

# Nitrogen-Doped Carbon Dots/TiO<sub>2</sub> Nanoparticle Composites for Photoelectrochemical Water Oxidation

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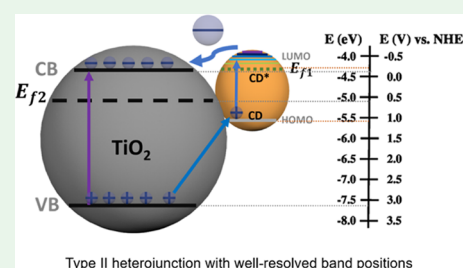


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**ABSTRACT:** Carbon dots on photoactive semiconductor nanomaterials have represented an effective strategy for enhancing their photoelectrochemical (PEC) activity. By carefully designing and manipulating a carbon dot/support composite, a high photocurrent could be obtained. Currently, there is not much fundamental understanding of how the interaction between such materials can facilitate the reaction process. This hinders the wide applicability of PEC devices. To address this need of improving the fundamental understanding of the carbon dots/semiconductor nanocomposite, we have taken the TiO<sub>2</sub> case as a model semiconductor system with nitrogen-doped carbon dots (NCDs). We present here with in-depth investigation of the structural hybridization and energy transitions in the NCDs/TiO<sub>2</sub> photoelectrode via high-resolution scanning transmission microscopy (HR-STEM), electron energy loss spectroscopy (EELS), UV–vis absorption, electrochemical impedance spectroscopy (EIS), Mott–Schottky (M–S), time-correlated single-photon counting (TCSPC), and ultraviolet photoelectron spectroscopy (UPS), which shed some light on the charge-transfer process at the carbon dots and TiO<sub>2</sub> interface. We show that N doping in carbon dots can effectively prolong the carrier lifetime, and the hybridization of NCDs and TiO<sub>2</sub> is able not only to extend TiO<sub>2</sub> light response into the visible range but also to form a heterojunction at the NCDs/TiO<sub>2</sub> interface with a properly aligned band structure that allows a spatial separation of the charges. This work is arguably the first to report the direct probing of the band positions of the carbon dot–TiO<sub>2</sub> nanoparticle composite in a PEC system for understanding the energy-transfer mechanism, demonstrating the favorable role of NCDs in the photocurrent response of TiO<sub>2</sub> for the water oxidation process. This study reveals the importance of combining structural, photophysical, and electrochemical experiments to develop a comprehensive understanding of the nanoscale charge-transfer processes between the carbon dots and their catalyst supports.



**KEYWORDS:** carbon dots, photoelectrocatalysis, heterojunction, charge transfer, band structure

## 1. INTRODUCTION

Photoelectrochemical (PEC) water splitting for hydrogen and oxygen production represents a promising technology for the conversion of solar energy to clean and renewable chemical fuels. Since the first report on PEC water splitting in 1972 using the TiO<sub>2</sub> photoelectrode,<sup>1</sup> many efforts have been made to improving the light conversion efficiency. To achieve the overall reaction, the water oxidation happening at the photoanode is a crucial step as it requires higher energy input. Several approaches have been reported in the literature to improve the performance of the photoanode materials, such as heteroatom doping,<sup>2</sup> nanostructuring,<sup>3</sup> etc. Among those, constructing heterojunctions in nanoscale materials like CdS/TiO<sub>2</sub>,<sup>4–8</sup> graphene/TiO<sub>2</sub>,<sup>9,10</sup> and carbon dots (CDs)/TiO<sub>2</sub><sup>11–15</sup> has been demonstrated to be an effective strategy. The enhanced PEC performance of the CdS/TiO<sub>2</sub> system is assigned to the electric-field-assisted charge transport at the interface with matched band alignments, which can improve the charge separation and prolong the photoinduced carrier

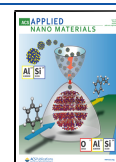
lifetime. In the case of graphene or reduced graphene oxide, those two-dimensional (2D) and zero band-gap materials serve as an electron mediator when coupled with TiO<sub>2</sub>, allowing an accelerated electron migration at the interface.

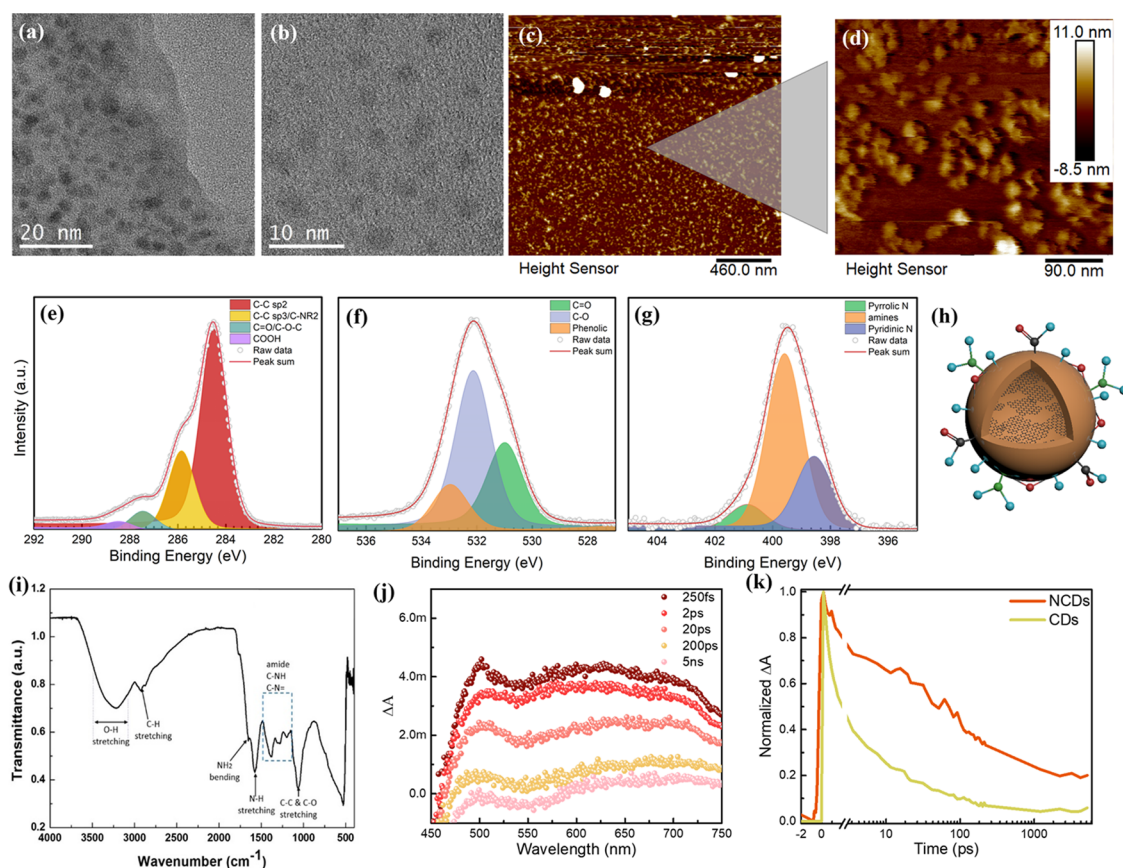
Carbon dots with size less than 10 nm have been demonstrated to act as photosensitizers for enhancing the performance of heterogeneous photocatalysts, due to their adjustable band potentials, excellent and tunable light-harvesting ability, and electron-transfer efficiency.<sup>12,16–20</sup> When doped with nitrogen,<sup>13,21,22</sup> carbon dots usually show an enhanced activity toward photodriven reactions both exper-

