Towards Fundamental Understanding of Interfaces in Carbon Nitride Photocatalytic and (Photo)electrochemical Systems

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Abstract

Photo(electro)catalysis is one of the promising approaches for solar-to-chemical conversion, which includes the splitting of water to produce hydrogen as an alternative solar fuel to traditional fossil fuels. Carbon nitride (CN\textsubscript{x}) has been recognized as the privileged particulate photocatalyst and emerging photoelectrode material for its hydrogen evolution ability, but the low charge mobility, fast charge recombination, and charge trapping of the pristine CN\textsubscript{x} stand in the way of better performance. Overcoming these challenges motivates the diverse modifications made to CN\textsubscript{x}. Post-synthetic modifications (i.e., the loading of cocatalysts) create new interfaces, for example, CN\textsubscript{x}|cocatalyst compared to CN\textsubscript{x}|electrolyte, which impacts the photo(electro)catalytic performance by creating new interfacial charge transfer pathways. Pre-synthetic modifications can also modify the interface (i.e., substrate) where CN\textsubscript{x} is grown to tune the CN\textsubscript{x} structure and diversify its properties. The lack of fundamental understanding or at least systematic investigation of these interfaces motivates my thesis studies. In the particulate system, I confirmed that cocatalysts accelerate the interfacial charge transfer at the CN\textsubscript{x}|cocatalyst interface, and surprisingly found that the transition metal Ni exhibited comparable hydrogen production ability to Pt. Meanwhile, a Ni \textit{in situ} photoreduction pathway, different from that observed with Pt, was revealed during the hydrogen evolution reaction mechanism. In the (photo)electrochemical system, I modified the substrate surface via aminosilanization. This interface modification produced a thinner and compact CN\textsubscript{x} layer, and different behavior in charge carrier dynamics (i.e., fewer deep traps) monitored by transient absorption spectroscopy, which is not seen when post-modifying the CN\textsubscript{x} with cocatalysts due to the high population of the traps in the bulk CN\textsubscript{x}. The faster charge transport with less charge trapping through the CN\textsubscript{x} layer as well as more efficient charge transfer at the CN\textsubscript{x}|substrate interface allow more charges to pass through the electrodes. The interface studies in two CN\textsubscript{x} systems concluded that the charge transfer at interfaces and charge transport in the bulk CN\textsubscript{x} are still challenging to address. Developing strategies to decrease or passivate the trap states in CN\textsubscript{x} or promote the rate of charge transfer across the interfaces remain promising directions to achieve optimized CN\textsubscript{x}-based photocatalytic and (photo)electrochemical systems.
Lay Summary

The key to addressing the energy crisis is to find alternatives to traditional fossil fuels. Solar energy is the most promising renewable energy resource and can be utilized to produce clean high-energy fuels. Carbon nitride (CNₙ) has the potential to split water to produce hydrogen and oxygen gas in well-designed solar-driven systems, either using CNₙ in powder form or preparing CNₙ films as electrodes. This thesis explores how effective strategies aimed at overcoming the difficulties of interfacial charge transfer, like introducing cocatalysts and modifying the substrate on which CNₙ is grown, can be. The interfaces between CNₙ and other materials serve as our research focuses and characterizations reveal that the defects in CNₙ and along the interface are problematic because they hinder the participation of charges in chemical reactions. My work points out the current challenges and provides a fundamental understanding of interfaces in CNₙ-based solar-utilizing devices.
Preface

Contributions from Dr. Robert Godin and Dr. Jian Liu include project design, instrument training, data acquisition, data analysis, and writing guidance. Emma Mitchell offered experimental training on hydrogen evolution reaction. Peter Osei Ohemeng provided the training on the Ocean Optics instrument. Sutripto Khasnabis helped with the data collection in transient absorption spectroscopy. Stephanie Busse helped with the plasma cleaning and aminosilanization process for the CNx-based photoelectrodes project. Dr. Isaac Li provided access to the TECAN Multifunctional Plate Reader and the plasma cleanser. Dr. Shrestha assisted with the SEM image collection. Samples for XPS were sent to 4D LABS at Simon Fraser University.

The thesis is composed of two first-author article papers supervised by Dr. Robert Godin and Dr. Jian Liu. The first was published in *ACS Catalysis*: Liu, C.; Liu, J.; Godin, R. ALD-Deposited NiO Approaches the Performance of Platinum as a Hydrogen Evolution Cocatalyst on Carbon Nitride. *ACS Catal.* 2023, 13, 573–586. Permission for using the manuscript in the thesis has been obtained from the journal. The second, not yet published, was submitted to *ACS Applied Materials & Interfaces* on June 27, 2023, titled Aminosilanized Interface Promotes Electrochemically-stable Carbon Nitride Films with Fewer Trap States on FTO for (Photo)electrochemical Systems (manuscript ID: am-2023-09284g). Supporting Information 1 mentioned in Chapter 3 can be found under DOI: 10.1021/acscatal.2c04795. Supporting Information 2 mentioned in Chapter 4 can be found in Appendix A: Supporting Information 2.

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Dedication

致我的父母，刘建华和吴素峰。
Chapter 1: Introduction

For over two centuries, the combustion of fossil fuels, namely coal, petroleum, and natural gas, has been the primary source of energy supply, but its associated environmental pollution has become a huge concern in terms of sustainability. In 2021, Net Zero by 2025: A Roadmap for the Global Energy Sector was published by the International Energy Agency (IEA), which set out a narrow but achievable pathway for reaching net zero emissions by 2050. However, in the short time since the report was published, much has changed. The global economy rebounded in 2021 from the COVID-19 pandemic with a global energy demand increase of 5.4%. The surging energy demand was partially met by the larger consumption of coal, causing 36.6 gigatonnes (Gt) of CO₂ emissions in 2021 and the largest annual increase in global CO₂ emissions ever recorded (1.9 Gt). Surge in demand, bottleneck in supply, severe global warming issue, goal to meet net-zero CO₂ emission by 2050, and the energy transition from traditional fossil fuels to renewables have been re-emphasized by IEA in their World Energy Outlook 2022 report. In the Stated Policies Scenario (STEPS), a global energy demand growth controlled at around 1% per year to 2030 can be met almost entirely by renewables.

Renewables, including solar, wind, hydropower, tidal, and geothermal, are alternatives to traditional fossil fuels, but not all of them can keep expanding on their existing installation scale, and their contribution to the world energy transition can be limited in the future. Wind electric energy costs $0.03-$0.20 per kWh, but the most appropriate places for the deployment of wind generators are offshore, which requires huge installation costs. Hydropower is almost the most economic electrical energy source, costing $0.03 per kWh. However, the expanding number of artificial water reservoirs and hydroelectric dams can cause environmental damage and disturb the ecosystem, for example, the natural spawning ground of fish. Tidal power plants can be considered as a specific type of hydropower plant, while it is only economically feasible for a few regions where the tidal vibration of the water is not less than 4 m. Geothermal energy is preferred...
in volcanic areas, but the total potential capacity of geothermal power plants is significantly low\(^6\), and it is predicted to account for a mere 1\% of renewables-based electricity generation in 2050\(^4,7\).

Till now, solar energy has been considered the most promising alternative energy source. This resource is remarkably enormous\(^8\) since the solar flux hitting the upper boundary of the Earth’s atmosphere is ca. 5.6\times10^{24} \text{ J per year}, almost 5000 times that of the annual energy demand of humanity\(^6\). Photovoltaics (PV) and thermal solar energy serve as two main routes in solar energy utilization. The former directly converts solar irradiation to electricity, and the latter uses solar radiation for heating a working medium (i.e., the solar water heater). In the 2022 IEA report, solar PV and wind are expected to account for 43\% of electricity generation worldwide in 2030, up from 28\% today\(^5\). The long-term goal is to decrease the cost of electric energy below $0.05 \text{ per kWh}$ (already at $0.10-0.15 \text{ per kWh}$ for solar power plants)\(^6\).

However, electricity and heat have encountered difficulties in being well-stored at a scaled-up level\(^9,10\). An alternative approach is to use high-energy chemicals for energy storage. When these chemicals, for example, hydrogen, are produced by converting solar energy to chemical bonds, they are termed solar fuels\(^11\). The solar-to-chemical conversion involves specialized materials and devices, mostly semiconductor-based photocatalysts and photoelectrode, that can absorb sunlight and catalyze chemical reactions. Solar fuels are easier to store as high-energy molecules in the long-term timescale and can be conveniently transported and distributed. National Renewable Energy Laboratory (NREL) has investigated the commercial energy-storing materials and applications, where hydrogen and gasoline have outcompeted batteries and capacitors in specific power and specific energy (Figure 1-1)\(^12\), and hydrogen exhibits the potential for being the leading energy-storing renewable energy.

In the rest of the introduction, we will start from the research gaps when utilizing semiconductors as essential materials for solar-to-chemical conversion, and introduce our
target material carbon nitride, semiconductor features, and underlying mechanisms of photocatalytic processes, in particular the charge transfer at interfaces that is important in this process. More technical details can be found in Chapter 2, including semiconductor band bending for interfacial charge transfer, charge trapping and its influence on charge transport, electrocatalytic measurements, and atomic layer deposition technique.

We would like to emphasize the significance of interface engineering at semiconductor|cocatalyst and semiconductor|substrate interfaces based on their contributions to the behavior of photocatalysts and photoelectrodes. These topics are expanded upon in Chapter 3 and Chapter 4.

Figure 1-1. The specific energy against the specific power of various energy-storing materials\(^\text{12}\).

1.1 Research direction

Photo(electro)catalysis is mainly based on semiconductor materials. Over the years, inorganic semiconductors have been discussed frequently in the photovoltaic and photo(electro)catalytic fields, like the widely used Si solar cells\(^\text{13}\), well-established Fe\(_2\)O\(_3\) and BiVO\(_4\) photoanodes for water oxidation\(^\text{14,15}\), and well-known particulate TiO\(_2\) photocatalyst for dye degradation\(^\text{16}\) and catalytic hydrogen generation\(^\text{17}\). Till 2009, the
discovery of carbon nitride (CN\textsubscript{x}) organic semiconductor has captured the attention of researchers for its intriguing metal-free feature (identified in Section 1.2) as well as photocatalytic water-splitting abilities\textsuperscript{18}. But typically, organic semiconductors process low surface reactivity, which calls for further surface modifications to improve their catalytic properties. The loading of the cocatalyst is regarded as the most straightforward method to supply surface reactive sites for redox reactions and thus brings the idea of heterojunctions – interfacing two complementary materials\textsuperscript{19}. Still, metal-based, especially noble metal-based (e.g., Pt, Pd, Ru), catalyst materials have dominated photo(electro)catalytic studies over the years, but noble metals are endangered by their low global reserves\textsuperscript{20,21} whilst heavy metals (e.g., Cd) have been tied to environmental pollution over several decades\textsuperscript{22}.

Interestingly, it was recently reported that nickel nitrides have superior catalytic properties comparable to Pt for photocatalytic hydrogen production\textsuperscript{23–26}, which shifts our focus back to the earth-abundant elements even when choosing cocatalyst materials. Nickel oxide, as a wide-band inorganic semiconductor, is brought to life by an industrialy viable technology, namely atomic layer deposition (see Section 2.5 and Chapter 3). Meanwhile, we realize that the interface between the organic semiconductor and inorganic semiconductor interface is less known, which brings us to the fundamental research questions and study CN\textsubscript{x}|NiO interface in Chapter 3, and the CN\textsubscript{x}|SnO\textsubscript{2} interface in Chapter 4.

Overall, our research aims to develop photo(electro)catalytic systems with earth-abundant elements from both light absorber and cocatalyst aspects, prepare transition metal oxide with favorable catalytic properties via state-of-art technique, and fill the research gaps in studying organic semiconductor|inorganic semiconductor interface.
1.2 Carbon nitride

Carbon nitride (CN_{x}, ideally graphite C_{3}N_{4}, realistically [C_{6}N_{9}H_{3}]_{n})^{27}, an organic semiconductor, was reported as a promising photocatalyst for hydrogen and oxygen evolution reactions in 2009 for the first time^{18}. Since then, CN_{x} has become the leading particulate photocatalyst for water splitting, and there are more than 20,000 publications on CN_{x} in the last five years. CN_{x} material is composed of earth-abundant elements mostly C and N, and its metal-free feature interests researchers^{28}. As a metal-free organic polymer, CN_{x} is formed by a π conjugated system of tri-s-triazine or heptazine rings^{29,30}, which interact with each other from terminal amino groups via hydrogen binding (Figure 1-2))^{31}. The delocalized π-electron system determines the optical and electronic properties of CN_{x}, which correlates to the visible light absorption of CN_{x} starting from 450 nm to the lower wavelength region^{32}. CN_{x} is regarded as a desirable photocatalyst candidate for its suitable optical band gap energy (~2.7 eV)^{33,34}, where the conduction band edge is more negative to the electrochemical potential of the H^{+}/H_{2} couple (0 V vs. NHE), and the valence band edge is more positive than that of the O_{2}/H_{2}O couple (1.23 V vs. NHE)^{57}, possessing driving force for initiating proton reduction and water oxidation reaction. Strikingly, CN_{x} can be easily prepared from various precursors (e.g., dicyanamide, urea, or thiourea) via thermal condensation^{57} and can be easily recognized by its yellow color^{38}. CN_{x} is thermally stable up to 600°C and chemically nonreactive in a large pH range^{39}, which helps it survive in harsh conditions with lesser degradation.

According to the aforementioned features, we have chosen CN_{x} as the target light absorber semiconductor, and have carefully investigated its optical properties, morphology, and synthesis. More specifically, we focused on its photocatalytic and (photo)electrochemical behavior, including hydrogen generation activity and stability, charge transfer, and charge transport abilities.
Figure 1-2. Chemical structure of heptazine-based CN$_x$. Hydrogen bonds are identified with blue ovals.

1.3 Semiconductors

Semiconductors can be classified as inorganic semiconductors (e.g., silicon) and organic semiconductors (carbon-based molecules or polymers) based on what material they are made from. Both inorganic and organic semiconductors maintain certain light-dependent electrical conductivity and can be utilized as optoelectronic devices (e.g., light-emitting diodes\textsuperscript{40,41}). They can also be distinguished by chemical composition, crystallinity, charge carrier mobility, etc. Typically, inorganic semiconductors have a crystalline structure with a high degree of order, which can be controlled through crystal growth techniques. In contrast, organic semiconductors are mostly disordered, amorphous, and more flexible. Moreover, inorganic semiconductors usually process a higher charge carrier mobility. For example, amorphous silicon\textsuperscript{42} has a charge carrier mobility of 1~10 cm$^2$ V$^{-1}$ s$^{-1}$, much higher than that of the representative organic semiconducting polymer poly(3-hexylthiophene) (P3HT)\textsuperscript{43} of 10$^{-4}$~10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. Up to now, inorganic semiconductors have been more frequently used in traditional electronic devices (e.g., commercial solar
panels\textsuperscript{13}), while organic semiconductors with tunable electronic and optical features are more commonly mentioned in emerging technologies, such as organic photovoltaics (OPVs)\textsuperscript{44,45}.

CN\textsubscript{x}, being an organic semiconductor, has advantages introduced in \textbf{Section 1.2}, but also challenges. Its low crystallinity or amorphous phase makes the identification of the chemical structure and defects challenging. Also, its relatively low charge carrier mobility makes it difficult for charge transport (\textbf{Section 2.3}) and interfacial charge transfer to outcompete fast charge recombination (\textbf{Section 1.4.2}) and beneficial to charge transport. Thus, these challenges and potential limitations have motivated our fundamental research on CN\textsubscript{x} material.

In this section, the energy diagram and Fermi level of semiconductors are introduced to further understand the basics of our semiconductor material.

\textbf{1.3.1 Energy diagram}

Energy diagrams are important for predicting the movement of electrons and holes in semiconductor materials. In molecular orbital (MO) theory, the interaction between two atoms is formed by one low-lying and another high-lying bonding atomic orbital\textsuperscript{46}. The number of MOs increases with the number of atoms (N), where N/2 MOs are usually occupied, leaving the other half unoccupied\textsuperscript{46}. When N goes up to about 200 atoms, the orbital levels get close in energy. A broad and continuous energy band of closely packed orbitals is formed, where the charges could move around freely\textsuperscript{46}. This can be seen as an 'empty' band and a 'filled' band in \textbf{Figure 1-3}.

In molecules, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) needs to be overcome by activation, such as the absorption of energy in the form of light, heat (high temperature), or electrical input.
In the energy band diagrams (Figure 1-4), the empty band is called the conduction band (CB), the filled band is the valence band (VB), and the gap between CB and VB is a forbidden energy gap or bandgap \( (E_g) \) where energy states do not exist ideally. A bandgap does not exist in metals since an occupied band overlaps with an unoccupied band, and thus the valence electrons can be easily moved to the conduction band\(^4\). Insulators have large bandgaps \((\geq 6 \text{ eV}, \text{ e.g., diamond, rubber})\)\(^4\), and very few electrons can be excited to the CB under thermal energy at room temperature. Thus, the material is a weak conductor of current. Semiconductors are defined as a type of material with a bandgap between that of metals and insulators. Upon appropriate photoexcitation (i.e., ultraviolet or visible light), electrons can be excited from the valence band to the conduction band, leaving the vacancy and net positive charges in the valence band, which are defined as holes (Figure 1-5). These photoexcited charge carriers can be used for subsequent photochemistry.

**Figure 1-3.** Interaction of atomic orbitals. LUMO and HOMO in molecular orbital theory.
Figure 1-4. Schematics of energy diagrams of metal, semiconductors, and insulators. CBE stands for the conduction band edge and VBE stands for the valence band edge.

Figure 1-5. Scheme of photoexcitation to a semiconductor.

### 1.3.2 Fermi level

The Fermi level is an essential concept for understanding the electronic properties of the semiconductor. The position of the Fermi level relative to the electrochemical potential of the redox reactions determines the flow of charge carriers and the corresponding driving force. From the statistical aspect, the Fermi level ($E_F$) is defined as the energy where the occupancy of an electronic state is 0.5 (50%) under equilibrium.
Alternatively, from the thermodynamic aspect, the Fermi level is indicative of the electrochemical potential of an electron in a solid. As shown in Figure 1-6, the intrinsic semiconductor has an equal number of mobile electrons and holes, with the $E_F$ in the middle of the band gap. For the n-type semiconductor, the Fermi level lies above the intrinsic level and is closer to the conduction band edge, indicating a higher number of mobile electrons. By contrast, a higher number of mobile holes exists in the p-type semiconductor, and the Fermi level lies closer to the valence band edge.

![Figure 1-6. Fermi level positions in different types of semiconductors under thermal equilibrium.](image)

It is worth mentioning the flipped directions of the energy level and electrochemical potential scales (Figure 1-7). The energy level in electronvolts (eV) is referenced to vacuum ($E = 0$ eV). Generally, materials have a negative work function because electrons in the solid are usually more stable than when in a vacuum. In contrast, electrochemical potentials are relative to a reference potential (e.g., standard hydrogen electrode or SHE). According to the International Union of Pure and Applied Chemistry (IUPAC), 0 V vs. SHE is calibrated at -4.44 V vs. vacuum. Given this relationship, we can align the energy scales in eV and electrochemical potentials in V. More detailed conversions between different standard potential scales can be found in Section 2.4.1.
1.4 Photocatalysis

Photocatalysis, a process of accumulating photogenerated charges in the presence of a light absorber to achieve chemical transformation, is inspired by natural photosynthesis\textsuperscript{48–50}. The chlorophylls in photosystems I and II can absorb photons with a maximum wavelength of ~700 nm, reducing nicotinamide adenine dinucleotide phosphate (NADP\textsuperscript{+}) to NADPH for energy supply and further complete the Calvin cycle\textsuperscript{48}. Its ability to drive chemical reactions upon solar energy prompts the emergence of photocatalysis and artificial photosynthesis. Strictly speaking, photocatalytic processes are thermodynamically favorable (\(\Delta G < 0\)), for example, the oxidation of phenol to hydroquinone by oxygen (\(\Delta G^\circ = -168 \text{ kJ/mol}\))\textsuperscript{51}. In contrast, photosynthetic processes are thermodynamically uphill (\(\Delta G > 0\)) and require extra photochemical energy input\textsuperscript{48}. Example reactions are water splitting (\(\Delta G^\circ = +237 \text{ kJ/mol}\))\textsuperscript{52} and CO\textsubscript{2} reduction to products such as CH\textsubscript{3}OH (\(\Delta G^\circ = +689 \text{ kJ/mol}\)), CH\textsubscript{4} (\(\Delta G^\circ = +800 \text{ kJ/mol}\))\textsuperscript{53,54}. Regardless of the clear distinction from a thermodynamic perspective, photocatalysts must consider light absorption, charge separation, and charge transfer processes. In this work, we adopt the broad definition of photocatalyst by the International Union of Pure and Applied Chemistry (IUPAC) as “catalyst able to produce, upon absorption of light, chemical transformations…”\textsuperscript{55}.
In this section, general photocatalytic processes, requirements for photocatalytic water splitting, as well as cocatalyst modification to the semiconductor are introduced.

1.4.1 General photocatalytic processes

A successful photocatalytic process involves multiple steps occurring in sequence or simultaneously\(^{55}\), which are illustrated in Figure 1-8, from step 1 to step 7. Light absorption comes first (step 1), and the band gap of the semiconductor determines the maximum wavelength it can absorb following the equation \(E_g(eV) = 1240/\lambda(nm)\)^{56}. The energy of a photon to be absorbed by a semiconductor is equal to or greater than the band gap in eV. For those aiming at utilizing visible light (380 to 700 nm), a band gap narrower than \(\sim 3.2\) eV is needed. When a photon is absorbed, its energy is transferred to generate an exciton, where an electron and a positively charged hole are held together by Coulombic force close in proximity\(^{57}\). The exciton might undergo recombination and thus prevent the photocatalytic process from being productive (step 2). Charge recombination is when the electron recombines with the hole to release the absorbed energy in the form of light or heat, corresponding to the radiative and non-radiative emissions, respectively. The dissociation of the exciton is known as charge separation (step 3). Separated charges then need to be transported to the surface of the semiconductor for redox reaction, during which the charges could be trapped (step 4), recombined (i.e., band-to-band recombination, step 6), released to the ground state from traps\(^{55}\) (step 7), or finally transported to the surface of the semiconductor (step 5). At the surface, the electron is consumed by an electron acceptor (A\(^+\)), whilst the hole reacts with an electron donor (D).

It is reported that photophysical processes proceed in a dramatically faster time scale compared to the surface chemical reaction. Typically, charge generation upon photoexcitation in the bulk occurs within several fs \((10^{-15}\) s), and charge transfer between bands and trap states takes place in ps \((10^{-12}\) s) to µs \((10^{-6}\) s); charge recombination within the bulk material and on the surface happens in ps to ns\(^{58}\). In contrast, surface chemical
surfaces, such as water splitting reactions, will not take place until ms to s time scale. Therefore, prolonging the charge carrier lifetime and extracting charges out from semiconductors more efficiently for redox reactions are significantly valued in photocatalysis.

Figure 1-8. General photocatalytic processes in organic semiconductors. Step 1: the absorption of photons; step 2: charge recombination; step 3: charge separation; step 4: charge trapping; step 5: charge transport; step 6: band-to-band charge recombination; step 7: charges released from the traps to the ground states.

1.4.2 Charge recombination and decay kinetics

Broadly speaking, electron-hole charge recombination is unproductive and can occur at any time to waste energy absorbed from the photons. Each step in the photocatalytic process must kinetically compete with charge recombination to be productive. Therefore, knowing the kinetics of the charge recombination helps to design artificial photosynthetic reactions.

As suggested by the Langevin theory, the idealized rate of charge recombination is dominated by Coulombic interactions when electrons and holes are in proximity, which indicates charge recombination is distance-dependent and spatial separation of the
electrons and holes lowers its recombination rate. In addition, the Langevin theory suggests that a high mobility of the charges increases the charge recombination rate\textsuperscript{59}. However, charge recombination is highly affected by the trap states in the materials\textsuperscript{60}. Firstly, charges tend to find those trap states of low energy and then are immobilized. If charges are trapped in shallow trap states near the CB edge and VB edge, they need thermal activation to reach the mobility edge to recover mobility\textsuperscript{61,62}. For those trapped in deep trap states, a longer time is required before detrapping or they are permanently localized\textsuperscript{62}. Successful charge recombination must go through a series of trapping and detrapping processes until a charge finds its recombination partner.

Researchers have built up models correlating the charge carrier densities ([n,p]) to the rate constant (k) and the time (t). Theoretically, in the absence of the trap states, the charges are mainly consumed by the recombination of electron-hole pairs, and the decay kinetic is described as a bimolecular, second-order process (\[ \frac{1}{[n,p]} = \frac{1}{[n,p]_0} + kt \])\textsuperscript{63}. Experimentally, the trap states are usually observed with an exponential distribution, and the decay kinetics of the charge carrier density follows the power law ([n, p] \propto t^{-\alpha}) instead\textsuperscript{60,64,65}.

For example, in CN\textsubscript{x}, charge carriers are generated within the fs time scale. However, they tend to get trapped on the ps time scale, and the as-calculated charge recombination follows a power-law decay\textsuperscript{66}. Though deep-trapped electrons surviving until μs to ms time scales are found, they are unreactive and have no contribution to photocatalytic activities\textsuperscript{66}. Hence, one of the challenges in optimizing photocatalytic systems is stopping charges from deep trapping. The introduction of Pt to the semiconductor can save the electrons from trapping, whereas Pt is introduced as a cocatalyst to facilitate the charge transfer\textsuperscript{67}. The electron transfer from CN\textsubscript{x} to Pt is reported to occur on the ns time scale and can compete with the charge trapping in the CN\textsubscript{x}\textsuperscript{66}. The loading of cocatalysts, like Pt, will be further discussed in Section 1.4.4.
1.4.3 Photocatalytic water splitting

All we want in photocatalysis are productive photocatalytic processes. More specifically, chemical transformations upon photoexcitation are preferred. Photocatalytic overall water splitting \((2H_2O \rightarrow 2H_2 + O_2)\) is one of the desirable reactions in the utilization of solar energy, as it produces high-energy hydrogen molecules while regenerating the starting material water during consumption without the release of any harmful and pollutant byproducts\(^{36,68}\). Overall water splitting is composed of two half-reactions, hydrogen evolution reaction (HER) or proton reduction \((2H^+ + 2e^- \rightarrow H_2)\) as well as oxygen evolution reaction (OER) or water oxidation \((2H_2O \rightarrow O_2 + 4H^+ + 4e^-)\)\(^{69}\). An appropriate band gap is needed for driving HER or OER. As drawn in Figure 1-9, semiconductor-based photocatalysts that are qualified for HER and OER have a conduction band edge (CBE) more negative than the redox potential of the \(H^+/H_2\) (0 V vs. NHE) and a valence band edge (VBE) more positive than redox potential of the \(H_2O/O_2\) (1.23 V vs. NHE) to be thermodynamically favorable\(^{33}\).

Though various materials are qualified for photocatalytic water splitting, there is still room for improving overall energy conversion efficiency. This requires high efficiencies in three sequential steps of the photocatalytic reaction: light harvesting, charge separation and transfer, and surface catalytic reaction. The first two steps can be mainly improved by adopting narrow band gap semiconductors and tuning physical properties (particle size and crystallinity), respectively\(^{19}\). For the third step, though matching band level and redox potentials have a certain effect on making charges possess thermodynamically sufficient driving force for water splitting, charges prefer to recombine if there are limited reaction sites on the surface of the semiconductor\(^{19}\). Loading cocatalysts on semiconductors has become a widely used approach to promote the third step, where the cocatalyst works as the reactive site to catalyze the reaction, thus accelerating the charge separation by continuously consuming the charges and forcing charges to move to redox reactions. For
example, OER cocatalysts (e.g., Co$_3$O$_4$, IrO$_2$) and HER cocatalysts (e.g., Pt) could separate the water oxidation and proton reduction reactions$^{70,71}$.

