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

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Marc-Antoine Stoeckel,<sup>f</sup> Paolo Samori,<sup>f</sup> Oliver Fenwick,<sup>a</sup> Ana Belen Jorge Sobrido,<sup>a</sup> Xinchun  
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17 **KEYWORDS:** Carbon dots, Photoelectrocatalysis, Heterojunction, Charge transfer, Band  
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19 structure

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24 **ABSTRACT**

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27 Carbon dots on photoactive semiconductor nanomaterials have represented an effective strategy  
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29 for enhancing their photoelectrochemical (PEC) activity. By carefully designing and manipulating  
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31 carbon dots/support composite, a high photocurrent could be obtained. Currently, there is not much  
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33 fundamental understanding of how the interaction between such materials can facilitate the  
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35 reaction process. This hinders the wide applicability in PEC devices. To address this need of  
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37 improving the fundamental understanding of carbon dots/semiconductor nanocomposite, we have  
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39 taken the TiO<sub>2</sub> case as a model semiconductor system with nitrogen-doped carbon dots (NCDs).  
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41 We present here with in-depth investigation of the structural hybridization and energy transitions  
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43 in the NCDs/TiO<sub>2</sub> photoelectrode *via* high-resolution scanning transmission microscopy (HR-  
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45 STEM), electron energy loss spectroscopy (EELS), UV-Vis absorption, electrochemical  
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47 impedance spectroscopy (EIS), Mott-Schottky (M-S), time-correlated single photon counting  
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49 (TCSPC) and ultra-violet photoelectron spectroscopy (UPS), which shed some light on the charge  
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51 transfer process at the carbon dots and TiO<sub>2</sub> interface. We show that N doping in carbon dots can  
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effectively prolong the carrier lifetime, and the hybridisation 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 heterojunction at the NCDs/TiO<sub>2</sub> interface with 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 carbon dots-TiO<sub>2</sub> nanoparticle composite in a PEC system for understanding the energy transfer mechanism, demonstrating the favourable role of NCDs in the photocurrent response of TiO<sub>2</sub> for 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.

## 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 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 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> carbon dots/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 photo-induced carrier lifetime. In the case of graphene or reduced graphene oxide, those 2D and zero bandgap

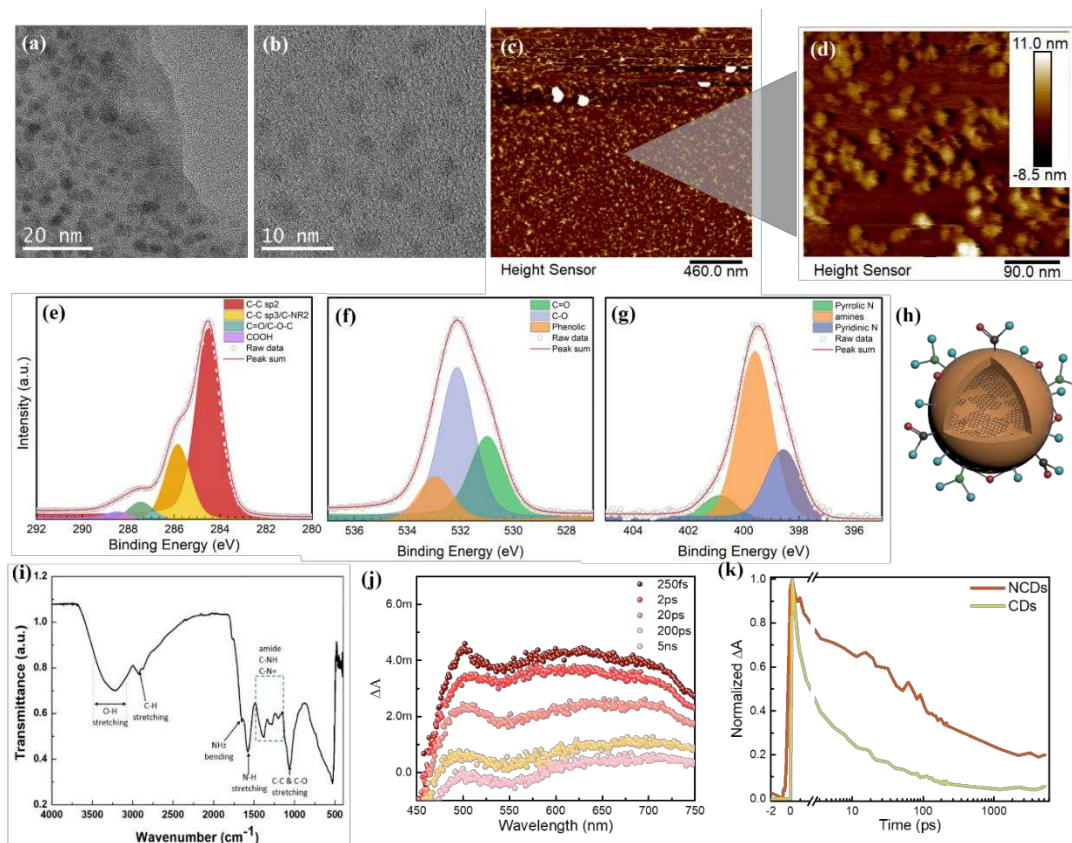
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3 materials serve as electron mediator when coupled with TiO<sub>2</sub>, allowing an accelerated electron  
4 migration at the interface.  
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8 Carbon dots with size less than 10 nm have been demonstrated to act as photosensitizers for  
9 enhancing the performance of heterogeneous photocatalysts, due to their adjustable band  
10 potentials, excellent and tunable light-harvesting ability, and electron transfer efficiency.<sup>12,16–20</sup>  
11  
12 When doped with nitrogen,<sup>13,21,22</sup> carbon dots usually show an enhanced activity towards photo-  
13 driven reactions both experimentally and theoretically.<sup>23,24</sup> Accordingly, the utilisation of nitrogen-  
14 doped carbon dots (NCDs) photosensitizers to facilitate PEC reactions started to attract  
15 attention.<sup>13,21,25</sup> However, owing to the complexity of NCDs compare to CdS and graphene in  
16 terms of chemical structure and energy states, the mechanism of NCDs in improving the PEC  
17 performance is still not well understood and explained.<sup>12,17,26</sup> Previous studies have indirectly  
18 demonstrated that the electronic coupling between the  $\pi$  states of the CDs and the conduction band  
19 of TiO<sub>2</sub> can form heterojunctions and impart the system for visible light absorption. The resulting  
20 heterojunction can efficiently separate the photo-generated electrons and holes, resulting in a lower  
21 recombination rate and a higher PEC activity.<sup>14</sup> Those effects can be greatly influenced by the  
22 intrinsic properties of CDs. For instance, the graphitisation degree can affect the charge transfer  
23 process,<sup>27</sup> the different N doping configuration (amines, amides, pyridinic, quaternary, N-oxides,  
24 etc.) can govern the light-harvesting ability,<sup>28</sup> while the functionality would determine the  
25 interaction with supporting materials.<sup>16,29</sup> Hence, it is of vital importance to develop a deeper  
26 understanding of the nanostructure of CDs and their interaction with the semiconductor materials  
27 and gain further insights on the dynamics of the charge exchange process at the materials interface.  
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51 In this paper, we exploit a broad arsenal of complementary advanced characterisation technique  
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3 NCDs at a fundamental level. Such studies reveal that N doping can effectively prolong the photo-  
4 induced carrier lifetime. A photoanode was prepared by decorating the as-synthesized NCDs onto  
5 a TiO<sub>2</sub> mesoporous film, which is used as a model semiconductor material to study the  
6 NCDs/semiconductor interaction. A detailed structural and PEC analysis showed that the  
7 nanoparticle composite possesses an improved visible light response as well as charge  
8 separation/transport ability, which resulted in a higher photocurrent value. In-depth  
9 characterisation of the NCD/TiO<sub>2</sub> nanocomposite by methods such as Mott-Schottky analysis,  
10 photoelectron spectroscopy in air, Kelvin probe and ultra-violet photoelectron spectroscopy was  
11 employed to evaluate the energy levels. Combined with electrochemical impedance spectroscopy  
12 (EIS) and in-situ photoluminescence quenching by time-correlated single photon counting  
13 (TCSPC), we present here the detailed mechanism for the interfacial charge transfer process.

## 2. Results and discussion



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

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17 NCDs were synthesized by solvothermal carbonisation of chitosan in ethanol solvent (4% w/v).  
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19 Several works on using chitosan to produce NCDs have been reported earlier.<sup>30-32</sup> Under mild  
20 conditions (HTC with 180 °C), the carbonisation and functionalisation will take place through  
21 chitosan dehydration, leading to the formation of NCDs. As illustrated in **Figure S1**, the precursor  
22 molecules go through decomposition to HMF and ammonia. The HMF molecule then go through  
23 ring opening to react with ammonia and form aminopentanal. Intermolecular condensation would  
24 occur at this stage in these intermediates. Pyridines would form from the reaction between amino  
25 groups and aldehyde, while the reaction between amino and keto groups results in the formation  
26 of pyrroles. Some amines remain free from reacting with other groups.<sup>33</sup> These functionalities are  
27 later identified in the structure of NCDs.