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**Figure 1.** Structural features of as-prepared NCDs: TEM (a) and high-resolution TEM (HR-TEM) (b) images; (c) overview AFM image on the mica substrate (Z-scale  $-6.0$  to  $7.9$  nm) and (d) high-resolution scanned image; X-ray photoelectron spectra (XPS): (e) C 1s, (f) O 1s, (g) N 1s, and corresponding Fourier transform infrared (FTIR) (i) spectrum; (h) schematic structure based on the characterizations (atoms in red: O, green: N, and blue: H); (j) femtosecond transient absorption spectra (fs-TAS) at different time decays and (k) normalized fs-TAS kinetics of NCDs and nondoped CDs measured at  $500$  nm (excitation wavelength:  $375$  nm).

imentally and theoretically.<sup>23,24</sup> Accordingly, the utilization of nitrogen-doped carbon dots (NCDs) photosensitizers to facilitate PEC reactions started to attract attention.<sup>13,21,25</sup> However, owing to the complexity of NCDs compare to CdS and graphene in terms of the chemical structure and energy states, the mechanism of NCDs in improving the PEC performance is still not well understood and explained.<sup>12,17,26</sup> Previous studies have indirectly demonstrated that the electronic coupling between the  $\pi$  states of the CDs and the conduction band (CB) of  $\text{TiO}_2$  can form heterojunctions and impart the system for visible-light absorption. The resulting heterojunction can efficiently separate the photogenerated electrons and holes, resulting in a lower recombination rate and a higher PEC activity.<sup>14</sup> Those effects can be greatly influenced by the intrinsic properties of CDs. For instance, the graphitization degree can affect the charge-transfer process,<sup>27</sup> the different N doping configuration (amines, amides, pyridinic, quaternary, N-oxides, etc.) can govern the light-harvesting ability,<sup>28</sup> while the functionality would determine the interaction with supporting materials.<sup>16,29</sup> Hence, it is of vital importance to develop a deeper understanding of the nanostructure of CDs and their interaction with the semiconductor materials and gain further insights on the dynamics of the charge-exchange process at the material interface.

In this paper, we exploit a broad arsenal of complementary advanced characterization techniques to understand the morphology, structure, and optical and electrochemical

properties of chitosan-derived NCDs at a fundamental level. Such studies reveal that N doping can effectively prolong the photoinduced carrier lifetime. A photoanode was prepared by decorating the as-synthesized NCDs onto a  $\text{TiO}_2$  mesoporous film, which is used as a model semiconductor material to study the NCD/semiconductor interaction. A detailed structural and PEC analysis showed that the nanoparticle composite possesses an improved visible-light response as well as charge-separation/-transport ability, which resulted in a higher photocurrent value. In-depth characterization of the NCD/ $\text{TiO}_2$  nanocomposite by methods such as Mott–Schottky (M–S) analysis, photoelectron spectroscopy in air (PESA), Kelvin probe, and ultraviolet photoelectron spectroscopy (UPS) was employed to evaluate the energy levels. Combined with electrochemical impedance spectroscopy (EIS) and in situ photoluminescence (PL) quenching by time-correlated single-photon counting (TCSPC), we present here the detailed mechanism for the interfacial charge-transfer process.

## 2. RESULTS AND DISCUSSION

NCDs were synthesized by solvothermal carbonization of chitosan in the ethanol solvent (4% w/v). Several works on using chitosan to produce NCDs have been reported earlier.<sup>30–32</sup> Under mild conditions (hydrothermal carbonization (HTC) with  $180$  °C), the carbonization and functionalization will take place through chitosan dehydration, leading to the formation of NCDs. As illustrated in Figure S1,

the precursor molecules go through decomposition to 5-hydroxymethylfurfural (HMF) and ammonia. The HMF molecule then goes through ring opening to react with ammonia and form aminopentanal. Intermolecular condensation would occur at this stage in these intermediates. Pyridines would form from the reaction between amino groups and aldehyde, while the reaction between amino and keto groups results in the formation of pyrroles. Some amines remain free from reacting with other groups.<sup>33</sup> These functionalities are later identified in the structure of NCDs.

Figure 1a,b shows the transmission electron microscopy (TEM) images of NCDs with spherical morphologies. The atomic force microscopy (AFM) images of the NCDs (Figure 1c,d) further prove that the sizes of those NCDs are uniformly distributed. The CDs are  $\sim 2$ –8 nm in height, with values obtained from cross-sectional topographic measurements, taken into account the broadening effect due to the finite size of the tip.