![Figure 1-9. Schematic illustration of HER and OER mechanisms. HER and OER cocatalysts are drawn in green and orange, respectively.](image)

1.4.4 CN$_x$/cocatalyst modification

We have introduced in Section 1.2 that CN$_x$ is one of the leading materials, especially for particulate photocatalytic hydrogen evolution. However, this material can be limited by its rapid charge recombination and low charge carrier mobility. A variety of modifications for countering the drawbacks of CN$_x$ have emerged$^{72}$, and cocatalyst modification is one that I focused on for this thesis. In this section, how a cocatalyst can affect the charge carrier dynamics and photocatalytic performance is introduced.

The charge carrier dynamics when using MoS$_2$ cocatalyst of different morphologies on carbon nitride nanosheet (CNNS) were reported by using femtosecond transient absorption spectroscopy (fs-TAS)$^{73}$. The average fs-TAS lifetime decreased in the order of CNNS (459 ps), MoS$_2$ monolayer/CNNS (293 ps), MoS$_2$ nanodot/CNNS (122 ps), and the faster decay is attributed to a faster electron transfer from CNNS to MoS$_2$. The electron transfer rate in MoS$_2$ nanodot/CNNS is ~5 times faster than MoS$_2$ monolayer/CNNS (5.96
x $10^9$ s$^{-1}$ vs. $1.23 \times 10^8$ s$^{-1}$), and electron injection efficiency in the former is 2 times higher than the latter (73.3% vs. 36.1%). And MoS$_2$ nanodot/CNNS exhibited an ~8 times higher photocatalytic HER performance than MoS$_2$ monolayer/CNNS (660 μmol g$^{-1}$ h$^{-1}$ vs. 83.8 μmol g$^{-1}$ h$^{-1}$) under visible light irradiation ($\lambda \geq 400$ nm) in the sacrificial environment.

Besides the metal-based cocatalysts, a metal-free CN$_x$/cocatalyst modification for HER is feasible with carbon dots (CDs). The amplitude-weighted average lifetime in time-resolved photoluminescence (trPL) decreased from 8.12 ns to 0.32 ns after the introduction of CDs$^{55,74}$, an indication of faster charge extraction. Also, 1 wt.% CDs/CN$_x$ has outperformed Pt/CN$_x$ in terms of the rate and efficiency of electron transfer from CN$_x$ to the cocatalyst, 6.4 times faster ($30.02 \times 10^8$ s$^{-1}$ vs. $4.69 \times 10^8$ s$^{-1}$) and 1.2 times higher (96% vs. 79%), respectively$^{74}$.

Therefore, it has previously been demonstrated that cocatalysts can have an impact on charge carrier dynamics and thus photoactivity. Noble metal and metal oxide cocatalysts on CN$_x$ were carefully investigated in Chapters 3 and 4.

### 1.5 Charge transfer at interfaces

Charge transfer at the interfaces is frequently discussed since its efficiency determines the amount of the charges passing through the interface and flowing to the target redox reactions. As drawn in Figure 1-10, in photocatalyst suspensions the semiconductor|cocatalyst interface (process 4), cocatalyst|electrolyte interface (process 5), and semiconductor|electrolyte interface (process 6) are the main processes investigated, where cocatalysts are added to facilitate the interfacial charge transfer and reduce the charge recombination rate. These interfaces are studied in Chapter 3. In (photo)electrochemical systems, processes from 4 to 6 remain relevant, but the semiconductor|substrate interface (process 2) emerges as a critical but less studied aspect. Semiconductor|substrate interface engineering is aimed at enhancing the interfacial contact of the electrochemical materials to substrates in physical proximity as
well as aligning the energy levels between the two layers. This highly influences the electrochemical performance of the photoelectrodes and is the focus of Chapter 4.

Figure 1-10. Charge pathways in particulate photocatalysts (left) and photoelectrodes (right). Process 1: external electron injection; process 2: charge transfer at CN$_x$|substrate interface; process 3: charge transport in bulk CN$_x$; process 4: charge transfer at CN$_x$|cocatalyst interface; process 5: charge transfer at cocatalyst|electrolyte interface; process 6: charge transfer at CN$_x$|electrolyte interface.

One example of better energy level alignment at the semiconductor|substrate interface could be the existence of dipoles between the electron transport layer (ETL) and electron selective layer (ESL) in perovskite solar cells. Those dipoles can tune the work function and energetics of the material by moving the vacuum level$^{75}$. A positive or negative work function shift up to several hundreds of meV is feasible, thus adjusting the energy level alignment at the interface with charge transport materials$^{76}$. Similarly, a 3-aminopropyltriethoxysilane (APTES) self-assembled monolayer was able to modify the interface between SnO$_2$ ESL and the perovskite layer since the terminal functional groups of APTES form dipoles on the SnO$_2$ surface, contributing to a better band energy
alignment for the enhanced photogenerated charge separation and charge extraction\textsuperscript{77}. In their work, the perovskite solar cell with APTES modified-SnO\textsubscript{2} ESL achieved a power conversion efficiency of 17\%, compared to 15\% in the non-APTES modified system\textsuperscript{77}, emphasizing the significance of semiconductor\|substrate interface engineering.

In this section, we start by introducing Marcus theory to study the fundamentals of electron transfer between molecules, and then the Marcus-Gerischer theory which describes the electron injection from the electrolyte into a wide-bandgap semiconductor through the semiconductor\|electrolyte interface.

### 1.5.1 Marcus theory of electron transfer

To study a (photo)chemical process, it is necessary to understand its kinetics and thermodynamics. Kinetics and thermodynamics are two branches of physical chemistry that investigate chemical reactions from different aspects. Kinetics focuses on the reaction rate, equilibrium, activation energy barrier ($\Delta G^*$), and mechanisms, and how those are affected by the concentration of species, temperature, and catalyst\textsuperscript{78}. In contrast, thermodynamics monitors the energy changes during the chemical reactions and tells whether a reaction is energetically favorable or unfavorable, which is always described by enthalpy, entropy, and free energy ($\Delta G^0$)\textsuperscript{78}. The Arrhenius Eyring equation (Equation 1-1) describes the kinetics of a chemical reaction, and its temperature dependence on the rate constant ($k$), where $A$ is the pre-exponential factor and $E_a$ is the activation energy\textsuperscript{61}.

$$k = A \exp\left(-\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (1-1)

As for the electron transfer, its rate ($k_{eT}$) between molecules (i.e., an electron donor and an accepter) can be described by the Marcus theory\textsuperscript{79} (Equation 1-2). Strikingly, kinetics is intimately related to thermodynamics. The relationship among free energy change ($\Delta G^0_{eT}$), activation barrier ($\Delta G^+_e$) and reorganization energy ($\lambda$) can be expressed by Equation 1-3 and drawn out by parabolas\textsuperscript{80,81} (Figure 1-11). Interestingly, the increase
in the absolute value of $\Delta G_{et}^0$ between the reactant and product does not guarantee a higher $k_{eT}$. The $k_{eT}$ maximum is achieved when $\lambda = -\Delta G_{et}^0$, which gives a $\Delta G_{et}^x = 0$. In addition, any further decreases of $\Delta G_{et}^0$ towards more negative values (i.e., more thermodynamically favored) leads to a higher $\Delta G_{et}^x$, and thus a slower $k_{eT}$.

$$k_{eT} = \frac{\pi}{\sqrt{h^2 \lambda k_B T}} \times H_{DA}^2 \times \exp \left( -\frac{(\lambda + \Delta G_{et}^0)^2}{4\lambda k_B T} \right) \quad (1-2)$$

$$\Delta G_{et}^x = \frac{(\lambda + \Delta G_{et}^0)^2}{4\lambda k_B T} \quad (1-3)$$

The term $\frac{\pi}{\sqrt{h^2 \lambda k_B T}}$ relates to the frequency factor, and the square of electronic coupling ($H_{DA}$) acts as the electronic factor, they all contribute to the $k_{eT}$, and the latter can be expressed by Equation 1-4:

$$H_{DA} = H_{DA}^0 \exp (-\beta_{el}(r_{DA} - r_{DA}^0)) \quad (1-4)$$

Where $H_{DA}^0$ is the electronic coupling at the Van der Waals limit; $\beta_{el}$ is the distance decay constant; $r_{DA}$ is the distance between the donor and acceptor; $r_{DA}^0$ is the distance between the donor and acceptor at the Van der Waals limit. $\hbar$ is the

From combining Equations 1-2 and 1-4, we see that the distance dependence of the electron transfer rate is exponential (Equation 1-5). For example, with the $\beta_{el}$ of 1 Å$^{-1}$, a decrease of 1 Å in $r_{DA}$ increases $k_{eT}$ by a factor of 7.4! This emphasizes that the interfacial contacts should be physically close to allow for faster electron transfer.

$$k_{eT} \propto \exp \left( -2\beta_{el}(r_{DA} - r_{DA}^0) \right) \quad (1-5)$$

Overall, the rate of electron transfer can be expressed by Marcus theory, and split into three components, 1) the pre-exponential factor which is related to the reorganization energy; 2) distance-dependent electronic coupling; 3) the correlation of activation barrier to free energy change. The theory assumes that electron transfer occurs with the reorganization of the electronic structure. Firstly, an electron is transferred from a donor molecule to an acceptor molecule, and the transfer energy is determined by the energy
difference between the donor and acceptor molecules. Next, the surroundings of the donor and acceptor molecules reorganize to accommodate the electron distribution, leading to changes in the positions and orientation of the atoms and molecules.

![Diagram of electron transfer](image)

Figure 1-11. Schematic illustration of (a) relationship among $\Delta G_{et}^0$, $\Delta G_{et}^0$, and $\lambda$; (b) $k_{et}$ plotted against $\Delta G_{et}^0$ in Marcus theory. $r$ and $p$ are subscripts for reactant and product, respectively.

### 1.5.2 Marcus-Gerischer theory of interfacial charge transfer

Based on the Marcus theory at the molecular level, the Marcus-Gerischer theory (MGT) was developed to describe excited-state electron injection at solid|liquid interfaces into wide-bandgap semiconductor$^{82,83}$. As an example, we consider the theoretical analyses of MGT as applied to a dye-sensitized solar cell (DSSC) system which is mainly composed of mesoporous oxide semiconductor, sensitizer dye, and $I^-/I_3^-$ based electrolyte$^{84}$. 

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Different from molecular electron transfer, electron transfer at the semiconductor|electrolyte interface involves a continuum of electronic states in the semiconductor\textsuperscript{85}. The electron transfer rate to all potential accepting states in the semiconductor electrode is the sum of the rate from each molecular state of a dye on the surface of the semiconductor to the different electronic states of the semiconductor. Thus, the interfacial charge transfer rate ($k_{eT}$) between sensitizers and a semiconductor can be expressed as \textbf{Equation 1-6} as the sum of all possible electron transfer rates in the semiconductor\textsuperscript{84}. $k_{eT}$ can be split into: $A$, the pre-exponential factor; $H^2$, the averaged electronic coupling between dye excited states and acceptor states in the semiconductor; $f(E, E_F)$, the Fermi-Dirac term for the electronic occupancy can be expressed by \textbf{Equation 1-7}; $\rho(E)$, the density of acceptor states of the semiconductor known as the DOS; and an exponential term related to the activation energy from Marcus theory\textsuperscript{86}. Typically, the DOS of metal oxide semiconductors is modeled with an exponential tail below the band edges due to the existence of the trap states ($\rho(E) \propto \exp(E/E_0)$), where $E_0$ represents the energetic distribution of the electronic states (more details in \textbf{Section 2.2}). The DOS in the conduction band and valance band should also be considered since they can act as electron acceptor and donor states, respectively.

\begin{equation}
k_{eT} = A \int H^2 (1 - f(E, E_F)) \rho(E) \exp \left( \frac{-(e \cdot E - e \cdot E_{ox}^* + \lambda)^2}{4\pi\lambda k_B T} \right) dE \tag{1-6}
\end{equation}

\begin{equation}
F(E, E_F) = \frac{1}{1 + e \exp \left( \frac{E - E_F}{k_B T} \right)} \tag{1-7}
\end{equation}

$E$ is the absolute potential of the acceptor state relative to NHE; $E_F$ is the Fermi level of the semiconductor; $E_{ox}^*$ is the redox potential of the dye excited state; $\lambda$ is the reorganization energy for electron injection in eV. The product of elementary charge ($e$) and potential gives the final units of energy ($E$) in eV.

From the expression of the MGT, the correlation of the $k_{eT}$ with applied biases is noticed. The Fermi level can be relocated under applied bias and thus changes the
occupancy as per the Fermi-Dirac term (more details in Section 2.1.2). For example, \( k_eT \), expressed as the photooxidation rate of the dye in perylene-sensitized electrodes, was found to be smaller with more negative applied bias\(^6\). Another example is that the applied bias could help to inject the charge carrier from the surface to the bulk of the semiconductor via an electric field in the space charge layer\(^7\).

The concepts regarding the interfacial charge transfer in the DSSC models are critical to our photoelectrochemical systems since they define the fundamentals of electron injection into the semiconductor and help to understand the charge transfer occurring at semiconductor|electrolyte interface as well as semiconductor|substrate interface under applied biases.

### 1.6 Research objective

The solar-to-fuel ability of particulate CN\(_x\) was first reported in 2009\(^1\), and CN\(_x\)-based (photo)electrochemical applications started a few years after. Researchers have investigated the versatile properties of CN\(_x\), including its chemical structure, optical and electronic properties, and chemical and thermal stability\(^8\)–\(^9\). However, the interface engineering between CN\(_x\) and other materials remains less studied, which serves as my motivation and builds up the whole project. I set out to study the CN\(_x\)|cocatalyst interface mainly in photocatalytic systems, and the CN\(_x\)|substrate interface in photoelectrochemical systems, with research objective as follows:

- To load NiO cocatalyst on CN\(_x\) via state-of-the-art ALD technique for maximizing the charge extraction ability of transition metal oxide, accelerating interfacial charge transfer at CN\(_x\)|cocatalyst interface (see Chapter 3).

In photocatalytic systems, diverse modifications to counteract the fast charge recombination and low charge carrier mobility in bulk CN\(_x\) that have been reported\(^7\),\(^8\)–\(^9\). They include narrowing the bandgap for more light absorption; morphology and dimensionality tuning to shorten the charge carrier diffusion length; defect control and
doping to redistribute spatial charges; introducing conductive material to improve conductivity; heterojunctions with cocatalysts (e.g., noble metal-based, transition metal-based, metal-free) to reduce the unfavorable charge recombination.

In Chapter 3, we adopted the idea of post-synthetic cocatalyst modification but tried out a new technique, atomic layer deposition (ALD). As most solution-processed modifications have issues with heterogeneity in cocatalyst size and distribution, we turned to ALD as it leads to superior thin film depositions with nanometer thickness and high conformity. NiO was chosen for its transition metal oxide properties and well-established ALD recipe, and this ALD-derived cocatalyst was layered on the Cx and help us compare with photodeposited Pt to explore whether the star-of-art technology could confer better cocatalyst capabilities to traditional metal oxide material during photocatalytic HER. Meanwhile, time-resolved photoluminescence (trPL) and photoinduced absorption spectroscopy (PIAS) are used to monitor the charge carrier dynamics, providing insights into the critical charge transfer at the semiconductor|cocatalyst interface.

- To modify the underlying substrate for a more efficient and robust Cx|substrate interface and identify its influence on morphology, optical properties, and photoelectrochemical performance (see Chapter 4).

As for the emerging Cx-based photoelectrochemical systems, existing review articles mainly stop at summarizing the Cx film growth approaches, including doctor-blade, liquid-based growth, vapor deposition, microcontact printing, and direct growth. The major issue in Cx-based (photo)electrodes is the difficulty of coating a conductive substrate with a uniform Cx layer while controlling its morphology, optical and photoelectrochemical properties. Thus the critical semiconductor|substrate interface in photoelectrodes is even less studied compared to current interface engineering on the particulate Cx heterojunctions between Cx and diverse cocatalysts. Also, the charge separation, charge transfer, and their correlations to structural, chemical, and photophysical properties are underexplained.
In Chapter 4, we adopted the direct growth method but pretreated the FTO (F-doped tin oxide coated glass) substrate with plasma cleaning and aminosilanization, and focused on the CNₓ|FTO interface. To understand how the photoelectrochemical system changes in response to this CNₓ|FTO interface modification, we have studied 1) morphology difference by scanning electron microscope (SEM); 2) changes in optical properties, especially the density of trap states by diffuse reflectance spectroscopy (DRS), photoluminescence (PL), and transient absorption spectroscopy (TAS); 3) charge transfer at the CNₓ|FTO interface, charge transport within CNₓ layer, and surface reaction kinetics at the CNₓ|electrolyte interface reflected by the electrochemical measurements; 4) also the electrochemical H₂ generation performance (mainly activity and stability). This fundamental study at the CNₓ|FTO is critical to designing CNₓ-based (photo)electrodes with enhanced photoelectrochemical ability and prolonged stability and deserves more attention.

Overall, I sought to explain how the different interfaces can impact photo(electro)catalytic processes and ultimately the activity and stability of particulate photocatalysts and photoelectrode for hydrogen production. These studies led to a better understanding of the current challenges and identified potential solutions.
Chapter 2: Charge dynamics details and methods

In this chapter, the critical band bending is introduced to understand the interfacial charge flow under irradiation for photocatalysis in Chapter 3, and under external bias for (photo)electrochemical processes in Chapter 4. Charge trapping and charge transport in polymers are next discussed for their influence on photoactivity. Also, techniques including atomic layer deposition used in Chapter 3 for cocatalyst deposition and electrochemical measurements utilized in Chapter 4 and are introduced.

2.1 Band bending

Band bending of the semiconductor is critical to photocatalysis and photoelectrocatalysis. Developing a band bending picture in terms of energy diagrams helps interpret the movement of the charges with the photocatalytic and photoelectrochemical processes and partially determines the behavior and performance of the applied materials. Band bending happens under a series of conditions, including in a dark environment or under stimuli from illumination and/or the applied bias.

2.1.1 Band bending in the dark

Conduction and valence bands bend (in terms of energy vs. distance) when the semiconductor contacts a metal or an electrolyte\(^ {47}\). As shown in Figure 2-1, an n-type semiconductor contacting an electrolyte is used as an example. The extent of band bending is dependent on the relative position of the Fermi level of the semiconductor and the electrochemical potential of the electrolyte.

Before contact, the semiconductor is characterized by its work function \( \chi \), electron affinity \( A \), and band gap, whilst the electrolyte has an electrochemical potential expressed by the Nernst equation, which could be described as its “Fermi level” (\( \phi_{\text{F,redox}} \))\(^ {47}\). Upon contact, when the Fermi level of the semiconductor is less positive than the electrochemical potential of the electrolyte, electrons would move from the semiconductor...
to the electrolyte, accumulating positive charges within the semiconductor near the surface, and this moves the Fermi level away from the conduction band edge and toward the valence band edge\textsuperscript{47}. The depletion of electrons is shown as an upward bending towards the semiconductor|electrolyte interface, and the band bending magnitude is $\Delta \phi_{SC} = \phi_F - \phi_{F,\text{redox}}$, where $\phi_F$ is the Fermi level of the semiconductor before contact. This depletion is most prominent at the surface and is minimized at a distance sufficiently far away from the surface, where the band edge energy remains flat\textsuperscript{47}. This distance is known as the depletion width ($W_{SC}$), which can be calculated according to Equation 2-1\textsuperscript{100}, and the space with which the charge redistribution occurs is called the space charge region (SCR).

$$W_{SC} = \sqrt{\frac{2\varepsilon_0 \varepsilon_{SC}}{q N_D} \left( \Delta \phi_{SC} - \frac{kT}{q} \right)} = \sqrt{\frac{2\varepsilon_0 \varepsilon_{SC}}{q N_D} \left( \phi_F - \phi_{F,\text{redox}} - \frac{kT}{q} \right)}$$ \hspace{1cm} (2-1)

where $\varepsilon_0 \varepsilon_{SC}$ is the dielectric constant of the semiconductor; $q$ is the electric charge; $N_D$ is the charge carrier concentration; $k$ is Boltzmann’s constant; and $T$ is the absolute temperature.

The relative positions of $\phi_F$ and the $\phi_{F,\text{redox}}$ determine the direction and degree of the band bending. For example, in an n-type semiconductor, if the Fermi level of the semiconductor is more positive than the electrochemical potential of the electrolyte ($\phi_F > \phi_{F,\text{redox}}$), electrons can be injected into the solid with a downward bending towards the semiconductor|electrolyte interface, and the condition is called accumulation (as more electrons are injected into the n-type semiconductor, making it more n-type) instead of depletion as introduced in Figure 2-1\textsuperscript{47}.

Theoretically, the more severe the band bending, the higher the driving force for the charge flow. However, the depletion of charges can form a built-in electric field to counteract the spontaneous flow of electrons from the semiconductor to the electrolyte, causing the Schottky barrier\textsuperscript{47}. The band bending at the semiconductor|metal interface is defined as the Schottky-type junction, which can hinder the interfacial charge transfer\textsuperscript{101}.  

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Not always problematic, the Schottky barrier can also separate photogenerated carriers and suppress the recombination of electrons and holes, thus improving the photocatalytic efficiency of the semiconductor\textsuperscript{102}.

Figure 2-1. Band diagrams of semiconductor\textpipe electrolyte interface, where the horizontal direction towards the left refers to distance from the interface to the bulk semiconductor. $\chi$ stands for work function and $A$ stands for electron affinity. $\phi_{\text{vac}}$, $\phi_{\text{CB}}$, $\phi_{\text{VB}}$, $\phi_{F}$, $\phi_{F,\text{redox}}$ are the electrical potentials of the vacuum, conduction band minimum, valance band maximum, the Fermi level of the semiconductor before or after contact, and the “Fermi level” of the redox electrolyte, respectively. $E(V \text{ vs. NHE})$ represents the electrochemical potentials are relative to the normal hydrogen electrode (NHE). (Adapted from ref. 47)

2.1.2 Band bending under applied bias

Band bending can also be controlled by the applied bias, influencing the charge separation capability at the semiconductor\textpipe electrolyte interface. To clarify, the applied bias ($V_{\text{appl.}}$) is determined versus a reference electrode (RE), which sets the Fermi level
position of the working electrode (WE), and we take the assumption that the Fermi level of the semiconductor equilibrates with the electrochemically-set Fermi level.

Exceptionally, band bending does not exist under the flat band condition, where $\phi_F = \phi_{F,\text{redox}}$, there is no net flow of electric charges through the interface, and the space charge region (SCR) does not exist (Figure 2-2, right)\textsuperscript{47}. The $V_{\text{appl.}}$ that leads to no band bending is called the flat band potential ($V_{FB}$)\textsuperscript{87}. As illustrated in Figure 2-2, the band bending can also be written as: $\Delta \phi_{SC} = \phi_F - \phi_{F,\text{redox}} = V_{FB} - V_{\text{appl.}}$. The bias dependence of $\Delta \phi_{SC}$ suggests that the capacitance of the SCR ($C_{SC}$) can be measured electrochemically, which is known as the Mott-Schottky method\textsuperscript{103,104}. The charges accumulated in the depletion region ($Q_{SC}$) is given in Equation 2-2, where $A$ is the semiconductor area.

$$Q_{SC} = \sqrt{2q\varepsilon_0\varepsilon_{SC}N_D A^2 \left(V_{FB} - V_{\text{appl.}} - \frac{kT}{q}\right)} \quad (2-2)$$

$$\frac{1}{C_{SC}^2} = \frac{1}{2q\varepsilon_0\varepsilon_{SC}N_D A^2} \left(V_{FB} - V_{\text{appl.}} - \frac{kT}{q}\right) \quad (2-3)$$

Furthermore, the Mott-Schottky equation (Equation 2-3) gives $C_{SC}$ as a function of the $V_{\text{appl.}}$, and a linear relationship between $1/C_{SC}^2$ and $V_{\text{appl.}}$ was found, and $V_{FB}$ is the intercept since $kT/q$ is usually negligible. Typically, flat band potential of n-type semiconductor lies 0.2~0.3V beneath the conduction band edge\textsuperscript{105-107}, and can be used to estimate the valence band edge according to the Mott-Schottky equation and band gap\textsuperscript{108,109}. Thus, $V_{FB}$ is critical to the electronic structure of the semiconductor and impacts on the (photo)electrocatalytic performance\textsuperscript{110}.
2.1.3 Band bending under illumination

The accumulation of charges and flow of charge under illumination is based on band bending. Appropriate illumination \((h\nu > E_g)\) produces photoexcited charges and breaks the equilibrium of charge distribution in the dark. This nonequilibrium leads to redistribution of charges in the space charge region (SCR), which generates new Fermi levels different from that of in the dark and are known as quasi-Fermi levels\textsuperscript{111}. Quasi-Fermi levels of electrons \((\phi_{F,n}^*)\) and holes \((\phi_{F,p}^*)\) split in the SCR since the charge carrier densities of electrons and holes can be independent of each other under illumination and this allows for both densities to be high. Still, using n-type semiconduction as an example (Figure 2-
3), when illumination strikes the semiconductor, a certain number of electrons and holes are generated. In n-type semiconductors, a relatively small difference in electron population exists when comparing dark and illuminated conditions since the majority of charge carriers are already electrons, and thus $\phi_{F,n} \approx \phi_F$. By contrast, the quasi-Fermi level of holes is significantly dependent on the photogenerated holes upon photoexcitation, showing a dramatic difference between the $\phi_{F,p}^*$ and $\phi_F$. The charge carrier densities lead to a difference between $\phi_{F,n}^*$ and $\phi_{F,p}^*$, which is the achievable photovoltage ($V_{ph}$) of the semiconductor|electrolyte system\textsuperscript{112}. Under strong irradiation, the system would approach the flat band condition, having the $\phi_{F,n}^*$ and $\phi_{F,p}^*$ energetically close to the conduction band edge and valence band edge, respectively.

![Band diagrams of an n-type photoanode under dark and illumination conditions. SC is short for semiconductor. (Adapted from ref. 47)](image)

### 2.2 Charge trapping and trap states

Charge trapping, one of the photophysical processes introduced in Section 1.4.1, is dependent on the trap states, which are spatially localized electronic states that exist in semiconductor bandgaps. The density of states (DOS) is one of the key concepts to understand charge carrier traps in semiconductors. Typically, DOS describes the
energetic distribution of electronic states within energy bands\textsuperscript{61}. For a perfectly ordered and crystalline semiconductor (e.g., crystalline Si), the band edges are well-defined, and the density of delocalized states has a $E/(eV)^{1/2}$ dependence and takes the form of a half-parabola\textsuperscript{113} (Figure 2-4a). In the semiconductor with weaker localization at the band edges (e.g., amorphous Si), an extended states tail extends into the band gap and creates localized states\textsuperscript{114}, which can be fitted in an exponential expression $g(E) = g_0 \times \exp(-E/E_0)$, where $g_0$ is the intrinsic density of the states, $E$ is the electronic energy, and $E_0$ is the breadth of the band tail in electronvolts\textsuperscript{115} (Figure 2-4b). We can also define a mobility edge, which is the threshold energy in the transition between localized trap states and delocalized states in the CB or VB\textsuperscript{116}. The DOS of the disordered polycrystalline and amorphous organic semiconductor film could also be approximated with a Gaussian distribution (Figure 2-4c)\textsuperscript{114,117} or an exponential distribution (Figure 2-4d)\textsuperscript{118}, which can be difficult to distinguish experimentally. The Gaussian distribution is further discussed in Section 2.3.

Figure 2-4. The DOS function of organic semiconductors that are (a) crystalline, (b) weakly-localized, polycrystalline/amorphous fitted with (c) Gaussian and (d) exponential models\textsuperscript{61}. 
A trap state is caused by the imperfection in the semiconductor, including the addition of the atom between perfect lattice sites, replacement or removal of the original atom at the same site. The introduction of a new atomic environment can bring new localized electronic states within the band gap, valence band (VB), as well as conduction band (CB) of the semiconductor. Adding states in the VB and CB does not influence much since they already have electronic states at those energies. On the contrary, the new electronic states have a marked effect on the charge carrier dynamics in the band gap for its previous lack of states at these energies. These trap states can capture electrons or holes depending on the energetic positions at a given temperature. As drawn in Figure 2-5, trap states are typically found below the mobility edges ($E_0$), where they can be shallow if located within a few $k_BT$ near the CB or VB edge or deep if they lie further than several $k_BT$ from the band edges. A shallow trap can capture a charge carrier temporarily until it is thermally activated to reach the mobility edge, while the low energy of deep traps severely impedes charges to escape thermally. They act as charge recombination centers where a trapped charge would localize spatially and eventually recombine with an oppositely-charged carrier, decreasing the overall lifetime of the charges.

