The Complex Role of Carbon Nitride as a Sensitizer in Photoelectrochemical Cells

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In the last years, enormous attention has been focused on the metal-free semiconductor graphitic carbon nitride (simplified as C3N4) with a bandgap of 2.7 eV, which holds a great promise in the fields of electrocatalysis,[1] bioimaging,[2] solar cells,[3] and especially photocatalysis.[4,5] Many approaches were introduced to enhance the photoactivity of C3N4, such as doping[6] with different heteroatoms and by surface area increase, usually by hard-templating method.[5] Recently, an easy, safe, and highly effective approach has been developed to promote the photocatalytic activity of C3N4, which employs supramolecular precursors for thermal polymerization into C3N4. The supramolecular complex is generated by combining different organic compounds (triazine derivatives) in solvents and then assemblies are formed because of noncovalent interactions such as hydrogen bonds. Typically, cyanuric acid-melamine system has been shown to yield preorganized micro/nanostructures and morphologies, and as a result enables the modification of optical and electrical properties of final C3N4 product and significant improvement of photoactivity.[5] Moreover, the final material composition can be tuned by the insertion of other molecules (e.g., barbituric acid) into the starting complex. As stated before, C3N4 features good stability over high temperature and corrosive chemical environments.[8] C3N4 has been frequently used in combination with other semiconductor materials, such as MoS2,[9] In2O3,[10] and Ag3PO4,[11] for better light harvesting. When the chemistry is successfully executed, heterojunctions are formed between C3N4 and the other component, which improve the charge separation process and the overall performance. However, while the high activity of C3N4 as photocatalyst is well understood and studied, its performance in photoelectrochemical cells (PEC) remained low due to a more complicated charge separation/transport process. In order to promote PEC performance, uniform, continuous, and well-attached thin film electrodes should be produced. Furthermore, it is crucial to better understand the photophysical properties and the chemical interactions of carbon nitride materials in such systems.

Herein, we carefully studied the chemical interactions alongside the photophysical properties of TiO2/C3N4 in a model photoelectrochemical cell. A TiO2/C3N4 hybrid thin film was prepared by an in situ vapor-transport growth mode, using cyanuric acid-melamine (CM) or cyanuric acid-melamine-barbituric acid (CMB) supramolecular complexes as the precursor (labeled here as TiO2/CM and TiO2/CMB, respectively). The hybrid materials were characterized using a range of techniques (summarized in Table S1, Supporting Information). After thermal polymerization, the 20-nm TiO2 nanoparticles were uniformly coated with 3–5 nm of C3N4 layers. The TiO2/C3N4 system showed unique electronic coupling, leading to a greatly modified electronic structure and enhanced optical absorption. Consequently, the visible-light driving photocurrent was raised by ~30 times for TiO2/C3N4 as compared with a comparable pristine TiO2 cell.

The material growth approach is developed on the basis of previous reports on improving photoactivities of C3N4,[12] with certain modifications, as schematically shown in Figure 1. First, mesoporous TiO2 thin film on fluorine-doped tin oxide (FTO) glass was prepared by a doctor-blade method using commercial paste followed by air-annealing. Second, CM or CMB precursor was placed on top of the substrate, fully covering the TiO2 film. Then the system was put in crucible, capped, and heated in nitrogen (detailed information is given in the Supporting Information).

The X-ray diffraction (XRD) patterns of the substrates are shown in Figure S1 (Supporting Information). Compared with bare FTO, the additional diffraction peaks confirmed the formation of TiO2 film, which was mainly composed of the anatase phase. After the growth of C3N4 layers, the TiO2 phase remained unchanged and no impurity peaks from, e.g., TiN or TiC were detected. It is noticeable that the diffraction patterns of C3N4 layer cannot be resolved because of its thinness (as shown in Figure 2) and the high crystallinity of TiO2 and FTO. However, the Fourier transform infrared spectroscopy spectra (Figure S1b, Supporting Information) of TiO2/CM and TiO2/CMB clearly demonstrated the vibration peaks at 1200–1650 cm−1, which correspond to the typical stretching modes of C3N4, as well as the typical N–H bending vibrations of the CMB supramolecular complexes. The ratio increased to 0.90 for TiO2/CMB, due to the incorporation of barbituric acid molecules into the precursor.