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

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51 To analyse the structure of the carbon core, the output of XRD and Raman spectroscopy  
52 techniques were compared. The X-ray diffraction (XRD) pattern (**Figure S2a**) displays a broad  
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3 peak centred at  $21^\circ$ , which has been demonstrated to be amorphous with turbostratic structure in  
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5 our previous study.<sup>31</sup> In theory, XRD involves X-rays interacting with electrons to reveal the  
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7 reciprocal space of crystalline lattice by diffraction, which does not give sufficient structural  
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9 information of packed carbon dots due to the less ordered structure. In this regard, Raman  
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11 spectroscopy uses long wavelength radiation and interacts with atoms, molecules or ions, which  
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13 can reveal the vibration frequencies of the system by scattering, providing information about the  
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15 chemical environments. Hence here Raman spectroscopy was carried out for the surface  
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17 characterisation of partially ordered carbon materials.<sup>34</sup> **Figure S2b** shows the Raman spectra ( $\lambda$   
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19 = 633 nm) of the NCDs. Two peaks centred at  $1382\text{ cm}^{-1}$  and  $1574\text{ cm}^{-1}$  can be seen, representing  
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21 the characteristic D and G bands for carbon materials, respectively, indicating a semi-crystalline  
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23 structure of the NCDs. The spectra show a significant level of noise-to-signal ratio, due to the  
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25 highly fluorescent background removal.  
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31 The X-ray photoelectron spectroscopy (XPS) spectra are shown in **Figure 1(e, f, g)**. They reveal  
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33 that the amine groups from chitosan are maintained on the surface of NCDs, and the carbon,  
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35 oxygen, nitrogen contents have been calculated to be 75.8%, 28.2% and 5.8%, respectively. Three  
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37 types of nitrogen species can be found in the material, which are pyridinic N (26%), amine groups  
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39 (64%) and pyrrolic N (10%), existing both on the surface as functional groups and incorporated  
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41 inside the core structure. It has been reported that different N-motifs show different charge  
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43 transportation properties, which will be beneficial for the PEC properties.<sup>28</sup> The Fourier transform  
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45 infrared (FTIR) spectrum in **Figure 1(i)** also confirms the existence of amine groups in the NCDs,  
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47 with  $\text{NH}_2$  bending at  $1648\text{ cm}^{-1}$  and N-H stretching at  $1576\text{ cm}^{-1}$ . The peaks between 1151 and  
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49  $1484\text{ cm}^{-1}$  are assigned to C-NH and C-N= amide groups.<sup>35,36</sup> A schematic profile representing the  
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51 structure of NCDs is shown in **Figure 1h**.  
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3 The optical properties of the NCDs are analyzed by UV-Vis absorption and photoluminescence.  
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5 As shown in **Figure S3a**, the UV-Vis absorption spectrum of NCD solution exhibits strong, broad  
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7 light absorption in the ultraviolet range, with an absorption peak at 270 nm, which tails off in the  
8  
9 visible region. The 270 nm absorption peak is due to the  $\pi \rightarrow \pi^*$  transition, while the visible light  
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11 absorption comes from  $n \rightarrow \pi^*$  transition.<sup>37,38</sup> The visible light response of the synthesized NCDs  
12  
13 is advantageous for use as a photosensitizer.<sup>14</sup> In **Figure S3b**, excitation-dependent emission was  
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15 observed in the blue-green light region depending on the excitation wavelength, indicating easy  
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17 access to the electronic states ( $n - \pi^*$ ,  $\pi - \pi^*$ ).<sup>39</sup> These interesting optical properties grant the  
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19 NCDs with potential applications in hybrid PEC design. Photoluminescence quantum yield ( $\Phi$ ) of  
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21 NCDs was calculated to be 8.7% referenced by quinine sulphate (QS).<sup>40</sup>  
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27 Our previous work has shown that the NCDs derived from chitosan are capable of generating  
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29 photocurrents under visible light irradiation, akin to the electronic structure of n-type  
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31 semiconductor, and the excited states of carbon dots upon interaction with light govern the photo-  
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33 induced activity.<sup>31</sup> To investigate the nature of stable surface paramagnetic defects, EPR  
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35 measurements were performed on NCD powder at room temperature in dark condition. In **Figure**  
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37 **S4**, the sharp isotropic EPR signals centred at  $g_{\text{iso}}=2.0035$  is expected to come from the presence  
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39 of carbon centred radical species present on the NCD surface, which could act as active sites for  
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41 redox reactions.  
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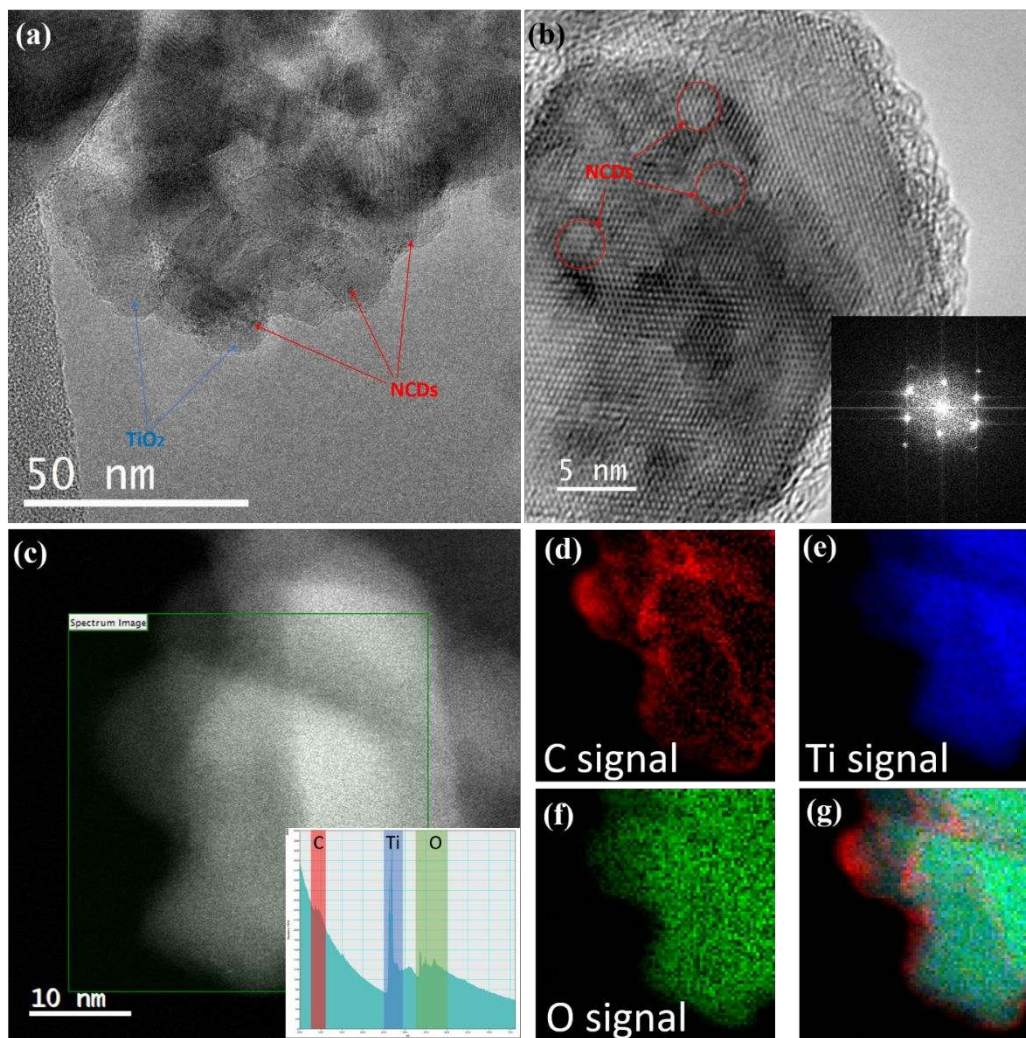
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45 The excited state photophysical properties of NCDs were investigated by mean of femtosecond  
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47 transient absorption spectroscopy (fs-TAS) which reveals that upon 375 nm photoexcitation,  
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49 NCDs gave rise to differential absorption signals that are spanning over the visible range from  
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51 450-750 nm on a ps timescale (**Figure 1j**). Features are centred near 500 nm and 625 nm, similar  
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53 to previously reported spectra of CDs.<sup>27,37</sup> The features showed up at shorter and longer  
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3 wavelenghtes are possibly assigned to core and surface states of CDs, respectively. This behaviour  
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5 is akin to that observed for graphitic carbon dots.<sup>27,41</sup> The decay lifetime kinetics at 500 nm were  
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7 fitted using a bi-exponential function into short (2.17 ps, 39%) and long (138.97 ps, 61%) lived  
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9 components. The extracted excitons lifetimes have been found being longer than any other  
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11 photosensitising materials reported to date.<sup>42,43</sup> The comparison of the decay profile of NCDs with  
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13 that of non-doped CDs in **Figure 1k** reveals that doping with N has largely prolonged the exciton  
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15 lifetime, being beneficial for the PEC process. This might be a result of N doping reducing  $\pi$ -  
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17 connections between  $sp^2$  domains, suppressing the interlayer non-radiative energy dissipation,<sup>21</sup>  
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19 and serve as electron donor to effectively scavenge holes to extend the lifetime of photogenerated  
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21 electrons.<sup>27</sup> Here we have demonstrated for the first time clear evidence and explanation of the  
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23 positive effect of N doping in carbon dots for the application as efficient photosensitizers. We have  
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25 applied the prepared NCDs to  $TiO_2$ , which is an ideal model semiconductor to study the effect of  
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27 the NCDs in the recombination rate of the photogenerated charge carriers in a PEC system.  
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29 Compared to inorganic semiconducting quantum dots, carbon dots consist of mostly  $sp^2$  carbon,  
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31 which helps the formation of a charge-transfer complex with  $TiO_2$  and thus resulting in more  
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33 efficient absorption and charge separation.<sup>44</sup>  
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40 The  $TiO_2$  thin film is fabricated by spin-coating a commercially available mesoporous titania  
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42 paste onto fluorine-doped tin oxide (FTO) coated glass substrate. To gain insight into the  
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44 morphology of the  $TiO_2$  film, we performed SEM top-view and cross-section imaging of the  
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46 NCDs/ $TiO_2$  film, with representative images portrayed in **Figure S5**. No major aggregation of the  
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48 nanoparticles can be observed. The thickness of the film was measured to be  $\sim 1 \mu m$  (from the  
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50 SEM cross-section), considered adequate to provide good charge carrier generation and collection  
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52 ability.<sup>45</sup> Brunauer-Emmett-Teller (BET) measurements showed that the  $TiO_2$  has a specific  
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3 surface area of 110 m<sup>2</sup>/g, higher than the commercial P25 (49 m<sup>2</sup>/g). The mesoporosity, as seen  
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5 from the SEM top view image guarantees sufficient light absorption and is also beneficial for  
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7 anchoring the NCDs on its surface and inside the TiO<sub>2</sub> films, providing more active sites for  
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9 reactions.<sup>14</sup>  
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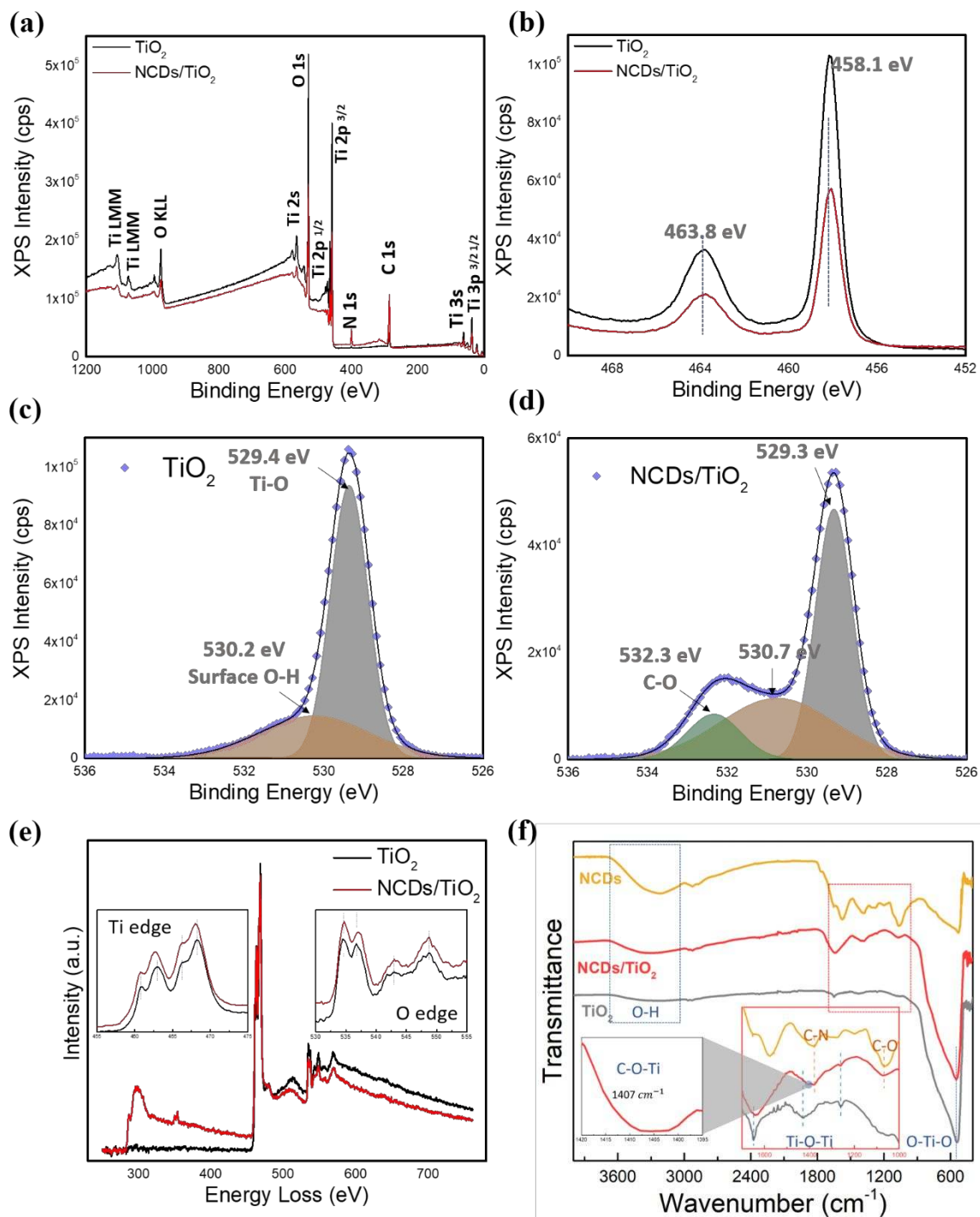
11  
12 **Figure S6** displays the XRD patterns of the TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> films. The dominant peak in  
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14 both samples are assigned to the (101) facet of anatase phase, which is considered to be the most  
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16 stable structure in anatase TiO<sub>2</sub>.<sup>46</sup> The diffraction patterns of NCDs/TiO<sub>2</sub> are in good match with  
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18 that of the TiO<sub>2</sub> which contains mostly anatase phase with small amount of rutile (JCPDS 01-084-  
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20 1286, 01-073-2224), indicating that the deposition of NCDs does not cause any obvious changes  
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22 in TiO<sub>2</sub> crystallinity.<sup>47</sup>  
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**Figure 2** TEM (a) and HR-TEM (b) of NCDs/TiO<sub>2</sub> (insert is the FFT patterns); (c) HAADF image of NCDs/TiO<sub>2</sub> and corresponding EELS spectra (inserted). The single element maps derived from the spectra: (d) C signal, (e) Ti signal, (f) O signal and (g) colour mix (red: C, blue: Ti, green: O).