Figure 2-5. Schematic of charge transport and charge recombination via shallow and deep trap states under thermal activation. The Y energy scale is drawn so that higher energy is upwards for both electrons and holes.
2.3 Charge transport in polymers

Charge transport in organic semiconductors, also one of the photocatalytic processes introduced in Figure 1-8, is crucial for solar energy conversion devices since how fast the charges transport does influence the photoactivity by changing the amount of charges transported to reactive sites within a specific time scale. Charge mobility is the term to describe the ability of electrons or holes to move through a specific material within an electric field in units of square centimeters per volt per second (cm² V⁻¹ s⁻¹), and it is affected by its crystal structure, chemical composition, and the impurities/defects⁶⁰,¹¹⁹. Broadly speaking, well-ordered materials tend to have a high charge mobility due to the lack of defects/traps that would localize charges and prevent charge carrier transport.

Multiple trap and release (MTR) and hopping transport are two classic models to describe charge transport in the organic semiconductor. In the MTR charge transport model (blue trace in Figure 2-6), charges keep moving within the delocalized states within the energy bands, being trapped by localized shallow trap states in the band gap and thermodynamically released back into the energy bands¹²⁰,¹²¹. With a high population of trap states, charge carriers hop from one localized trap state to another with the help of thermal activation, which is called hopping transport (orange trace in Figure 2-6)¹²². A high density of trap states reduces the charge mobility because of the high probability of charges being trapped, and complex trapping and de-trapping processes are involved. This reduced charge mobility could be associated with the shortening of charge carrier diffusion length, adversely affecting the charge transport to the semiconductor|electrolyte interface¹²³. Hence, the optimal charge mobility for transporting charges to the surface for subsequent redox reactions is often the focus of the studies.
Figure 2-6. The trap DOS function includes shallow traps from tail states and deep traps in the band gap (left). The energy diagram of an organic semiconductor with trap states. (right). (Adapted from ref. 61)

The correlation between trap DOS and effective transport energy is further discussed. The DOS function to describe the trap states within the band gap is referred to as the trap DOS, which is often found to be a Gaussian\textsuperscript{124} or an exponential distribution\textsuperscript{125,126}. The right panel in Figure 2-6 illustrates the deep trap states in the Gaussian distribution (red curve) and shallow traps in the exponential distribution (black curve). As mentioned before, researchers have found that organic semiconductors have a broad Gaussian distribution of electronic states\textsuperscript{117}. For Gaussian-shaped DOS ($g(E)$) expressed in Equation 2-4, the effective transport energy ($E_{tr}$) is defined as the energy at which the charge carrier equilibrium is established after hopping between the localized states\textsuperscript{21}, and is inversely correlated to the density of localized states (Equation 2-5).

\[
g(E) = \frac{N_i}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{E^2}{2\sigma_i^2}\right) + \frac{N_t}{\sqrt{2\pi}\sigma_t} \exp\left(-\frac{(E - E_t)^2}{2\sigma_t^2}\right) 
\]

\[
E_{tr} \cong 1.2kT \left(\frac{6\gamma^3}{\pi N}\right)^{\frac{1}{3}}
\]
Where \( N_i \) and \( N_t \) are the total densities of intrinsic states and traps, respectively; \( \sigma_i \) and \( \sigma_t \) is Gaussian vibrations of the intrinsic states and trap distributions, respectively; \( E_t \) is the energy of the trap DOS maximum; \( k \) is the Boltzmann constant; \( T \) is the temperature; \( \gamma \) is the inverse localization radius; \( N \) is the total density of localized states. To summarize, we have established that the charge mobility and thus charge transport in organic semiconductors are sensitive to the trap state distribution.

2.4 Electrochemical measurements

Based on photocatalysis, photoelectrochemical (PEC) application for water splitting can be achieved with an external applied bias. It spatially separates the half-reactions to different electrodes, where proton reduction occurs at the photocathode and water oxidation occurs at the photoanode. To decrease the complexity of the photoelectrochemical system, the fundamentals of electrochemical processes are first introduced as the background information for Chapter 4.

In this section, we will explain the setup and classification of the electrochemical measurements. In addition, the thermodynamics that govern the redox processes and bias-induced charge transfer will be discussed. Finally, the critical parameters for evaluating the electrocatalytic performance of the electrodes will be introduced.

2.4.1 Three-electrode electrochemical cell

Electrocatalytic measurements are used in Section 4.2.4, conducted in a three-electrode electrochemical cell connected to a potentiostat that supplies the external voltage. The overall chemical reaction in the electrochemical cell is made up of two independent half-reactions taking place at two electrodes. The one of interest occurs on the working electrode (WE), and the other occurs on the counter electrode (CE), and thus the circuit is completed with ionic current flowing through the electrolyte. The applied potential is the applied external bias with respect to the reference electrode (RE), which is
equivalent to controlling the energy of the electrons within the WE\textsuperscript{128}. By driving the electrode to a more negative potential, the energy of the electrons rises, reaching a high enough level to transfer into vacant electronic states in the electrolyte, and thus electrons flow from electrode to electrolyte. More specifically, a reduction current occurs\textsuperscript{128}. Similarly, an oxidation current could happen with a more positive applied potential. RE calibrates the measured/observed electrode potential of both the WE and CE to a known standard potential scale, whose standard potential is measured as the redox potential of a specific redox couple.

The electrochemical potential of a redox couple is determined by the ratio of the oxidized and reduced species, which is given in the Nernst equation\textsuperscript{128} (Equation 2-6).

\[
E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{red}]}{[\text{ox}]} \quad \text{(2-6)}
\]

Where \(E\) is the measured/observed electrode potential; \(E^\circ\) is the standard electrode potential; \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); \(T\) is the temperature in Kelvin; \(n\) is the number of electrons evolved in the reaction; \(F\) is the Faraday constant (96485 C mol\(^{-1}\)).

The standard hydrogen electrode (SHE), one of the common standard potential scales, is measured under the equilibrium of \(2H^+ + 2e^- \rightleftharpoons H_2\) in a 1 M acidic solution (pH=0) under 1 bar H\(_2\)(g)\textsuperscript{129}. The standard electrode potential of \(2H^+(aq)/H_2(g)\) is defined as zero volts, and the Nernst equation can be further taken to Equation 2-7 to add a consideration for pH:

\[
E = E^\circ - \frac{RT}{nF} \ln \frac{p_{H_2}}{[H^+]^2} = E^\circ - \frac{0.059V}{2} \log \frac{1}{[H^+]^2} = E^\circ - 0.059V \times pH \quad \text{(2-7)}
\]

The SHE is collected in strict conditions. To compare potentials in different pHs more conveniently we can use the reversible hydrogen electrode (RHE). Unlike other reference electrodes, its potential is not fixed and deviates from that of SHE according to Equation 2-7\textsuperscript{129}. When H\(_2\)(g) stays as 1 bar under T=298.15 K, and the activity of H\(^+\)
decreases (pH increases), the value of E decreases by 59 mV per pH unit. The zero potential of the RHE changes with pH value and mirrors the shift in redox potentials of the proton reduction and water oxidation half-reactions, making their potentials pH-independent.

Silver chloride aqueous electrode is the reference electrode mainly used in this work, it relies on the equilibrium between the solid silver and solid salt (silver chloride) in a potassium chloride solution of a given molarity\textsuperscript{128}, and its standard potential is given by

**Equation 2-8:**

\[
E_{Ag/AgCl}^\theta = E_{Ag/AgCl}^o - 0.059 \log[Cl^-] = 0.222V - 0.059V \log[Cl^-] \tag{2-8}
\]

\[E_{Ag/AgCl}^\theta = 0.194 \text{ V vs. NHE} \] when using 3M KCl at 25° C. The observed electrode potential with a Ag/AgCl reference electrode can be converted into RHE potentials\textsuperscript{130} following **Equation 2-9:**

\[E_{vs.RHE} = E_{Ag/AgCl} + 0.059V \times pH + E_{Ag/AgCl}^\theta \tag{2-9}\]

For example, using an Ag/AgCl KCl(3M) reference electrode in an electrolyte of pH=7, 0 V vs. Ag/AgCl can be converted to 0.607 V vs. RHE. The conversion among different standard potential scales is illustrated in **Figure 2-7.**

![Figure 2-7. Conversion between some standard potential scales.](image-url)
2.4.2 Thermodynamics and redox processes

The link between the redox potential of half-reactions and the thermodynamics of the overall reaction (Δ𝐺) is introduced in this section. Theoretically, a redox reaction can spontaneously occur if the charge transfer is energetically favorable or exergonic (Δ𝐺 < 0)\textsuperscript{131}.

\[ ΔG = -nFE_{rxn}^o \]  
\[ E_{rxn}^o = E_{cathode (reduction)}^o - E_{anode (oxidation)}^o \]  

The potential difference between the reduction reaction at the cathode and the oxidation reaction at the anode is the standard potential of a redox reaction (E\textsubscript{rxn}^o). n is the number of electrons evolved in the reaction and F is the Faraday constant of 96485 C mol\textsuperscript{-1}.

Holes flowing out of a semiconductor \((PC^* (h^+) \rightarrow PC + h^+)\) can be seen as a reduction process, where \(E_{cathode (reduction)}^o = E_{VB}^o\), and \(E_{VB}^o\) can be seen as the ground state redox potential of the semiconductor. In contrast, an electron flowing out of a semiconductor \((PC^* (e^-) \rightarrow PC + e^-)\) is regarded as an oxidation process, where \(E_{anode (oxidation)}^o = E_{CB}^o\), and \(E_{CB}^o\) can be seen as the excited state redox potential.

As drawn in Figure 2-8, electrons in the conduction band can participate in a reduction half-reaction if the electron acceptor has a more positive redox potential than the conduction band edge. The processes can be written as: \(E_{rxn}^o = E_1^o - E_{CB}^o < 0, \Delta G > 0\), energetically unfavorable; \(E_{rxn}^o = E_2^o - E_{CB}^o > 0, \Delta G < 0\), energetically favorable.

In contrast, holes in the valence band could transfer to the hole acceptor if it has a more negative redox potential than the valence band edge. Based on the energetics, the processes can be written as: \(E_{rxn}^o = E_{VB}^o - E_3^o > 0, \Delta G < 0\), energetically favorable; \(E_{rxn}^o = E_{VB}^o - E_4^o < 0, \Delta G > 0\), energetically unfavorable.
Based on the energetics of the semiconductor and redox potentials of the redox reactions, the feasibility of the charge transfer can be conveniently recognized, which benefits the selection of an appropriate semiconductor for a specific redox reaction when designing the photocatalytic and photoelectrochemical systems.

Figure 2-8. Schematic illustration of charge flow based on the redox potential of the half-reactions and the energetics of the semiconductor.

2.4.3 Bias-induced charge transfer in organic semiconductor

We have described the band bending of semiconductors that occurs under applied bias in Section 2.1.2. Now we want to convey that bias-induced band bending can lead to a powerful driving force for charge transfer across the interface, and this is further discussed in Section 4.2.4. Upon polarization through the applied bias in the presence of a counter electrode, a varying applied bias continuously shifts the Fermi level in the working electrode.

The redox reactions are kicked off when the position of the Fermi level relative to the redox potential of the redox couple allows the thermodynamic flow of the charges to
where the energy is lower. In other words, negatively charged electrons would like to flow from more negative electrochemical potential to more positive electrochemical potential.

Figure 2-9. An n-type semiconductor with Fermi level located differently under applied biases or not in the dark. EC HER and OER are short for electrochemical hydrogen evolution reaction and oxygen evolution reaction.

As shown in Figure 2-9, with a new Fermi level position that is more electrochemically positive than the H2O/O2 couple, the system can transfer holes from the valence band across the interface for water oxidation. Similarly, the applied bias can relocate the Fermi level to where it is more negative than the H+/H2 couple, initiating proton reduction by flowing the electrons to the redox couple. In the latter circumstance, the band bending is relieved and the flat band condition is potentially achieved with a more negative applied bias. Though the barrier inhibiting electrons from crossing the interface is lowered and electrons could cross the semiconductor|electrolyte interface more thermodynamically, band bending is regarded as a more powerful driving force to flow charges to the surface.

Similar discussions are found in semiconductor|metal heterojunction, where the field-induced charge transfer at the semiconductor|metal interface could be switched by
reversing the external electric field, and the role of the metal could be altered electrically between the electron acceptor and electron donor under the positive or negative voltage, respectively\textsuperscript{132}.

2.4.4 Common electrochemical measurements

Electrochemistry correlates the flow of electrons to chemical transformations, and electrochemical measurements are used as a powerful tool to probe electron transfer in redox reactions\textsuperscript{133}. Common electrochemical measurements as well as electrochemical impedance spectroscopy are introduced in this section.

2.4.4.1 Cyclic voltammetry, linear scan voltammetry, and chronoamperometry

In electrochemical reactions, for example, in HER, the rate of H\textsubscript{2} generation is proportional to the number of electrons transferred from the reactants to products. In an electrochemical measurement, this is reflected as the current density and can be obtained by techniques such as cyclic voltammetry (CV), linear scan voltammetry (LSV), and chronoamperometry. Each measurement is performed under different types of controlled conditions. For example, the applied potential in CV is continuously changing over time in a sawtooth pattern, but it is swept linearly in LSV, and fixed in chronoamperometry.

CV can be used to investigate electron transfer-initiated chemical reactions, and it is plotted as the current (I) that passes the electrode against the applied potential. As shown in Figure 2-10, IUPAC convention states that the applied potentials are shown as low to high potentials from left to right\textsuperscript{133}. The cathodic/reduction peak is caused by linear sweeping from higher to low potentials, showing a negative current. Oppositely, the anodic/oxidation peak and positive current contributed to the reversed sweep direction. Half-wave potential (E\textsubscript{1/2}) is defined as the potential in the middle of cathodic and anodic peak potentials\textsuperscript{134}, used as a straightforward way to estimate the redox potential for redox couples\textsuperscript{135}. CV can also provide information about the stability\textsuperscript{136} and reversibility\textsuperscript{137} of
electrochemical processes by observing the changes in peak amplitudes and positions after continuous cyclic sweeping. The experimental results and data analysis when using CV tools can be found in Sections 4.2.1 and 4.2.3.

Figure 2-10. IUPAC convention of CV scans with current against potential.$^{133}$

LSV is another commonly used tool to study the redox behavior of electroactive species, in which the potential is swept linearly from one potential to another (see details in Section 4.2.4). LSV is typically applied in simpler systems with fewer different redox processes. The current density at a specific potential conveniently represents the reaction rate, and this current-potential characteristic can further provide information for onset potential, Tafel slope, and overpotential, which are introduced in Section 2.4.5. In photoelectrocatalytic systems, chopped light LSV can monitor the photocurrent and transient current response upon photoexcitation$^{138,139}$, from which the degree of charge recombination can be analyzed$^{140}$.

Chronoamperometry can be classified into two modes. Potentiostatic mode holds the potential as a constant and measures the current to collect an I-t plot (used in Section 4.2.5), and galvanostatic mode keeps the current constant and records the potential change against time (V-t plot). Similar to LSV scans, the I-t plot gives photocurrent under certain potentials (e.g., open circuit potential, 1.23 V vs. RHE), and the behavior of charge recombination can be analyzed from the transient current response as well$^{141,142}$. 
2.4.4.2 Electrochemical impedance spectroscopy

The similarity between an electrochemical reaction and an electric circuit is that inputting a voltage would output a corresponding electrical/current signal. This input-output relationship allows correlating the electrochemical reactions to electrical circuits and is accepted as the basics of electrochemical impedance spectroscopy (EIS) technique, which is used in Section 4.2.6.

Impedance (Z) is used as a general term when current is impeded in a circuit, and resistance (R) describes the special impedance under direct current conditions\(^{143}\). The whole electrochemical reaction can be expressed as an impedance, whilst EIS is a technique to measure the impedance of an electrochemical system as a function of frequency. It applies a small sinusoidal voltage to the system in a frequency range and collects the resulting current response\(^{143}\). Impedance usually changes with frequency and behaves differently within the varying frequency range. For example, a capacitor behaves like a low impedance (i.e., short circuit) at high frequencies and like a high impedance (i.e., open circuit) at low frequencies. In contrast, a resistor behaves like a constant impedance throughout the frequency regime. From there, the results can be analyzed to provide information about the charge flow in the system, such as the resistance and capacitance of the electrolyte, the charge transport resistance, the interfacial charge transfer resistance, and the double-layer capacitance. These values can be further used to explain the mechanisms and kinetics of the electrochemical reaction.

Total Impedance \(Z (Z=Z_{\text{Im}}+jZ_{\text{Re}})\) is composed of imaginary (\(Z_{\text{Im}}\)) and real (\(Z_{\text{Re}}\)) components\(^{143}\), where the former is usually capacitive, and the latter is resistive, and thus impedance can be expressed as the vector sum of the capacitance and the resistance of the circuit. The imaginary versus real impedance is known as the Nyquist plot, and the Bode plot is plotted with phase angle \(\phi\) against frequency\(^{144}\). \(\phi\) represents the phase shift between the applied sinusoidal voltage and the resulting delayed sinusoidal current\(^{144}\) and can be calculated from \(\tan \phi = |Z_{\text{Im}}|/|Z_{\text{Re}}|\). As shown in Figure 2-11, the smaller value at \(Z_{\text{Re}}\)
axis corresponds to the behavior at the high-frequency region, and $Z_{Re}$ axis thus displays, from left to right, the data points obtained from high frequency to low frequency.

Figure 2-11. An example of tridimensional impedance\textsuperscript{144}, where $Z''$ and $Z'$ stands for the imaginary part ($Z_{Im}$) and real part ($Z_{Re}$) of the impedance, respectively.

Electrical components bring physical meaning to the EIS. The correlation of the equivalent circuit and Nyquist plot can be simplified\textsuperscript{144} as presented in Figure 2-12. Resistor (R) has no imaginary part and is shown as a dot on the $Z_{Re}$ axis in the Nyquist plot, corresponding to the resistance in ohm. A capacitor (C) alone has the real part at $Z_{Re}=0$, shown as a vertical line overlapped with the $Z_{Im}$ axis (Figure 2-12a). When a capacitor is in series with a resistor, the R-C circuit is shown as a vertical line in parallel to the $Z_{Im}$ axis and perpendicular to the $Z_{Re}$ axis, intersecting at $Z_{Re}=R_1$ (Figure 2-12b). When the capacitor is in parallel to a resistor, the circuit is written as RC, a semicircle is shown, and its diameter equals to $Z_{Re}=R_2$, which is typically interpreted as the interfacial charge transfer resistance (Figure 2-12c). In addition, when $R_1$ is series with the RC branch, the circuit is written as $R(RC)$, and the semicircle shifts to higher values by a constant resistance $R_1$, which is usually regarded as the solution resistance of the electrolyte (Figure 2-12d). A Warburg impedance ($Z_w$), an element for mass transfer or diffusion\textsuperscript{144}, usually appears at the intermediate frequency regime as a straight line with a slope of 1.
in the Nyquist plot\textsuperscript{145} and disappears at extremely high frequencies where mass transfer does not occur (Figure 2-12e).

When $Z_w$ is introduced to the equivalent circuit, a classic model $R(C(RW))$ is thus built up in Figure 2-12f. $C_2$, the double layer capacitance, originates from the non-active ions around the electrode|electrolyte interface, which changes the charge distribution but does not drive the chemical reactions; charge transfer resistance $R_2$ in series with Warburg impedance $Z_w$ compose the faradaic impedance, arising from the reactive species near the electrode|electrolyte interface, where charge transfer and mass transfer exist. Charge transfer dominates the high-frequency region (kinetically-controlled region), while mass transfer takes the lead on the low-frequency region (diffusional-controlled region)\textsuperscript{146}. The ideal model is designed for the planar electrode, and the straight line of the impedance diffusion may deviate from $45^\circ$ due to the roughness of the electrode\textsuperscript{147}. Therefore, in the realistic equivalent circuit model $R(Q(RW))$, a constant phase element (CPE or Q) instead of $C$ is used\textsuperscript{148}. Furthermore, the electrode roughness could bring inhomogeneity of the electric field and double-layer capacitance variation at the electrode/electrolyte interface, causing the suppressed or rotated semicircle (Figure 2-12g)\textsuperscript{148,149}.

Figure 2-12. Schematic illustration of equivalent circuits and corresponding Nyquist plots.
2.4.5 Electrocatalytic performance and critical parameters

Electrocatalytic performance is a term describing the ability of a material to catalyze electrochemical reactions. It is evaluated based on its activity (the rate of product generation or current density), selectivity (the ability to catalyze a specific reaction and produce a certain product), stability (the duration of maintaining its activity and selectivity under working conditions), durability (resistance towards the degradation of the materials), morphology, and surface area (the amount of reactive sites). Electrocatalytic performance is determined by a series of critical parameters, including the onset potential, overpotential, exchange current density, Tafel slope, and the Faradaic efficiency, which are introduced in the following sections.

2.4.5.1 Onset potential and overpotential

The onset potential is often defined as the least negative (positive) potential at which the faradic current is monitored or the reduction (oxidation) reaction product is produced under certain conditions\textsuperscript{150}. The overpotential ($\eta$), discussed in Section 4.2.4, is the additional potential versus the thermodynamic redox potential that is applied to the working electrode to initiate an electrochemical reaction or to drive a redox reaction at a certain rate\textsuperscript{128,130}. The overpotential at the arbitrary 10 mA cm\textsuperscript{-2} is often used to evaluate the performance of an electrode\textsuperscript{151,152}. This is because the theoretical onset overpotential value has a huge difference compared to the experimental values since the kinetic constraints are not considered while calculating the thermodynamics of the overpotential\textsuperscript{153}. Notably, 10 mA cm\textsuperscript{-2} is approximately the metric current density expected for a solar-to-fuel conversion device to exhibit 10% efficiency under 1 sun illumination (AM 1.5 or 1000 W m\textsuperscript{-2})\textsuperscript{154,155}.

Overpotential is caused by various losses during the electrochemical processes, including activation barrier, kinetic losses, mass transport limitation, and ohmic resistance\textsuperscript{153}. For example, the theoretical water splitting voltage is 1.23 V vs. RHE, which
is composed of two half-reactions (HER at 0 V vs. RHE; OER at 1.23 V vs. RHE)\textsuperscript{151}. With overpotential, a potential more negative than 0 V vs. RHE would be required to initiate the hydrogen evolution process, and a potential more positive than 1.23 V vs. RHE is necessary for oxygen generation (Figure 2-13). Smaller overpotentials are always preferred to reduce the extra energy input. Superior HER processes show overpotentials close to 0 V, typically in tens of millivolts\textsuperscript{8,156}. However, OER is a more complicated four-electron evolved reaction, it usually has larger overpotential up to a few hundred millivolts\textsuperscript{8}.

![Figure 2-13. Overpotential in HER and OER processes.](image)

**2.4.5.2 Tafel slope and exchange current density**

Generally, the current is limited wholly or partially by the reaction rate, which is related to the electro-reactants transported to the electrode surface. Under the condition that mass transport is not an issue, interfacial dynamics affect the current, under which the current is often related exponentially to the overpotential $\eta$, and the equation is known as the Tafel equation\textsuperscript{157} (Equation 2-12). The Tafel slope simply describes the increase in overpotential when the reaction rate increases by a factor of ten (Figure 2-14), and this parameter is used in Section 4.2.4 to evaluate the electrocatalytic performance of the CN\textsubscript{x} electrode.

$$\eta = a + b \log j$$

(2-12)
\[ a = \frac{2.3RT}{\alpha F} \times \log j_0 \]  
\[ b = -\frac{2.3RT}{\alpha F} \]  

Here \( j \) represents the current density in A cm\(^{-2}\); \( b \) is the Tafel slope in V decade\(^{-1}\); \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); \( \alpha \) is the cathodic transfer coefficient; \( F \) is the faraday constant (96485 C mol\(^{-1}\)) ; \( T \) is the temperature in Kelvin. Thus, the exchange current density \( j_0 \) can be determined from a Tafel analysis.

Figure 2-14. An example of a current-overpotential curve with the slope as Tafel plots for anodic and cathodic sides\(^{128}\).

Tafel slope analysis is mainly dependent on the characteristic current density-potential (J-V) curve, and its values correlate to the onset potentials of the redox reactions. It is widely reported that a low Tafel slope is correlated with a low onset potential and a high exchange current density\(^{158-160}\), which assumes that the change in the reaction rate is solely due to the change of the rate constant under different applied potentials. However, more than one factor could affect the current density versus applied potentials. In Francàs et al.'s research\(^{161}\) on water oxidation electrocatalysts, FeOOHNiOOH and Ni(Fe)OOH electrodes exhibited similar electrocatalytic performance towards the water oxidation
reaction, shown as almost overlapped J-V curves. However, FeOOH-NiOOH tends to accumulate more charges while it has a slower rate constant compared to Ni(Fe)OOH at the same applied potentials, leading to a similar activity overall. In addition, the non-uniform density of states exists in these materials since the accumulated charges are not linear with the applied bias\textsuperscript{162}. Not solely the reaction constants but also the density of states determine the reaction rate, and the potential dependence of these two factors were observed. Furthermore, though the reaction order calculated from the spectroelectrochemical study was the same for the two electrodes, the corresponding Tafel slopes were different. Thus, they stated that the different Tafel slopes depend more on the change of charge density upon applied biases instead of being indicative of different reaction mechanisms. Therefore, a combination of reaction kinetics and charge accumulation synergistically contributed to the J-V behavior and thus affected the Tafel slope is revealed.

2.4.5.3 Faraday efficiency

The Faraday efficiency (FE), also known as the faradaic efficiency\textsuperscript{163}, is defined as the ratio of the charges consumed by the reaction to the charges passed through the system (Equation 2-15). Especially, in (photo)electrocatalytic processes in which gases are produced (e.g., HER and OER), the FE can be further clarified to the ratio of the experimentally collected gas to the amount of theoretically calculated gas based on the (photo)electrochemical current (Equation 2-16). The FE of a specific reaction is usually lower than 100% mostly because the secondary reactions are ongoing\textsuperscript{164}. A high value of the FE indicates a high selectivity to the target product.

\[
FE = \frac{\text{the amount of charges passed through}}{\text{the amount of charges consumed}} \times 100\% \quad (2-15)
\]

\[
FE = \frac{\text{experimental amount of target product}}{\text{theoretical amount of target product}} \times 100\% \quad (2-16)
\]
2.5 Atomic layer deposition

Atomic layer deposition (ALD) is chosen as one of the methods to deposit cocatalysts on our light absorber material for better photocatalytic performance in chapter 3 (see Section 3.2.1). ALD has developed as a state-of-the-art technique for its thin film deposition of uniformity on complex three-dimensional topographies\textsuperscript{165}. Its deposition is mainly based on the gas-solid reactions of two gaseous reactants. More specifically, the reactant made of the metal compound is usually called “precursor,” and the other non-metal compound is “reactant.” The saturating, irreversible, and separated gas-solid reactions between the precursor and the reactant make it outcompete other thin film deposition approaches (e.g., chemical vapor deposition (CVD))\textsuperscript{166}.

Typically, one ALD cycle is composed of four steps as follows (Figure 2-15)\textsuperscript{166}. Firstly, in step 1a, the gas-solid reaction happens with the precursor (Reactant A or precursor) chemically absorbed on the substrate. Secondly, evacuation is conducted to remove unreacted precursors and gaseous byproducts in step 1b. Thirdly, in step 2a, the second gas-solid reaction occurs with a non-metal reagent (Reactant B) reacting with the absorbed precursor. Finally, the second evacuation proceeded to remove the unreacted reactant and gaseous byproduct in step 2b. One ALD cycle of four steps is thus completed, after which the thickness increase is defined as growth per cycle (GPC) to evaluate the growth rate of the ALD processes.
Figure 2-15. Schematic illustration of a ALD reaction cycle consisting of four steps (from bottom to up)\textsuperscript{166}.