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vibrations while $A_{1g} + B_{1g(2)}$ and $E_{g(2)}$ are Ti–O stretching vibrations. The spectra demonstrated that after C$_3$N$_4$ growth the intensity of $E_{g(1)}$ mode was significantly increased and the peak showed slight blue shift, meaning the enhancement of the bending vibration. On the contrary, $A_{1g}$ and $E_{g(2)}$ modes were broadened and shifted to lower wavenumbers, suggesting the increasing of lattice disorder and weakening of the stretching vibrations. The structure evolution of TiO$_2$ indicated the strong interaction between TiO$_2$ and C$_3$N$_4$, as discussed in more detail later in this manuscript.

Atomic force microscopy was employed to characterize the surface of the TiO$_2$ and TiO$_2$/C$_3$N$_4$ substrates (Figure S2, Supporting...
Information). The morphology and roughness of the substrates were not changed after thermal polymerization (with CM or CMB), e.g., no generation of disordered layers on top was found as reported before.\textsuperscript{12,15} The cross-section scanning electron microscopy images also confirmed the absence of extra top layer (Figure S3a, Supporting Information) and only the mesoporous structure of the primary TiO\textsubscript{2} film was observed (Figure S3b,c, Supporting Information). On the contrary, it is very interesting to find out that the TiO\textsubscript{2} nanoparticles were uniformly coated by a thin C\textsubscript{3}N\textsubscript{4} layer (3–5 nm), as illustrated by high-resolution transmission electron microscopy (HRTEM) images in Figure 2a. Further evidence of the successful C\textsubscript{3}N\textsubscript{4} deposition is given by the electron energy loss spectroscopy (EELS) spectra (Figure 2b). Compared with pristine TiO\textsubscript{2}, TiO\textsubscript{2}/CM and TiO\textsubscript{2}/CMB show the transitions of 1s $\rightarrow$ $\pi^*$ and 1s $\rightarrow$ $\sigma^*$ in both carbon K edge and nitrogen K edge. More importantly, the relative intensities of the two transitions (the 1s $\rightarrow$ $\pi^*$ transition peaks are very sharp and intense for TiO\textsubscript{2}/CM and TiO\textsubscript{2}/CMB) demonstrated that the outer layers of the TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} nanoparticles exclusively consisted of $sp^2$ hybridized carbon and nitrogen atoms,\textsuperscript{16} which further proves the thin layers are composed of carbon nitride. Corresponding selected area electron diffraction patterns illustrates that the C\textsubscript{3}N\textsubscript{4} does not have obvious impact on the crystallinity of the TiO\textsubscript{2} nanoparticles (Figure S4, Supporting Information). It is worth noting that we randomly studied $\approx$ 10 different spots and we found that all the TiO\textsubscript{2} nanoparticles were coated with C\textsubscript{3}N\textsubscript{4} (Figure S5, Supporting Information). In addition, line-scanning energy-dispersive X-ray spectroscopy shows that the nitrogen and carbon contents remain constant across the TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} film (Figure S3d, Supporting Information). Therefore, it is reasonable to assume that the growth of C\textsubscript{3}N\textsubscript{4} took place all across the TiO\textsubscript{2} film. Besides, we found that the CM complex (with and without the TiO\textsubscript{2}) did not show a liquid-phase intermediate up to 500 °C (Figure S6, Supporting Information), such that no liquid would penetrate into the TiO\textsubscript{2} thin film during the growth. These facts as well as the thickness ($\approx$ 7 μm) and the mesoporous structure of the TiO\textsubscript{2} film, we can suppose that during the heating process an in situ vapor-transport growth of the C\textsubscript{3}N\textsubscript{4} layers occurred. Specifically, sublimation of the CM precursor would be triggered at elevated temperature in the sealed crucible (around 430 °C based on TG-DSC curves, Figure S6b, Supporting Information) and the resulted vapor precursor can transport downward to the TiO\textsubscript{2} substrate driven by concentration gradient. This process is followed by redeposition at the TiO\textsubscript{2} nanoparticles driven by surface energy minimization, as schemed in Figure 1b. Afterwards, thermal polymerization of the precursor towards C\textsubscript{3}N\textsubscript{4} occurred on the surface of the TiO\textsubscript{2} nanoparticles with further temperature increase (Figure 1c) and the phase transformations of CM precursor were monitored by XRD measurement (Figure S6d–g, Supporting Information). The growth could have been terminated by several reasons: (1) the oxide surfaces are preferentially coated by C\textsubscript{3}N\textsubscript{4} due to surface energy effects; this effect levels off at about 5-nm thickness; (2) the transport of the vapor as well as the thickening of C\textsubscript{3}N\textsubscript{4} layer is slowed down or even prohibited because of space limitations.