To analyze the structure of the carbon core, the outputs of X-ray diffraction (XRD) and Raman spectroscopy techniques were compared. The X-ray diffraction (XRD) pattern (Figure S2a) displays a broad peak centered at  $21^\circ$ , which has been demonstrated to be amorphous with a turbostratic structure in our previous study.<sup>31</sup> In theory, XRD involves X-rays interacting with electrons to reveal the reciprocal space of crystalline lattice by diffraction, which does not give sufficient structural information of packed carbon dots due to the less ordered structure. In this regard, Raman spectroscopy uses long-wavelength radiation and interacts with atoms, molecules, or ions, which can reveal the vibration frequencies of the system by scattering, providing information about the chemical environments. Hence, here Raman spectroscopy was carried out for the surface characterization of partially ordered carbon materials.<sup>34</sup> Figure S2b shows the Raman spectra ( $\lambda = 633$  nm) of the NCDs. Two peaks centered at  $1382$  and  $1574\text{ cm}^{-1}$  can be seen, representing the characteristic D and G bands for carbon materials, respectively, indicating a semicrystalline structure of the NCDs. The spectra show a significant level of noise-to-signal ratio, due to the highly fluorescent background removal.

The X-ray photoelectron spectra (XPS) are shown in Figure 1e–g. They reveal that the amine groups from chitosan are maintained on the surface of NCDs, and the carbon, oxygen, nitrogen contents have been calculated to be 75.8, 28.2, and 5.8%, respectively. Three types of nitrogen species can be found in the material, which are pyridinic N (26%), amine groups (64%), and pyrrolic N (10%), existing both on the surface as functional groups and incorporated inside the core structure. It has been reported that different N-motifs show different charge-transportation properties, which will be beneficial for the PEC properties.<sup>28</sup> The Fourier transform infrared (FTIR) spectrum in Figure 1i also confirms the existence of amine groups in the NCDs, with  $\text{NH}_2$  bending at  $1648\text{ cm}^{-1}$  and N–H stretching at  $1576\text{ cm}^{-1}$ . The peaks between  $1151$  and  $1484\text{ cm}^{-1}$  are assigned to C–NH and C–N= amide groups.<sup>35,36</sup> A schematic profile representing the structure of NCDs is shown in Figure 1h.

The optical properties of the NCDs are analyzed by UV–vis absorption and photoluminescence. As shown in Figure S3a, the UV–vis absorption spectrum of the NCD solution exhibits strong, broad light absorption in the ultraviolet range, with an absorption peak at 270 nm, which tails off in the visible region. The 270 nm absorption peak is due to the  $\pi \rightarrow \pi^*$  transition,

while the visible-light absorption comes from  $n \rightarrow \pi^*$  transition.<sup>37,38</sup> The visible-light response of the synthesized NCDs is advantageous for use as a photosensitizer.<sup>14</sup> In Figure S3b, excitation-dependent emission was observed in the blue-green light region depending on the excitation wavelength, indicating easy access to the electronic states ( $n-\pi^*$ ,  $\pi-\pi^*$ ).<sup>39</sup> These interesting optical properties grant the NCDs with potential applications in hybrid PEC design. Photoluminescence quantum yield ( $\Phi$ ) of NCDs was calculated to be 8.7% referenced by quinine sulfate (QS).<sup>40</sup>

Our previous work has shown that the NCDs derived from chitosan are capable of generating photocurrents under visible-light irradiation. Akin to n-type semiconductor, the excited states of carbon dots upon interaction with light govern the photoinduced activity.<sup>31</sup> To investigate the nature of stable surface paramagnetic defects, electron paramagnetic resonance (EPR) measurements were performed on NCD powder at room temperature in dark conditions. In Figure S4, the sharp isotropic EPR signals centered at  $g_{\text{iso}} = 2.0035$  are expected to come from the presence of carbon-centered radical species present on the NCD surface, which could act as active sites for redox reactions.

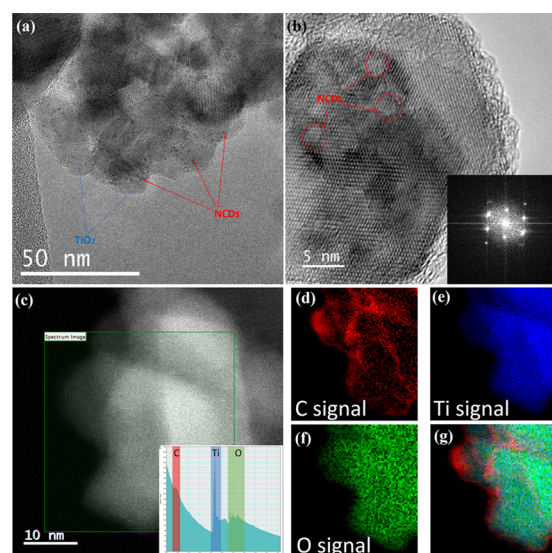
The excited-state photophysical properties of NCDs were investigated by means of femtosecond transient absorption spectroscopy (fs-TAS), which reveals that upon 375 nm photoexcitation, NCDs gave rise to differential absorption signals that are spanning over the visible range from 450 to 750 nm on a ps timescale (Figure 1j). Features are centered near 500 and 625 nm, similar to previously reported spectra of CDs.<sup>27,37</sup> The features that showed up at shorter and longer wavelengths are possibly assigned to the core and surface states of CDs, respectively. This behavior is akin to that observed for graphitic carbon dots.<sup>27,41</sup> The decay lifetime kinetics at 500 nm were fitted using a biexponential function into short- (2.17 ps, 39%) and long (138.97 ps, 61%)-lived components. The extracted exciton lifetimes have been found being longer than any other photosensitizing materials reported to date.<sup>42,43</sup> The comparison of the decay profile of NCDs with that of nondoped CDs in Figure 1k reveals that doping with N has largely prolonged the exciton lifetime, being beneficial for the PEC process. This might be a result of N doping reducing  $\pi$ -connections between  $\text{sp}^2$  domains, suppressing the interlayer nonradiative energy dissipation,<sup>21</sup> and serve as an electron donor to effectively scavenge holes to extend the lifetime of photogenerated electrons.<sup>27</sup> Here, we have demonstrated for the first time clear evidence and explanation of the positive effect of N doping on carbon dots for the application as efficient photosensitizers. We have applied the prepared NCDs to  $\text{TiO}_2$ , which is an ideal model semiconductor to study the effect of the NCDs on the recombination rate of the photogenerated charge carriers in a PEC system. Compared to inorganic semiconducting quantum dots, carbon dots consist of mostly  $\text{sp}^2$  carbon, which helps the formation of a charge-transfer complex with  $\text{TiO}_2$  and thus resulting in more efficient absorption and charge separation.<sup>44</sup>