In addition, the ALD technique stands out for its saturating and irreversible reactions, which are called self-limiting or self-terminating characteristics\textsuperscript{165}. Specifically, the saturating feature allows the same amount of reactants absorbed on different parts of three-dimensional substrates, which is independent of available reactants, exposure, and purge times. The other irreversible feature guarantees that the desorption will not occur over time. Interestingly, the partial pressure of the vaporized reactant or precursor would not influence the amount of material adsorbed on the substrate for the saturating and irreversible reactions\textsuperscript{165}. As shown in Figure 2-16, only case A is qualified for the atomic layer deposition since it is irreversible and saturated after a certain period of time, automatically leading to the same amount of materials adsorbed on the substrates no
matter how complicated the surface morphology is. Then the timely purging prevents the precursor and reactant from reacting in the gas phase, which allows the same amount of material to be deposited per cycle.

Figure 2-16. Schematic illustration of five types of adsorptions\textsuperscript{166}. (a) qualified irreversible and saturating adsorption for ALD processes. (b) reversible and saturating adsorption. (c) combination of reversible and irreversible saturating adsorption. (d) irreversible non-saturating adsorption. (e) irreversible saturating adsorption before saturation. The dashed vertical line denotes the end of precursor or reactant pulse. (Adapted from ref. \textsuperscript{166})

What is more, ALD processes have a weak dependence on temperature, which is not the case in CVD. Generally, CVD processes are strongly temperature-dependent and the growth rate in the surface-reaction-limited regime follows the Arrhenius-type relationship, which increases exponentially with the deposition temperature. However, ALD growth per cycle (GPC) could slightly increase or decrease, stay constant, or maximize as a function of the temperature (Figure 2-17). It was found that per 100° C increase during the ALD processes of Al\textsubscript{2}O\textsubscript{3} using AlMe\textsubscript{3} and H\textsubscript{2}O only led to a linear decrease in growth per cycle by about 20% within the temperature range of 180° C to 300 °C\textsuperscript{167}. 
Overall, the ALD technique has realized deposition accuracy by achieving precisely controlled thickness and extremely homogenous surface and has been utilized as a sophisticated tool in material modification in photocatalysis\textsuperscript{168,169} and thin film deposition in photo(electro)chemical applications\textsuperscript{170–172}.

![Diagram](image)

Figure 2-17. Schematic illustration of weak temperature-dependent ALD growth per cycle. Growth per cycle (a) decreases with temperature, (b) increases with temperature, (c) is temperature-independent, and (d) maximizes at a specific temperature. (Adapted from ref. 166)
Chapter 3: ALD-Deposited NiO Approaches the Performance of Platinum as a Hydrogen Evolution Cocatalyst on Carbon Nitride

Chapter 3 is based on my first-author paper published on *ACS catalysis*: Liu, C.; Liu, J.; Godin, R. ALD-Deposited NiO Approaches the Performance of Platinum as a Hydrogen Evolution Cocatalyst on Carbon Nitride. *ACS Catal.* 2023, 13, 573–586. https://doi.org/10.1021/acscatal.2c04795. The experiments, data analysis, and manuscript writing contributed to this project were conducted on my own, under the supervision of my two supervisors, Dr. Jian Liu and Dr. Robert Godin. The content is reprinted with permission from ref. 256. Copyright 2023, American Chemical Society. The formatting is adjusted according to the thesis format. Supporting information 1 mentioned in this chapter can be found under DOI: 10.1021/acscatal.2c04795, where Figure SX represents Figure S3-X in this chapter, the same for the tables.

3.1 Introduction

The efficient utilization of solar energy, the most promising renewable energy resource, remains one of the pressing objectives for addressing the energy crisis as well as mitigating catastrophic climate change in the 21st century. To realize conversion from sunlight to chemical energy as an alternative to traditional fossil fuel energy, semiconductor photocatalysis has been widely studied and has the benefit of effective energy storage in energy-dense chemical molecules (i.e., solar fuels)48. Photocatalytic hydrogen evolution reaction (HER, $2H^+ + 2e^- \rightarrow H_2$) is the half-reaction of the overall water splitting ($2H_2O \rightarrow 2H_2 + O_2$) and is regarded as a desirable reaction due to the high energy density of hydrogen and its pollution-free product173,174. Further development of photocatalytic solar energy conversion to generate high-energy solar fuels is needed to address the global energy crisis and is in line with the “Net Zero by 2050” report from the International Energy Agency (IEA)4 which states that massive deployment of all available clean and efficient energy technologies is required to stay on track for net zero CO$_2$.
emissions in the energy sector by 2050. This is needed to limit the increase of average global temperatures to 1.5 °C as targeted in the Paris Agreement.

Metal-free carbon nitride (CN$_x$) material emerged as a photocatalyst for water splitting half-reactions in 2009\textsuperscript{18}. CN$_x$ is made from earth-abundant elements and inexpensive precursors. In addition, it has a suitable optical band gap (2.7 eV) for visible light absorption, strong reduction ability for hydrogen generation and carbon dioxide reduction, facile synthetic approaches, and high (photo)chemical stability\textsuperscript{38}. Though CN$_x$ is one of the leading materials for particulate photocatalytic solar energy conversion so far, the performance of systems coupled with water oxidation is still too low for widespread use. Limitations of pristine CN$_x$ include limited light absorption of the solar spectrum, faster charge recombination compared to the kinetically competing redox reactions, and low charge carrier mobility ($\mu_h$: $1.7 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ from field effect measurements)$^{175,176}$ compared to 2D organic materials, for instance, boron carbon nitride ($\mu_h/\mu_e$: 5-20 cm$^2$ V$^{-1}$ s$^{-1}$)$^{177,178}$ and CN$_x$ monolayer ($\mu_e$: 1617.52 cm$^2$ V$^{-1}$ s$^{-1}$)$^{179}$, and other organic conjugated polymers, like common poly-3-hexylthiophene (P3HT) material ($\mu_h$: $10^{-4} \sim 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$)$^{180}$.

The photocatalytic solar fuel production process can be separated into four steps: light absorption by the light absorber, charge generation of electron-hole pairs, charge transport to the surface of the semiconductor, and interfacial charge transfer for surface redox reactions\textsuperscript{55}. Only photogenerated charges that are transported to the surface of the semiconductor can participate in the chemical redox reactions. Then, charges that have thermodynamically sufficient redox potentials enable the reaction to occur, but charge recombination still could happen if there is a lack of suitable reactive sites on the photocatalyst\textsuperscript{19}. The addition of a cocatalyst on the surface can extract charges from the photocatalyst, suppressing unproductive charge recombination and promoting the surface redox reaction. As a result, the photocatalytic ability is enhanced\textsuperscript{36}.
Noble metal-based cocatalysts, including Pt, Pd, Ru, Ag, and Ir, have been extensively explored for their notable impact on accelerating the HER\textsuperscript{181}. Nevertheless, their use in scaled-up applications is severely restricted by their low global reserves and/or high cost\textsuperscript{20,21}. Hence, researchers shifted their focus to more abundant transition metal-based HER cocatalysts\textsuperscript{8}, including metal phosphides (Co\textsubscript{2}P, Ni\textsubscript{2}P, NiCoP)\textsuperscript{182,183}, metal sulfides (CdS and MoS\textsubscript{2} quantum dots)\textsuperscript{184,185}, metal carbides\textsuperscript{186}, and other metal complexes\textsuperscript{187,188}. However, satisfactory HER activities are accompanied by complicated synthesis methods and poor stabilities, preventing widespread use.

Thus, nickel oxide (NiO\textsubscript{x}) cocatalysts, as one of the metal oxides, have attracted attention due to their easier fabrication, lower cost, and long-lasting chemical stability. In Deng’s work\textsuperscript{189}, the hierarchical CdS/NiO nanospheres were constructed by a microwave-assisted wet chemical process, and the synergistic effect brought by this p-n heterojunction led to an apparent quantum yield (AQY) of 11.65% towards HER under solar simulation. Overall water splitting was even demonstrated by \textit{in situ} photodepositing an ultrathin NiO layer on the Zn\textsubscript{1-x}Cd\textsubscript{x}S photocatalyst, with an AQY approaching 0.66\%\textsuperscript{190}. Furthermore, NiO\textsubscript{x} has a decent carrier mobility of $\sim 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and the assembly of the sol-gel derived NiO\textsubscript{x} thin film on perovskite solar cells helped reach a power conversion efficiency of 17.03% because of the faster hole extraction, suppressed recombination, and well-aligned energy levels between the perovskite layer and NiO\textsubscript{x}\textsuperscript{191}. In a paper published in 2018\textsuperscript{192}, Liu \textit{et al.} synthesized amorphous NiO-decorated graphitic carbon nitride (NiO/g-C\textsubscript{3}N\textsubscript{4}) by post-annealing of Ni(OH)\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}, and applied it to water reduction under visible light illumination. The inner electric field created by NiO/g-C\textsubscript{3}N\textsubscript{4} heterojunction allowed the photogenerated electrons to transfer from the photocatalyst to the cocatalyst and therefore promoted the photogenerated charge carrier migration as well as separation. Later, in the work of Zhang \textit{et al.}\textsuperscript{193}, a nickel complex (NiL) and NiO\textsubscript{x} were incorporated into CN\textsubscript{x} in sequence to prepare yNiL/NiO\textsubscript{x}/CN\textsubscript{x} through a bimolecular nucleophilic substitution reaction. The NiL complex worked as the cocatalyst, while the NiO\textsubscript{x}
nanoparticles were the hole transporting medium. The optimized ternary hybrid system exhibited an AQY of 1.46% at 450 nm under sacrificial conditions, which is the best AQY previously reported for the Ni/NiO<sub>x</sub> with CN<sub>x</sub> towards photocatalytic HER.

The reported NiO synthesis so far has concentrated on traditional solution-processed approaches (e.g., hydrothermal and thermal decomposition)<sup>194</sup>, while its disadvantages, such as uneven coating particle size and heterogeneous distribution, are becoming increasingly apparent<sup>195</sup>. Atomic layer deposition (ALD) is a state-of-the-art technique for achieving uniform deposition on the complex three-dimensional substrate with conformal morphology, and this technique is gaining attention for its self-terminating gas-solid reactions, which are independent of available reactant, exposure, and purge times<sup>166</sup>. Therefore, it has boosted the deposition accuracy by achieving precisely controlled thickness and an extremely homogenous surface.

Herein, we decorated flake-like CN<sub>x</sub> with NiO by plasma-enhanced atomic layer deposition (PEALD). The CN<sub>x</sub> was calcinated as a film after a dip-coating process that produced a thiourea layer on the FTO substrate. The optimized NiO/CN<sub>x</sub> heterostructure as a particulate photocatalyst showed the highest AQY of 3.1% (at 405 nm) for H<sub>2</sub> production compared to previously reported NiO/CN<sub>x</sub> systems and exhibited a significant 54% of the H<sub>2</sub> production performance compared to Pt/CN<sub>x</sub> with the benchmark Pt cocatalyst. For Pt/CN<sub>x</sub> materials, H<sub>2</sub> production starts immediately upon light irradiation. However, this is not the case for our NiO/CN<sub>x</sub> heterostructures, which showed a noticeable induction period after illumination. A similar phenomenon was observed when using NiCl<sub>2</sub> as an alternative Ni precursor to photodeposit metallic Ni species on the surface of CN<sub>x</sub>. We propose that the induction period is related to reversible redox processes involving different oxidation states of Ni that can be formed under light irradiation. To reveal the underlying mechanism and explain the mechanism that differs from the benchmark Pt/CN<sub>x</sub>, photoinduced absorption spectroscopy (PIAS) was used to monitor the charge carrier dynamics on the seconds timescale.
3.2 Result and discussion

3.2.1 Particulate photocatalyst and morphology

NiO/CN\textsubscript{x} was synthesized by thermal polymerization of CN\textsubscript{x} and ALD deposition of NiO, as shown in Figure 3-1. Based on Qin’s work published in 2020\textsuperscript{196}, a uniform ca. 30 μm thick layer of CN\textsubscript{x} was formed on fluorine-doped tin oxide (FTO)-coated glass by dipping the slides in hot saturated aqueous thiourea solution and then calcinating at 500 °C for 2 h (Figure S3-1a). The FTO-coated glass was chosen for the subsequent deposition since CN\textsubscript{x} robust film formation fails on the bare glass substrate (Figure S3-2). The ALD growth of NiO on the CN\textsubscript{x}/FTO was done using bis(cyclopentadienyl)nickel and plasma-processed oxygen as the Ni precursor and co-reagent, respectively\textsuperscript{197}. The growth rate was determined to be 0.1 nm per cycle. We name the samples with the number of NiO ALD cycles indicated in brackets; NiO(20)/CN\textsubscript{x}, NiO(50)/CN\textsubscript{x}, NiO(65)/CN\textsubscript{x}, and NiO(150)/CN\textsubscript{x} were prepared and correspond to CN\textsubscript{x} decorated with 2, 5, 6.5, and 15 nm thick NiO films, respectively. Thus, four different cocatalyst loadings were obtained and further studied.

Morphological characterization of CN\textsubscript{x} and NiO/CN\textsubscript{x} was conducted by Scanning Electron Microscope (SEM). The dip-coating technique grows a ca. 30 μm thick CN\textsubscript{x} film (Figure S3-1a) with a flake-like structure with distinct voids around 20 μm in diameter or smaller (Figure S3-1b). Such a 3D porous structure exposes sufficient specific area for further cocatalyst loading and should offer abundant reactive sites for photocatalytic reactions. The porous CN\textsubscript{x} structures were conserved after NiO modification (Figure 3-2b-e). The peeling and grinding during sample preparation broke a proportion of the CN\textsubscript{x} protrusions, while the flake-like morphology was well preserved (Figure 3-2a vs. Figure S3-1b). Deposited NiO was detected by Energy-dispersive X-ray spectroscopy (EDS), showing an even distribution of Ni atoms over the CN\textsubscript{x} area and increasingly more Ni and O content from 0 to 150 ALD cycles of NiO as determined by the increase in the blue and
green color that corresponds to Ni (Figure 3-2f to Figure 3-2j). The quantitative elemental composition can be found in Table S3-2 and corroborates the increase in Ni for more ALD cycles.

Figure 3-1. Schematic illustration of NiO/CNx synthesis. The thiourea layer was recrystallized on the FTO substrate by dip-coating method, and then thermally treated to produce CNx. The CNx was coated with various NiO content via different number of ALD cycles, and then scratched off to give particulate NiO/CNx photocatalyst.

Figure 3-2. Top-view SEM images and EDS elemental mapping of (a,f) CNx, (b,g) NiO(20)/CNx, (c,h) NiO(50)/CNx, (d,i) NiO(65)/CNx, and (e,j) NiO(150)/CNx.
3.2.2 Chemical structures and optical properties

To examine the functional groups and chemical structures of CN\textsubscript{x} and NiO-functionalized CN\textsubscript{x}, the Fourier-transform infrared spectroscopy (FTIR) technique was used (Figure 3-3a). In Figure S3-3, the sharp peaks at 804 cm\textsuperscript{-1} correspond to the prominent characteristic peak of CN\textsubscript{x}, showing the breathing mode of the heptazine core, which identifies the successful formation of CN\textsubscript{x}\textsuperscript{29,198}. The presence of the peaks around 1200-1650 cm\textsuperscript{-1} originates from C=N stretching modes in the material\textsuperscript{198,199}. The N-H and OH stretching vibrations were observed as a broad peak around 3200 cm\textsuperscript{-1}. The FTIR peaks confirm the melon structure in all CN\textsubscript{x} and NiO(20, 50, 65, 150)/CN\textsubscript{x}, while the NiO loading is too limited to be detected.

Ultraviolet-visible Diffuse Reflectance Spectroscopy (UV-vis DRS) was used to examine the electronic and optical properties of our opaque materials. As displayed in Figure 3-3b, the DRS spectra were dominated by the CN\textsubscript{x} component. All traces have strong absorption peaks in the UV range assigned to \pi-\pi* electronic transitions in the heptazine rings of CN\textsubscript{x}\textsuperscript{193}, and the typical CN\textsubscript{x} semiconductor absorption onset in the blue spectral range (ca. 450 nm) was observed. The band gap energy (E\textsubscript{g}) was quantified by Tauc plots (Figure S3-4). For direct electronic transitions, the band gaps were determined to be 2.85 eV, 2.84, 2.89, 2.85, and 2.78 eV for CN\textsubscript{x}, NiO(20)/CN\textsubscript{x}, NiO(50)/CN\textsubscript{x}, NiO(65)/CN\textsubscript{x}, and NiO(150)/CN\textsubscript{x}, respectively. The band gap fluctuating by no more than 0.1 eV after various NiO decorations indicates an insignificant difference in the band structure and that CN\textsubscript{x} acts as the dominant light absorber. The shape of the optical absorption varied slightly when changing the NiO loading. The NiO/CN\textsubscript{x} samples exhibited an additional absorbance tail toward 450-800 nm, which becomes more obvious with increased NiO loading (Figure 3-3b). This is consistent with the change of the sample color from yellow to blackish yellow as the content of the NiO increased from 0 to 150 ALD cycles, shown in Figure S3-5. NiO, in addition to behaving as a typical wide bandgap semiconductor that absorbs ultraviolet light, may have absorbance within the visible region.
attributed to the formation of interband states caused by defects such as oxygen vacancies or other impurities\(^{200,201}\). Zhang’s paper on Ni/NiO@g-C\(_3\)N\(_4\) revealed a comparable optical absorbance increase from UV to 800 nm with increased Ni/NiO content\(^{202}\). Similarly, in our work, the promoted absorption in the visible range suggests that NiO/CN\(_x\) heterojunction could utilize more proportion of incident solar irradiation. However, the absorption by the cocatalyst can be detrimental to the photocatalytic activity when increasing the content, blocking the optical collection ability of the photocatalyst and resulting in a shading effect\(^{203,204}\).

Steady-state photoluminescence (PL) spectra provide insights into emissive charge carriers and photophysical characteristics in semiconductor materials. Herein, emission spectra were collected under 405 nm excitation at room temperature. The intense emission peak of bulk CN\(_x\) was observed at 480 nm (Figure 3-3c). For pristine CN\(_x\), the PL peak at 480 nm can be attributed to the n-\(\pi^*\) transitions, and it is further related to the band-to-band recombination of electron-hole pairs\(^{205}\). With the NiO cocatalysts, a significant quenching of the PL was noticed. The maximum emission intensity (ca. 480 nm) weakened to 84\%, 85\%, 58\%, and 33\% of that of bulk CN\(_x\) with NiO(20, 50, 65, 150) deposition, respectively. Similar quenched PL results were reported in previous work when adding NiO as a cocatalyst on graphitic carbon nitride, and authors stated that NiO composite limited charge recombination and gave rise to efficient charge separation\(^{202,206,207}\). However, we consider that the weakened emission intensity from the NiO/CN\(_x\) may be attributed to NiO absorbing the excitation and/or the emission light. To draw the conclusion of whether the electron-hole recombination is suppressed by the NiO component, more detailed characterization is required.
Figure 3-3. (a) FTIR, (b) UV-vis DRS, and (c) steady-state PL spectra of CNₓ, NiO(20)/CNₓ, NiO(50)/CNₓ, NiO(65)/CNₓ, and NiO(150)/CNₓ.

3.2.3 Charge carrier dynamics and charge trapping

Time-resolved photoluminescence (trPL) was performed to investigate the photoexcited carrier recombination and charge separation. The samples were excited by 350 nm excitation, and the emission spectra were obtained after different lag times from 0 to 2000 μs. The rapid decay before 120 μs is caused by the decay of the excitation flash and is excluded from the kinetic analysis (Figure S3-6). In Figure S3-7, the highest intensity at each lag time was extracted and plotted against log time. After 2000 μs, CNₓ and NiO(20, 50, 65, 150)/CNₓ fluorescence intensity decayed to similar values of 4.7%,
5.0%, 6.1%, 4.7%, and 6.4% of the intensity at 120 μs for the same sample, respectively. The relationship between intensity and lag time follows the power law (Equation 3-1):

\[ I = kt^{-\alpha} \]  

(3-1)

Where \( I \) indicates the fluorescence intensity; \( t \) indicates the lag time; \( k \) is the power law decay constant; and \( \alpha \) is the power law exponent. A similar \( \alpha \) of around 1 (Figure 3-4a) was determined for all samples, indicating the similar charge recombination behavior of all samples in the range of 120 μs to 2000 μs. As expected from an \( \alpha \sim 1 \), the fluorescence intensity of all samples also follows the second-order kinetic decay, which suggests that bimolecular charge recombination dominates the decay kinetic (Figure S3-8). Despite the differences we observed in the slope of the second-order kinetics, we determined that the rate constants are similar for all samples. This is attributed to the fact that we monitor the PL intensity, not the concentration of charge carriers, which is affected by the different optical properties of the films (see the Discussions on trPL 2nd order reaction kinetics section in Supporting Information 1 for further discussion).
Figure 3-4. (a) Log-log plot of the trPL intensity against the lag time. (b) Emission energy against the lag time of all samples. (c) Schematic illustration of trap states distribution and emission energy changes.

The energy of the emission maximum was determined at every lag time. In Figure 3-4b, it is seen that the emission energy of all samples decreased from ~2.6 eV to ~2.2 eV after 2000 μs, indicating a red-shift of the emission over the microsecond timescale. Typically, a decrease of the emission energy over time implies the presence of the charge carrier trapping and the associated loss in electrochemical potentials of the excited charges\textsuperscript{210}. At a short lag time, more trap states are filled, showing the higher emission energy with electronic transitions closer to band edges. At long lag times, charge
recombination will deplete charges, leading to only lower energy states being filled with electrons and corresponding smaller emission energy. The similar behavior of all samples in trPL measurement indicates that the NiO cocatalyst is not affecting the charge carrier dynamics of the heterojunction, presumably because of the high population of trap states in bulk CNx.

3.2.4 Photocatalytic hydrogen evolution reaction

The photocatalytic performance of the prepared catalysts towards HER was evaluated under 405 nm visible light irradiation (10 mW/cm², 2 cm² area) in a 10% v/v TEOA aqueous solution. From Figure 3-5, with 2 mg/mL photocatalyst in 10 mL solution, the hydrogen evolution rate of NiO(20)/CNx, NiO(50)/CNx, NiO(65)/CNx, and NiO(150)/CNx was 1.4, 1.5, 3.9, and 1.1 μmol·h⁻¹, corresponding to an AQY of 1.1%, 1.2%, 3.1%, and 0.8%, respectively. In Figure S3-10, the activities of NiO(20, 50, 65, 150)/CNx after 2 h HER process were preserved at 94%, 73%, 103%, and 99%, respectively. The optimal NiO(65)/CNx exhibited 83% of initial activity after 5 h HER process, showing promising stability of the material. Bulk CNx is unable to drive the water reduction reaction under the same conditions, shown as the flat blue trace after 1 h of light irradiation in Figure 3-5a. With the NiO cocatalyst, the activity improved with increasing NiO loading up to 65 cycles of NiO deposition and then decreased. The trend can be interpreted as growth in interfacial surface area or reactive sites at low NiO levels followed by detrimental light absorption at higher loadings. 3 wt.% Pt was introduced as the benchmark cocatalyst on CNx, and the Pt/CNx exhibited a hydrogen evolution rate of 5.20 μmol·h⁻¹ with 5.7% AQY in the same condition applied to NiO/CNx. Thus, after the optimization of NiO content on the CNx photocatalyst, the NiO(65)/CNx reached around 54% of the photocatalytic activity of Pt towards proton reduction (AQY at 405 nm of 3.1% for the NiO(65)/CNx vs. 5.7% for the Pt/CNx), a significant activity considering that the NiO precursor is 17 times cheaper (Price per gram of ~12 CAD for NiCp₂ vs. ~202 CAD for H₂PtCl₆ from the supplier Sigma Aldrich).
Figure 3-5. (a) Photocatalytic H₂ evolution of all samples using 2 mg/mL photocatalyst in 10 mL 10% v/v TEOA aqueous sacrificial solution under 405 nm light irradiation. (b) AQY and (c) hydrogen evolution rate of all samples.

3.2.5 Ni in situ photoreduction and potential mechanism

Interestingly, an induction period was observed with all NiO/CNₓ samples at the beginning of the HER. In Figure 3-6, all HER traces with NiO can be separated into three stages. During the first 200-400 s, no hydrogen was produced, and the hydrogen concentration remained extremely low. The following stage is where an upward curvature appeared. An arbitrary threshold of 0.1 μmol H₂ in the 10 mL reaction solution was reached
in the range of 600 s to 900 s after the start of irradiation, taking longer with increasing NiO content (Table S3-4). This second stage with the upward curvature displayed a noticeable extension from 15 to 22 minutes as the NiO loading increased. Finally, a steady \( \text{H}_2 \) evolution rate, observed as the section with a consistent slope, was achieved in the third stage. Typically, the photodeposition process shows an induction period, which is the common method for photoreducing cocatalyst precursors and forming reactive species for photocatalysis. In our case, Pt cocatalyst was introduced by photoreducing the Pt\(^{4+}\) in \( \text{H}_2\text{PtCl}_6 \) to Pt\(^0\) on the CN\(_x\) surface. In Figure 3-6f and Figure S3-11, the induction period was seen during the Pt photodeposition, and the steady \( \text{H}_2 \) generation rate can be interpreted as the completion of the Pt deposition. Next, the reactant solution was purged with inert gas to remove the generated \( \text{H}_2 \). Finally, the HER activity test for Pt/CN\(_x\) started, in which process the generated \( \text{H}_2 \) is linearly proportional to the light irradiation duration, and no induction period was seen.
Figure 3-6. H\textsubscript{2} evolution and linear fitting of (a) NiO(20)/CN\textsubscript{x}, (b) NiO(50)/CN\textsubscript{x}, (c) NiO(65)/CN\textsubscript{x} and (d) NiO(150)/CN\textsubscript{x}. Photocatalytic processes of (e) 3 wt.% Ni photodeposition (1\textsuperscript{st} run) and 3 wt.% Ni/CN\textsubscript{x} HER (2\textsuperscript{nd} run) and (f) 3 wt.% Pt photodeposition (1\textsuperscript{st} run) and 3 wt.% Pt/CN\textsubscript{x} HER (2\textsuperscript{nd} run). The abscissa intercept of the slopes, used to quantify the induction period, is indicated with arrows in panels e) and f). 20 mg photocatalyst was used, and a linear fitting was taken after reaching a steady hydrogen evolution rate. Dashed horizontal lines are drawn at 0.1 µmol H\textsubscript{2} amount to highlight the induction period.
The possibility of having mixtures of Ni oxidation states (e.g., NiO) in the ALD-derived Ni-based cocatalyst complicates the verification of the Ni reactive species in the induction period. Therefore, NiCl₂ was chosen as a control Ni precursor for its precise initial oxidation state (Ni²⁺). 3 wt.% of Ni was photodeposited on the CNₓ surface using the same condition as the HER, in which the Ni²⁺ ions were increasingly photoreduced to Ni⁰ to form the catalytic sites. The induction period was reproduced both during the initial photodeposition and the subsequent hydrogen evolution process (Figure 3-6e). Given the similar behavior of the NiO and NiCl₂ samples, we propose that the same reactive Ni⁰ species are formed during the induction period and that the conversion between Ni²⁺ and Ni⁰ species is most likely reversible. Surprisingly, with the 3 wt.% NiCl₂-based deposition, the Ni/CNx heterostructure still exhibited 39% of hydrogen generation activity compared to Pt (AQY of 2.2% for the Ni/CNx vs. 5.7% for the Pt/CNx), though there is a ca. 70 times price difference between the two precursors (Price per gram of ~3 CAD for NiCl₂·6H₂O vs. ~202 CAD for H₂PtCl₆ from the supplier Sigma Aldrich). The much lower cost would make the Ni-based cocatalyst more economically feasible despite the loss in activity.