TEM and HR-TEM were used to investigate the morphologies of the NCDs/TiO<sub>2</sub> nanoparticles further. TEM image (**Figure 2a**) of the prepared NCDs/TiO<sub>2</sub> nanoparticles taken at low-magnification shows some dark spots dispersed on the surface of the TiO<sub>2</sub>, revealing that the NCDs have been effectively deposited onto TiO<sub>2</sub>. In the HR-TEM images, the NCDs became less obvious, leaving only contrast differences due to the small particle size and less crystalline nature

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3 of the NCDs compared to TiO<sub>2</sub> nanoparticles, as determined by TEM and XRD (**Figure 1 and**  
4 **S2**). The observed lattice spacing of 0.35 nm for TiO<sub>2</sub> nanoparticles correspond to the (101) plane  
5 of anatase TiO<sub>2</sub>, as can be seen from XRD patterns in **Figure S6**. To further resolve the presence  
6 of NCDs, high-angle annular dark-field image (HAADF) was taken on several TiO<sub>2</sub> nanoparticles  
7 under high magnification. As seen in **Figure 2c**, NCDs are difficult to discern through the dark-  
8 field image due to the light element contrast. At the same area electron energy loss spectra (EELS)  
9 was scanned. It is known that EELS is better than EDS at detecting light elements due to the  
10 smaller energy window. Here we chose to look at 250 - 750 eV, which contains the characteristic  
11 spectra of carbon, nitrogen, titanium and oxygen, as illustrated in **Figure 2c** inserted. The spectra  
12 of C, Ti and O are very distinctive, while no signal can be seen from N, probably due to the low  
13 nitrogen amount in the NCDs (N 5.8%) also loaded in small amounts on the TiO<sub>2</sub> (~2.4%  
14 calculated from the mass loss in **Figure S7**). The EELS maps of individual elements along with  
15 the colour mix are shown in **Figure 2(d-g)**. The mapping of the NCDs on TiO<sub>2</sub> infers the  
16 heterostructure formation, which may promote the charge separation within the hybrid system,  
17 corroborating the improved PEC activity.<sup>48</sup>  
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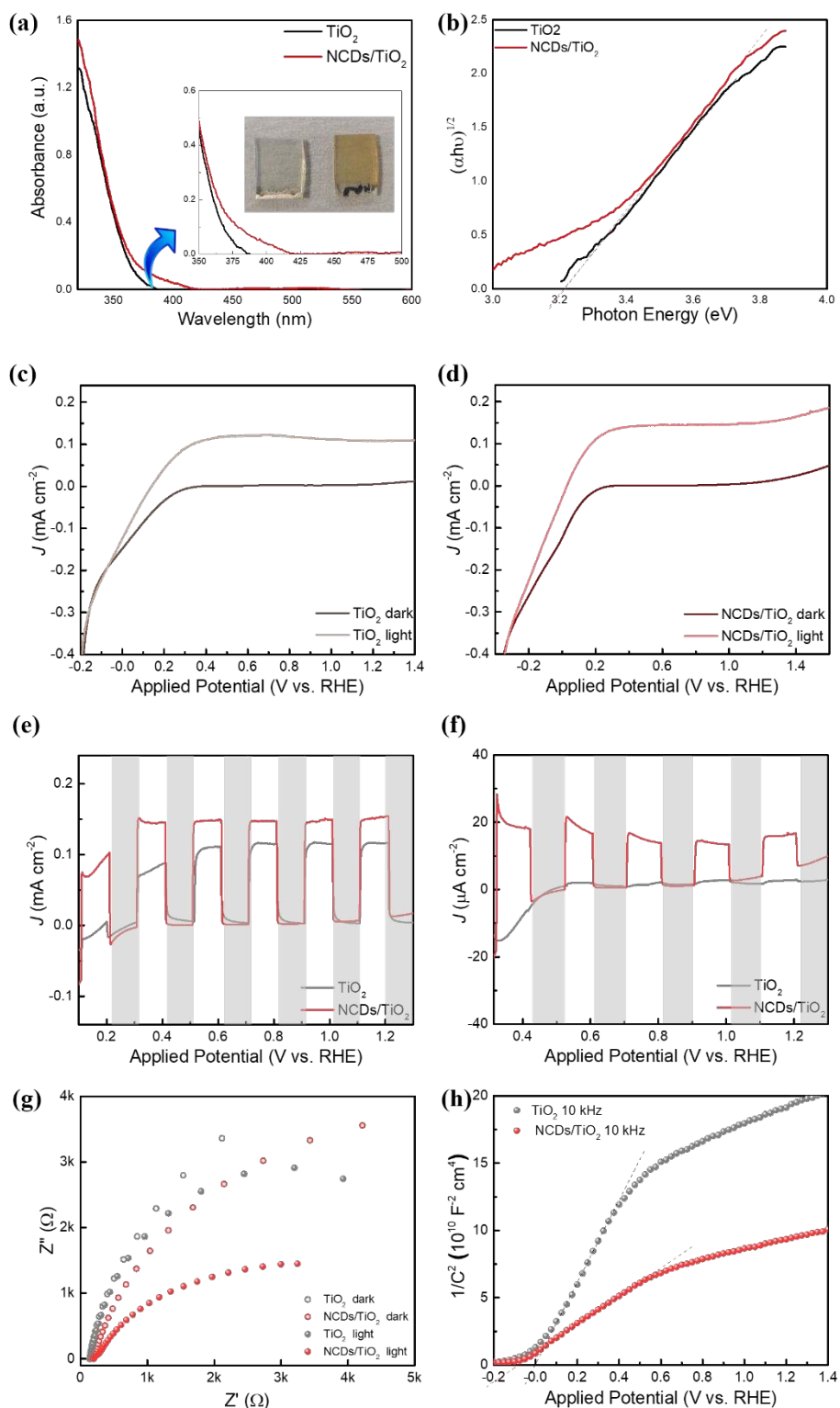


**Figure 3** Comparison of XPS survey spectra (a) and Ti 2p high-resolution spectra (b) of the TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> films; O 1s spectra of (c) TiO<sub>2</sub> and (d) NCDs/TiO<sub>2</sub>. (e) EELS spectra of TiO<sub>2</sub> (black) and NCDs/TiO<sub>2</sub> (red) and (f) FTIR signals.