The chemical states of the material systems were investigated by X-ray photoelectron spectroscopy (XPS), \textit{(Figure 3a,b)}. The pristine TiO\textsubscript{2} substrate showed typical binding energies of 458.4 and 529.6 eV for Ti 2p\textsubscript{3/2} and O 1s. After carbon nitride growth the Ti 2p\textsubscript{1/2} and O 1s peaks shifted to higher binding energies.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure3}
\caption{(a) Ti 2p and (b) O 1s XPS spectra, (c) schematic chemical structure of TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} and (d) UV–vis absorption spectra of the TiO\textsubscript{2}, TiO\textsubscript{2}/CM, TiO\textsubscript{2}/CMB substrates, and C\textsubscript{3}N\textsubscript{4} powders made from pure CM and CMB.}
\end{figure}
(458.8 and 530.0 eV, respectively). Significantly, the binding energy of Ti–O–C bonding appears at 532.8 eV in the O 1s spectrum (Figure 3b). In addition, the C 1s spectrum also clearly shows the C–O bonding at 286.7 eV (Figure S7a, Supporting Information), implying the formation of direct electronic coupling between TiO$_2$ and C$_3$N$_4$, which is responsible for the positive shifts of the Ti 2p$_{3/2}$ and the O 1s peaks because C$_3$N$_4$ acts apparently as a strong electron withdrawing group on the TiO$_2$ surface. Interestingly, this kind of chemical interaction between TiO$_2$ and C$_3$N$_4$ has not been reported previously although a few TiO$_2$/C$_3$N$_4$ composites were prepared$^{[17,18]}$ indicating the peculiarity of the in situ vapor transport based growth mode of C$_3$N$_4$ on mesoporous TiO$_2$. In addition, the shift of Ti 2p$_{3/2}$ peak to higher binding energies implies that nitrogen doping of TiO$_2$ during the synthesis could be excluded. Moreover, no Ti–C or Ti–N coordination schemes were detected. We note that free C$_3$N$_4$ powders made from CM complex did not show any C–O or C=O bonds (Figure S8, Supporting Information), indicating that the generation of C–O bonding is due to the chemical coupling between TiO$_2$ and C$_3$N$_4$ (Figure 3c).

The N 1s XPS spectra are shown in Figure S7a (Supporting Information) and the spectrum of TiO$_2$/CM was fitted into several binding energies (Figure S7c, Supporting Information). The main peak at 398.7 and 399.8 eV can be attributed to the C–N–C coordination and tertiary nitrogen N–(C)$_3$ groups, respectively.$^{[13]}$ The peak at 400.8 eV resulted from the bonding of C–N–H. The C 1s spectrum is shown in Figure S7b (Supporting Information) (fitted curve in Figure S7d, Supporting Information), demonstrating the occurrence of C–N–C group with binding energy at 288.3 eV. The N and C spectrum corresponds well with that of typical C$_3$N$_4$ samples.

The UV–vis absorption spectra are shown in Figure 3d. The pristine TiO$_2$ substrate showed a clear absorption edge at 400 nm, corresponding to the bandgap of 3.1 eV of anatase. After thermal polymerization with the supramolecular precursors, the absorption of TiO$_2$/CM was strongly enhanced in the visible-light range, and the edge shifted to ≈600 nm and beyond for TiO$_2$/CMB (see also Figure S9, Supporting Information). It is important to note that corresponding to the XPS measurements, the optical absorption is fundamentally different from that of C$_3$N$_4$ made from pure CM and CMB, N-doped or C-decorated TiO$_2$$^{[19]}$ and conventional TiO$_2$/C$_3$N$_4$ composites. Given the promotion of light absorption, we investigated the photocurrents (Figure 4a) of the substrates under visible light.