To gain more insight into the induction period, we photodeposited 3 wt.% Ni from NiCl₂ onto TiO₂. A Pt/TiO₂ reference sample was also prepared. As was seen for CNₓ, the induction period disappeared after Pt was deposited on TiO₂ (Figure S3-11). Montoya et al.’s investigation of in situ photo-reduced Ni on TiO₂ displayed a similar induction period under UV light irradiation, suggesting the induction period is a general process when using nickel as the photocatalytic HER cocatalyst²¹¹. Further inspired by Cui et al.’s work of core/shell Ni/NiO on TiO₂ facilitating hydrogen production under visible light condition²¹², we tested the HER ability of Ni/TiO₂ 405 nm illumination. However, no hydrogen was evolved, presumably due to the sensitivity of the TiO₂ composition (80% anatase and 20% rutile) on band structure since the work function of Ni is close to the CB of TiO₂ and reduces the thermodynamic driving force for electron transfer to Ni²⁺,²¹²,²¹³ (Figure S3-12).
Photoinduced absorption spectroscopy (PIAS) was performed to investigate the charge carrier dynamics and the cause of the induction period for Ni-based cocatalysts\textsuperscript{214}. PIAS signals were probed under the HER active condition during and after irradiating with a 395 nm LED at 10 mW/cm\textsuperscript{2} for 3 seconds. The continuous excitation was applied to monitor the accumulation of photogenerated charges, presumably electrons since holes are quenched by the hole scavenger TEOA, which occurs under active conditions. In \textbf{Figure 3-7a}, by extracting the %Abs peak value at 3 s when the most photogenerated charges are accumulated, the transient absorption spectra of CN\textsubscript{x}, 3 wt.% Pt/CN\textsubscript{x}, and NiO(150)/CN\textsubscript{x} can be obtained, revealing the optical behavior of the photoinduced species. The relative error from the standard deviation of the spectra data is analyzed around 4%, but we estimate the total error to be 10% due to the manual setup of samples in the experimental apparatus. The thicker NiO(150)/CN\textsubscript{x} was chosen for the PIAS measurements instead of the better-performing NiO(65)/CN\textsubscript{x} to increase the chance of observing a signal related to charges located in the NiO layer. Neither NiO nor Pt cocatalyst altered the PIAS spectra of CN\textsubscript{x}, implying we are not probing the reactive species in the cocatalyst. We attribute the lower amplitude of PIAS spectra in the samples with cocatalyst to partial absorption of the excitation light pulse, resulting in a lower amount of photogenerated charges. While these results could also point to lower charge accumulation due to charge transfer to the cocatalysts, this seems unlikely based on the similarity of the growth and decay kinetics. PIAS signal decay traces of the three samples in 10% v/v TEOA/H\textsubscript{2}O were probed at specific wavelengths in the visible region (\textbf{Figure 3-7b} and \textbf{Figure S3-13}). Still, a negligible difference in decay kinetics was observed, although the samples have different activities toward HER as shown in \textbf{Figure 3-5}. It is reported that CN\textsubscript{x} has photogenerated electrons that have a lifetime in the microsecond to second timescale, while charge carrier trapping dominates the charge-consuming pathway, making these charges deeply trapped, unable to transfer to the surface and participate in the redox reactions\textsuperscript{66}. Because of the high population of photocatalytically
inactive electron trap states in bulk CN, we conclude that the signal from the trapped charges dominates and precludes the detection of reactive species even with the help of the Pt cocatalyst. Further work is foreseen to match the light absorber thickness, charge carrier mobility, and charge diffusion length, transferring the charges to the interface of the carbon nitride and cocatalysts. Detailed information about experimenting on diverse variables (dry/wet, air/argon, with hole scavenger/without hole scavenger) can be found in the Supporting information 1 (Figure S3-14 to Figure S3-16).

X-ray photoelectron spectroscopy (XPS) was carried out to investigate the chemical bonding and identify the nickel species formed on the surface of the photocatalysts. In Figure 3-8a, the C 1s spectrum of CN showed three carbon environments with consistent peak positions to the literature\textsuperscript{215,216}. The peak seen at 284.8 eV was attributed to adventitious carbon. Moreover, the peak observed around 286 eV resulted from a C-O type environment. These two carbon peaks presumably come from carbon impurities and
surface contamination. The dominant peak around 288 eV indicates the N-C=N environment in the heptazine-based CNₓ structure. The N 1s spectrum of CNₓ is also consistent with the literature (Figure 3-8b)\textsuperscript{31}. The nitrogen peak located at 398.8 eV represents pyridinic nitrogen (C=N-C) in CNₓ. The peak observed at 400.0 eV shows the N-H linkages or NH₂ groups. The leftmost peak shown at 401.3 eV indicates the tertiary nitrogen N(C)\textsubscript{3} in CNₓ\textsuperscript{217}. For the O 1s spectrum of CNₓ, oxygen composition mainly comes from surface contamination, including C-O linkage, surface-adsorbed H₂O, or hydroxyl groups (Figure S3-17a)\textsuperscript{218,219}. With the Ni component, metal-oxygen peaks appear (Figure S3-17b to Figure S3-17d): peaks at around 529~531 eV and 532 eV correspond to the Ni-O and Ni-OH, respectively\textsuperscript{220}.

Also, it is worthwhile to mention the distinct XPS spectra of the photodeposited Ni/CNₓ and ALD-derived NiO(65)/CNₓ brought by the different preparation approaches. The photodeposition process contributes to the morphology of Ni nanoparticles scattered around the surface of the CNₓ, which is the cause of Ni/CNₓ having similar carbon, nitrogen, and oxygen environments compared to bulk CNₓ. However, ALD deposition leads to a conformal NiO nanofilm on the surface of the CNₓ and explains why the features of CNₓ are partially hidden for NiO(65)/CNₓ due to the surface sensitivity of the XPS technique. Therefore, the peaks are ascribed to the C, O, and N environments on the surface/interface of the NiO; the C 1s peak with the lowest binding energy is assigned to the C-Ni environment, potentially from residual NiCp₂ (Figure S3-18a, b)\textsuperscript{221}; the rightmost N 1s peak presumably related to the Ni\textsuperscript{0}-N environment (Figure S3-19b); the O 1s peak located at the low binding energy might refer to the adsorbed oxygen states in the porous CNₓ structure, relating to atomic oxygen with an ionic Ni-O\textsuperscript{222} or plasma-processed oxygen species (Figure S3-17c).

Ni 2p spectra were analyzed among the as-prepared NiO(65)/CNₓ, NiO(65)/CNₓ after HER, Ni/CNₓ after HER, and Ni/TiO₂ after HER (Figure 3-8c to Figure 3-8f). Ni\textsuperscript{ii} species were found in all Ni-containing samples, yet metallic Ni\textsuperscript{0} species at 851~853 eV
were only detected after the hydrogen evolution reaction. This confirms our hypothesis that Ni$^0$ species are formed under irradiation. Peaks around 856 and 874 eV are assigned to Ni 2p $3/2$ and Ni 2p $1/2$ peaks of Ni$^{II}$ species, respectively. The peaks observed around 862 and 880 eV are shake-up satellites of Ni 2p $3/2$ and Ni 2p $1/2$ peak, respectively$^{223}$. After the hydrogen evolution reaction, the NiO component in ALD-derived NiO/CNₓ dominates the Ni 2p spectrum$^{224}$, and the Ni$^{II}$ species in Ni/CNₓ and Ni/TiO₂ arise from both NiO and Ni(OH)$_2$$^{225,226}$. The peak approaching 850 eV in Figure 3-8d, e, and f confirms the presence of Ni$^0$ in samples that underwent HER$^{218,227,228}$. Estimated by the peak area, it was noticed that NiO(65)/CNₓ after HER has the highest amount of Ni$^0$ species (7%), followed by Ni/CNₓ after HER (5%), and finally Ni/TiO₂ after HER (2%). The trend in the amount of Ni$^0$ species in the samples conforms with the trend in the HER activity, strongly suggesting that the activity difference among NiO/CNₓ samples is caused by Ni$^0$ content. Combined with the photocatalytic activities, we propose that photogenerated electrons are consumed at Ni$^0$ reactive sites for hydrogen evolution and that a higher proportion of Ni$^0$ is beneficial to the proton reduction since more photoexcited electrons are participating in the interfacial charge transfer. No HER is observed with Ni/TiO₂ despite the fact that Ni$^0$ is observed, presumably due to the conduction band edge (CBE) of TiO₂ being more positive than CNₓ, resulting in the sluggish kinetics of electrons transferring from TiO₂ to Ni that hampers the accumulation of enough reactive nickel species for proton reduction$^{229,230}$. 
Figure 3-8. XPS (a) C 1s and (b) N 1s spectra of CN₉. (c-f) XPS Ni 2p spectra of NiO(65)/CNₓ, NiO(65)/CNₓ after HER, Ni/CNₓ, and Ni/TiO₂ after HER.

We surveyed the literature to differentiate the reaction mechanisms between noble and transition metal-based photocatalysts in electrocatalytic and photocatalytic hydrogen evolution. Creus et al.’s research on ligand-capped Ru nanoparticles (NPs) for electrocatalytic hydrogen evolution reaction revealed the oxidation of Ru⁰ to RuO₂ under air exposure and that RuO₂ can be fully reduced to Ru⁰ after long enough bulk electrolysis in the reductive environment (1 M H₂SO₄ instead of 1 M NaOH)²³¹. A partially surface oxidized Ru/RuO₂ NPs outcompeted commercial Pt/C in alkaline solution, while in the acidic environment, a continuous decrease of Ru⁴⁺ for generating more reactive metallic Ru⁰ for electrocatalytic HER is noticed. Later in Kwak et al.’s work, CNₓ was functionalized with single Ni atoms for photocatalytic hydrogen evolution, and the coexistence of Ni⁰ and Ni⁺ species was confirmed after sample preparation²²⁷. The Ni peak positions and the ratio of Ni⁰/Ni⁺ remain almost identical after HER, suggesting the well-maintained Ni oxidation states. Different from Ru metal, the stabilization of having both Ni oxidation states under catalytic conditions on the surface of the photocatalyst might be achievable, though the
oxidation of the Ni\(^0\) in the ambient atmosphere during the characterization process should be seriously considered.

Based on previous work and our XPS analysis, we hypothesize that Ni reduction is occurring in situ and stabilizes the catalytically active species on the CN\(_x\). For the ALD-deposited NiO/CN\(_x\), NiO was formed as a conformal film on the surface of CN\(_x\), and the conversion from NiO to metallic Ni begins when irradiating the sample under active conditions. As drawn in Figure 3-9a, the outer NiO that is more exposed to the reactants in solution will be photoreduced to Ni\(^0\) first, forming a thin metallic Ni layer on the surface of the NiO film. Then the Ni in situ photoreduction continues consuming electrons and goes deeper into the NiO film. It is not until adequate NiO is converted to Ni metal that electrons can flow to protons and evolve hydrogen molecules. During this process, photoexcited electrons are totally consumed reducing NiO while holes are scavenged by TEOA, and proton reduction has not started, which corresponds to the first stage in the HER trace (the induction period). The second stage involves both photoreduction and proton reduction, and the upward curve of hydrogen generation can be interpreted as more and more Ni\(^0\) active species are formed for HER. Though the majority of the cocatalyst may remain as NiO, a dynamic equilibrium between NiO and Ni\(^0\) species will be achieved in the third stage, exhibiting a steady hydrogen evolution rate. For the case using NiCl\(_2\) as the Ni precursor, Ni\(^{2+}\) ions are photoreduced to Ni\(^0\) species on the surface of the CN\(_x\), and then these Ni\(^0\) species accumulate to clusters and finally grow into Ni nanoparticles which are embedded on the CN\(_x\) as reactive sites for HER\(^{227}\). Similarly, these Ni NPs could be oxidized to NiO or Ni(OH)\(_2\) under noncatalytic conditions, and a reversible conversion from Ni\(^{III}\) to Ni\(^0\) happens again once the light is on.
Till now, the mechanism of the induction period has been disentangled, but it is intriguing that the induction period seems to be reproducible without air exposure. The reproducibility of the induction period with both NiO/CN\textsubscript{x} and Ni/CN\textsubscript{x} was verified by restarting hydrogen production right after purging the system with inert gases (Figure S3-21 as an example for NiO(65)/CN\textsubscript{x}). Even on subsequent HER runs the induction period is evident, implying that the transformation of Ni\textsuperscript{0} to Ni\textsuperscript{II} can also proceed in an oxygen-free environment. A possible mechanism is drawn in Figure 3-9b. With the light illumination, charges are generated in the light absorber CN\textsubscript{x}, then transported to Ni\textsuperscript{0} active sites for evolving hydrogen molecules. Meanwhile, excess holes are scavenged by TEOA.
Once the light irradiation stops, we suggest that metallic Ni can be oxidized by flowing electrons back into electron trap states of CN$_x$, which contributes to the reproducible feature of the Ni induction period. More explanations about band bending and Fermi level of the system could be found in the Supporting information 1.

3.3 Experimental section

Chemicals and substrates. All the chemical reagents were used as received with no further purification. Thiourea (≥99.0%), triethanolamine (TEOA) (>99%), Bis(cyclopentadienyl)nickel (nickelocene, NiCp$_2$) (>95%), chloroplatinic acid hydrate (H$_2$PtCl$_6$) (≥99.9%), fluorine-doped tin oxide (FTO)-coated glass (surface resistivity ~7 Ω/sq, thickness 2.2 mm), and titanium oxide (TiO$_2$, 80% anatase and 20% rutile) were purchased from Sigma-Aldrich. Nickel(II) chloride (anhydrous 98%, NiCl$_2$·6H$_2$O), ethanol (reagent grade alcohol, 100%), and acetone (≥99.5%) were purchased from VWR. Detergent (Sparkleken) was obtained from Fisher Scientific. Millipore water (18.2 ΩM cm resistivity at 20°C) was generated by a Direct-Q® water purification system.

Synthesis of CN$_x$/FTO and CN$_x$. The fluorine-doped tin oxide-coated (FTO) glass slides were sonicate-cleaned using detergent, acetone, ethanol, and water in sequence, then dried at 60°C. An aqueous thiourea solution was made by adding 27 g thiourea to 30 g water at 70°C. Clean FTO slides were then dip-coated with a layer of recrystallized thiourea by dipping into the saturated thiourea aqueous solution and taking it out immediately. After drying, subsequent dipping can be done to increase the thickness of the thiourea layer and the final CN$_x$ layer. A single dipping step was performed to yield the sample used for photocatalysis. Thicker 3 dipping step samples were made for PIAS characterization to ensure an optically opaque film. After thoroughly drying at 60°C for 1 h, thiourea/FTO slides were positioned in a quartz tube and calcinated in a nitrogen atmosphere for 2 h at 500°C with a heat ramp of 5°C per min. CN$_x$/FTO with a uniform
light yellow CNx layer on the FTO slides was formed for subsequent cocatalyst deposition (ALD or photodeposition).

For the cocatalyst photodeposition process, the CNx layer was scratched off the substrate using a surgical blade and thoroughly ground in the mortar as a bulk CNx photocatalyst.

**Synthesis of NiO/CNx.** Nickelocene and oxygen were chosen as the Ni source and oxidizing co-reagent, respectively. The NiCp2 container was kept at 95°C to continuously vaporize the precursor. The gaseous Ni precursor was transported into the reaction chamber by an Ar carrier gas with a flow rate of 10 sccm. The co-reagent O2 was ionized by a plasma generator of 300 W RF power, then pulsed into the chamber with a flow rate of 50 sccm. The chamber pressure was controlled at around 300 mPa during the deposition process. The deposition temperature was set at 250°C, which is the proper temperature within the ALD growth window. One deposition cycle consists of a 500 ms pulse of NiCp2, a 15 s decay for precursor adsorption, a 10 s oxygen pulse, a 15 s plasma duration for O2 to react with adsorbed Ni precursor, and another 10 s pulse of Ar to purge out the residual precursor and by-products. NiO was deposited on the CNx/FTO cycle by cycle, and the ALD growth rate was determined to be 0.1 nm per cycle by depositing NiO on the silicon wafer and measuring the thickness of the NiO layer using a DektakXT® profilometer. NiO(20)/CNx, NiO(50)/CNx, NiO(65)/CNx, NiO(150)/CNx were defined as CNx/FTO deposited with 20, 50, 65, and 150 cycles of NiO. NiO decorated CNx was scratched off the substrate using a surgical blade and ground for subsequent characterization and experiment as a particulate NiO/CNx photocatalyst.

**Photodeposition of Pt and Ni cocatalysts.** Differentiated from ALD-derived NiO cocatalyst, Pt and Ni metal cocatalysts were deposited on CNx through photodeposition using chloroplatinic acid hydrate and nickel chloride as corresponding cocatalyst precursors, respectively. 20 mg bulk CNx powder, scratched from the FTO substrate, was transferred to 10 mL 10% v/v TEOA-H2O solution, either 84 μL 15 mg/mL H2PtCl6 or 132
μL 10 mg/mL NiCl₂ stock solution was added to the reaction solution to load a 3 wt.% cocatalyst on CNₓ. The suspension was irradiated using 405 nm LED under 10 mW/cm² for around 1h to prepare 3 wt.% Pt/CNₓ or Ni/CNₓ, then was purged with Ar for subsequent photocatalytic hydrogen evolution reaction measurements.

Photocatalytic hydrogen evolution reaction. Photocatalytic activities of CNₓ with three types of cocatalysts (ALD-deposited NiO, photodeposited Pt and photodeposited Ni) were measured under 405 nm LED in sacrificial conditions using TEOA as a hole acceptor. The 405 nm light source was calibrated to simulate the amount of G_{AM1.5} (1000 W/m²) light that is absorbed by CNₓ. This is estimated to be 100 W/cm² or 10 mW/cm² (Figure S3-22). For NiO decorated CNₓ, no photodeposition of additional cocatalyst was needed. For 3 wt.% Pt/CNₓ and Ni/CNₓ, the HER was proceeded after the photodeposition and subsequent purging with Ar. A 10 mL 10% v/v TEOA-H₂O reaction solution with photocatalyst density of 2 mg/mL was irradiated until the a constant hydrogen evolution rate was obtained, seen as a steady slope in the increasing H₂ concentration. The reactant solution was purged with Ar and tested at least in duplicate. The hydrogen concentration in the solution was determined using a Unisense hydrogen microprobe sensor. The voltage readout from the Unisense Microsensor Multimeter was calibrated with known H₂ concentrations (0 and 20 μM H₂) in Millipore water at 25°C.

The apparent quantum yield (AQY) can be calculated by the following equations.

\[
AQY \, (\%) = \frac{nR}{I}
\]  

(3-2)

Where \( n \) is the number of electrons involved in the reaction (2 electrons per H₂ molecule); \( R \) is the photocatalytic hydrogen evolution rate (mol/s); \( I \) is the moles of photons reaching the samples per second (einstein/s) and is determined by:

\[
I = \frac{P_{total}}{E_{photon}} = \frac{P \times Lighting \, area}{h \frac{c}{\lambda} \times N_A}
\]  

(3-3)
Where $P_{\text{total}}$ is the total energy per second under specific light power density (J/s); $E_{\text{photon}}$ is the energy of a mole of photons from the light with the wavelength of $\lambda$ (J/mol); $P$ is the power density of the light (W/m$^2$); lighting area is the area that light is hitting on the sample (m$^2$); $h$ is Planck’s constant (J·s); $c$ is the speed of light (m/s), $\lambda$ is the wavelength of the irradiation light (m); $N_A$ is the Avogadro’s constant ($6.02 \times 10^{23}$ mol$^{-1}$).

**Characterization.** Scanning Electron Microscopy (SEM) and Energy Dispersive spectrometer (EDS) were performed on the 10 nm thick Pt/Pd coated sample using the Tescan Mira 3 XMU Scanning Electron Microscope (working distance of 15 mm, beam intensity of 15.00, and accelerating voltage of 20 kV) and the Oxford X-Max Energy dispersive spectrometer, respectively. Fourier-transform Infrared Spectroscopy (FTIR) was obtained by the Thermo Electron Nicolet 6700 Spectrometer with a diamond ATR attachment and an XT-KBr beam splitter. UV-vis Diffuse Reflectance Spectroscopy (UV-vis DRS) was collected on an Ocean Optics Maya 2000 PRO spectrometer with deuterium/halogen UV-vis light source and integrating sphere accessory, while steady-state Photoluminescence (PL) spectroscopy was measured by replacing the broadband light source with 405 nm laser diode excitation. For the measurement, the fine powder sample was placed on a glass microscope slide and compressed using a quartz slide through which the light was directed to the sample. Time-resolved PL was acquired with a TECAN Multifunctional Plate Reader, the fine powder sample was placed and firmly pressed into the 96 well plates with 350 nm light exciting from the bottom, and the emission was monitored every 5 nm from 400 nm to 700 nm. The X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Analytical Axis UL TRA spectrometer with a monochromatized Al Ka line source (150 W). Survey scans were obtained using the scan rate of 1 eV per step, with a pass energy of 160 eV. High-resolution spectra were obtained at a 0.1 eV step size, with a pass energy of 20 eV. A calibration procedure was conducted following the ISO 15472 international procedure, and Al and Mg X-ray sources were used to calibrate the energy scale linearity. XPS fitting was conducted using the Shirley
background and Gaussian-Lorentzian sum lineshapes with 90% Gaussian character and 10% Lorentzian in a customized XPS fitting MATLAB application, which is accessible at https://github.com/SolarSpec/XPSfitting. The FWHM was set at 1 ~ 2 eV ± 10% for C 1s and N 1s, ~ 2 eV ± 10% for O 1s, 1.2 eV ± 50% for Ti 2p, and ~ 5 eV ± 50% for Ni 2p spectra analysis. The binding energy was calibrated to the adventitious C-C environment at 284.8 eV in the C 1s spectra. Photoinduced Absorption Spectroscopy (PIAS) setup consists of a 395 nm excitation LED, a 95 W oriel lamp probing light source, and an Oriel Cornerstone monochromator. The sample was mounted on the stage in the middle of the light path, and the excitation was set at 10 mW cm$^{-2}$ for 3 s, followed by a 15 s decay. Long pass and band pass filters were used for obtaining the specific probe wavelengths. Kinetic traces were averaged for 32 traces for wavelengths ≥ 650 nm and 64 traces for wavelengths ≤ 600 nm. The acquisition algorithm was written in the LabView environment to control the PIAS system. Data were processed using customized MATLAB scripts accessible at https://github.com/SolarSpec/PIASgui. The profilometry was measured by the DektakXT® stylus surface profiler.

3.4 Conclusions

The NiO/CN$_x$ was prepared through thermal polymerization/condensation and atomic layer deposition. The optimized NiO(65)/CN$_x$ heterostructure evolved H$_2$ at a rate of 3.9 μmol·h$^{-1}$ (AQY of 3.1%) with the photocatalyst density of 2 mg/mL in 10% v/v TEOA aqueous solution under 405 nm visible light irradiation (10 mW/cm$^2$, 2 cm$^2$ area). Notably, the activity with the ALD-derived NiO-based cocatalyst approaches 54% of the photocatalytic hydrogen evolution performance of 3 wt.% Pt/CN$_x$ with expensive Pt. At the same time, the 3 wt.% Ni/CN$_x$ deposited from simple NiCl$_2$ showed an AQY of 2.2%, which is 39% of the activity of that Pt benchmark. Considering costs, the Ni cocatalysts are up to 70 times lower than Pt-based cocatalysts while preserving a significant activity. The performance-to-cost ratio is much improved for the Ni-based cocatalyst versus using Pt.
Additionally, compared to air-sensitive catalysts (i.e., phosphides), NiO catalyst demands no strict storage requirements (i.e., oxygen-free) and could be activated in catalytic conditions for hydrogen generation, which further controls the cost when it comes to large-scale production. Admittedly, the ALD technique increases the sample fabrication cost, but we demonstrate that the enhanced surface control of the Ni cocatalyst enables it to outcompete alternatives made by traditional synthesis. The fine control of the modification conditions of ALD (e.g., low-temperature deposition, atomic level controlled film properties, high conformality, easily re-workable feature, high-level efficiency, and high productivity) qualifies it as a competitive technique for industrialization on a long-term scale. For instance, the ALD-derived anodic aluminum oxide (AAO) template, which is a widely used nanoporous membrane for photoanode nanofabrication so far\textsuperscript{232,233}. Forge Nano company, at the frontline of industry-scale ALD, is capable of processing up to 30,000 kg power per day with the flexibility of inputting eight precursors at any time using the combination of gas, liquid, and solid precursors, which demonstrates the success of the industrialization of the ALD technique and its competitive edge even when producing complex materials. As mentioned in their white papers\textsuperscript{234}, a fast deposition of up to 30 nm per minute Al\textsubscript{2}O\textsubscript{3} ALD coating at all-in costs of \(~\text{CAD 1.3 per 300 mm wafer}\) is achieved when using trimethylaluminum as the precursor (\(~\text{CAD 1 per mL}\))\textsuperscript{235}, indicating that ALD process costs at a scaled-up level can be competitive with wet chemical routes.

During the hydrogen evolution reaction, we find an induction period before the production of H\textsubscript{2} for all Ni-based heterostructures, which we relate to the \textit{in situ} Ni reduction. Supported by XPS analysis of the samples before and after HER, we interpret the mechanism as a photoreduction of Ni species from higher oxidation states to Ni\textsuperscript{0} reactive species that promote proton reduction. The induction period completes when a dynamic equilibrium is achieved between the photoreduction to Ni\textsuperscript{0} species and the oxidation through electrons flowing black to CN\textsubscript{x}. Our work filled the gap of ALD-derived
Ni/NiO\textsubscript{x} on CN\textsubscript{x} for photocatalysis and succeeded in achieving an improved understanding of the charge flow at the Ni/CN\textsubscript{x} interface.

Finally, we applied a photoinduced absorption spectroscopy system for monitoring the charge carrier dynamics under long-time pulses. We observed a large population of trapped charges in the CN\textsubscript{x} that lowers the charge mobility and leads to immobilized charges (presumably electrons), which prevents negligible charges from reaching the cocatalyst/light absorber interface. So, we emphasize the significance of the promotion of light absorber materials since cocatalyst modification of the benchmark Pt cocatalyst cannot extract enough charges from the bulk CN\textsubscript{x} that contains excess trap states. To design a more promising NiO/CN\textsubscript{x} heterojunction, work could be done to shorten the distance that charges need to travel (i.e., thinner photoelectrode or smaller photocatalyst particle size) and synthesize the materials with fewer trap states to make longer-lived charges sufficiently reactive for redox reactions.
Chapter 4: Aminosilanized Interface Promotes Electrochemically-stable Carbon Nitride Films with Fewer Trap States on FTO for (Photo)electrochemical Systems

Chapter 4 is based on my other first-author research paper submitted to ACS Applied Materials & Interfaces on June 27, 2023. The experiments of the project were 95% conducted by myself, the data analysis and manuscript writing were finished on my own. Coauthors are Stephanie Busse, who conducted plasma cleaning optimization and helped with the aminosilanization process, also Dr. Jian Liu and Dr. Robert Godin, who supervised the project. The manuscript is reproduced with permission from the journal. Supporting Information 2 mentioned in this chapter can be found in Appendix A: Supporting Information 2.

4.1 Introduction

In the context of the energy crisis, researchers have spent the last few decades working on developing renewable energy sources. (Photo)electrocatalytic water splitting is one of the most desirable ways to realize solar-to-chemical conversion with sufficient efficiency and has achieved scaled-up production\cite{236}. Carbon nitride (CN\textsubscript{x}), a polymer semiconductor, was first reported in 2009 for its favorable hydrogen generation ability with visible light\cite{18}. This semiconductor material has a band gap of \(\sim 2.7\) eV and suitable band positions\cite{237}, and thus can drive reactions such as overall water splitting (\(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2\)), which is composed of two half-reactions: proton reduction (\(2\text{H}^+ + 2e^- \rightarrow \text{H}_2\), hydrogen evolution reaction, HER), and water oxidation (\(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-\), oxygen evolution reaction, OER)\cite{96}. CN\textsubscript{x} can be synthesized easily from earth-abundant and inexpensive nitrogen-rich precursors, for example, urea, dicyandiamide, cyanamide, and melamine\cite{238}. CN\textsubscript{x} also has high thermal stability and is not volatile up to 600 °C and it is chemically stable in a large pH range\cite{81}.