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

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35 The formation of NCDs/TiO<sub>2</sub> hybrid has been further confirmed by FTIR analysis. **Figure 3f**  
36 shows that the spectra of NCDs/TiO<sub>2</sub> display typical vibration of O-Ti-O at 550 cm<sup>-1</sup>, as well as  
37 C-N, C-O stretching at 1378 and 1067 cm<sup>-1</sup>, confirming the presence of NCDs in the hybrid  
38 sample. A new absorption peak arises between the Ti-O-Ti and C-N bond at 1407 cm<sup>-1</sup>, which is  
39 possible through the C-O-Ti bond formation.<sup>52</sup> Based on the above results, it can be concluded that  
40 the NCDs are loaded on the TiO<sub>2</sub> *via* chemical absorption.  
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**Figure 4** optoelectronic properties of  $\text{TiO}_2$  and  $\text{NCDs}/\text{TiO}_2$  films: (a) UV-Vis absorption (inserted are the digital pictures of the films: left:  $\text{TiO}_2$ , right:  $\text{NCDs}/\text{TiO}_2$ ); (b) tauc plot of  $\text{TiO}_2$  and

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3 NCDs/TiO<sub>2</sub> with indirect band gap; LSV curves of (c) TiO<sub>2</sub> and (d) NCDs/TiO<sub>2</sub> under dark and  
4 light conditions; the chopped photocurrent response of the two samples under (e) full spectrum  
5 and (f) visible light ( $\lambda > 420$  nm) illumination; (g) EIS Nyquist plots under simulated solar light  
6 illumination (100 kHz – 0.1 Hz, 0.3V vs. RHE, 100 mW cm<sup>-2</sup>) and (h) Mott-Schottky plots with  
7 10 kHz frequency under dark condition at equilibrium.  
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15 Light absorption is one of the essential factors determining the PEC performance of electrode  
16 materials. UV-Vis-NIR spectroscopy is employed to characterise the optical properties of the TiO<sub>2</sub>  
17 films and their respective NCD hybrids. As shown in **Figure 4a**, pure TiO<sub>2</sub> show no absorption  
18 above 385 nm owing to the intrinsic wide band gap of anatase TiO<sub>2</sub> (3.2 eV). Compared to the  
19 pristine TiO<sub>2</sub> film, the NCD decorated films show enhanced visible light absorption tails up to 425  
20 nm for NCDs/TiO<sub>2</sub>. Therefore, the presence of NCDs plays a critical role in boosting the visible  
21 light absorption of the composites, which is important for visible-light-driven  
22 photoelectrocatalytic activity. No bandgap narrowing can be observed from the Tauc plot (**Figure**  
23 **4b**), indicating that the NCDs are only present on the surface without disrupting the crystalline  
24 structure of TiO<sub>2</sub>, in line with the STEM and XRD results.  
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38 PEC measurements were performed on the aforementioned TiO<sub>2</sub> films to investigate the photo-  
39 induced charge transfer behaviour. **Figure 4c-f** show the linear sweep voltammetry (LSV) of the  
40 photoelectrodes under simulated solar light irradiation (electrolyte: 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous  
41 solution; scan rate: 5 mV/s). Clearly, the NCDs/TiO<sub>2</sub> photoanode showed enhanced photo-  
42 response compared to pure TiO<sub>2</sub>; the NCDs/TiO<sub>2</sub> displays a saturation photocurrent of 0.15 mA  
43 cm<sup>-2</sup> at 0.3V vs RHE, approximately two times higher than that of the pristine TiO<sub>2</sub> (0.08 mA cm<sup>-2</sup>)  
44 under the same conditions. This may be the effect of the formation of heterojunctions at the  
45 NCDs/TiO<sub>2</sub> interface, which can effectively separate the photo-induced charge carriers. The  
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3 expected PEC results under visible light ( $\lambda > 420$  nm) further depict the enhanced charge  
4 separation of TiO<sub>2</sub> by hybridising NCDs. While TiO<sub>2</sub> electrode showed no obvious photo-response  
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6 in this region, the NCDs/TiO<sub>2</sub> generated photocurrent of 17  $\mu\text{A cm}^{-2}$ , owing to the slightly  
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8 enhanced visible absorption of NCDs. Consequently, based on the above results, the  
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10 photosensitization effect of NCDs on the photocurrent generation of NCDs/TiO<sub>2</sub> heterostructures  
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12 was unambiguously ascertained under both simulated solar and visible light illuminations.  
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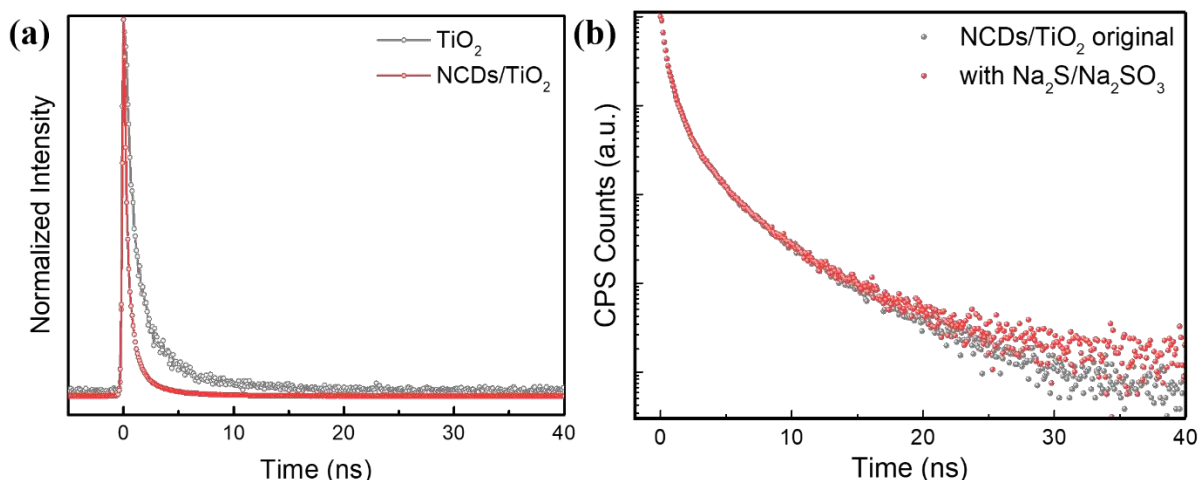
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17 The distribution of the photocurrent between UV and visible light is given in **Figure S8**. Nearly  
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19 half of the enhanced photo-carrier generation of NCDs/TiO<sub>2</sub> is attributed to the higher visible light  
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21 absorption, due to the photosensitization ability of NCDs. The rest of the improved photocurrent  
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23 may arise from a more efficient charge separation and transportation because of the formed  
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25 heterojunction between TiO<sub>2</sub> and NCDs.<sup>29,53</sup> Stability test was performed on the NCDs/TiO<sub>2</sub>  
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27 photoelectrode. As seen from **Figure S9**, NCDs/TiO<sub>2</sub> exhibit a current density decrease in the first  
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29 2000s, but with time proceeds, the electrode became more stable, with less than 25 % current  
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31 density drop. Future work is needed to improve the stability of this hybridized material.  
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36 The electron-hole pair separation efficiency were further analysed with EIS measurements. In  
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38 the Nyquist plots, the charge transfer process at the electrode/electrolyte interface is represented  
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40 by the diameter of the semicircle at low frequency; a smaller diameter indicates a lower charge  
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42 transfer resistance. **Figure 4g** shows the Nyquist plots of the TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> photoanodes  
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44 from 100 kHz to 0.1 Hz under simulated solar light illumination (0.3V vs RHE). The prepared  
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46 NCDs/TiO<sub>2</sub> show a smaller semi-circular diameter compare to TiO<sub>2</sub> under light illumination,  
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48 revealing that the NCDs/TiO<sub>2</sub> electrode possesses less photo-induced charge transfer resistance in  
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50 the interface of electrode and electrolyte, highlighting the key benefit of NCDs in improving  
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52 charge separation efficiency and enhancing photoelectrochemical activity. Compare with the EIS  
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3 performed under dark conditions, we can tell that the charge transfer resistance of NCDs/TiO<sub>2</sub>  
4 electrode decreased faster by light illumination compared with pristine TiO<sub>2</sub>. This proves that  
5 NCDs provided photosensitised electrons to TiO<sub>2</sub> and separated the electron-hole pairs more  
6 efficiently, thereby decreasing the impedance under light.<sup>54</sup> Additionally, the Mott-Schottky (M-  
7 S) measured at 10 kHz reveals a higher carrier density after NCDs deposition (**Figure 4h**) from  
8 the smaller slope of NCDs/TiO<sub>2</sub> curve.<sup>50,55</sup> To minimise the effect of surface state capacitance and  
9 the double-layer capacitance at the electrode/electrolyte interface, the frequency of the M-S  
10 measurements was chosen to be fast enough to limit the effective filling and unfilling of the  
11 electrodes' surface state, as well as restrain the building up of double layer capacitance. On that  
12 note, even though this analysis is derived from an ideal planar electrode model, the calculation of  
13 carrier density for a relative comparison is still reasonable.<sup>56</sup> Measurements at different frequency  
14 (1 kHz and 3 kHz) can be found in **Figure S10**. The carrier density ( $N_D$ ) can be estimated by the  
15 equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \left( V - V_{fb} - \frac{k_B T}{e} \right)$$