**Figure 4.** a) Photocurrent response of pristine TiO$_2$, TiO$_2$/CM, and TiO$_2$/CMB substrates under white light (λ > 410 nm). The measurement was carried out in a three-electrode system, Pt as the counter and Ag/AgCl as the reference electrode and 0.1 M Na$_2$S solution as the electrolyte. The light was chopped manually. b) Schematic energy diagrams in the TiO$_2$/C$_3$N$_4$ system under light excitation and the proposed charge transfer mechanism (path 1, 2, and 3, charge excitation and transfer; path 4, 5, and 6, charge recombination). c) Cyclic voltammetry, d) chemical capacitance (C$_k$), and e) $R_{rec}$ of pristine TiO$_2$, TiO$_2$/CM, and TiO$_2$/CMB substrates obtained in the dark.
light illumination (λ > 410 nm) using a typical three-electrode setup in Na₂S (0.1 m) aqueous solution without applying bias. As expected, the pristine TiO₂ showed low photocurrent (0.045 mA cm⁻²) because of its poor visible-light absorption. The photoactivity was significantly enhanced for TiO₂/CM and the photocurrent reached 1.4 mA cm⁻², mostly related to the improved light absorption and to the recombination inhibition as will show later in the manuscript. The photocurrent decreased to 0.7 mA cm⁻² for TiO₂/CMB although it showed further enhanced light absorbance. The decrease of the photocurrent is probably due to higher defects levels (because of a too high carbon doping) which can result in higher recombination of charge carriers. In order to further study the photoactivity of carbon nitride, we measured the photocurrent versus the light intensity (Figure S10, Supporting Information). The photocurrent profile showed a typical solar cell behavior and can be well fitted into a linear model for both TiO₂/CM and TiO₂/CMB. Furthermore, we note that the photocurrent profiles can be divided into two parts, namely the current increased more quickly at low light intensity (<2000 µmol m⁻² s⁻¹) than at higher light intensity (up to 20000 µmol m⁻² s⁻¹). This can be understood due to the enhanced recombination of the photogenerated charge carriers at high illumination intensities. The TiO₂/C₃N₄ substrates also illustrated considerable photocurrent under blue light (465 nm), i.e., 0.65 and 0.24 mA cm⁻² for TiO₂/CM and TiO₂/CMB (Figure S11, Supporting Information), while pristine TiO₂ did not show any noticeable photoresponse. Besides, the hydrophilicity of TiO₂ substrate was checked before and after C₃N₄ sensitization and there was no obvious change based on contact angle measurement (Figure S12, Supporting Information), indicating the improvement of photocurrent should be ascribed to modified electronic/optical properties.

Combining with the chemical coupling between TiO₂ and C₃N₄ as revealed by XPS alongside the unique absorption spectra, we suppose that a novel, interface bound energy transition was created in this system. Normally speaking, upon absorption of light with energy higher than 2.7 eV (bandgap of C₃N₄), electrons in the ground state (HOMO) of C₃N₄ are excited to the conduction band and are relaxing to the lowest unoccupied molecular orbital (LUMO). From there, they usually transfer to the TiO₂ conduction band (CB) due to the difference in energy (path 1 and 2, Figure 4b). The thermodynamically favorable electron injection is thereby driving charge separation. Subsequently, the negative charges transport through the TiO₂ nanoparticles and reach the conducting transparent electrode, while holes transfer to the electrolyte. In the present case, however, we suggest that the strong electronic coupling enables hybridization between the two semiconductors, and new molecular orbitals are generated at the interface (Figure S13, Supporting Information), according to the molecular orbital theory. We note that it differs from the conventional heterojunction due to the strong chemical coupling. Consequently, photoinduced charge transition can take place between the new levels (blue arrow), which have significantly narrower energy gap and thus results in optical absorption far beyond the bandgap of either C₃N₄ or TiO₂. This TiO₂/C₃N₄ can be considered as a joint electronic system and behaves in the way of charge-transfer complex. Similar phenomenon was previously observed in carbon@TiO₂ nanocomposite, wherein a “dyade” structure was suggested to describe the properties.

Furthermore, the electronic coupling can enable an alternative charge transfer (under illumination) from C₃N₄ HOMO directly into the unoccupied states in TiO₂ CB (path 3, Figure 4b). This kind of transfer has also been demonstrated between TiO₂ and other sensitizers such as catechol. However, one of the key issues arising from this transition is the fast recombination at the interface of TiO₂/C₃N₄, induced by the electron transition back from the metal oxide to the C₃N₄ (path 4, Figure 4b) which would severely diminish the photocurrent. This can explain the relatively low photocurrent obtained from TiO₂/C₃N₄ system compared with standard sensitized solar cells (≈10 mA cm⁻²), although the absorption was strongly extended to the visible light range. Moreover, the obtained photovoltage (Figure S14, Supporting Information) in the C₃N₄/TiO₂ cell is relatively low (~170 mV). The photovoltage in PEC is the energy gap between the TiO₂ Fermi level (electrons) and the chemical potential of the electrolyte (holes) and for the normal TiO₂ PEC cell in Na₂S electrolyte the photovoltage is ~300 mV. The decreased photovoltage can be explained by (1) the downshift of the TiO₂ energy level with respect to the electrolyte (2) the high recombination rate limits the electron concentration in the TiO₂ (3) the negative potential of the Na₂S electrolyte.