Particulate CNₙ is privileged as a photocatalyst for water splitting and pollutant degradation and is more familiar to researchers since typical thermal treatment synthesis produces CNₙ as free powder. CNₙ is also investigated in photoelectrochemical (PEC) systems and electrocatalysis. Those systems physically separate the two half-reactions to suppress efficiency-limiting back-reactions, and make it easier to collect pure gas products. In contrast to the well-established particulate CNₙ photocatalyst, more investigations are needed on CNₙ materials to produce optimal (photo)electrodes. A continuous CNₙ film is desired for (photo)electrochemical devices, as it is critical to improve light absorption with lesser reflection and scattering losses, enhance charge separation and transport with molecules closer in proximity, and ensure proper contact between the (photo)electrode and electrolyte. However, the direct growth of CNₙ film on substrates is challenging; on the one hand, the large particle size of CNₙ and its insolubility in most solvents makes it challenging to attach the CNₙ powder to the substrates through post-annealing methods; on the other hand, one-step polymer condensation of growing CNₙ directly on the substrates has harsh demands on the thermal stability (up to 600°C) of the substrate materials.

The direct growth of CNₙ thin film on substrates for overall water splitting is of great interest in PEC systems. To date, CNₙ-based photoanodes have been investigated, especially under the standard electrolysis potential of 1.23 V RHE (V vs. reversible hydrogen electrode) under AM 1.5G illumination. However, there are fewer studies regarding using CNₙ as a photocathode at potentials more negative than 0 V vs. RHE, partially because CNₙ as an n-type semiconductor typically generates band bending that promotes the accumulation of holes at the electrolyte interface which makes interfacial reductive chemistry more challenging.

Key to the development of CNₙ (photo)electrodes is the interface between CNₙ materials and substrates. Unfortunately, this critical semiconductor|substrate interface has been much less studied compared to optimizing the synthetic conditions of the CNₙ. An
undesirable semiconductor|substrate interface, for instance, weak adhesion of the semiconductor to the substrate and the inefficient charge transfer through the interface, kills the stability of the electrode, causing the detachment of the functional material from the supporting substrate. An interesting way to address this is the idea of “gas pressure sinter”, where CN
${}_x$
 is grown on FTO under high vapor pressure of the CN
${}_x$
 precursor, leading to strong adhesion of the CN
${}_x$
 film to FTO. Physically pressing the CN
${}_x$
 layer closer to the substrate to create intimate contact does not guarantee efficient charge transfer at the CN
${}_x$|FTO interface. Trap states along this interface can adversely affect the charge migration and cause charge recombination. An unmatched energy band between semiconductor and substrates can form a Schottky barrier and also hinder the charge transfer. Crystal facet engineering in crystalline semiconductors enables the anisotropic growth of a crystal in a certain direction for tailoring the charge transfer at the interface, but this is of great challenge to amorphous organic semiconductors. In perovskite solar cells, another solar energy utilizing device, it was found that the introduction of dipoles can align the energy band between adjacent two layers, and a work function shift up to several hundreds of meV is feasible. In Yang et al.’s work, they found that APTES molecules can align the energy band between SnO
${}_2$
 and the perovskite layer since the terminal functional groups of APTES form dipoles, and those terminal groups can passivate the trap states at the perovskite surface via hydrogen bonding to reduce charge trapping and trap-state-induced charge recombination, increasing the power conversion efficiency. This interface engineering targeted the band alignment but we also see the possibility of APTES working as a covalent linker, which is worthwhile to be tried out in amorphous semiconductors for creating an intimate and adhesive semiconductor|substrate interface via covalent chemical bonds.

In efforts to access all-organic PEC systems for water splitting and other energy applications, we sought to investigate CN
${}_x$-based (photo)electrodes. We first conducted electrochemical measurements of CN
${}_x$ on FTO-coated glass but quickly encountered
stability issues and film lift-off, which prompted us to modify the FTO and improve the contact between the CN\textsubscript{x} layer and FTO substrates. We adopted the idea that an APTES cross-linker can strengthen the interaction between CN\textsubscript{x} layer and FTO substrate through covalent bonds, passivate the existing trap states in CN\textsubscript{x} material, and then promote the electrochemical stability of CN\textsubscript{x} electrodes. Considering the complexity of photoelectrochemical pathways, we decided to investigate the CN\textsubscript{x}/FTO interface without light irradiation to pave the pathways for future photoelectrochemical applications. We surprisingly found that the interface modification has the potential to influence the growth of CN\textsubscript{x} over the substrate on a length scale of tens of micrometers from the morphology, optical property, especially the population of trap states, physical adhesion, electrochemical stability, and activity.

4.2 Result and discussion

4.2.1 Contact angle and hydrophilicity

We first attempted to prepare CN\textsubscript{x}/FTO electrodes following the procedure in our previous work\textsuperscript{256} where the FTO glass is dipped in saturated thiourea solution to crystalize the CN\textsubscript{x} precursor on the surface. Thiourea was chosen as the CN\textsubscript{x} precursor since it is reported that sulfur atoms could work as the molten mediator to initialize the growth of the CN\textsubscript{x} on the FTO glass\textsuperscript{257}. The FTO glass was ultrasonically cleaned with detergent, acetone, ethanol, and ultrapure water in sequence and with no further modifications. After thermal treatment to form the CN\textsubscript{x} layer, this initial CN\textsubscript{x}/FTO electrode was unstable and easily broken under HER conditions (< 0 V vs. RHE), shown as cracked or lifted films (Figure S4-1).

The lifting of the CN\textsubscript{x} film prompted us to devise a strategy to improve the CN\textsubscript{x}/FTO interface. In this work, we use ‘CN\textsubscript{x}/FTO interface’ to simplify the interfaces between CN\textsubscript{x} and all FTO substrates, including p-FTO\textsubscript{NH\textsubscript{2}} (plasma-cleaned and aminosilanized), p-FTO (plasma-cleaned), and FTO (non-plasma cleaned), as illustrated in Figure 4-1. We first
introduced the plasma cleaning and then turned to (3-aminopropyl)triethoxysilane (APTES), an organosilane molecule that is frequently used in silane-based functionalization\textsuperscript{258}, as a way to incorporate a covalent bridge between the FTO glass and the CN$_x$. The bifunctional APTES can bind to the hydroxyl groups exposed on the oxide surfaces through the silane moiety on one side, leaving the primary amino group available for incorporation into the CN$_x$ polymer backbone as a bridge between heptazine rings (Figure S4-2). The result would be a grafting of CN$_x$ on FTO through covalent bonds. The FTO glass was thus modified firstly by a 5 min plasma cleaning and secondly by a 24 h soaking in the mixture of 8.6 ml APTES with 20 ml toluene.

Figure 4-1. Schematic illustration of substrate cleaning, aminosilanization, and CN$_x$ electrode preparation.

We measured the contact angle of water droplets (5 µL of ultrapure water) on p-FTO$_{NH_2}$ and p-FTO to evaluate the success of the modification. As shown in Figure 4-2a, FTO glass that was ultrasonically cleaned in solvents had a contact angle of ~85°, showing the hydrophobic nature of its surface and pointing to residual carbon-based contamination from the ambient environment. The hydrophobic coating would impede surface modification and motivated us to use plasma cleaning for thorough cleaning. A 5 min
plasma cleaning under ambient air at a pressure of 0.5 Torr was chosen. Longer plasma treatment was seen to adversely affect the conductivity of the FTO material. After the plasma cleaning, the surface of the resulting p-FTO was highly hydrophilic and had contact angles of around 11°, which indicates the elimination of the organic contamination and the exposure of the hydrophilic -OH groups at the FTO surface. Aminosilanization was conducted immediately after the plasma cleaning, since the hydrophilicity of the FTO surfaces was decreased after exposure to air for 24 h (Figure S4-3), by soaking the p-FTO in the APTES-toluene mixture for 24 h. APTES was adsorbed on the substrate surface via hydrogen bonding and proton transfer between the terminal amino groups and the exposed hydroxyl groups\(^{259}\), and APTES from monolayer to multilayers in the thickness of a few hundred of Å is achievable with the control of the soaking time\(^{260}\). The p-FTO\(_{\text{NH2}}\) showed a slight contact angle decrease (~8°) compared to p-FTO, suggesting the hydrophilicity is well preserved or slightly improved after the aminosilanization. The increased hydrophilicity after plasma cleaning and aminosilanization increases the wettability of the surface to melted thiourea, which leads to a more spread out layer on the substrates during the polymer condensation and forms a thinner and more homogeneous CN\(_x\) layer.

Following the contact angle measurement, cyclic voltammetry (CV) was used to identify the attached amine groups after aminosilanization by detecting the electrochemical activity of the FTO surfaces towards ferrocene/ferrocenium. As seen in Figure 4-2b, a quasi-reversible redox reaction was seen in the p-FTO CV trace, showing the redox potential (i.e., the average of peak anodic and cathodic potential) of 0.19 V vs. Ag/Ag\(^+\) for the ferrocene/ferrocenium redox couple, which is close to the reported value (0.08 V vs. Ag/Ag\(^+\), 10 mM) with an 0.1 V offset\(^{261}\). The same measurement with the p-FTO\(_{\text{NH2}}\) showed a disappearance of the redox peaks and a decrease in current density from ~16 to ~1 \(\mu\)A cm\(^{-2}\). These results imply the electrode surface is covered by an
insulating layer that inhibits electron transfer between the FTO and the ferrocene redox couple in the organic solvent, supporting complete APTES coverage.

Figure 4-2. (a) The contact angle of FTO, p-FTO, p-FTO\textsubscript{NH\textsubscript{2}}. (b) CV of p-FTO\textsubscript{NH\textsubscript{2}} and p-FTO towards ferrocene (0.1 mM) in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 50 mV s\textsuperscript{-1} where a non-aqueous Ag/AgNO\textsubscript{3} was used as the reference electrode.

4.2.2 Morphological and structural characterizations

Following the successful modification of the FTO, we proceeded to grow CN\textsubscript{x} films on (non)aminosilanized substrates to evaluate the effect of the aminosilane on the resulting CN\textsubscript{x} layer. CN\textsubscript{x}/p-FTO\textsubscript{NH\textsubscript{2}} and CN\textsubscript{x}/p-FTO electrodes were prepared by dipping p-FTO\textsubscript{NH\textsubscript{2}} and p-FTO in 0.9 g/mL thiourea/water mixture three times to recrystallize a thiourea layer, and then thermally treated at 500°C for 2 h in N\textsubscript{2}. Scanning electron microscope (SEM) was used to observe the morphologies of CN\textsubscript{x} electrodes at the surfaces and cross-sections. Figure 4-3a, b shows CN\textsubscript{x}/p-FTO\textsubscript{NH\textsubscript{2}} and CN\textsubscript{x}/p-FTO both had flake-like and porous CN\textsubscript{x} morphologies at the surface. The former has smaller pores of ~5 μm compared to ~30 μm for CN\textsubscript{x}/p-FTO. The cross-sectional images are shown in Figure 4-3c, d. CN\textsubscript{x} on p-FTO\textsubscript{NH\textsubscript{2}} forms a more compact layer, while porous features of CN\textsubscript{x}/p-FTO were throughout the film leaving voids at the CN\textsubscript{x}/FTO interface. Underlayer gaps were formed during the layer-by-layer dip-coating, and the subsequent polymer condensation further preserved its porosity with the vaporization of hydrogen sulfide.
Close contact between the CN\textsubscript{x} layer and the FTO substrate is preferred since it potentially enables more efficient charge transfer across the interface to enhance the (photo)electrochemical performance\textsuperscript{138}. In addition, the surface terminations affected the thickness of the CN\textsubscript{x} layers grown. For the CN\textsubscript{x}/p-FTO it was ca. 130 μm while the CN\textsubscript{x}/p-FTO\textsubscript{NH2} has a thinner layer with a thickness of ~ 60 μm.

Figure 4-3. Top-view and cross-sectional SEM images of as-prepared (a, c) CN\textsubscript{x}/p-FTO\textsubscript{NH2} and (b, d) CN\textsubscript{x}/p-FTO electrodes. Top view images of (e) CN\textsubscript{x}/p-FTO\textsubscript{NH2}, (f) CN\textsubscript{x}/p-FTO, (g) Pt/CN\textsubscript{x}/p-FTO\textsubscript{NH2}, and (h) Pt/CN\textsubscript{x}/p-FTO electrodes after electrochemical measurements.
Fourier-transform infrared spectroscopy (FTIR) was used to verify the synthesis of CNx and identify its functional groups. In Figure 4-4a, the sharp peak at 804 cm\(^{-1}\) is one of the most prominent characteristic infrared absorption peaks of CNx materials, indicating the presence of the heptazine rings\(^{29}\). The multiple peaks within 1100-1650 cm\(^{-1}\) were attributed to the stretching vibration of CN heterocycles (C-N and C=\(\equiv\)N) in heptazine-derived repeating units\(^{262}\). Moreover, the broadening peak between 3000 and 3500 cm\(^{-1}\) is caused by the stretching modes of \(-\text{NH}_2\), \(-\text{NH}\), \(-\text{OH}\) groups\(^{37}\). The successful synthesis of typical heptazine-based CNx was confirmed in CNx/p-FTONH\(_2\) and CNx/p-FTO. Both showed spectra of high similarity, suggesting closely related chemical structures. No signatures of residual thiourea were seen in the FTIR spectra of the CNx films (Figure S4-4).

The colors of the CNx grown on p-FTONH\(_2\) and p-FTO were noticeably different, with CNx on p-FTONH\(_2\) being a lighter yellow compared to the orange color on p-FTO (Figure S4-5). Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was used to quantitatively investigate the optical properties of the films (Figure 4-4b). Similar absorption onsets around 450 nm were noticed for both samples, but a stronger absorption tail between 450 and 600 nm is evident for CNx/p-FTO, in line with the color differences observed by the eye. Tauc plots were used to determine bandgaps of 2.89 eV and 2.87 eV for CNx/p-FTONH\(_2\) and CNx/p-FTO, respectively (Figure 4-4c). In addition, a tail deviating from the linear portion from \(\sim 2.9\) eV to smaller energies could be seen. This is known as the Urbach tail\(^{263}\) and was analyzed in Figure 4-4d. The slope of the linear fits is proportional to \(1/E_u\) where \(E_u\) describes the energy level distribution of defect states in the materials\(^{264}\). The Urbach tail energy of CNx/p-FTONH\(_2\) was 217 meV/dec compared to 294 meV/dec for CNx/p-FTO, suggesting that CNx/p-FTONH\(_2\) has fewer trap states extending into the bandgap than CNx/p-FTO.

Photoluminescence of CNx/p-FTONH\(_2\) and CNx/p-FTO was collected under the continuous light excitation of 405 nm (Figure 4-4e). An intense emission peak was
measured at ~480 nm and represents the band-to-band recombination of electron-hole pairs\textsuperscript{37}, which are assigned to n-\pi * electronic transitions\textsuperscript{205,265}. CN\textsubscript{\textit{x}}/p-FTO has a lower PL intensity, which is consistent with more deep trapping and non-radiative recombination compared to CN\textsubscript{\textit{x}}/p-FTO\textsubscript{NH2}.

To provide more insights into the trap states, transient absorption spectroscopy (TAS) was used to detect non-emissive states in the CN\textsubscript{x}. CN\textsubscript{\textit{x}}/p-FTO\textsubscript{NH2} and CN\textsubscript{\textit{x}}/p-FTO electrodes were photoexcited using a 355 nm pulsed laser from the front CN\textsubscript{x} side, and the $\mu$s-TAS kinetic decay of photogenerated charges at the probe wavelength of 800 nm was collected. CN\textsubscript{\textit{x}}/p-FTO\textsubscript{NH2} showed a lower absorption amplitude than CN\textsubscript{\textit{x}}/p-FTO on the $\mu$s-s timescale (Figure 4-4f), which is assigned to a lower density of unreactive trapped electrons in the CN\textsubscript{x}\textsuperscript{66}. Both $\mu$s-TAS decays are linear on log-log plots (Figure 4-4g), indicating a power law decay with exponential tail states of trapped charges in the CN\textsubscript{x}\textsuperscript{60,64,65}. The power law exponent $\alpha$ were 0.27 and 0.25 for CN\textsubscript{\textit{x}}/p-FTO\textsubscript{NH2} and CN\textsubscript{\textit{x}}/p-FTO, respectively. The energetic distribution of trap states can be determined from the $\alpha$ values. Consistent in trends and values with the Urbach tails analyzed from the DRS spectra, the CN\textsubscript{\textit{x}}/p-FTO\textsubscript{NH2} has a narrower distribution of trap states (94 meV) compared to CN\textsubscript{\textit{x}}/p-FTO (126 meV), consistent with having less deep trap states in CN\textsubscript{\textit{x}}/p-FTO\textsubscript{NH2}. Detailed calculations can be found in Supporting Information 2.
Figure 4-4. (a) FTIR, (b) DRS, (c) Tauc plot, (d) Urbach tail, (e) PL, (f) TAS decay kinetics, and (g) TAS in the log-log scale of CNₓ/p-FTO NH₂ and CNₓ/p-FTO.
4.2.3 Electrochemical surface area

Electrochemical measurements were used to evaluate the electrochemical performance of the CNₙ on (non)aminosilanized FTO substrates in 0.1 M Na₂SO₄ (pH=7) and explain the differences seen in morphologies and optical properties. Electrochemical surface area (ECSA) is used as a critical parameter to reflect the reactive area of the materials²⁶⁶. We determined the ECSA by adding K₃[Fe(CN)₆] to the Na₂SO₄ electrolyte as an inorganic electron mediator to promote faradaic processes. CV scans in 5 mM K₃[Fe(CN)₆] - 0.1M Na₂SO₄ clearly resolved the redox processes on the bare FTO substrates (Figure 4-5). When the CNₙ layer was added, the current densities were reduced, consistent with the CNₙ layer having low conductivity²⁴⁴. The response observed is attributed to the exposed FTO areas so that a lower ECSA represents better surface coverage of the CNₙ film on the FTO. ECSA was calculated from the Randles-Sevcik equation¹²⁸ according to Equation 4-1, where the peak height is linearly proportional to the root of the scan rate. This equation can be taken to Equation 4-2 by dividing the electrode area to determine the relative ratio between ECSA and the geometry area of the electrode (P_ECSA to Geometry).

\[
i_p = (2.69 \times 10^5)n^{\frac{3}{2}}AD_0^{\frac{1}{2}}C_0^{\frac{1}{2}}v^{\frac{1}{2}}
\]

\[
j_p = (2.69 \times 10^5)n^{\frac{3}{2}}P_{ECSA to Geometry}D_0^{\frac{1}{2}}C_0^{\frac{1}{2}}v^{\frac{1}{2}}
\]

A is the ECSA in cm²; \(i_p\) is the peak current in amperes (A); \(j_p\) is the peak current density in A cm⁻²; \(n\) is the number of electrons evolved in the oxidation reaction (\(n=1\) in our case); \(D_0\) is the diffusion coefficient of the redox species in cm² s⁻¹; \(C_0\) is the concentration of the redox specie in the electrolyte in mol cm³. Specifically, \(D_0\) of Fe(CN)₆⁴⁻ (7.35×10⁻⁶ cm² s⁻¹) and Fe(CN)₆³⁻ (8.96×10⁻⁶ cm² s⁻¹) are used for calculating the ECSA from the anodic peak and the cathodic peak, respectively²⁶⁷.
Figure 4-5. (a) Cyclic voltammetry of p-FTO\textsubscript{NH2} in 5 mM K\textsubscript{3}[Fe(CN)\textsubscript{6}] - 0.1M Na\textsubscript{2}SO\textsubscript{4} from 10 to 110 mV s\textsuperscript{-1} with a 10 mV s\textsuperscript{-1} step within the potential range of 0.4 V to 1.2 V vs. RHE. (b) Peak cathodic or anodic current density as a function of the $v^{1/2}$, $v$ is the scan rate in the unit of V s\textsuperscript{-1}.

The $P_{ECSA \ to \ Geometry}$ of all samples at oxidative and reductive sides were listed in Table 4-1. CN\textsubscript{x} coverage is estimated to be on the order of $\sim$ 98-99% for both p-FTO\textsubscript{NH2} and p-FTO electrodes, and a slightly higher coverage was noticed in CN\textsubscript{x}/p-FTO\textsubscript{NH2} than CN\textsubscript{x}/p-FTO, consistent with the cross-sectional SEM images where CN\textsubscript{x}/p-FTO is more porous throughout the CN\textsubscript{x} film, resulting in electrolyte being able to penetrate deeper to the CN\textsubscript{x}/FTO interface (Figure 4-3c, d). A decrease of ca. 2~3% in $P_{ECSA \ to \ Geometry}$ was found between the p-FTO\textsubscript{NH2} and p-FTO, indicating the attached APTES slightly passivated the FTO surfaces in the aqueous environment.

Table 4-1. $P_{ECSA \ to \ Geometry}$ in percentage for CN\textsubscript{x}/p-FTO\textsubscript{NH2}, CN\textsubscript{x}/p-FTO, p-FTO\textsubscript{NH2}, and p-FTO.

<table>
<thead>
<tr>
<th></th>
<th>$P_{ECSA \ to \ Geometry}$ (%) at the anodic side</th>
<th>$P_{ECSA \ to \ Geometry}$ (%) at the cathodic side</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN\textsubscript{x}/p-FTO\textsubscript{NH2}</td>
<td>1.1 $\pm$ 0.2</td>
<td>1.1 $\pm$ 0.4</td>
</tr>
<tr>
<td>CN\textsubscript{x}/p-FTO</td>
<td>2.0 $\pm$ 0.7</td>
<td>1.8 $\pm$ 0.7</td>
</tr>
<tr>
<td>p-FTO\textsubscript{NH2}</td>
<td>69 $\pm$ 3</td>
<td>58.2 $\pm$ 0.7</td>
</tr>
<tr>
<td>p-FTO</td>
<td>71 $\pm$ 5</td>
<td>61 $\pm$ 4</td>
</tr>
</tbody>
</table>
4.2.4 Electrocatalytic hydrogen evolution activity

Clearly, CN$_x$ grown on p-FTO$_{NH2}$ and p-FTO have different morphology, which can lead to a difference in electrochemical performance. To better focus on the CN$_x$|FTO interface, we have photodeposited Pt cocatalyst on the surface of the CN$_x$ layer, which gives us two more CN$_x$ electrodes, Pt/CN$_x$/p-FTO$_{NH2}$ and Pt/CN$_x$/p-FTO. Pt, as a benchmark HER electrocatalyst, possesses low overpotential at 10 mA cm$^{-2}$ at all pH values and thus was added to minimize reactivity differences due to the CN$_x$ surfaces.

Linear scan voltammetry (LSV) was used to collect the potential-current density curve of CN$_x$ electrodes and FTO substrates in 0.1 M Na$_2$SO$_4$ (pH=7) (Figure 4-6a). At -0.5 V RHE, the given current density from the highest to the lowest followed the order of Pt/CN$_x$/p-FTO$_{NH2}$, Pt/CN$_x$/p-FTO, CN$_x$/p-FTO$_{NH2}$, CN$_x$/p-FTO, p-FTO$_{NH2}$, and p-FTO. The corresponding Tafel slopes were given in Figure 4-6b and Table S4-1. The overpotential needed for the CN$_x$ electrodes to increase the current density by a factor of ten is distinct from the FTO substrates with values less than one-half of them (~200 to 300 mV dec$^{-1}$ with CN$_x$ films vs. >600 mV dec$^{-1}$ for FTO substrates), which confirms charges passing through the CN$_x$ layer. Interestingly, the addition of Pt did not minimize the Tafel slope as was expected. We attribute this effect to the Tafel slope being not limited by the proton reduction reaction but rather by the conductivity of the CN$_x$ film and the difficulty of charges to reach the interface with the electrolyte. As reported by Zhang et al.$^{245}$, the electrical conductivity of CN$_x$ is lower than 1x10$^{-10}$ S m$^{-1}$, and this low conductivity limits the charges reaching the CN$_x$ surfaces and gives a high Tafel slope.

The chronoamperometry (I-t) and the corresponding electrocatalytic H$_2$ evolution rates were collected synchronously in 0.1 M Na$_2$SO$_4$ (pH=7) in the range of -0.3V to -0.8V vs. RHE (Figure S4-7). The initial applied bias of each CN$_x$ electrode was set to -0.3V vs. RHE (the least negative potential we detected any H$_2$). A potential shift to the negative by 0.1 V was applied when a steady hydrogen evolution rate and a stabilized chronoamperometric response were monitored simultaneously. This process was
repeated until the electrode became unfunctional, showing cracks or lifted edges. The breaking point of the electrode always gives a sharp spike in the I-t plot, which can be interpreted as the formation and detachment of the large hydrogen bubbles lifting the CN_x film and subsequent rushing of the electrolyte to the CN_x|FTO interface, causing a momentary circuit change. The presence of these spikes further confirms that the observed current response was not coming from the substrates since the breaking point of the FTO substrates was always observed as a step-like or unsmoothed current increase. With these data, we calculated the Faraday efficiency towards HER (FE_H2) according to Equation 4-3:

\[
FE_{H2}(\%) = \frac{\text{experimental \ \mu mol \ of \ } H_2}{\text{theoretical \ \mu mol \ of \ } H_2} \times 100% = \frac{\text{experimental \ \mu mol \ of \ } H_2}{\frac{I \times t}{z \times F}} = \frac{H_2 \text{ evolution rate \ (\mu mol/s)}}{\frac{I_s}{z \times F}}
\]

(4-3)

Where I is the time-dependent current in amperes; I_s is the stabilized current in amperes corresponding to a stabilized HER rate; t is the time in seconds; z is the number of transferred electrons, which is 2 for evolving hydrogen molecules; F is the Faraday constant (96485 C mol\(^{-1}\)).

The current density, H_2 evolution rate, and FE_H2 of four CN_x electrodes as a function of applied bias and their corresponding ratios relative to CN_x/p-FTO were plotted in Figure 4-6c to Figure 4-6h. In Figure 4-6c, either aminosilanization or Pt cocatalyst increased the current, and a similar enhancement in the current of the two was noticed compared to CN_x/p-FTO (Figure 4-6d). Pt/CN_x/p-FTO_NH2 with both modifications boosted the current density over CN_x/p-FTO by a factor of 7 at -0.3 V vs. RHE and still higher than 3 times at -0.8 V RHE. We now discuss the correlation between current density and HER rate. Overall, H_2 evolution rates increased when going to more negative potentials for all CN_x electrodes (Figure 4-6e), and the comparison of the four electrodes is shown in Figure 4-6f. CN_x/p-FTO_NH2 had similar H_2 evolution rates compared to the CN_x/p-FTO, inconsistent
with the higher current density measured. Pt/CNx/p-FTO displayed slightly higher HER rates than CNx/p-FTO at less negative potentials (-0.3 V to -0.5 V vs. RHE) while the impact of Pt diminished as the potential went further negative. Pt/CNx/p-FTO_{NH2} boosted the HER rates, with the highest ratio of 11 at -0.3 V vs. RHE and 3.1 at -0.6 V vs. RHE, but the ratios were not as large as in the current density. The differences in HER rates among electrodes kept narrowing and were found to be undistinguishable at -0.7 V vs. RHE, approaching the operating limit of the FTO substrates\(^{270}\). Clearly, the increase in the \(H_2\) evolution rate did not follow the pace of the current density increase. We propose that the current response is the collection of faradaic (e.g., current contributing to HER) and non-faradaic (e.g., initial charging of the semiconductor layer in Figure S4-7) processes, and either introducing Pt on CN\(_x\) surfaces or APTES at the CN\(_x\)/FTO interface introduced other electrochemical processes. In the absence of Pt, the rate of electrons consumed at the CN\(_x\) surface can limit the current. Adding Pt enables the quick consumption of the electrons at the CN\(_x\) surface, leading to a higher HER rate, and thus the current starts to be limited by electrons reaching the surface by charge transfer at the CN\(_x\)/FTO interface and charge transport through the CN\(_x\) layer. The distinct difference in HER rates between Pt/CNx/p-FTO\(_{NH2}\) and Pt/CNx/p-FTO suggests that the APTES modification helps electrons to reach the CN\(_x\) surface, presumably due to the promoted charge transfer at the CN\(_x\)/FTO interface and less charge trapping during charge transport in thinner CN\(_x\) layer. The behavior of Pt/CNx/p-FTO\(_{NH2}\) emphasizes the significance of modification to the CN\(_x\)/FTO interface as well as the CN\(_x\) surface for accelerating the HER kinetic.