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17 Where  $e = 1.6 \times 10^{-19} \text{ C}$ ,  $\varepsilon_0 = 8.86 \times 10^{-12} \text{ F m}^{-1}$ ,  $\varepsilon = 55$  for (101) facet anatase TiO<sub>2</sub> with  
18 a small amount of rutile,<sup>55,57</sup> and C is the capacitance. By using these values, we obtain the average  
19 donor densities of  $8.44 \times 10^{18} \text{ cm}^{-3}$  and  $2.67 \times 10^{19} \text{ cm}^{-3}$  for TiO<sub>2</sub> and NCDs/TiO<sub>2</sub>  
20 electrodes, respectively. The extrapolation of the M-S plot to the x- intercept gives flat potential  
21 of the electrode, in which the NCDs modified TiO<sub>2</sub> show a slightly negative potential than that of  
22 TiO<sub>2</sub>, by 0.1 V, which may due to the hybridised band structure of NCDs and TiO<sub>2</sub> and favours  
23 the migration of photoinduced electrons from NCDs to TiO<sub>2</sub>.<sup>39</sup>



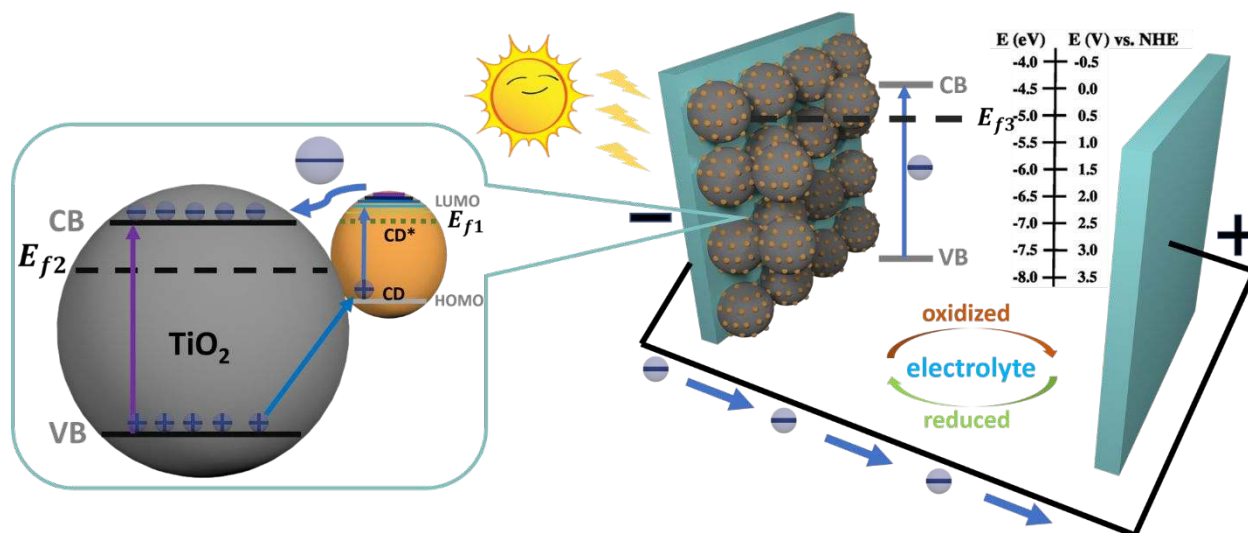
**Figure 5** (a) TCSPC decay profile of TiO<sub>2</sub> (grey) and NCDs/TiO<sub>2</sub> (red); (b) decay profiles of NCDs/TiO<sub>2</sub> with (red) and without (grey) the presence of hole scavenger Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>. The excitation wavelength for all the experiments is 405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

To further study and gain greater insight into the charge transfer properties in NCDs/TiO<sub>2</sub> heterostructure, Time-correlated Single Photon Counting measurement was performed on pristine TiO<sub>2</sub> and NCDs decorated sample. From **Figure 5a** we can observe a 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 were 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 NCDs/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 ns to 1.75 ns after adding hole scavengers (**Figure S11**). This is probably due to the efficient charge separation in the

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3 NCDs/TiO<sub>2</sub> system, with photogenerated electrons transferred to TiO<sub>2</sub> and holes transported to the  
4 surface of NCDs.<sup>59,60</sup>  
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8 Combined ultraviolet photoemission spectroscopy (UPS) and photoelectron spectroscopy in air  
9 (PESA) techniques provide insights into the electronic structure and energy band positions of the  
10 NCDs/TiO<sub>2</sub> materials. The value of ionisation potential of NCD powders from PESA in **Figure**  
11 **S12a** was determined to be 5.5 eV ± 0.02 eV, corresponding to the energy of the highest occupied  
12 electronic state (HOMO) of NCDs. The Fermi level of NCDs ( $E_{f1}$ ) was probed directly by Kelvin  
13 probe and was determined to be -4.3 eV. The UV/Vis absorption spectrum of NCDs in **Figure S2a**  
14 suggests a relatively large energy gap of 3.5 eV, leaving the lowest unoccupied electronic state  
15 (LUMO) at -2 eV. However, the excitation-dependent PL of NCDs (**Figure S2b**) indicates  
16 individual energy states of NCDs, which allows energy transitions extending up to 500 nm (2.48  
17 eV).<sup>31</sup> The valence band edge and Fermi level ( $E_{f2}$ ) of TiO<sub>2</sub> from UPS are -7.65 eV and -5.22 eV,  
18 respectively (**Figure S12b**), similar to the reported band position of anatase phase TiO<sub>2</sub>.<sup>61,62</sup> The  
19 band gap ( $E_g$ ) was calculated to be 3.21 eV from Tauc plot (**Figure 4b**), from which according to  
20  $E_g = E_C - E_V$ , the conduction band (CB) edge is estimated to be -4.44 eV, above the H<sup>+</sup>/H<sub>2</sub>  
21 reduction potential. As to the NCDs/TiO<sub>2</sub>, the measured Fermi level ( $E_{f3}$ ) is -5.16 eV by UPS, in  
22 between that of NCDs and TiO<sub>2</sub>, consistent with the observation in the PEC Mott-Schottky  
23 measurements mentioned previously. A continuous distribution of valence band states is observed  
24 up to ~3.6 eV in UPS concerning the Fermi level, indicating there are mid-states existing within  
25 the bandgap of the nanocomposite. These states are likely formed at the NCDs/TiO<sub>2</sub> interface and  
26 will promote hole transport from the valence band of TiO<sub>2</sub> to the HOMO band of NCDs.<sup>63</sup>  
27 Moreover, the ionization energy of NCDs at 5.5 eV, much smaller than the energy for TiO<sub>2</sub> (7.65  
28 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  
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the first report that directly probes the band positions of carbon dots-TiO<sub>2</sub> photoelectrode in a PEC system for understanding the energy transfer mechanism.



**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.

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 HOMO band on to LUMO band, where they are effectively transferred through TiO<sub>2</sub> into the circuit under positive bias, resulted in a higher photocurrent response.

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

19 In summary, a facile solvothermal method was employed to synthesise nanoscale NCDs with  
20 good optical and PEC response in the UV-visible range. This type of carbon dots can be applied  
21 as a photosensitizer for improving the PEC activity of TiO<sub>2</sub> and used as a model system to  
22 understand the fundamental mechanism of sensitisation using NCDs. The obtained NCDs/TiO<sub>2</sub>  
23 electrode exhibits a higher photocurrent compared to the pristine TiO<sub>2</sub>, with an even greater  
24 enhancement under visible light illumination. A variety of complementary techniques such as HR-  
25 STEM, EELS, UV-Vis absorption, EIS, M-S, TCSPC and UPS were performed to investigate the  
26 optoelectronic properties, photo-induced charge transfer and band structure of the hybrid. The  
27 results reveal that the improved PEC activity for the NCDs/TiO<sub>2</sub> arises from the synergistic effect  
28 of NCDs combined with TiO<sub>2</sub>, which expand the light response into visible range as well as form  
29 type II heterojunction at the interface with well-resolved band position probing which have been  
30 reported for the first time. We show here the charge transfer process between NCDs and TiO<sub>2</sub>,  
31 with in-depth analysis of the energy transitions to develop a comprehensive fundamental  
32 understanding on the favoured role of NCDs in the photoelectrocatalytic reactions. The importance  
33 of combining structural, photophysical and electrochemical assays on systematically improve the  
34 charge transfer process between carbon dots and their catalyst counterparts is also addressed here.  
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3 Future work will focus on tuning the carbon dots properties and optimising the hybridisation with  
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5 other photoelectrocatalytic systems or z-schemes for enhanced photocatalytic performances.  
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## 10 **ASSOCIATED CONTENT**

### 11 12 13 **Supporting Information**

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15 The supporting Information is available free of charge on the ACS Publications website.  
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18 More characterizations on NCDs/TiO<sub>2</sub>'s morphology and chemical/physical properties. (PDF)  
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### 30 **Author Contributions**

31  
32 The manuscript was written through contributions of all authors. All authors have given approval  
33 to the final version of the manuscript. HL produced the NCDs/TiO<sub>2</sub> materials and performed all  
34 the basic characteristic techniques; SD helped with the TAS and TCSPC measurements; MD, JSK  
35 measured the fermi level while MAS, PS and OF helped with UPS and PESA analysis; HL, QG,  
36 YF, ABJ, XW and MMT co-wrote the paper. All authors have contributed to revise the manuscript.  
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### 39 **Notes**

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41 The authors declare no competing financial interest.  
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## 19 REFERENCES