The  $\text{TiO}_2$  thin film is fabricated by spin coating a commercially available mesoporous titania paste onto a fluorine-doped tin oxide (FTO)-coated glass substrate. To gain insight into the morphology of the  $\text{TiO}_2$  film, we performed scanning electron microscopy (SEM) top-view and cross-section imaging of the NCDs/ $\text{TiO}_2$  film, with representative images portrayed in Figure S5. No major aggregation of the nanoparticles can be observed. The thickness of the film

was measured to be  $\sim 1 \mu\text{m}$  (from the SEM cross-section), considered adequate to provide good charge carrier generation and collection ability.<sup>45</sup> Brunauer–Emmett–Teller (BET) measurements showed that the  $\text{TiO}_2$  has a specific surface area of  $110 \text{ m}^2 \text{ g}^{-1}$ , higher than that of the commercial P25 ( $49 \text{ m}^2 \text{ g}^{-1}$ ). The mesoporosity, as seen from the SEM top-view image, guarantees sufficient light absorption and is also beneficial for anchoring the NCDs on its surface and inside the  $\text{TiO}_2$  films, providing more active sites for reactions.<sup>14</sup>

Figure S6 displays the XRD patterns of the  $\text{TiO}_2$  and NCDs/ $\text{TiO}_2$  films. The dominant peaks in both samples are assigned to the (101) facet of the anatase phase, which is considered to be the most stable structure in anatase  $\text{TiO}_2$ .<sup>46</sup> The diffraction patterns of NCDs/ $\text{TiO}_2$  are in good match with that of the  $\text{TiO}_2$ , which contains mostly the anatase phase with small amount of rutile (JCPDS 01-084-1286 and 01-073-2224), indicating that the deposition of NCDs does not cause any obvious changes in  $\text{TiO}_2$  crystallinity.<sup>47</sup>

TEM and HR-TEM were used to investigate the morphologies of the NCDs/ $\text{TiO}_2$  nanoparticles further. TEM image (Figure 2a) of the prepared NCDs/ $\text{TiO}_2$  nanoparticles



**Figure 2.** TEM (a) and HR-TEM (b) of NCDs/ $\text{TiO}_2$  (the inset is the fast Fourier transform (FFT) patterns); (c) HAADF image of NCDs/ $\text{TiO}_2$  and corresponding EELS spectra (inset). The single element maps derived from the spectra: (d) C signal, (e) Ti signal, (f) O signal, and (g) color mix (red: C, blue: Ti, green: O).

taken at low magnification shows some dark spots dispersed on the surface of the  $\text{TiO}_2$ , revealing that the NCDs have been effectively deposited onto  $\text{TiO}_2$ . In the HR-TEM images, the NCDs became less obvious, leaving only contrast differences due to the small particle size and less crystalline nature of the NCDs compared to  $\text{TiO}_2$  nanoparticles, as determined by TEM and XRD (Figures 1 and S2). The observed lattice spacing of  $0.35 \text{ nm}$  for  $\text{TiO}_2$  nanoparticles corresponds to the (101) plane of anatase  $\text{TiO}_2$ , as can be seen from XRD patterns in Figure S6. To further resolve the presence of NCDs, a high-angle annular dark-field image (HAADF) was taken on several  $\text{TiO}_2$  nanoparticles under high magnification. As seen in Figure 2c, NCDs are difficult to discern through the dark-field image due to the light element contrast. In the same area, electron energy loss spectra (EELS) were scanned. It is known that EELS is better than energy-dispersive spectrometry

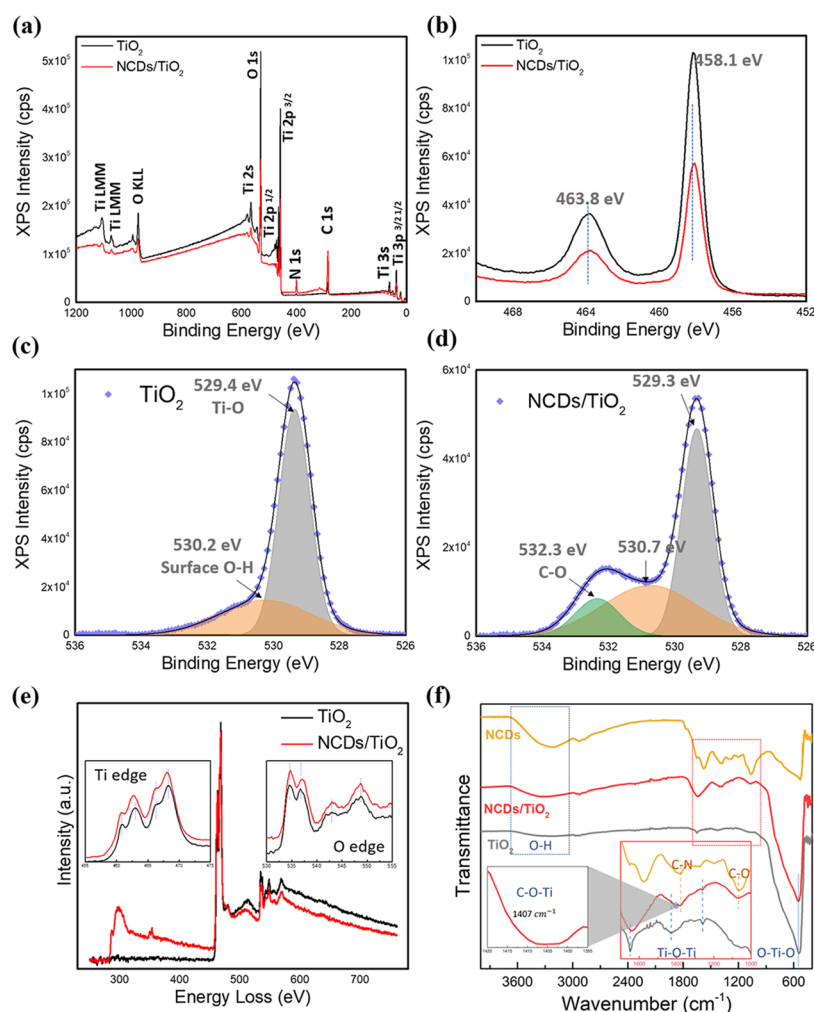
(EDS) at detecting light elements due to the smaller energy window. Here, we chose to look at  $250\text{--}750 \text{ eV}$ , which contains the characteristic spectra of carbon, nitrogen, titanium, and oxygen, as illustrated in the inset of Figure 2c. The spectra of C, Ti, and O are very distinctive, while no signal can be seen from N, probably due to the low nitrogen amount in the NCDs (N 5.8%) also loaded in small amounts on the  $\text{TiO}_2$  ( $\sim 2.4\%$  calculated from the mass loss in Figure S7). The EELS maps of individual elements along with the color mix are shown in Figure 2d–g. The mapping of the NCDs on  $\text{TiO}_2$  infers the heterostructure formation, which may promote the charge separation within the hybrid system, corroborating the improved PEC activity.<sup>48</sup>