A deeper analysis of the photoelectrochemical behavior of the TiO₂/C₃N₄ heterostructures was carried out by means of cyclic voltammetry and impedance spectroscopy. Figure 4c shows the cyclic voltammery curves obtained for both CM and CMB-modified TiO₂ substrates and the comparison with pristine TiO₂ electrodes. These curves show the classical capacitive behavior of TiO₂ under cathodic bias related to the increased density of states as we approach the conduction band of the material. In addition, the reduction peak (at ~0.6 V vs Ag/AgCl for pristine TiO₂), which reflects electron transfer from the TiO₂ CB to localized surface/trap state was clearly shifted for the C₃N₄-modified TiO₂ substrates to more positive potentials, underlining the existence of new electron transfer mechanisms in the dyadic material. In order to characterize this shift further, electrochemical impedance spectroscopy (EIS) in dark was carried out. Figure S15 (Supporting Information) shows an example of the complex plane plots recorded on the tested samples. The obtained impedance spectra were fitted by using the well-known models applied to liquid DSSCs. The adapted model employed in the present study is shown as Figure S16 (Supporting Information). The extracted chemical capacitance for TiO₂, Cₚ, is plotted in Figure 4d as a function of the reference electrode potential and monitors the exponential density of states of TiO₂ below the conduction band.

The slope of the Cₚ versus the potential in the semi-logarithmic scale is similar for all the electrodes, which indicates that the sensitization with C₃N₄ does not significantly modify the density of interband states of TiO₂. However, a clear anodic shift of about ~ 200 mV is observed for Cₚ of the C₃N₄-sensitized TiO₂ electrodes. The anodic shift (increase of capacitance at the same voltage) can be attributed to (1) downshift of the energy bands (Figure S17a, Supporting Information) with respect to the electrolyte due to the exponential distribution of the electronic states in TiO₂ (more states are exposed to the electrolyte) or (2) distribution broadening of the TiO₂ density of states (Figure S17b, Supporting Information). However,
Based on the slopes of capacitance versus potential, we can exclude the band broadening, further proving the strong electronic interactions between the materials. Figure 4f shows the recombination resistance ($R_{\text{rec}}$), of electrons in the conduction band of TiO$_2$ with accepting species in the electrolyte (we note that in the TiO$_2$/C$_3$N$_4$ recombination rates cannot be obtained by this measurement). In order to compare the $R_{\text{rec}}$ among different samples, we have corrected the applied voltage to a common equivalent conduction band, ($V_{\text{ecl}}$) in order to analyze this parameter on the basis of a similar density of electrons (i.e., the same distance between the electron Fermi level and TiO$_2$ CB), since $R_{\text{rec}}$ depends on the density of electrons in the TiO$_2$ CB.[20] The lowest $R_{\text{rec}}$ values are obtained for pristine TiO$_2$ and the highest ones for the TiO$_2$/CM electrode (i.e., the lowest recombination rate), indicating that C$_3$N$_4$ obtained with the CM precursor inhibits the charge recombination from the TiO$_2$ to the electrolyte. However, the $R_{\text{rec}}$ for TiO$_2$/CMB is lower compared to TiO$_2$/CM, except for a small interval of approximately 300 mV, and approaches that of pristine TiO$_2$ at the highest applied voltages tested in the present study, which explains well the lower photocurrent found and showed in Figure 4a.

In conclusion, a study of carbon nitride as a potential stable solid-state sensitizer for TiO$_2$ electrodes with a novel dyadetype structure for improved visible-light activity is reported. The synthesis carried out by in situ, vapor transport growth of C$_3$N$_4$ coatings onto the nanoparticles of TiO$_2$ mesoporous thin film produced a strong chemical coupling, indicated by the generation of a direct Ti–O–C bond. This bonding enabled creation of additional molecular orbitals at the interface, resulting in a strong red-shift of the optical absorption. The chemical and photophysical properties of the new hybrid materials were further investigated by EIS, confirming that C$_3$N$_4$ acts as a surface dipole structure downshifting the energy levels over the TiO$_2$ surface. We strongly believe that this work opens new possibilities to achieve more efficient C$_3$N$_4$-based photocatalysts and electrochemical cells by optimizing the electron communication between the organic semiconductor and the supporting metal oxide substrate alongside the hole acceptor. Moreover, the fundamental understandings on the photophysical properties and the chemical interactions provide the opportunity to design refined types of communicating hybrid systems, such as nitrogen doped carbon at metal oxides.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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