As displayed in Figure 4-6g, the \(FE_{H2}\) for CN\(_x\) electrodes in 0.1 M \(Na_2SO_4\) peaked around -0.6 V vs. RHE with 46.1%, 37.3%, 57.7%, and 70.5% for Pt/CNx/p-FTO\(_{NH2}\), Pt/CNx/p-FTO, CNx/p-FTO\(_{NH2}\), and CNx/p-FTO, respectively, and decreased afterward. Unmodified CNx/p-FTO electrode has a higher \(FE_{H2}\) than other CNx electrodes except for Pt/CNx/p-FTO\(_{NH2}\) at -0.3 V vs. RHE (Figure 4-6h) since the modification involves electrochemical processes other than HER. Moreover, the \(FE_{H2}\) increased by 40~60%
within ca. 300 mV, but under applied bias as negative as -0.6 V vs. RHE, the FE$_{H_2}$ values were still much lower than 100%, the FE$_{H_2}$ of Pt at only -0.2 V vs. RHE (Figure S4-9). The low FE$_{H_2}$ values appear to be linked to the low conductivity of the CN$_x$ materials seen in ECSA measurement. As reported by Biswas et al., the water splitting efficiency of inorganic semiconductor-based photoelectrodes is linear to the conductivity of the light-absorbing material$^{271}$. With a stronger external applied bias to increase the electrical conductivity, charge transport and charge transfer efficiency close to 100% can be achieved for water oxidation in an inorganic semiconductor photoanode$^{272}$. In analogy, we suggest the CN$_x$ can be more conductive under further negative applied bias with more electrons injected, and this can affect the efficiency of charge transfer at the CN$_x$|FTO interface as well as the charge transport through the CN$_x$ layer, causing more charges reaching the CN$_x$ surface. The increase in conductivity can explain the increase in FE$_{H_2}$ but no further than -0.6 V RHE, the likely FTO limiting potential. Consistent with what we noticed in current density and HER kinetics, the addition of Pt did not boost the selectivity of charges flowing to the HER because the population of charges reaching the surface is limited, and thus the surface chemistry at the CN$_x$|electrolyte interface is not necessarily limiting the charge flux through the electrode.

The decrease in FE$_{H_2}$ after -0.6 V RHE may also be due to the mass transfer limitation. The FE$_{H_2}$ for CN$_x$ electrodes peaked on the order of 10 to 50 μA cm$^{-2}$ and then decreased (Figure 4-6i and Figure S4-11). Typically, mass transfer limitations don’t appear until a few mA cm$^{-2}$ in inorganic semiconductor electrodes$^{273}$. The decrease in FE$_{H_2}$ at lower current density in our case can be due to the hydrogen bubble generation and detachment since the enlarging hydrogen bubbles which are not detached in time can induce the local inhibition of the mass transfer at the surfaces$^{274}$. Not only at surfaces, but the permeation of the electrolyte can also cause mass transfer issues beneath the CN$_x$ surface. It was found that Na$_2$SO$_4$ electrolyte can diffuse to the FTO surface through ‘pinholes’ of 50 nm in diameter on the Ti layer with a thickness of a few micrometers during
PEC water splitting, completely detaching the functional inorganic semiconductor from the FTO substrate, as reported by Krysa et al.\textsuperscript{275}. Consistent with our observation, as potential went further negative, the back side of the FTO substrates started showing scattered ‘shadows,’ and eventually a millimeter-sized bubble was trapped beneath the CN\textsubscript{x} layer. This was seen to occur even on compact CN\textsubscript{x}/p-FTO\textsubscript{NH2} electrode (Figure S4-12), a clear indication that the electrolyte can permeate the CN\textsubscript{x} layer and hydrogen molecules are generated and detained at the CN\textsubscript{x}/FTO interface. As reported by Li et al., a porous 3D architecture with ordered channels can be synthesized for a better bubble release in water electrolysis, which solves the mass transfer problem caused by gas bubbles blocking a large portion of the catalytically active surface area and efficiently decreasing the ohmic loss\textsuperscript{276}. A similar concept has been advanced for CN\textsubscript{x}-based nanosized heteroarrays, but the majority of them are based on CN\textsubscript{x} being guest materials to decorate other semiconductors (e.g., TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, and CdS)\textsuperscript{277}. 
Figure 4-6. (a) Linear scan voltammetry and (b) corresponding Tafel slopes of Pt/CN\textsubscript{x}/p-FTO\textsubscript{NH2}, Pt/CN\textsubscript{x}/p-FTO, CN\textsubscript{x}/p-FTO\textsubscript{NH2}, CN\textsubscript{x}/p-FTO, p-FTO\textsubscript{NH2}, and p-FTO in 0.1 M Na\textsubscript{2}SO\textsubscript{4} at the scan rate of 1 mV s\textsuperscript{-1} from 0 V to -0.5 V vs. RHE. (c) The stabilized current density, (e)
H$_2$ evolution rate, (g) $\text{FE}_{\text{H}_2}$ of Pt/CN$_x$/p-FTO$_{\text{NH}_2}$, Pt/CN$_x$/p-FTO, CN$_x$/p-FTO$_{\text{NH}_2}$, and CN$_x$/p-FTO electrodes against applied bias in the range of -0.3 V to -0.8 V RHE with 0.1 V intervals in 0.1 M Na$_2$SO$_4$ and (d, f, h) their ratios relative to the CN$_x$/p-FTO electrode, respectively. (i) $\text{FE}_{\text{H}_2}$ of four CN$_x$ electrodes plotted against the current density.

4.2.5 Electrochemical stability measurement

The erosion of the electrolyte at the CN$_x$|FTO interface and concerning CN$_x$ film detachment issue led us to analyze the electrochemical stability of CN$_x$ electrodes. Firstly, our initial attempts on CN$_x$/FTO$_{\text{NH}_2}$ (substrate non-plasma cleaned but aminosilanized) and CN$_x$/FTO (substrate non-plasma cleaned) demonstrated their limited stability. They do not stay functional at potentials more negative than -0.1 V vs. RHE, consistent with the residual surface contamination identified by contact angle measurements, which severely impedes the formation of an electrochemical-stable CN$_x$ electrode. Plasma cleaning is necessary to produce stable electrodes.

Secondly, to quantify the electrochemical stability of the CN$_x$ electrodes, we integrated the current over time in chronoamperometric curves (Figure S4-7) and determined the amount of charge (Coulombs) passing through the electrode before the electrode broke and the CN$_x$ film lifted (Figure 4-7). CN$_x$/p-FTO$_{\text{NH}_2}$ on average passed 0.6 C of charge, 2.4 times that of CN$_x$/p-FTO (~0.25 C). CN$_x$/p-FTO with more exposed FTO, as determined by the ECSA measurements, induces more hydrogen generated at the CN$_x$|FTO interface and thus has weaker electrochemical stability. Also, Pt/CN$_x$/p-FTO$_{\text{NH}_2}$ allowed ~1 C of charge to pass through, 2.5 times that of Pt/CN$_x$/p-FTO (~0.4 C). Clearly, the aminosilanization at the CN$_x$|FTO interface contributed to more charges the electrode can pass before failure, which is presumably due to the easier charge transfer at the CN$_x$|FTO interface. The impact of Pt prolonging the electrochemical lifetime was also investigated. The ratios of passed charges between Pt/CN$_x$/p-FTO vs. CN$_x$/p-FTO and Pt/CN$_x$/p-FTO$_{\text{NH}_2}$ vs. CN$_x$/p-FTO$_{\text{NH}_2}$ were 1.6 and 1.7, respectively. Finally, combining both
modifications resulted in Pt/CN\(_x/p\)-FTO\(_{NH2}\) passing 4 times the charges of the CN\(_x/p\)-FTO. The synergy with the optimized redox reaction at the surface (in contact with the electrolyte) and promoted charge transfer at the CN\(_x\)/FTO interface further enhance the electrochemical stability.

A prolonged electrochemical lifetime can be achieved by letting the electrode work at less negative potentials, presumably due to limiting the formation of large H\(_2\) bubbles that cause film lift-off. The most stable sample was Pt/CN\(_x\)/FTO\(_{NH2}\) which stayed functional until 8.9 C charges passed, surviving for 20 h in total from applied potentials of -0.3 V vs. RHE for 1 h, -0.4 V vs. RHE for 2 h, -0.5 V vs. RHE for ~5 h, -0.6 V vs. RHE for 10 h, and -0.7 V vs. RHE for ~1 h. More details about the electrochemical stability can be found in Figure S4-13.

![Figure 4-7](image)

**Figure 4-7.** The averaged charges passed before failure for Pt/CN\(_x/p\)-FTO\(_{NH2}\), Pt/CN\(_x/p\)-FTO, CN\(_x/p\)-FTO\(_{NH2}\), and CN\(_x/p\)-FTO in 0.1 M Na\(_2\)SO\(_4\). The chronoamperometric response corresponding to HER at applied potentials ranging from -0.3 V to -0.8 V vs. RHE at 0.1 V intervals was integrated by time individually and summed to calculate the number of passed charges.

The morphology of broken representative CN\(_x\) electrodes after the electrochemical measurements were taken by SEM (Figure 4-3e to Figure 4-3h). The photodeposited Pt made the electrode surface smoother, with most voids filled with Pt nanoparticles. No
matter if Pt cocatalyst is present or not, CN\textsubscript{x} on p-FTO is more likely to bulge with cracks (Figure S4-14), while CN\textsubscript{x} on p-FTO\textsubscript{NH2} tends to maintain the CN\textsubscript{x} as a whole film and has lifted edges.

### 4.2.6 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) can monitor faradaic and non-faradaic processes simultaneously, through which the impedance during the electrochemical processes could be disentangled\textsuperscript{278}. EIS measurements were conducted in 0.1M Na\textsubscript{2}SO\textsubscript{4}, in the absence and presence of an additional 5 mM K\textsubscript{3}[Fe(CN)\textsubscript{6}] under dark conditions. The electrodes were preconditioned at a bias of -0.5V vs. RHE before the EIS measurement, allowing for a more accurate simulation of the HER process\textsuperscript{143}. 10 min preconditioning was applied to CN\textsubscript{x} electrodes to allow sufficient time to reach equilibrium, while p-FTO\textsubscript{NH2}, p-FTO, and FTO only needed 1 min of preconditioning. The total impedance |Z| and Bode phase plots were given in Figure S4-15 and Figure S4-16, and the Nyquist plots were plotted as imaginary impedance versus real impedance in Figure 4-8a, b and Figure S4-17a, b.

The Bode plots in an inert electrolyte give insight into the ionic permeation of polymer electrode surface to small ions (i.e., Na\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} in our case)\textsuperscript{279} (Figure S4-17c). Generally, ionic permeation favors low frequencies (< 2 Hz), where a lower \(\phi\) suggests a higher ionic permeation ability with \(\phi\) close to ~80° implying that the substrate behaves closer to an ideal capacitor\textsuperscript{280}. The \(\phi\) of the four CN\textsubscript{x} electrodes were lower, being 60° at 1 Hz and 0.1 Hz, reflecting that all electrodes are well ion-permeable.

The prominent peak in Bode plots (Figure S4-16) can be expressed with an RC (resistor and capacitor) branch in the equivalent circuit\textsuperscript{281}. It describes that the impedance is dominated by a single process, usually the interfacial charge transfer at the CN\textsubscript{x}|electrolyte interface at this low frequency (~10 Hz). Though the low conductivity of CN\textsubscript{x} can lead to a large charge transport resistance (R\textsubscript{tr}), shown as a straight line at about...
a few hundred-hertz regions in the Nyquist plot\textsuperscript{282}, it was not seen in our case, which can be related to the preconditioning allowing for adequate electron accumulating in the conduction band of the CN\textsubscript{x}\textsuperscript{283,284}. The equivalent circuits were thus modeled based on Randle’s circuit\textsuperscript{285} to explain the Nyquist plot (inserts in Figure 4-8\textbf{a, b}). The Warburg element (\(W_1\)) is needed in the case of CN\textsubscript{x} electrodes to fit the upward tail in the right-hand side of the Nyquist plot. Instead of an ideal capacitor element, a constant phase element (CPE) was used to describe the non-ideality associated with non-faradaic processes\textsuperscript{286}. 

\(Q_1\), the characteristic parameter of CPE, can be converted to its equivalent capacitance (C) according to \textbf{Equations 4-4} and \textbf{4-5}\textsuperscript{286}.

\[
C_1 = Q_1(\omega_{\text{max}}'')^{n-1} \tag{4-4}
\]

\[
C_2 = \frac{(Q_1R_{ct})^{\frac{1}{n}}}{R_{ct}} \tag{4-5}
\]

where \(\omega_{\text{max}}''\) is the angular frequency corresponding to the maximum imaginary part of the impedance and \(n\) describes how CPE is close to capacitance in the range of 0 to 1.

The fitted Nyquist plots are in Figure S4-18 and Figure S4-19, and best fit parameters (\(R_1, R_2, W_1, Q_1, n, C_1, C_2\)) are listed in Table S4-2. We see that the FTO substrates had \(n\) values quite close to 1, while \(n\) was ca. 0.75 in the CN\textsubscript{x} electrode, shown as the depressed semicircle in the Nyquist plot. This is related to the non-homogeneity of the electrode surface, for example, the surface roughness\textsuperscript{148}. The capacitance is assigned to accumulated charges at the CN\textsubscript{x}/electrolyte interface. CN\textsubscript{x}/p-FTO had a \(C_1\) value of ca. 300 \textmu F cm\textsuperscript{-2}, which is 100~200 \textmu F cm\textsuperscript{-2} lower than other CN\textsubscript{x} electrodes, indicating that the least charges are accumulated at the surface of the CN\textsubscript{x}/p-FTO.

From the Nyquist plots, we obtained \(R_1\) of \(\sim 30\ \Omega\) (representing the total resistance of the electrolyte, back contact, and all wires) with the FTO substrates, and the value increased by 30~300 \(\Omega\) when calcinating the CN\textsubscript{x} layer on the top. The interfacial charge transfer resistance \(R_{ct}\) is correlated to the kinetics of the Faradaic reactions (i.e., HER)
and the thickness of the charge transfer layer. A smaller $R_{ct}$ can be correlated to a faster reaction rate and a thinner charge-transferring layer\textsuperscript{287,288}. The $R_{ct}$ of CN$_x$ electrodes in different electrolytes was analyzed in Figure 4-8c to distinguish the impact from different modifications to the interfacial charge transfer at the CN$_x$|electrolyte interface. In 0.1 M Na$_2$SO$_4$ electrolyte, CN$_x$/p-FTO$_{NH2}$ had a $R_{ct}$ ca. 40% smaller than that of CN$_x$/p-FTO (~3300 $\Omega$ vs. ~5100 $\Omega$). Again, the modification at the CN$_x$|FTO interface influencing the CN$_x$|electrolyte interface was seen. The addition of Pt narrowed the difference in $R_{ct}$ to 10% (~3700 $\Omega$ for Pt/CN$_x$/p-FTO$_{NH2}$ vs. ~4100 $\Omega$ for Pt/CN$_x$/p-FTO) since it optimized the CN$_x$ surfaces. Interestingly, with a faster one-electron redox reaction, the APTES modification alone decreased the $R_{ct}$ by 55% even comparable to the impact of the Pt, and Pt/CN$_x$/p-FTO$_{NH2}$ with both modifications caused a 90% decrease in $R_{ct}$ compared to that of CN$_x$/p-FTO.

The Warburg impedance was compared in Figure 4-8d to study the mass transfer and ion diffusion in the CN$_x$ electrodes. The classic diffusion-controlled Warburg impedance has a slope of 45° on a planar electrode\textsuperscript{288}, and a decreased Warburg slope is seen on porous electrodes\textsuperscript{289}, like our CN$_x$ electrodes. In Kundu et al.’s work on Zinc batteries, a Warburg tail similar to ours was seen and assigned to its porous structure\textsuperscript{290}. CN$_x$/p-FTO$_{NH2}$ consistently showed a smaller Warburg impedance compared to CN$_x$/p-FTO, which can be related to its morphology with a decreased pore volume (Figure 4-3). The Warburg impedance decreased after the photodeposited Pt cocatalyst filled the pores, causing the surfaces to be smoother and closer to flat substrates with less diffusion through the film.
Figure 4-8. EIS conducted under -0.5 V vs. RHE. (a) Nyquist plot of Pt/CNₓ/p-FTO NH₂, Pt/CNₓ/p-FTO, CNₓ/p-FTO NH₂, CNₓ/p-FTO, and (b) p-FTO NH₂, p-FTO in 0.1 M Na₂SO₄. (c) R<sub>ct</sub> and (d) Warburg resistance of four CNₓ electrodes in 0.1 M Na₂SO₄ and 5 mM K₃[Fe(CN)₆]-0.1 M Na₂SO₄. In the equivalent circuit, R₁ includes the resistance of the electrolyte, back contact, and all wires; R₂ (Rₚ) is the interfacial charge transfer resistance at the CNₓ|electrolyte interface in Ω; σ represents the Warburg impedance in Ω s<sup>1/2</sup>; Q₁ is the constant phase element (CPE).

4.2.7 Physical robustness

The physical robustness was tested by sonicating the electrodes in water in 5 mins increments up to 30 mins and taking digital photographs (Figure S4-20). CNₓ/p-FTO had an outstanding adhesion, showing CNₓ firmly attached to the substrate after the full 30
mins of sonication, as did CNₓ/FTO (Figure S4-21). As reported by Shalom et al.²⁹¹, CNₓ is bonded to the hydroxylated surface of silica via Si-O-NH-bonds, which can be further taken as Sn-O-NH when CNₓ contacts SnO₂ surfaces. Unexpectedly, the CNₓ layer of CNₓ/p-FTO_{NH₂} started to fall off after the first 5 min, and only a small portion of the film remained on the substrate at the end, conflicting with our expectation that the APTES layer would serve as a covalent bridge between the CNₓ and the supporting substrates. Jin et al.’s TGA analysis on APTES-silica surfaces²⁹² found that the decomposition of chemically bonded APTES starts at ca. 500°C due to the cleaving of the C-Si bond that is initiated at 450-510°C in an N₂ atmosphere²⁹³. While in Jafarzadeh et al.’s work, the PL peak assigned to ATPES in aminopropyl-modified silica nanoparticles was only partially quenched after 2 h calcination at 500°C, suggesting that APTES was not fully decomposed with the protection of the silica network. Hence, in our case, it is likely that only a certain number of bonded APTES groups are cleaved during the thermal treatment for CNₓ synthesis, leading to a CNₓ layer with a hydrophobic propyl chain appended to it, which would not have desirable interactions with the hydroxylated surface of the FTO.

4.3 Experimental section

Chemicals and substrates. All of the chemical reagents were purchased from commercial suppliers and used with no further purification. Thiourea (≥99.0%), toluene (anhydrous, 99.8%), chloroplatinic acid hydrate (H₂PtCl₆) (≥99.9%), triethanolamine (TEOA) (>99.0%), ferrocene (98%), tetrabutylammonium hexafluorophosphate (for electrochemical analysis, ≥99.0%), potassium hexacyanoferrate (K₃[Fe(CN)₆]) (ACS reagent, ≥99.0%), sodium sulfate (ACS reagent, ≥99.0%), acetonitrile (HPLC, ≥99.9%), fluorine-doped tin oxide (FTO) coated glass (surface resistivity ~7 Ω/aq, thickness 2.2 mm) were purchased from Sigma-Aldrich. (3-Aminopropyl)triethoxysilane (APTES) (98%) was purchased from Alfa Aesar. Acetone (≥99.5%) and ethanol (reagent grade alcohol, 100%)
were purchased from VWR. Ultrapure water (18.2 MΩ cm resistivity at 20°C) was obtained from a Direct-Q water purification system.

**Preparation of p-FTO and p-FTO\textsubscript{NH2}.** Commercial FTO-coated glass slides (1.0 cm x 2 cm) were plasma cleaned for 5 mins at a high Radio Frequency (RF) level (18W) under chamber pressure of 0.5 Torr and carrier gas of air to produce p-FTO. Aminosilanization was conducted right after the plasma cleaning to prepare aminosilanized FTO-coated glass slides (p-FTO\textsubscript{NH2}). p-FTOs were firstly placed in the staining jar, which was rinsed with ethanol, completely dried at 60°C in an oven, and cooled down to room temperature. Next, anhydrous toluene was added to the APTES to prepare an APTES-toluene mixture (8.6 mL APTES per 20 mL), and the mixture was thoroughly mixed before transferring it into the jar. The staining jar was capped and firmly wrapped with Parafilm to block the moisture and keep the mixture transparent and clean. The soaking lasted for 24 h, and the sides were taken out and cleaned with acetone, ethanol, and ultrapure water in sequence to remove the physically bonded APTES.

**Preparation of CN\textsubscript{x}/p-FTO and CN\textsubscript{x}/p-FTO\textsubscript{NH2}.** p-FTOs were coated with a layer of thiourea film by dipping the slides into 70°C aqueous thiourea solution (0.9 g mL\textsuperscript{-1}) and taken out immediately. 5 mins interval was instituted before the next dipping. Three dips in total per slide were conducted. The prepared thiourea/p-FTO were dried at 60°C in an oven for subsequent use. Thiourea/p-FTO slides were placed in a glass tube capped with aluminum foil and then calcinated in a tube furnace at 500°C for 2 h with a heat ramp of 5°C per minute under N\textsubscript{2} flow to produce CN\textsubscript{x}/p-FTO. The CN\textsubscript{x}/p-FTO\textsubscript{NH2} was prepared by replacing the substrate with p-FTO\textsubscript{NH2} and repeating the same procedures.

**Preparation of Pt/CN\textsubscript{x}/p-FTO and Pt/CN\textsubscript{x}/p-FTO\textsubscript{NH2}**. The Pt cocatalyst was introduced to the surface of the CN\textsubscript{x} layer through photodeposition. Electrodes (1.0 cm x 2 cm of CN\textsubscript{x}/p-FTO or CN\textsubscript{x}/p-FTO\textsubscript{NH2}) were vertically placed one at a time in a quartz cuvette containing 10 mL of 1 mM H\textsubscript{2}PtCl\textsubscript{6} in 10% v/v TEOA/H\textsubscript{2}O, with the CN\textsubscript{x} layer facing the light. The solution was purged with Ar for 15 min to remove the dissolved oxygen in
the solution before turning the 405 nm LED light on. The illumination of 10 mW cm\(^{-2}\) lasted for 1 h, with the system well-sealed and stirred to form Pt/CN\(_x/p\)-FTO or Pt/CN\(_x/p\)-FTO\(_{\text{NH2}}\). The electrodes were washed with ethanol to remove the residual TEOA and then dried at room temperature for subsequent use.

**Electrochemical measurements.** The electric connection of the working electrodes to the wire was conducted in the following steps. Firstly, a ca. 2 mm x 2 mm area of the CN\(_x\) layer was scratched off using a surgical blade to expose the underlying conductive FTO layer. Secondly, the exposed FTO surface was connected to the wire by pasting a silver conductive epoxy (MG Chemicals, #83315-15G) at the joint and heated at 65°C for 2 h to cure. Lastly, to achieve a waterproof electric connection, a layer of marine epoxy (LePage Marine Epoxy, #1919323, Henkel) was coated on top to fully cover the dried conductive epoxy and any exposed wire. Electrochemical measurement was conducted in a quartz electrochemical cell using a Palmsens4 potentiostat. The electrolyte was fully purged with Ar between scans to create an inert electrochemical environment. The CV responses of p-FTO\(_{\text{NH2}}\) and p-FTO towards ferrocene/ferrocenium were tested using 0.1 mM ferrocene with 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with the scan rate of 50 mV s\(^{-1}\) in the potential range of -1 V to 1 V vs. Ag/Ag\(^+\) (non-aqueous Ag/AgNO\(_3\), 10 mM, as the reference electrode) and Pt wire as the counter electrode. The CV responses of Pt/CN\(_x/p\)-FTO\(_{\text{NH2}}\), Pt/CN\(_x/p\)-FTO, CN\(_x/p\)-FTO\(_{\text{NH2}}\), CN\(_x/p\)-FTO, p-FTO\(_{\text{NH2}}\), and p-FTO towards ferrocyanide/ferricyanide were tested in aqueous 5 mM K\(_3[\text{Fe(CN)}_6]\) -with 0.1M Na\(_2\)SO\(_4\) from 10 to 110 mV s\(^{-1}\) with 10 mV s\(^{-1}\) steps within the potential range of 0.4 V to 1.2 V vs. RHE (-0.2 V to 0.6 V vs. Ag/AgCl), where the aqueous Ag/AgCl (3 M KCl) and Pt wire were used as the reference electrode and counter electrode, respectively. The LSV scans of all electrodes were conducted in 0.1 M Na\(_2\)SO\(_4\) electrolyte at the scan rate of 1 mV s\(^{-1}\) from 0 V to -0.5 V vs. RHE; the CV scans were scanned between 0.5 V and -0.5 V vs. RHE with the scan rate of 1 mV s\(^{-1}\) or 10 mV s\(^{-1}\) in 0.1 M Na\(_2\)SO\(_4\) electrolyte. The chronoamperometry was conducted in 0.1 M Na\(_2\)SO\(_4\) electrolyte.
under the bias of -0.3 V to -0.8 V vs. RHE with 0.1 V intervals. The EIS measurement was conducted in 0.1 M Na$_2$SO$_4$ or 5 mM K$_3$[Fe(CN)$_6$] with 0.1 M Na$_2$SO$_4$ electrolytes, with an $E_{dc}$ of -0.5 V vs. RHE and $E_{ac}$ of 10 mV. CN$_x$-contained electrodes and FTO substrates were preconditioned at -0.5 V vs. RHE for 10 min and 1 min, respectively. The frequency range was from 100000 Hz to 0.01 Hz.

Characterization. Plasma cleaning proceeded with a PDC-32G Harrick plasma cleanser (115V) using air as the carrier gas. The contact angle was measured using a home-built apparatus, a SAMSUNG PL200 camera was fixed on the optical table, and a stage was lifted to the focus of the camera lens with a convex lens placed in between to focus on the cross-section. Images were taken with the slide horizontally placed on the stage, and the contact angle analysis was finished using Fiji software. Scanning electron microscopy (SEM) was obtained using a Tescan Mira 3 XMU scanning electron microscope (working distance of 18 mm, beam intensity of 15.00, and an accelerating voltage of 20 kV) with the sample coated with 10 nm thick Pt/Pd. Fourier-transform infrared spectroscopy (FTIR) was collected using a Thermo Electron Nicolet 6700 spectroscopy equipped with a diamond ATR attachment and an XT-KBr beam splitter. UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was measured using an Ocean Optics Maya 2000 PRO spectrometer, and a deuterium/halogen light source was connected to the integrating sphere accessory through which the light was directed to the sample slide. The photoluminescence (PL) was collected on the Ocean Optics system by replacing the broad-band light with a 405 nm laser diode excitation, and the slide was kept under the integrating sphere. Transient absorption spectroscopy (TAS) was collected based on a home-built microsecond TAS setup, where a Surelite Continuum Nd: YAG laser generates laser pulses at 355 nm laser with the fluence of 100 uJ cm$^{-2}$, and a 95 W oriel lamp was used to probe the transient changes in absorption at 800 nm upon photoexcitation. The sample electrode was mounted on the stage in the ambient air and excited by a pulsed laser, and the signal was averaged over 512 scans. The transient absorption changes
Upon photoexcitation were acquired by a photodiode using custom LabVIEW code and processed with MATLAB code available at https://github.com/SolarSpec/SpectraBuilder. Electrochemical measurements were conducted with a PalmSen4 potentiostat. The hydrogen concentration in the aqueous phase was probed by a Unisense hydrogen microprobe sensor. Physical robustness measurement was tested using a Branson M2800 ultrasonic cleaner (40 kHz).