The chemical structure of the NCDs/ $\text{TiO}_2$  was analyzed by XPS. Compared to the pristine  $\text{TiO}_2$ , the survey spectrum (Figure 3a) of NCDs/ $\text{TiO}_2$  showed higher intensity in C and N peaks, which originates from the NCDs. The deconvoluted high-resolution signals of Ti 2p (Figure 3b) show no shift in the binding energy, suggesting that there is no disruption of the  $\text{TiO}_2$  structure after anchoring of the NCDs. The peaks at  $458.1$  and  $463.8 \text{ eV}$  are originated from the pair of  $\text{Ti } 2p_{3/2}$  and  $\text{Ti } 2p_{1/2}$ , respectively, assigned to the  $\text{Ti}^{4+}$  sp peaks of  $\text{TiO}_2$ . Figure 3c shows the O 1s spectra of  $\text{TiO}_2$ , in which the peaks at  $529.4$  and  $530.2 \text{ eV}$  arise from Ti–O and surface O–H groups in  $\text{TiO}_2$ , respectively.<sup>49</sup> After depositing NCDs, the surface O–H peak shifted towards higher binding energy, suggesting that the chemical environment has been changed due to the interaction between the  $\text{TiO}_2$  and NCDs and the formation of the Ti–O–C bond.<sup>11</sup> The O 1s spectrum also showed a peak at  $532.3 \text{ eV}$  corresponding to C–O bonds, which is also present in the O 1s spectra of NCDs (Figure 1f). The energy shift can also be observed in high-resolution EELS spectra at Ti and O edges after depositing NCDs (Figure 3e), suggesting a chemical environment change around surface Ti and O atoms.<sup>50,51</sup>

The formation of the NCD/ $\text{TiO}_2$  hybrid has been further confirmed by FTIR analysis. Figure 3f shows that the spectra of NCD/ $\text{TiO}_2$  display typical vibration of O–Ti–O at  $550 \text{ cm}^{-1}$ , as well as C–N, C–O stretching at  $1378$  and  $1067 \text{ cm}^{-1}$ , confirming the presence of NCDs in the hybrid sample. A new absorption peak arises between the Ti–O–Ti and C–N bond at  $1407 \text{ cm}^{-1}$ , which is possibly because of the C–O–Ti bond formation.<sup>52</sup> Based on the above results, it can be concluded that the NCDs are loaded on the  $\text{TiO}_2$  via chemical absorption.

Light absorption is one of the essential factors determining the PEC performance of electrode materials. UV–vis–NIR spectroscopy is employed to characterize the optical properties of the  $\text{TiO}_2$  films and their respective NCD hybrids. As shown in Figure 4a, pure  $\text{TiO}_2$  shows no absorption above  $385 \text{ nm}$ , owing to the intrinsic wide band gap of anatase  $\text{TiO}_2$  ( $3.2 \text{ eV}$ ). Compared to the pristine  $\text{TiO}_2$  film, the NCD-decorated films show enhanced visible-light absorption tails up to  $425 \text{ nm}$  for NCDs/ $\text{TiO}_2$ . Therefore, the presence of NCDs plays a critical role in boosting the visible-light absorption of the composites, which is important for visible-light-driven photoelectrocatalytic activity. No band-gap narrowing can be observed from the Tauc plot (Figure 4b), indicating that the NCDs are only present on the surface without disrupting the crystalline structure of  $\text{TiO}_2$ , in line with the scanning transmission microscopy (STEM) and XRD results.

PEC measurements were performed on the aforementioned  $\text{TiO}_2$  films to investigate the photoinduced charge-transfer



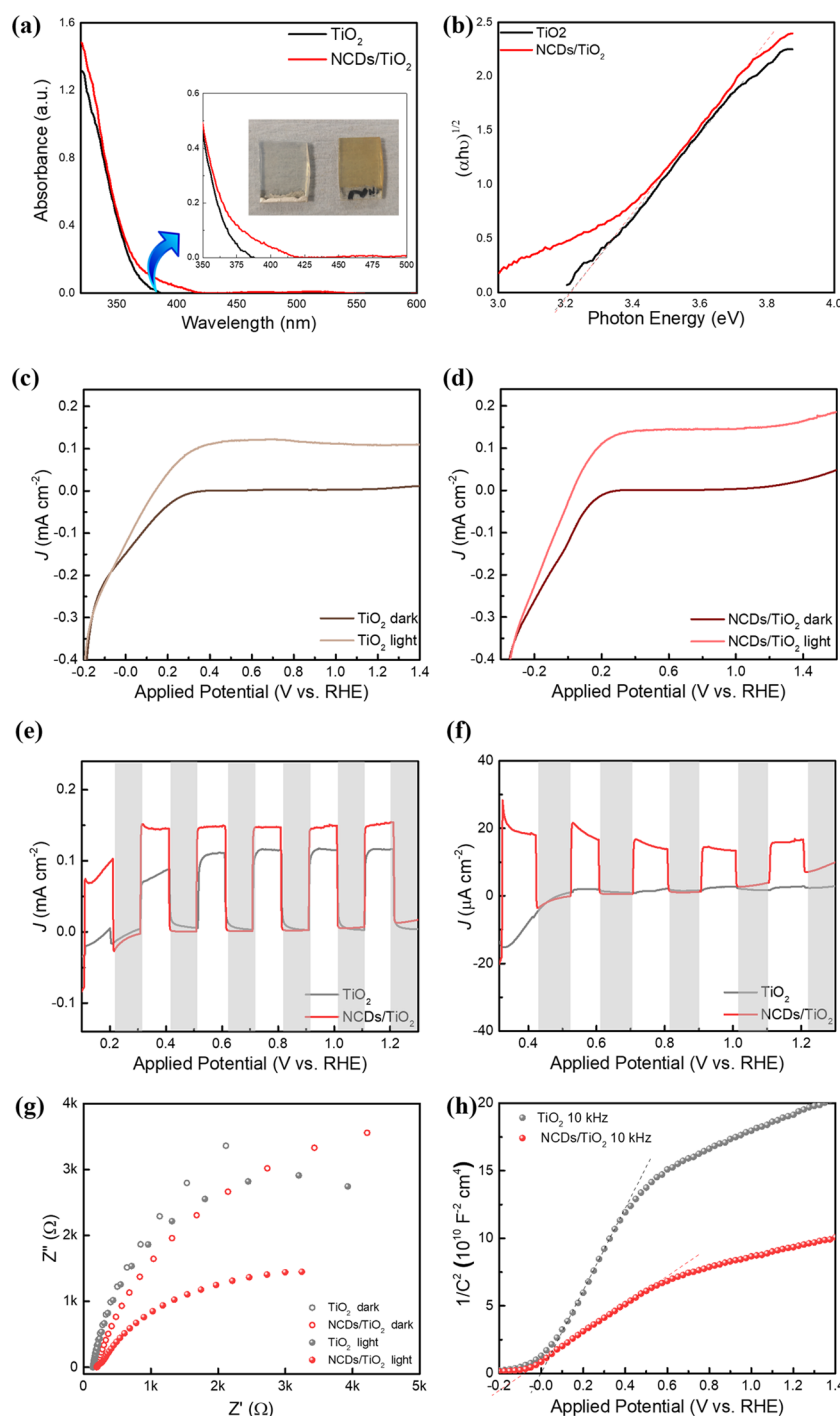
**Figure 3.** Comparison of XPS survey spectra (a) and Ti 2p high-resolution spectra (b) of the  $\text{TiO}_2$  and NCDs/ $\text{TiO}_2$  films; O 1s spectra of (c)  $\text{TiO}_2$  and (d) NCDs/ $\text{TiO}_2$ . (e) EELS spectra of  $\text{TiO}_2$  (black) and NCDs/ $\text{TiO}_2$  (red) and (f) FTIR signals.