- 20  
21  
22 (1) Fujishima, A., & Honda, K. Electrochemical Photolysis of Water One and Two-  
23 Dimensional Structure of Poly ( L-Alanine ) Shown by Specific Heat Measurements at Low.  
24 *Nature* **1972**, *238*, 37–38.  
25  
26  
27  
28  
29  
30 (2) Zhao, L.; Chen, X.; Wang, X.; Zhang, Y.; Wei, W.; Sun, Y.; Antonietti, M.; Titirici, M. M.  
31 One-Step Solvothermal Synthesis of a Carbon @TiO<sub>2</sub> Dyade Structure Effectively  
32 Promoting Visible-Light Photocatalysis. *Adv. Mater.* **2010**, *22* (30), 3317–3321.  
33  
34  
35  
36  
37  
38 (3) Yoo, I. han; Kalanur, S. S.; Seo, H. A Nanoscale p–n Junction Photoelectrode Consisting  
39 of an NiO<sub>x</sub> Layer on a TiO<sub>2</sub>/CdS Nanorod Core-Shell Structure for Highly Efficient Solar  
40 Water Splitting. *Appl. Catal. B Environ.* **2019**, *250* (February), 200–212.  
41  
42  
43  
44  
45  
46 (4) Tada, H.; Mitsui, T.; Kiyonaga, T.; Akita, T.; Tanaka, K. All-Solid-State Z-Scheme in CdS–  
47 Au–TiO<sub>2</sub> Three-Component Nanojunction System. *Nat. Mater.* **2006**, *5* (10), 782–786.  
48  
49  
50  
51 (5) Zhao, H.; Hu, Z.; Liu, J.; Li, Y.; Wu, M.; Van Tendeloo, G.; Su, B. L. Blue-Edge Slow  
52 Photons Promoting Visible-Light Hydrogen Production on Gradient Ternary 3DOM TiO<sub>2</sub>-  
53 Au-CdS Photonic Crystals. *Nano Energy* **2018**, *47* (December 2017), 266–274.  
54  
55  
56  
57  
58  
59  
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- 1  
2  
3 (6) Sant, P. A.; Kamat, P. V. Interparticle Electron Transfer between Size-Quantized CdS and  
4 TiO<sub>2</sub> Semiconductor Nanoclusters. *Phys. Chem. Chem. Phys.* **2002**, *4* (2), 198–203.  
5  
6  
7  
8  
9 (7) Lee, Y.-L.; Chi, C.-F.; Liao, S.-Y. CdS/CdSe Co-Sensitized TiO<sub>2</sub> Photoelectrode for  
10 Efficient Hydrogen Generation in a Photoelectrochemical Cell. *Chem. Mater.* **2010**, *22* (3),  
11 922–927.  
12  
13  
14  
15  
16 (8) Zhang, F.; Zhang, C.-L.; Wang, W.-N.; Cong, H.-P.; Qian, H.-S. Titanium  
17 Dioxide/Upconversion Nanoparticles/Cadmium Sulfide Nanofibers Enable Enhanced Full-  
18 Spectrum Absorption for Superior Solar Light Driven Photocatalysis. *ChemSusChem* **2016**,  
19 *9* (12), 1449–1454.  
20  
21  
22  
23  
24  
25  
26 (9) Xiong, Z.; Luo, Y.; Zhao, Y.; Zhang, J.; Zheng, C.; Wu, J. C. S. Synthesis, Characterization  
27 and Enhanced Photocatalytic CO<sub>2</sub> Reduction Activity of Graphene Supported TiO<sub>2</sub>  
28 Nanocrystals with Coexposed {001} and {101} Facets. *Phys. Chem. Chem. Phys.* **2016**, *18*  
29 (19), 13186–13195.  
30  
31  
32  
33  
34  
35  
36 (10) Lu, Y.; Cheng, X.; Tian, G.; Zhao, H.; He, L.; Hu, J.; Wu, S. M.; Dong, Y.; Chang, G. G.;  
37 Lenaerts, S.; Siffert, S.; Van Tendeloo, G.; Li, Z. F.; Xu, L. L.; Yang, X. Y.; Su, B. L.  
38 Hierarchical CdS/m-TiO<sub>2</sub>/G Ternary Photocatalyst for Highly Active Visible Light-  
39 Induced Hydrogen Production from Water Splitting with High Stability. *Nano Energy* **2018**,  
40 *47* (September 2017), 8–17.  
41  
42  
43  
44  
45  
46  
47  
48 (11) Yu, H.; Zhao, Y.; Zhou, C.; Shang, L.; Peng, Y.; Cao, Y.; Wu, L.-Z.; Tung, C.-H.; Zhang,  
49 T. Carbon Quantum Dots/TiO<sub>2</sub> Composites for Efficient Photocatalytic Hydrogen  
50 Evolution. *J. Mater. Chem. A* **2014**, *2* (10), 3344.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (12) Tian, J.; Leng, Y.; Zhao, Z.; Xia, Y.; Sang, Y.; Hao, P.; Zhan, J.; Li, M.; Liu, H. Carbon  
4 Quantum Dots/Hydrogenated TiO<sub>2</sub> Nanobelt Heterostructures and Their Broad Spectrum  
5 Photocatalytic Properties under UV, Visible, and near-Infrared Irradiation. *Nano Energy*  
6 **2015**, *11*, 419–427.  
7  
8  
9  
10  
11  
12  
13 (13) Chen, P.; Wang, F.; Chen, Z. F.; Zhang, Q.; Su, Y.; Shen, L.; Yao, K.; Liu, Y.; Cai, Z.; Lv,  
14 W.; Liu, G. Study on the Photocatalytic Mechanism and Detoxicity of Gemfibrozil by a  
15 Sunlight-Driven TiO<sub>2</sub>/Carbon Dots Photocatalyst: The Significant Roles of Reactive  
16 Oxygen Species. *Appl. Catal. B Environ.* **2017**, *204*, 250–259.  
17  
18  
19  
20  
21  
22  
23 (14) Wang, Q.; Huang, J.; Sun, H.; Zhang, K.-Q.; Lai, Y. Uniform Carbon Dots@TiO<sub>2</sub> Nanotube  
24 Arrays with Full Spectrum Wavelength Light Activation for Efficient Dye Degradation and  
25 Overall Water Splitting. *Nanoscale* **2017**, *9*, 16046–16058.  
26  
27  
28  
29  
30  
31 (15) Liang, Z.; Hou, H.; Fang, Z.; Gao, F.; Wang, L.; Chen, D.; Yang, W. Hydrogenated TiO<sub>2</sub>  
32 Nanorod Arrays Decorated with Carbon Quantum Dots toward Efficient  
33 Photoelectrochemical Water Splitting. *ACS Appl. Mater. Interfaces* **2019**, *11* (21), 19167–  
34 19175.  
35  
36  
37  
38  
39  
40  
41 (16) Shi, W.; Guo, F.; Zhu, C.; Wang, H.; Li, H.; Huang, H.; Liu, Y.; Kang, Z. Carbon Dots  
42 Anchored on Octahedral CoO as a Stable Visible-Light-Responsive Composite  
43 Photocatalyst for Overall Water Splitting. *J. Mater. Chem. A* **2017**, *5* (ii), 19800–19807.  
44  
45  
46  
47  
48  
49 (17) Martins, N. C. T.; Ângelo, J.; Girão, A. V.; Trindade, T.; Andrade, L.; Mendes, A. N-Doped  
50 Carbon Quantum Dots/TiO<sub>2</sub> Composite with Improved Photocatalytic Activity. *Appl.*  
51 *Catal. B Environ.* **2016**, *193*, 67–74.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (18) Wang, B.; Deng, Z.; Fu, X.; Li, Z. MoS<sub>2</sub>/CQDs Obtained by Photoreduction for Assembly  
4 of a Ternary MoS<sub>2</sub>/CQDs/ZnIn<sub>2</sub>S<sub>4</sub> Nanocomposite for Efficient Photocatalytic Hydrogen  
5 Evolution under Visible Light. *J. Mater. Chem. A* **2018**, *6* (40), 19735–19742.  
6  
7  
8  
9  
10  
11 (19) Feng, J.; Liu, G.; Yuan, S.; Ma, Y. Influence of Functional Groups on Water Splitting in  
12 Carbon Nanodots and Graphitic Carbon Nitride Composites: A Theoretical Mechanism  
13 Study. *Phys. Chem. Chem. Phys.* **2017**, *19*, 4997–5003.  
14  
15  
16  
17  
18 (20) Luo, H.; Papaioannou, N.; Salvadori, E.; Roessler, M. M.; Ploenes, G.; Eck, E. R. H.;  
19 Tanase, L. C.; Feng, J.; Sun, Y.; Yang, Y.; Danaie, M.; Belen Jorge, A.; Sapelkin, A.;  
20 Durrant, J.; Dimitrov, S. D.; Titirici, M. Manipulating the Optical Properties of Carbon Dots  
21 by Fine-Tuning Their Structural Features. *ChemSusChem* **2019**, *12* (19), 4335–4335.  
22  
23  
24  
25  
26  
27  
28 (21) Shi, R.; Li, Z.; Yu, H.; Shang, L.; Zhou, C.; Waterhouse, G. I. N.; Wu, L. Z.; Zhang, T.  
29 Effect of Nitrogen Doping Level on the Performance of N-Doped Carbon Quantum  
30 Dot/TiO<sub>2</sub> Composites for Photocatalytic Hydrogen Evolution. *ChemSusChem* **2017**, *10*  
31 (22), 4650–4656.  
32  
33  
34  
35  
36  
37  
38 (22) Yan, M.; Hua, Y.; Zhu, F.; Gu, W.; Jiang, J.; Shen, H.; Shi, W. Fabrication of Nitrogen  
39 Doped Graphene Quantum Dots-BiOI/MnNb<sub>2</sub>O<sub>6</sub> p-n Junction Photocatalysts with  
40 Enhanced Visible Light Efficiency in Photocatalytic Degradation of Antibiotics. *Appl.*  
41 *Catal. B Environ.* **2017**, *202*, 518–527.  
42  
43  
44  
45  
46  
47  
48 (23) Sk, M. A.; Ananthanarayanan, A.; Huang, L.; Lim, K. H.; Chen, P. Revealing the Tunable  
49 Photoluminescence Properties of Graphene Quantum Dots. *J. Mater. Chem. C* **2014**, *2* (34),  
50 6954–6960.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (24) Otyepka, M.; Kalytchuk, S.; Rogach, A. L.; Zbořil, R.; Sudolská, M.; Nachtigallová, D.;  
4  
5 Holá, K. Graphitic Nitrogen Triggers Red Fluorescence in Carbon Dots. *ACS Nano* **2017**,  
6  
7 *11* (12), 12402–12410.  
8  
9  
10  
11 (25) Zhang, Y. Q.; Ma, D. K.; Zhang, Y. G.; Chen, W.; Huang, S. M. N-Doped Carbon Quantum  
12  
13 Dots for TiO<sub>2</sub>-Based Photocatalysts and Dye-Sensitized Solar Cells. *Nano Energy* **2013**, *2*  
14  
15 (5), 545–552.  
16  
17  
18 (26) Liang, Z.; Hou, H.; Fang, Z.; Gao, F.; Wang, L.; Chen, D.; Yang, W. Hydrogenated TiO<sub>2</sub>  
19  
20 Nanorod Arrays Decorated with Carbon Quantum Dots toward Efficient  
21  
22 Photoelectrochemical Water Splitting. *ACS Appl. Mater. Interfaces* **2019**, *11* (21), 19167–  
23  
24 19175.  
25  
26  
27  
28 (27) Martindale, B. C. M.; Hutton, G. A. M.; Caputo, C. A.; Prantl, S.; Godin, R.; Durrant, J. R.;  
29  
30 Reisner, E. Enhancing Light Absorption and Charge Transfer Efficiency in Carbon Dots  
31  
32 through Graphitization and Core Nitrogen Doping. *Angew. Chemie - Int. Ed.* **2017**, *56*,  
33  
34 6459–6463.  
35  
36  
37  
38 (28) Hu, R.; Li, L.; Jin, W. J. Controlling Speciation of Nitrogen in Nitrogen-Doped Carbon Dots  
39  
40 by Ferric Ion Catalysis for Enhancing Fluorescence. *Carbon N. Y.* **2017**, *111*, 133–141.  
41  
42  
43  
44 (29) Xie, S.; Su, H.; Wei, W.; Li, M.; Tong, Y.; Mao, Z. Remarkable Photoelectrochemical  
45  
46 Performance of Carbon Dots Sensitized TiO<sub>2</sub> under Visible Light Irradiation. *J. Mater.*  
47  
48 *Chem. A* **2014**, *2* (39), 16365–16368.  
49  
50  
51  
52 (30) Yang, Y.; Cui, J.; Zheng, M.; Hu, C.; Tan, S.; Xiao, Y.; Yang, Q.; Liu, Y. One-Step  
53  
54 Synthesis of Amino-Functionalized Fluorescent Carbon Nanoparticles by Hydrothermal  
55  
56  
57  
58  
59  
60