4.4 Conclusions

Our work has broken down the complexity of the photo(electrode) systems and explored the CN\textsubscript{x} thin film purely under the electrochemical conditions without light irradiation to pave the pathways for its further being utilized as the photocathode in harsh photoelectrochemical environments. We filled the knowledge gap of the fundamental studies at the CN\textsubscript{x}|FTO interface, pointed out the existing issues (i.e., electrolyte penetration, film detachment) and potential solutions, and emphasized the importance of the back contact interface for the optimization of CN\textsubscript{x}-based (photo)electrochemical devices.

We have reported a direct growth of a CN\textsubscript{x} layer on p-FTONH\textsubscript{2}, a plasma-cleaned and aminosilanized FTO substrate, where APTES was introduced as a bifunctional covalent linker to bond the CN\textsubscript{x} layer to the hydroxylated FTO surface. The critical CN\textsubscript{x}|FTO interface and resulting CN\textsubscript{x} electrodes were carefully investigated from hydrophilicity, morphology, optical properties, electrochemical performance, and physical robustness. We surprisingly found that the modification at the interface influenced the CN\textsubscript{x} on the length scale of tens of micrometers, exemplified by CN\textsubscript{x} layer thicknesses of 60 μm and 130 μm with and without the APTES modification, respectively. The CN\textsubscript{x} layers have pore sizes from a few micrometers to tens of micrometers, and the CN\textsubscript{x} film grown on the p-FTONH\textsubscript{2} was denser and more compact. We found that the high permeability of the porous CN\textsubscript{x} was problematic since it erodes the electrode stability at the CN\textsubscript{x}|FTO interface.
The formation of H\textsubscript{2} bubbles at the FTO interface causes the detachment of the functional materials during the (photo)electrochemical processes. Mass transfer limitations at low current densities of 10 to 50 μA cm\textsuperscript{-2} were observed, which we attribute to bubble aggregation in the porous network, blocking the reactive sites and hindering the HER process. Increasing the CN\textsubscript{x} surface hydrophobicity for a faster bubble detachment or preparing CN\textsubscript{x} with ordered structures for better mass transfer could be ways to accelerate the (photo)electrochemical HER. For example, well-ordered crystalline nanocones with CN\textsubscript{x} being host materials growing on Si wafer has been synthesized using plasma sputtering reaction deposition\textsuperscript{295}, and this strategy could be leveraged to improve product bubble release.

Interestingly, as verified by the DRS and TAS measurements, modification of the FTO surface was able to reduce the distribution of trap states in CN\textsubscript{x}/p-FTO\textsubscript{NH2} compared to CN\textsubscript{x}/p-FTO. The lower Urbach tail energy and corresponding lower density of deep traps in CN\textsubscript{x}/p-FTO\textsubscript{NH2} decreased charge trapping during charge transport to the CN\textsubscript{x} interface with the electrolyte. The improved charge transport through the CN\textsubscript{x} film of CN\textsubscript{x}/p-FTO\textsubscript{NH2}, both from a decreased thickness and a reduction in the density of deep trap states, led to increased electrocatalytic current density and HER rates. With Pt/CN\textsubscript{x}/p-FTO exhibiting a comparable HER rate to CN\textsubscript{x}/p-FTO but Pt/CN\textsubscript{x}/p-FTO\textsubscript{NH2} showing a much higher HER rate than both, we conclude that HER on CN\textsubscript{x} electrodes is predominantly limited by whether charges can reach the surface rather than by surface reaction limitations.

Overall, we observe that the CN\textsubscript{x}/FTO interface modification has a significant impact on the properties of the grown CN\textsubscript{x} layer and spatially far beyond the immediate interface. More efforts to understand CN\textsubscript{x}/substrate interface engineering and how it affects the properties of the CN\textsubscript{x} layer are warranted. Based on the presumed cleavage of the Si-C bond of ATPES during the polymer condensation, more thermally stable strategies should be explored. A thin layer of metal added to the FTO could bring the chance of forming interfacial coordination bonds. As reported recently, the \textit{sp}^{2} N→Ti
coordination bonds were found between CNₓ and Ti-FTO substrate²⁵¹, leading to an expedited charge transfer from the semiconductor to the supporting substrate. We found no correlation between physical adhesion and electrochemical stability of the CNₓ films, emphasizing the need to evaluate both separately. Ultimately, the importance of interfacial charge transfer and potential limitations motivate the optimization of every interface in (photo)electrode systems.
Chapter 5: Conclusion

This work aims at optimizing CN$_x$ material for photo(electro)catalysis and focuses on how interface modifications impact the morphology, optical property, HER activity, and stability of CN$_x$-based photocatalysts and photoelectrodes. The semiconductor|cocatalyst interface in a particulate system was described in chapter 3 and the semiconductor|substrate interface in an electrochemical system was described in chapter 4. We concluded that the major limitation of CN$_x$ is unproductive charge recombination and charge trapping and pointed out the direction for future work on CN$_x$ material.

Interface engineering impacts interfacial charge transfer, the key to productive photo(electro)catalytic processes. In chapter 3, the CN$_x$|cocatalyst interface was studied. Particulate CN$_x$ alone did not produce hydrogen since photoexcited charges were wasted by severe bulk and surface recombination. HER activity was observed when cocatalysts (Pt or Ni) were deposited on CN$_x$, an indication that cocatalysts prevent charge carrier recombination and promote proton reduction. NiO(65)/CN$_x$, and 3 wt.% Ni/CN$_x$ exhibited 54% and 39% of the HER activity of 3 wt.% Pt/CN$_x$ under ~1 sun illumination. The difference in exchange current density between Ni and Pt metals can reach one order of magnitude, but it is reported in the HER volcano plot that the logarithm of the exchange current density of metal catalysts is proportional to the hydrogen adsorption free energy and also to the potential at a constant HER current density (10 mA cm$^{-2}$). Thus, Ni cocatalyst can still exhibit HER activity within a factor of two compared to Pt despite having an exchange current density ten times smaller. This further suggests cocatalysts vary in charge extraction abilities and the charge transfer at the CN$_x$|cocatalyst interface.

In chapter 4, the CN$_x$|FTO and the CN$_x$|Pt interfaces were investigated in CN$_x$ electrodes. In the dark, the accelerated charge transfer at the CN$_x$|Pt interface could not boost HER rate alone indicating that HER is limited by the charges reaching the CN$_x$ surface. Electrons reach the surface via charge transfer at the CN$_x$|FTO interface and charge transport through the CN$_x$ layer, highlighting that these processes ultimately dictate
the HER activity. APTES modification at the CN_x|FTO interface resulted in a thinner and more compact CN_x layer, which allows more charges to pass through and reach the CN_x surface. Additionally, this CN_x|FTO interface changed the morphology of the CN_x surface and eventually resulted in a lower interfacial charge transfer resistance at the CN_x|electrolyte and CN_x|Pt interfaces.

The modifications at various interfaces also cause different charge trapping properties during charge transport. In chapter 3, the charge carrier dynamics of ALD-derived NiO/CN_x and CN_x within 2000 μs upon photoexcitation were monitored by time-resolved photoluminescence (trPL). Similar behavior in power law decay and emission energy shift was obtained. This points to similar charge recombination during this timescale and that the NiO cocatalyst does not affect the charge carrier dynamics because of the high population of trap states in bulk CN_x. The similarities in transient absorption spectra and photoinduced absorption spectroscopy (PIAS) signal decays of Pt/CN_x, NiO/CN_x, and CN_x further confirm that trapped charges dominated the PIAS signal. Hence, in our case, the post-synthetic modification did not help suppress charge trapping in the as-prepared CN_x. Meanwhile, we found that pre-synthetic modification which influences the CN_x growth can tune the density of the trap states. In chapter 4, ATPES modification led to CN_x of lesser deep trap states grown on the p-FTO_NH2 than p-FTO substrates, verified by lower Urbach tail energy calculated from the DRS, higher PL intensity from reduced non-radiative recombination, and fewer trapped charges in addition to a narrower trap distribution that leads to shallower traps as determined by transient absorption spectroscopy (TAS). In addition, if the electronic properties of the CN_x can be tuned by the underlayer onto which it is grown or its surroundings during the polymer condensation, the chemical composition of the crucibles and the residual contamination might lead to lab-to-lab and batch-to-batch variations of CN_x materials.

Typically, (photo)electrodes of good adhesion to the supporting substrates show decent (photo)electrochemical activity. The reconsideration of the relationship between
electrochemical performance and physical robustness is raised based on the observations in chapter 4. We observed that CN\textsubscript{x}/p-FTO\textsubscript{NH2} is more electrochemically stable but less physically adhered compared to CN\textsubscript{x}/p-FTO. The lift-off issue in solar utilizing devices has led to the study of improved adhesion\textsuperscript{275}, and the importance of substrate pretreatment (e.g., ultrasonication in solvents\textsuperscript{298}, RF plasma\textsuperscript{275}) to remove surface contamination has previously been recognized. In our work, we sought to improve the physical adhesion but ended up having an adverse impact due to the limited thermal stability of the APTES at 500°C. However, the CN\textsubscript{x} grown on aminosilanized FTO has advantages on HER rates, current density, and electrochemical stability over that of the CN\textsubscript{x}/p-FTO. It is even interesting that CN\textsubscript{x}/FTO electrode, the one with severe film lift-off issue under electrochemical operation at reductive potentials, outcompeted CN\textsubscript{x}/p-FTO\textsubscript{NH2} in physical adhesion. A similar observation can be found in Kuhl et al.’s work on metal oxide-hydroxide electrocatalysts for OER\textsuperscript{299}, where Co(OH)\textsubscript{2} are highly catalytically active but poor in substrate adhesion, whilst Co\textsubscript{3}O\textsubscript{4} are of high hardness with enhanced adhesion to the underlying substrate but low in OER activity. Therefore, we suggest that the physical adhesion can be contradictory to the (photo)electrochemical stability, especially in our case, the CN\textsubscript{x}/FTO interface of good adhesion cannot guarantee efficient charge transfer, easily ruining the electrode electrochemically.

5.1 Research limitations

Despite we have contributed to reasoning about the changes in the photo(electro)catalytic behaviors to the corresponding post or pre-synthetic modifications, this work has limitations. Firstly, the photocatalytic performance comparison between using ALD-derived NiO and photodeposited Ni cocatalyst on CN\textsubscript{x} could have been further investigated. The optimization of photodeposited Ni content, instead of 3 wt.\%, can be tried out to explore the interfacial charge transfer limit of Ni-based cocatalyst on CN\textsubscript{x}. Secondly, the insolubility property of CN\textsubscript{x} makes it challenging to conduct the atomic layer
deposition (ALD) since the pre-modified powder is typically drop-casted adhesively on the substrate for subsequent usage in the vacuum. The direct growth of CN$_x$ on FTO allows us to proceed with the ALD process, but it restricts the possibility of modifying nanostructured and morphology-controlled CN$_x$ (e.g., nanosheet or hollow sphere). Also, the CN$_x$ film prepared for the ALD is around 30 μm, a certain degree of CN$_x$ surface may have been inaccessible to the ALD process due to blocking from the substrate. More even cocatalyst deposition can be achieved by lowering or even minimizing the thiourea density in water (now it is kept as 2 mg mL$^{-1}$), but that is a contribution at the expense of efficiency. Thirdly, this direct growth method had a similar restriction in the photoelectrode project, where the electrode thickness is relatively thicker than the charges can diffuse in the bulk CN$_x$ material, which limits the (photo)electrochemical performance. Lastly, more efforts on investigating the photoelectrochemical activity (i.e., under light) of the CN$_x$ electrodes in chapter 4 could be made, and thus a more complicated charge flow between the light absorber material and back contact could be studied based on the fundamental understanding of electrochemical behavior in the dark.

5.2 Future directions

Going forward, charge transport in the bulk CN$_x$ and charge transfer at interfaces will still be major limitations in building an optimized CN$_x$-based photo(electro)catalytic system. To address the former issue, the morphology control to shorten charge transport length is a straightforward approach due to the low charge mobility of pristine CN$_x$. Fabrication strategies have been proposed to synthesize CN$_x$ in various nanostructures, including porous nanolayers$^{300}$, hollow sphere$^{70}$, and 3D ordered strcuture$^{301}$. Similarly, in photoelectrochemical cells, thin functional materials in the range of nanometers are preferred. However, the extension of charge carrier diffusion length is needed since this length can be shorter than the minimized particle size or film thickness. Modification strategies (e.g., heteroatom doping$^{302,303}$, hybrids$^{304,305}$) have come up to enhance the
charge mobility, prolong carrier lifetime, and the electron diffusion length up to tens of μm is achievable\textsuperscript{306}. As for the charge transfer at the interfaces, we have proposed that the deep traps in the semiconductor are problematic. Though effort has been put into defect engineering, the identification and quantification of various defects (e.g., N-vacancy, C-vacancy, amino defect, cyano defect) in CN\(_x\) are still challenging\textsuperscript{307–311}. The difficulties in passivating ill-defined detrimental defects severely impede the process of CN\(_x\) material optimization. Developing advanced strategies to decrease the density of trap states\textsuperscript{66} to prolong the charge carrier lifetime and passivating the traps\textsuperscript{312} to reduce the energy losses from charge recombination still needs more attention.

To conclude, our work conducted the interface engineering on CN\(_x\)-based photocatalysts and electrodes, investigated the fundamental understanding toward CN\(_x\)|substrate, CN\(_x\)|cocatalyst, and CN\(_x\)|electrolyte interfaces, suggested the potential solution for addressing the interfacial charge transfer and charge transport issues in the photocatalytic and (photo)electrochemical systems.
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Appendices

Appendix A: Supporting Information 2

Discussions on the Urbach tail energy and the μs-TAS kinetic decay. The $\alpha$ parameter determined from the linear slope of the log-log plots of the TAS decays is related to a characteristic temperature ($T_0$)\(^{313}\) (Equation S4-1) from which the characteristic energy of the distribution ($E_{dist}$) (Equations S4-2 and S4-3) can be calculated.

\[
\alpha = \frac{T}{T_0} \quad \text{(S4-1)}
\]

\[
E_u \approx E_{dist} = k_B T_0 \quad \text{(S4-2)}
\]

\[
E_u = \frac{k_B T}{\alpha} \quad \text{(S4-3)}
\]

Where $\alpha$ is the power law exponent; $E_u$ is the Urbach tail energy; $T$ is the temperature; $T_0$ is characteristic temperature of the distribution; $k_B$ is the Boltzmann constant; $k_B T_0$ is the characteristic energy; $k_B T$ is 25.7 in the unit of meV. $\alpha$ is derived from the $E_{dist}$ in the exponential form, which is similar to the relationship between $K/S$ and $E_u$.

\[
\alpha \sim \exp \left( -\frac{E}{E_{dist}} \right) = \exp \left( -\frac{E}{k_B T_0} \right)
\]

\[
\frac{K}{S} \sim \exp \left( \frac{E}{E_u} \right)
\]

For CN$_x$/p-FTO$_{NH_2}$:

The Urbach tail energy calculated from the DRS spectra is 217 and 294 meV/dec for CN$_x$/p-FTO$_{NH_2}$ and CN$_x$/p-FTO, respectively. To compare the Urbach tail and $E_{dist}$ energies, two representations of the distribution of trap states, we need to consider unit conversion. We convert the Urbach tail energy from meV/dec to the unit of meV (effectively meV/e since it is a term in an exponential):
\[ E_u = 217 \frac{meV}{dec} \times \log(e) = 217 \frac{meV}{dec} \times 0.434 \frac{dec}{e} = 94 \frac{meV}{e} \rightarrow 95 \, meV \]

Compared to:

\[ E_{\text{dist}} = \frac{25.7 \, meV}{0.27} = 95 \, meV \]

For CNx/p-FTO:

\[ E_u = 294 \frac{meV}{dec} \times \log(e) = 294 \frac{meV}{dec} \times 0.434 \frac{dec}{e} = 128 \frac{meV}{e} \rightarrow 128 \, meV \]

\[ E_{\text{dist}} = \frac{25.7 \, meV}{0.25} = 103 \, meV \]

**Discussion on band structure under applied bias.** As shown in Scheme S4-1, band bending occurs when the CNx semiconductor contacts the electrolyte, and the electric field drives the electron across the barrier to reach the surface. In the dark, there is a small proportion of electrons in the valence band thermodynamically exciting into the conduction band. With external biases, the relocation of the Fermi level in the semiconductor is feasible, which results in a smaller energy difference between the Fermi level and the conduction band minimum for more negative applied potentials. More electrons are injected into the conduction band under these conditions, and these electrons can be driven to the surface of the semiconductor for redox reactions. As an n-type potential, a Fermi level close to the flat band potential could be approached, and this leads to nearly no barrier at the semiconductor|electrolyte interface and further helps with the interfacial charge transfer, but it narrows the space charge region due to the decreasing Fermi levels offset and weaker band bending.
Scheme S4-1. Schematic illustration of the proton reduction and band bending of $\text{CN}_x$ in the dark, with external applied bias ($V_{\text{appl.}}$) or larger applied bias. RE represents the electrochemical potential of the reference electrode.
Figure S4-1. Chronoamperometry of CNx/FTO under 0 V RHE with digital photos inserted.

Figure S4-2. The scheme of different types of interactions among APTES, hydroxylated FTO substrate, and CNx layer.

Figure S4-3. The contact angle of 5 µL ultrapure water droplets on p-FTO and p-FTO_{NH2} after 24h.
Discussions on reductive peaks seen in LSV scans of CN\textsubscript{x} electrodes. The first LSV scan of CN\textsubscript{x}-containing electrodes was accompanied by a sharp cathodic peak at \( \sim -0.4 \) V vs. RHE (Figure S4-6). The cathodic current is due to the accumulation of the electrons into the conduction band of the CN\textsubscript{x}, and the cathodic peak is presumably caused by the reduction of the CN\textsubscript{x} surface states\textsuperscript{28,230}. In such a circumstance, electrons would not significantly flow to HER, and the proton reduction reaction suppressed\textsuperscript{314}. A less obvious anodic peak in Figure S4-6e was observed. This implies that the discharge of accumulated electrons is almost irreversible, in line with the dramatically quenched cathodic peak in the second scan. The quenching suggests the electrons start transferring to the HER instead of continuously accumulating with the CN\textsubscript{x}; more specifically, the HER starts dominating. All data in Figure 4-6 were collected after this activation process.
Figure S4-6. LSV scans from 0.2V vs. RHE to -0.5V vs. RHE at a scan rate of 1 mV s⁻¹ in 0.1 M Na₂SO₄ (a-d). CV scans of CN₁₅/p-FTO as an example at a scan rate of 1 mV s⁻¹ in 0.1 M Na₂SO₄ (e).
Figure S4-7. Representative chronoamperometry (I-t) plots of Pt/CN_x/p-FTO_{NH2} (a, b), Pt/CN_x/p-FTO (c, d), CN_x/p-FTO_{NH2} (e, f), and CN_x/p-FTO in 0.1 M Na_2SO_4 (g, h).
Figure S4-8. Representative chronoamperometry plots of FTO (without plasma cleaning), p-FTO, p-FTO$_{NH2}$ in 0.1 M Na$_2$SO$_4$.

Figure S4-9. The FE$_{H2}$ of Pt wire working electrode calculated under -0.2 V RHE.

$\text{FE}_{H2} = 2 \times 96485 \text{ (C mol}^{-1}) \times 2.2E-05 \text{ (μmol s}^{-1}) / 4 μA = 1.06 = 106\%.$
Figure S4-10. CV scans to Pt/CN \textsubscript{x}/p-FTO\textsubscript{NH2}, Pt/CN\textsubscript{x}/p-FTO, CN\textsubscript{x}/p-FTO\textsubscript{NH2}, and CN\textsubscript{x}/p-FTO, p-FTO\textsubscript{NH2}, p-FTO, and FTO at scan rate of 10 mV s\textsuperscript{-1} in 0.1 M Na\textsubscript{2}SO\textsubscript{4}.

Table S4-1. Averaged Tafel slope

<table>
<thead>
<tr>
<th></th>
<th>Averaged Tafel slope (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CN\textsubscript{x}/p-FTO\textsubscript{NH2}</td>
<td>221 ± 11</td>
</tr>
<tr>
<td>Pt/CN\textsubscript{x}/p-FTO</td>
<td>240 ± 24</td>
</tr>
<tr>
<td>CN\textsubscript{x}/p-FTO\textsubscript{NH2}</td>
<td>233.3 ± 0.4</td>
</tr>
<tr>
<td>CN\textsubscript{x}/p-FTO</td>
<td>280 ± 40</td>
</tr>
<tr>
<td>p-FTO\textsubscript{NH2}</td>
<td>600 ± 300</td>
</tr>
<tr>
<td>p-FTO</td>
<td>900 ± 400</td>
</tr>
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</table>
Figure S4-11. $\text{FE}_2\text{H}_2$ against the current density for Pt/CN$_x$/p-FTO$_{\text{NH}_2}$, Pt/CN$_x$/p-FTO, CN$_x$/p-FTO$_{\text{NH}_2}$, and CN$_x$/p-FTO, respectively.

Figure S4-12. Representative digital images of electrode during the electrochemical measurement taken from the back side (a) after sample preparation, (b) scattered “shadows”, and (c) trapped bubbles beneath the CN$_x$ film.
Figure S4-13. Electrochemical lifetime of Pt/CNx/p-FTO_{NH2}, Pt/CNx/p-FTO, CNx/p-FTO_{NH2}, and CNx/p-FTO in 0.1 M Na2SO4.

Figure S4-14. Pt/CNx/p-FTO before and after EC HER.
Figure S4-15. Total impedance as a function of the frequency for six types of samples in two different electrolytes. The electrode was pretreated with a 10 min bias of -0.5 V vs. RHE ahead of the EIS measurement.
Figure S4-16. Bode phase angle as a function of the frequency for six types of samples in two different electrolytes. The electrode was pretreated with a 10 min bias of -0.5 V vs. RHE ahead of the EIS measurement.
Figure S4-17. (a) Nyquist plot of Pt/CN_x/p-FTO_{NH2}, Pt/CN_x/p-FTO, CN_x/p-FTO_{NH2}, and CN_x/p-FTO in 5 Mm K₃[Fe(CN)₆]-0.1M Na₂SO₄; electrodes were pretreated with the applied potential at -0.5 V vs. RHE for 10 min. (b) Nyquist plot of p-FTO_{NH2} and p-FTO in 5 Mm K₃[Fe(CN)₆]-0.1 M Na₂SO₄ treated with applied potential at -0.5 V vs. RHE for 1 min in advance. Bode plots and total impedance |Z| of Pt/CN_x/p-FTO_{NH2}, Pt/CN_x/p-FTO, CN_x/p-FTO_{NH2}, and CN_x/p-FTO, p-FTO_{NH2}, and p-FTO in 0.1 M Na₂SO₄ (c, d) and 5 mM K₃[Fe(CN)₆]-0.1 M Na₂SO₄ (e, f).
Figure S4-18. Nyquist plots of Pt/CNx/p-FTONH2, Pt/CNx/p-FTO, CNx/p-FTONH2, and CNx/p-FTO, p-FTONH2, p-FTO, and FTO fitted with the equivalent circuit in 0.1M Na2SO4.
Figure S4-19. Nyquist plots of Pt/CN_x/p-FTO_NH2, Pt/CN_x/p-FTO, CN_x/p-FTO_NH2, and CN_x/p-FTO, p-FTO_NH2, and p-FTO fitted with equivalent circuit in 5mM K3[Fe(CN)6]-0.1M Na2SO4.
Table S4-2. Fitted EIS parameters in 0.1 M Na$_2$SO$_4$ and 5 mM K$_3$[Fe(CN)$_6$]-0.1 M Na$_2$SO$_4$. $C_1$ is calculated from Equation 4-4, and $C_2$ is calculated from Equation 4-5. SD subscript stands for the standard deviation.

<table>
<thead>
<tr>
<th>EIS parameters in 0.1 M Na$_2$SO$_4$</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$W_1$ (Ω s$^{1/2}$)</th>
<th>$Q_{1\text{Avg.}}$</th>
<th>$Q_1$ SD</th>
<th>$n$</th>
<th>$C_1$</th>
<th>$C_1$ SD</th>
<th>$C_2$</th>
<th>$C_2$ SD</th>
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</thead>
<tbody>
<tr>
<td>Pt/CN$<em>x$/p-FTO$</em>{NH2}$</td>
<td>106±24</td>
<td>3731±1780</td>
<td>90</td>
<td>2.62E-04</td>
<td>1.75E-04</td>
<td>0.74</td>
<td>4.10E-04</td>
<td>3.33E-04</td>
<td>2.52E-04</td>
<td>1.77E-04</td>
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<tr>
<td>Pt/CN$_x$/p-FTO</td>
<td>61±12</td>
<td>4140±1625</td>
<td>237±33</td>
<td>2.18E-04</td>
<td>7.94E-05</td>
<td>0.75</td>
<td>3.99E-04</td>
<td>2.05E-04</td>
<td>2.04E-04</td>
<td>7.25E-05</td>
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<tr>
<td>CN$<em>x$/p-FTO$</em>{NH2}$</td>
<td>320±259</td>
<td>3250±934</td>
<td>187±94</td>
<td>2.64E-04</td>
<td>9.37E-05</td>
<td>0.77</td>
<td>4.34E-04</td>
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<td>2.55E-04</td>
<td>1.05E-04</td>
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<td>CN$_x$/p-FTO</td>
<td>142±144</td>
<td>5121±242</td>
<td>375±106</td>
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<td>p-FTO$_{NH2}$</td>
<td>32±2</td>
<td>30970±110</td>
<td>17</td>
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<td>3.56E-05</td>
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<td>3.09E-07</td>
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<td>p-FTO</td>
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<td>FTO</td>
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<td>3.46E-06</td>
<td>3.40E-05</td>
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EIS parameters in 5 mM K$_3$[Fe(CN)$_6$]-0.1 M Na$_2$SO$_4$
<table>
<thead>
<tr>
<th></th>
<th>R₁ (Ω)</th>
<th>R₂ (Ω)</th>
<th>W₁ (Ω s⁻¹/²)</th>
<th>Q₁ Avg.</th>
<th>Q₁ SD</th>
<th>n</th>
<th>Calculated capacitance (F cm⁻²)</th>
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<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁</td>
</tr>
<tr>
<td>Pt/CNx/p-FTO NH₂</td>
<td>23</td>
<td>444</td>
<td>14</td>
<td>5.53E-04</td>
<td>0.72</td>
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<td>5.53E-04</td>
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<tr>
<td>Pt/CNx/p-FTO</td>
<td>100±59</td>
<td>1821±669</td>
<td>98±20</td>
<td>3.37E-04</td>
<td>5.76E-05</td>
<td>0.74</td>
<td>4.97E-04</td>
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<tr>
<td>CNx/p-FTO NH₂</td>
<td>115±52</td>
<td>1774±149</td>
<td>293±61</td>
<td>3.15E-04</td>
<td>2.87E-05</td>
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<tr>
<td>CNx/p-FTO</td>
<td>353±446</td>
<td>3933±1319</td>
<td>890±863</td>
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<td>1.11E-04</td>
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<td>2.96E-04</td>
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<tr>
<td>p-FTO NH₂</td>
<td>33±10</td>
<td>16585±2850</td>
<td>NA</td>
<td>3.35E-05</td>
<td>2.89E-06</td>
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<tr>
<td>p-FTO</td>
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<td>1.37E-06</td>
<td>0.95</td>
<td>3.64E-05</td>
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</tbody>
</table>
Figure S4-20. Digital photos of CNx/p-FTO and CNx/p-FTO\textsubscript{NH2} taken every 5 mins within 30 min ultrasonication in water.

Figure S4-21. Digital photo of CNx/FTO after ultrasonication in water for 30 minutes.