behavior. Figure 4c–f shows the linear sweep voltammetry (LSV) of the photoelectrodes under simulated solar light irradiation (electrolyte: 0.2 M  $\text{Na}_2\text{SO}_4$  aqueous solution; scan rate:  $5 \text{ mV s}^{-1}$ ). Clearly, the NCD/ $\text{TiO}_2$  photoanode showed enhanced photoresponse compared to pure  $\text{TiO}_2$ ; the NCD/ $\text{TiO}_2$  displays a saturation photocurrent of  $0.15 \text{ mA cm}^{-2}$  at 0.3 V vs RHE, approximately 2 times higher than that of the pristine  $\text{TiO}_2$  ( $0.08 \text{ mA cm}^{-2}$ ) under the same conditions. This may be the effect of the formation of heterojunctions at the NCDs/ $\text{TiO}_2$  interface, which can effectively separate the photoinduced charge carriers. The expected PEC results under visible light ( $\lambda > 420 \text{ nm}$ ) further depict the enhanced charge separation of  $\text{TiO}_2$  by hybridizing NCDs. While the  $\text{TiO}_2$  electrode showed no obvious photoresponse in this region, the NCD/ $\text{TiO}_2$  generated photocurrent of  $17 \mu\text{A cm}^{-2}$ , owing to the slightly enhanced visible absorption of NCDs. Consequently, based on the above results, the photosensitization effect of NCDs on the photocurrent generation of NCDs/ $\text{TiO}_2$  heterostructures was unambiguously ascertained under both simulated solar and visible-light illuminations.

The distribution of the photocurrent between UV and visible light is given in Figure S8. Nearly half of the enhanced photocarrier generation of NCDs/ $\text{TiO}_2$  is attributed to the higher visible-light absorption, due to the photosensitization ability of NCDs. The rest of the improved photocurrent may

arise from a more efficient charge separation and transportation because of the formed heterojunction between  $\text{TiO}_2$  and NCDs.<sup>29,53</sup> The stability test was performed on the NCDs/ $\text{TiO}_2$  photoelectrodes. As seen from Figure S9, NCD/ $\text{TiO}_2$  exhibits a current density decrease in the first 2000s, but with time proceeds, the electrode became more stable, with less than 25% current density drop. Future work is needed to improve the stability of this hybridized material.

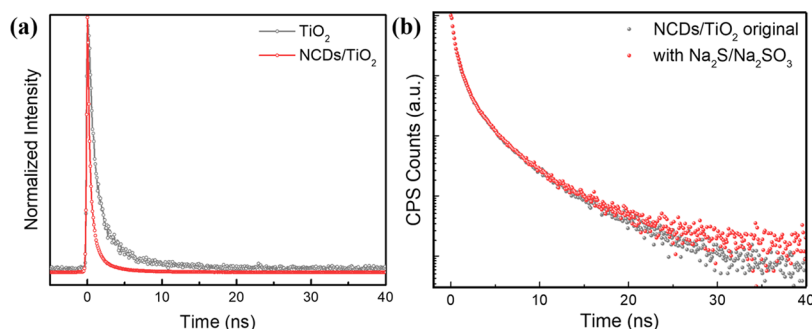
The electron–hole pair separation efficiency was further analyzed with EIS measurements. In the Nyquist plots, the charge-transfer process at the electrode/electrolyte interface is represented by the diameter of the semicircle at low frequency; a smaller diameter indicates a lower charge-transfer resistance. Figure 4g shows the Nyquist plots of the  $\text{TiO}_2$  and NCDs/ $\text{TiO}_2$  photoanodes from 100 kHz to 0.1 Hz under simulated solar light illumination (0.3 V vs RHE). The prepared NCD/ $\text{TiO}_2$  shows a smaller semicircular diameter compare to  $\text{TiO}_2$  under light illumination, revealing that the NCD/ $\text{TiO}_2$  electrode possesses less photoinduced charge-transfer resistance in the interface of the electrode and electrolyte, highlighting the key benefit of NCDs in improving charge-separation efficiency and enhancing photoelectrochemical activity. Compared with the EIS performed under dark conditions, we can tell that the charge-transfer resistance of the NCDs/ $\text{TiO}_2$  electrode decreased faster by light illumina-