- 1  
2  
3 Carbonization of Chitosan. *Chem. Commun.* **2012**, *48*, 380–382.  
4  
5  
6  
7 (31) Zhang, D.-W.; Papaioannou, N.; David, N. M.; Luo, H.; Gao, H.; Tanase, L. C.; Degoussé,  
8 T.; Samori, P.; Sapelkin, A.; Fenwick, O.; Titirici, M.-M.; Krause, S. Photoelectrochemical  
9 Response of Carbon Dots (CDs) Derived from Chitosan and Their Use in Electrochemical  
10 Imaging. *Mater. Horizons* **2018**, *5*, 423–428.  
11  
12  
13  
14  
15  
16 (32) Marinovic, A.; Kiat, L. S.; Dunn, S.; Titirici, M. M.; Briscoe, J. Carbon-Nanodot Solar Cells  
17 from Renewable Precursors. *ChemSusChem* **2017**, *10* (5), 1004–1013.  
18  
19  
20  
21  
22 (33) Shu, C.-K. Degradation Products Formed from Glucosamine in Water. *J. Agric. Food*  
23 *Chem.* **1998**, *46* (3), 1129–1131.  
24  
25  
26  
27 (34) Ortega-Liebana, M. C.; Chung, N. X.; Limpens, R.; Gomez, L.; Hueso, J. L.; Santamaria,  
28 J.; Gregorkiewicz, T. Uniform Luminescent Carbon Nanodots Prepared by Rapid Pyrolysis  
29 of Organic Precursors Confined within Nanoporous Templating Structures. *Carbon N. Y.*  
30 **2017**, *117*, 437–446.  
31  
32  
33  
34  
35  
36  
37 (35) Yang, M.; Li, B.; Zhong, K.; Lu, Y. Photoluminescence Properties of N-Doped Carbon Dots  
38 Prepared in Different Solvents and Applications in PH Sensing. *J. Mater. Sci.* **2018**, *53*,  
39 2424–2433.  
40  
41  
42  
43  
44  
45 (36) Santos, C. I. M.; Mariz, I. F. A.; Pinto, S. N.; Gonçalves, G.; Bdikin, I.; Marques, P. A. A.  
46 P.; Neves, M. G. P. M. S.; Martinho, J. M. G.; Maçôas, E. M. S. Selective Two-Photon  
47 Absorption in Carbon Dots: A Piece of the Photoluminescence Emission Puzzle. *Nanoscale*  
48 **2018**, *10* (26), 12505–12514.  
49  
50  
51  
52  
53  
54  
55 (37) Strauss, V.; Margraf, J. T.; Dolle, C.; Butz, B.; Nacken, T. J.; Bauer, W.; Peukert, W.;  
56  
57  
58  
59  
60

- 1  
2  
3 Spiecker, E.; Clark, T.; Guldi, D. M. Carbon Nanodots – Towards a Comprehensive  
4 Understanding of Their Photoluminescence. *J. Am. Chem. Soc.* **2014**, *49*, 17308–17316.  
5  
6  
7  
8  
9 (38) Sudolská, M.; Dubecký, M.; Sarkar, S.; Reckmeier, C. J.; Zbořil, R.; Rogach, A. L.;  
10 Otyepka, M. Nature of Absorption Bands in Oxygen-Functionalized Graphitic Carbon Dots.  
11 *J. Phys. Chem. C* **2015**, *119*, 13369–13373.  
12  
13  
14  
15  
16 (39) Li, Y.; Li, P.; Wang, J.; Yang, Y.; Yao, W.; Wei, Z.; Wu, J.; Yan, X.; Xu, X.; Liu, Y.; Zhu,  
17 Y. Water Soluble Graphitic Carbon Nitride with Tunable Fluorescence for Boosting Broad-  
18 Response Photocatalysis. *Appl. Catal. B Environ.* **2018**, *225* (November 2017), 519–529.  
19  
20  
21  
22  
23  
24 (40) Sahu, S.; Behera, B.; Maiti, T. K.; Mohapatra, S. Simple One-Step Synthesis of Highly  
25 Luminescent Carbon Dots from Orange Juice: Application as Excellent Bio-Imaging  
26 Agents. *Chem. Commun.* **2012**, *48*, 8835–8837.  
27  
28  
29  
30  
31  
32 (41) Guin, J. P.; Guin, S. K.; Debnath, T.; Ghosh, H. N. Chemically Clean Single-Step Oxido-  
33 Reductive Synthesis of Green Luminescent Graphene Quantum Dots as Impending  
34 Electrocatalyst. *Carbon N. Y.* **2016**, *109*, 517–528.  
35  
36  
37  
38  
39 (42) Shi, X. F.; Xia, X. Y.; Cui, G. W.; Deng, N.; Zhao, Y. Q.; Zhuo, L. H.; Tang, B. Multiple  
40 Exciton Generation Application of PbS Quantum Dots in ZnO@PbS/Graphene Oxide for  
41 Enhanced Photocatalytic Activity. *Appl. Catal. B Environ.* **2015**, *163*, 123–128.  
42  
43  
44  
45  
46  
47 (43) Shi, X.; Kim, S.; Fujitsuka, M.; Majima, T. In Situ Observation of NiS Nanoparticles  
48 Depositing on Single TiO<sub>2</sub> Mesocrystal for Enhanced Photocatalytic Hydrogen Evolution  
49 Activity. *Appl. Catal. B Environ.* **2019**.  
50  
51  
52  
53  
54  
55 (44) Lee, K.; Yoon, H.; Ahn, C.; Park, J.; Jeon, S. Strategies to Improve the Photocatalytic  
56  
57  
58  
59  
60