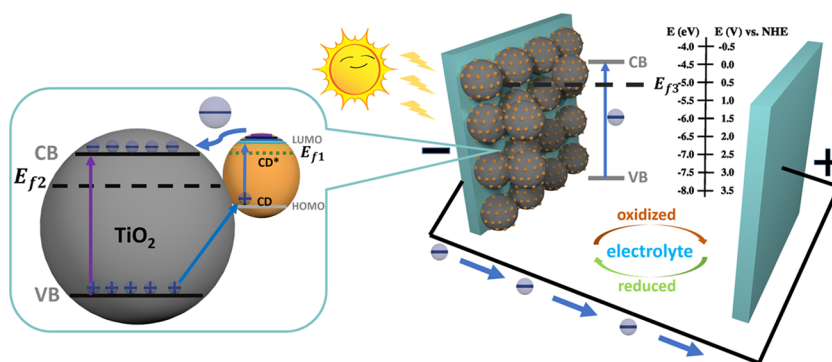
**Figure 4.** Optoelectronic properties of  $\text{TiO}_2$  and  $\text{NCDs/TiO}_2$  films: (a) UV–vis absorption (the inset is the digital pictures of the films: left:  $\text{TiO}_2$ , right:  $\text{NCDs/TiO}_2$ ); (b) Tauc plot of  $\text{TiO}_2$  and  $\text{NCDs/TiO}_2$  with indirect band gap; linear sweep voltammetry (LSV) curves of (c)  $\text{TiO}_2$  and (d)  $\text{NCDs/TiO}_2$  under dark and light conditions; the chopped photocurrent response of the two samples under (e) full-spectrum and (f) visible-light ( $\lambda > 420 \text{ nm}$ ) illumination; (g) EIS Nyquist plots under simulated solar light illumination ( $100 \text{ kHz}$  to  $0.1 \text{ Hz}$ ,  $0.3 \text{ V}$  vs reversible hydrogen electrode (RHE),  $100 \text{ mW cm}^{-2}$ ) and (h) Mott–Schottky plots with  $10 \text{ kHz}$  frequency under dark conditions at equilibrium.

tion compared with pristine  $\text{TiO}_2$ . This proves that NCDs provided photosensitized electrons to  $\text{TiO}_2$  and separated the electron–hole pairs more efficiently, thereby decreasing the impedance under light.<sup>54</sup> Additionally, the Mott–Schottky (M–S) plot measured at  $10 \text{ kHz}$  reveals a higher carrier density after NCD deposition (Figure 4h) from the smaller slope of the  $\text{NCD/TiO}_2$  curve.<sup>50,55</sup> To minimize the effect of surface state capacitance and the double-layer capacitance at the electrode/electrolyte interface, the frequency of the M–S

measurements was chosen to be fast enough to limit the effective filling and unfilling of the electrodes' surface state, as well as restrain the building up of the double-layer capacitance. On that note, even though this analysis is derived from an ideal planar electrode model, the calculation of carrier density for a relative comparison is still reasonable.<sup>56</sup> Measurements at different frequencies ( $1$  and  $3 \text{ kHz}$ ) can be found in Figure S10. The carrier density ( $N_D$ ) can be estimated by the equation



**Figure 5.** (a) TCSPC decay profile of TiO<sub>2</sub> (gray) and NCDs/TiO<sub>2</sub> (red); (b) decay profiles of NCD/TiO<sub>2</sub> with (red) and without (gray) the presence of the hole scavenger Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>. The excitation wavelength for all of the experiments is 405 nm, and the emission is recorded at 520 nm.



**Figure 6.** Proposed formation of the heterostructure with band alignments and charge transfer at the surface of TiO<sub>2</sub> and NCDs under light irradiation.

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 A^2 e N_D} \left( V - V_{fb} - \frac{k_B T}{e} \right)$$

where  $e = 1.6 \times 10^{-19}$  C,  $\epsilon_0 = 8.86 \times 10^{-12}$  F m<sup>-1</sup>,  $\epsilon = 55$  for (101) facet anatase TiO<sub>2</sub> with a small amount of rutile,<sup>55,57</sup> and  $C$  is the capacitance. By using these values, we obtain the average donor densities of  $8.44 \times 10^{18}$  and  $2.67 \times 10^{19}$  cm<sup>-3</sup> for TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> electrodes, respectively. The extrapolation of the M–S plot to the  $x$ -intercept gives the flat potential of the electrode, in which the NCD-modified TiO<sub>2</sub> shows a slightly negative potential than that of TiO<sub>2</sub>, by 0.1 V, which may be due to the hybridized band structure of NCDs and TiO<sub>2</sub>, and favors the migration of photoinduced electrons from NCDs to TiO<sub>2</sub>.<sup>39</sup>

To further study and gain greater insight into the charge-transfer properties in NCDs/TiO<sub>2</sub> heterostructures, time-correlated single-photon counting measurement was performed on pristine TiO<sub>2</sub> and the NCD-decorated sample. From Figure 5a, we can observe faster photoluminescence (PL) decay after depositing NCDs, which clearly indicate the existence of charge transfer between NCDs and TiO<sub>2</sub>, suppressing the radiative charge recombination in TiO<sub>2</sub>.<sup>43</sup> The PL quenching of the samples was tested *in situ* in an electrolyte with the presence of hole scavengers (Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>). It is advised that the presence of hole scavengers can effectively react with photogenerated holes and enrich the electrons in a photocatalyst system,<sup>58</sup> facilitate charge separation, and prevent electron–hole recombination, leading to a lower PL and shorter PL lifetime. Comparing the decay profiles of NCD/TiO<sub>2</sub> with/without hole scavengers in Figure 5b, it can be seen that the PL lifetime remained almost identical, suggesting a negligible PL quenching process. In

comparison, the PL lifetime of TiO<sub>2</sub> has dramatically decreased from 3.14 to 1.75 ns after adding hole scavengers (Figure S11). This is probably due to the efficient charge separation in the NCDs/TiO<sub>2</sub> system, with photogenerated electrons transferred to TiO<sub>2</sub> and holes transported to the surface of NCDs.<sup>59,60</sup>

Combined ultraviolet photoemission spectroscopy (UPS) and photoelectron spectroscopy in air (PESA) techniques provide insights into the electronic structure and energy band positions of the NCDs/TiO<sub>2</sub> materials. The value of the ionization potential of NCD powders from PESA in Figure S12a was determined to be  $5.5 \pm 0.02$  eV, corresponding to the energy of the highest occupied electronic state (highest occupied molecular orbital (HOMO)) of NCDs. The Fermi level of NCDs ( $E_{F1}$ ) was probed directly by the Kelvin probe and was determined to be  $-4.3$  eV. The UV/vis absorption spectrum of NCDs in Figure S2a suggests a relatively large energy gap of 3.5 eV, leaving the lowest unoccupied electronic state (lowest unoccupied molecular orbital (LUMO)) at  $-2$  eV. However, the excitation-dependent PL of NCDs (Figure S2b) indicates individual energy states of NCDs, which allows energy transitions extending up to 500 nm (2.48 eV).<sup>31</sup> The valence band (VB) edge and Fermi level ( $E_{F2}$ ) of TiO<sub>2</sub> measured from UPS are  $-7.65$  and  $-5.22$  eV, respectively (Figure S12b), similar to the reported band position of anatase phase TiO<sub>2</sub>.<sup>61,62</sup> The band gap ( $E_g$ ) was calculated to be 3.21 eV from the Tauc plot (Figure 4b), from which according to  $E_g = E_C - E_V$ , the conduction band (CB) edge is estimated to be  $-4.44$  eV, above the H<sup>+</sup>/H<sub>2</sub> reduction potential. As to the NCD/TiO<sub>2</sub>, the measured Fermi level ( $E_{F3}$ ) is  $-5.16$  eV by UPS, in between that of NCDs and TiO<sub>2</sub>, consistent with the observation in the PEC Mott–Schottky measurements

mentioned previously. A continuous distribution of valence band states is observed up to  $\sim 3.6$  eV in UPS concerning the Fermi level, indicating that there are midstates existing within the band gap of the nanocomposite. These states are likely formed at the NCD/TiO<sub>2</sub> interface and will promote hole transport from the valence band of TiO<sub>2</sub> to the HOMO band of NCDs.<sup>63</sup> Moreover, the ionization energy of NCDs at 5.5 eV, much smaller than the energy for TiO<sub>2</sub> (7.65 eV), clear suggests a transfer of holes from TiO<sub>2</sub> to NCDs.<sup>63</sup> To the best of our knowledge, this is the first report that directly probes the band positions of carbon dots–TiO<sub>2</sub> photoelectrodes in a PEC system for understanding the energy-transfer mechanism.

Based on the above results, a schematic diagram of the PEC mechanism is depicted in Figure 6. Under full-spectrum irradiation, the electrons on the HOMO of NCDs and valence band (VB) of TiO<sub>2</sub> can be effectively excited to the LUMO/CB, respectively. The electrons from the LUMO band of NCDs can then quickly transfer to the CB of the TiO<sub>2</sub> due to its deeper energy level. The holes left in the VB of TiO<sub>2</sub> then transfer to the NCDs, where it can react with the electrolyte for oxidation reactions. The accumulated electrons in TiO<sub>2</sub> would then go into the external circuit to the counter electrode where reduction reactions take place, resulting in a higher measured photocurrent. While under visible-light irradiation, the higher photoactivity is induced by obtaining a new absorption band through interfacial charge transfer.<sup>44</sup> Electrons in NCDs were excited from the HOMO band onto the LUMO band, where they are effectively transferred through TiO<sub>2</sub> into the circuit under positive bias, resulting in a higher photocurrent response.

Our work has therefore shown that in this hybrid system, the energy levels are arranged such that a photon excites an electron–hole pair on the NCDs with a subsequent electron transfer to the TiO<sub>2</sub>, which would then be transferred to the counter electrode. This leaves a hole in the valence band of the NCDs residing at  $-5.5$  eV, providing a site for electron transfer from OH<sup>−</sup>, which is the electron donor (D) in the electrolyte solution. The conversion of D<sup>+</sup> from D with NCD/TiO<sub>2</sub> as photocatalysts under illumination produces the photocurrent, completing the PEC circuit.

### 3. CONCLUSIONS

In summary, a facile solvothermal method was employed to synthesize nanoscale NCDs with good optical and PEC responses in the UV–visible range. This type of carbon dots can be applied as a photosensitizer for improving the PEC activity of TiO<sub>2</sub> and used as a model system to understand the fundamental mechanism of sensitization using NCDs. The obtained NCDs/TiO<sub>2</sub> electrode exhibits a higher photocurrent compared to the pristine TiO<sub>2</sub>, with an even greater enhancement under visible-light illumination. A variety of complementary techniques such as high-resolution STEM (HR-STEM), EELS, UV–vis absorption, EIS, M–S, TCSPC, and UPS were performed to investigate the optoelectronic properties, photoinduced charge transfer, and band structure of the hybrid. The results reveal that the improved PEC activity for the NCD/TiO<sub>2</sub> arises from the synergistic effect of NCDs combined with TiO<sub>2</sub>, which expands the light response into visible range as well as forms type II heterojunction at the interface with well-resolved band position probing, which has been reported for the first time. We show here the charge-transfer process between NCDs and TiO<sub>2</sub>, with an in-depth analysis of the energy transitions to develop a comprehensive

fundamental understanding of the favored role of NCDs in the photoelectrocatalytic reactions. The importance of combining structural, photophysical, and electrochemical assays to systematically improve the charge-transfer process between carbon dots and their catalyst counterparts is also addressed here. Future work will focus on tuning the carbon dot properties and optimizing the hybridization with other photoelectrocatalytic systems or z-schemes for enhanced photocatalytic performances.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.9b02412>.

More characterizations on NCDs/TiO<sub>2</sub>'s morphology and chemical/physical properties; potential carbon dots formation mechanism, XRD and Raman spectra, optical properties, EPR signal, SEM images, XRD patterns, thermogravimetric analysis patterns, photocurrent profile, PEC stability test, Mott–Schottky plots, TCSPC decay profile, PESA and UPS spectra (Figures S1–S12) (PDF)

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## Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. H.L. produced the NCDs/TiO<sub>2</sub> materials and performed all of the basic characteristic techniques; S.D. helped with the TAS and TCSPC measurements; M.D. and J.-S.K. measured the Fermi level, while M.-A.S., P.S., and O.F. helped with UPS and PESA analyses; H.L., Q.G., Y.F., A.B.J.S., X.W., and M.-M.T. co-wrote the paper. All authors have contributed to revise the manuscript.

## Notes

The authors declare no competing financial interest.

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