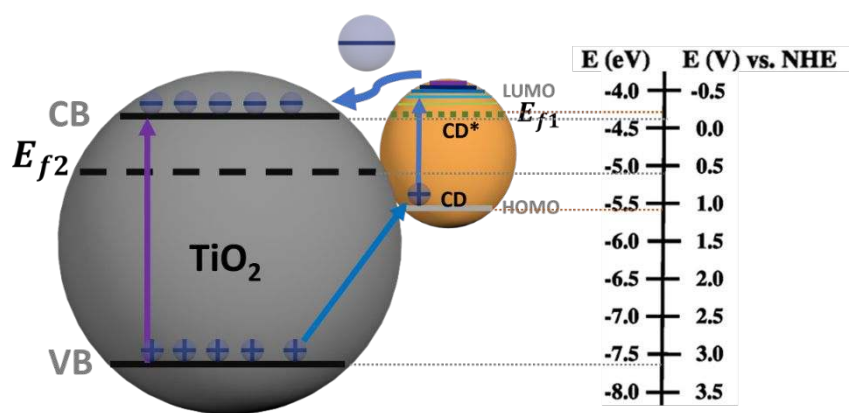


- 1  
2  
3 Activity of TiO<sub>2</sub>: 3D Nanostructuring and Heterostructuring with Graphitic Carbon  
4  
5 Nanomaterials. *Nanoscale* **2019**, *11* (15), 7025–7040.  
6  
7  
8  
9 (45) Chen, Z.; Dinh, H. N.; Miller, E. *Photoelectrochemical Water Splitting: Standards,*  
10  
11 *Experimental Methods, and Protocols*; Springer, 2013.  
12  
13  
14 (46) Wang, H.; An, T.; Selloni, A. Effect of Reducible Oxide-Metal Cluster Charge Transfer on  
15  
16 the Structure and Reactivity of Adsorbed Au and Pt Atoms and Clusters on Anatase TiO<sub>2</sub>.  
17  
18 *J. Chem. Phys.* **2017**, *146* (18), 184703.  
19  
20  
21  
22 (47) Nie, Y. C.; Yu, F.; Wang, L. C.; Xing, Q. J.; Liu, X.; Pei, Y.; Zou, J. P.; Dai, W. L.; Li, Y.;  
23  
24 Suib, S. L. Photocatalytic Degradation of Organic Pollutants Coupled with Simultaneous  
25  
26 Photocatalytic H<sub>2</sub> Evolution over Graphene Quantum Dots/Mn-N-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>  
27  
28 Composite Catalysts: Performance and Mechanism. *Appl. Catal. B Environ.* **2018**, *227*  
29  
30 (October 2017), 312–321.  
31  
32  
33  
34 (48) Tian, J.; Leng, Y.; Zhao, Z.; Xia, Y.; Sang, Y.; Hao, P.; Zhan, J.; Li, M.; Liu, H. Carbon  
35  
36 Quantum Dots/Hydrogenated TiO<sub>2</sub>nanobelt Heterostructures and Their Broad Spectrum  
37  
38 Photocatalytic Properties under UV, Visible, and near-Infrared Irradiation. *Nano Energy*  
39  
40 **2015**, *11*, 419–427.  
41  
42  
43  
44 (49) Yu, L.; Shao, Y.; Li, D. Direct Combination of Hydrogen Evolution from Water and  
45  
46 Methane Conversion in a Photocatalytic System over Pt/TiO<sub>2</sub>. *Appl. Catal. B Environ.*  
47  
48 **2017**, *204*, 216–223.  
49  
50  
51  
52 (50) Xu, Y.; Zhang, C.; Zhang, L.; Zhang, X.; Yao, H.; Shi, J. Pd-Catalyzed Instant  
53  
54 Hydrogenation of TiO<sub>2</sub> with Enhanced Photocatalytic Performance. *Energy Environ. Sci.*  
55  
56  
57  
58  
59  
60

- 1  
2  
3 **2016**, *9* (7), 2410–2417.  
4  
5  
6  
7 (51) D’Angelo, D.; Bongiorno, C.; Amato, M.; Deretzis, I.; La Magna, A.; Fazio, E.; Scalese, S.  
8 Oxygen Functionalities Evolution in Thermally Treated Graphene Oxide Featured by EELS  
9 and DFT Calculations. *J. Phys. Chem. C* **2017**, *121* (9), 5408–5414.  
10  
11  
12  
13  
14 (52) Rajender, G.; Kumar, J.; Giri, P. K. Interfacial Charge Transfer in Oxygen Deficient TiO<sub>2</sub>-  
15 Graphene Quantum Dot Hybrid and Its Influence on the Enhanced Visible Light  
16 Photocatalysis. *Appl. Catal. B Environ.* **2018**, *224* (October 2017), 960–972.  
17  
18  
19  
20  
21  
22 (53) Raziq, F.; Sun, L.; Wang, Y.; Zhang, X.; Humayun, M.; Ali, S.; Bai, L.; Qu, Y.; Yu, H.;  
23 Jing, L. Synthesis of Large Surface-Area g-C<sub>3</sub>N<sub>4</sub> Comodified with MnO<sub>x</sub> and Au-TiO<sub>2</sub> as  
24 Efficient Visible-Light Photocatalysts for Fuel Production. *Adv. Energy Mater.* **2018**, *8* (3),  
25 2–11.  
26  
27  
28  
29  
30  
31  
32 (54) Tzeng, W. J.; Wu, M. L.; Lin, L. J.; Chang, H. Y. Chalcogenide Photosensitized Titania  
33 Nanotube Arrays. *J. Alloys Compd.* **2015**, *651* (December 2015), 483–489.  
34  
35  
36  
37 (55) Goossens, A.; Schoonman, J. Mott-Schottky Analysis of Nanometer-Scale. *J. Electrochem.*  
38 *Soc.* **1997**, *144* (5), 1723–1727.  
39  
40  
41  
42 (56) Luo, Z.; Wang, T.; Zhang, J.; Li, C.; Li, H.; Gong, J. Dendritic Hematite Nanoarray  
43 Photoanode Modified with a Conformal Titanium Dioxide Interlayer for Effective Charge  
44 Collection. *Angew. Chemie - Int. Ed.* **2017**, *56* (42), 12878–12882.  
45  
46  
47  
48  
49  
50 (57) Kim, J. Y.; Jung, H. S.; No, J. H.; Kim, J. R.; Hong, K. S. Influence of Anatase-Rutile Phase  
51 Transformation on Dielectric Properties of Sol-Gel Derived TiO<sub>2</sub> Thin Films. *J.*  
52 *Electroceramics* **2006**, *16* (4), 447–451.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (58) Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. *Chem.*  
4  
5 *Soc. Rev.* **2009**, *38* (1), 253–278.  
6  
7  
8 (59) Ma, Z.; Zhang, Y.-L.; Wang, L.; Ming, H.; Li, H.; Zhang, X.; Wang, F.; Liu, Y.; Kang, Z.;  
9  
10 Lee, S.-T. Bioinspired Photoelectric Conversion System Based on Carbon-Quantum-Dot-  
11  
12 Doped Dye–Semiconductor Complex. *ACS Appl. Mater. Interfaces* **2013**, *5* (11), 5080–  
13  
14 5084.  
15  
16  
17 (60) Liu, R.; Huang, H.; Li, H.; Liu, Y.; Zhong, J.; Li, Y.; Zhang, S.; Kang, Z. Metal Nanoparticle  
18  
19 / Carbon Quantum Dot Composite as Photocatalyst for High Efficiency Cyclohexane  
20  
21 Oxidation. *Acs Catal.* **2014**, *4*, 328–336.  
22  
23  
24  
25 (61) Scanlon, D. O.; Dunnill, C. W.; Buckeridge, J.; Shevlin, S. A.; Logsdail, A. J.; Woodley, S.  
26  
27 M.; Catlow, C. R. A.; Powell, M. J.; Palgrave, R. G.; Parkin, I. P.; Watson, G. W.; Keal, T.  
28  
29 W.; Sherwood, P.; Walsh, A.; Sokol, A. A. Band Alignment of Rutile and Anatase TiO<sub>2</sub>.  
30  
31 *Nat. Mater.* **2013**, *12* (9), 798–801.  
32  
33  
34  
35 (62) Kashiwaya, S.; Morasch, J.; Streibel, V.; Toupance, T.; Jaegermann, W.; Klein, A. The  
36  
37 Work Function of TiO<sub>2</sub>. *Surfaces* **2018**, *1* (1), 73–89.  
38  
39  
40  
41 (63) Saha, A.; Moya, A.; Kahnt, A.; Iglesias, D.; Marchesan, S.; Wannemacher, R.; Prato, M.;  
42  
43 Vilatela, J. J.; Guldi, D. M. Interfacial Charge Transfer in Functionalized Multi-Walled  
44  
45 Carbon Nanotube@TiO<sub>2</sub> Nanofibres. *Nanoscale* **2017**, *9* (23), 7911–7921.  
46  
47  
48  
49  
50  
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52  
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54  
55  
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59  
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## Table of Contents



Type II heterojunction with well-resolved band positions

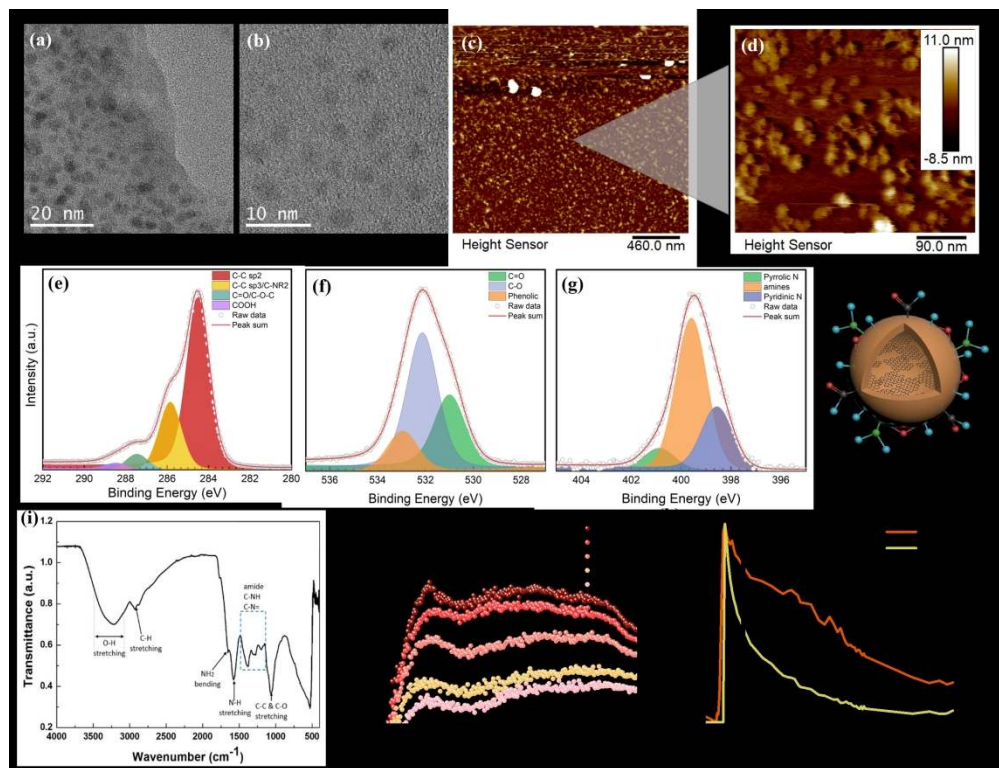


Figure 1 Structural features of as-prepared NCDs: TEM (a) and HR-TEM (b) images; (c) an overview AFM image on mica substrate (Z scale -6.0 to 7.9 nm) and (d) high-resolution scanned image; XPS spectra: (e) C 1s, (f) O 1s, (g) N 1s and corresponding FTIR (i) spectrum; (h) a schematic structure based on the characterizations (atoms in red: O, green: N and blue: H); (j) fs-TAS spectra at different time delays and (k) normalized fs-TAS kinetics of NCDs and non-doped CDs measured at 500 nm, samples were excited at 375 nm.

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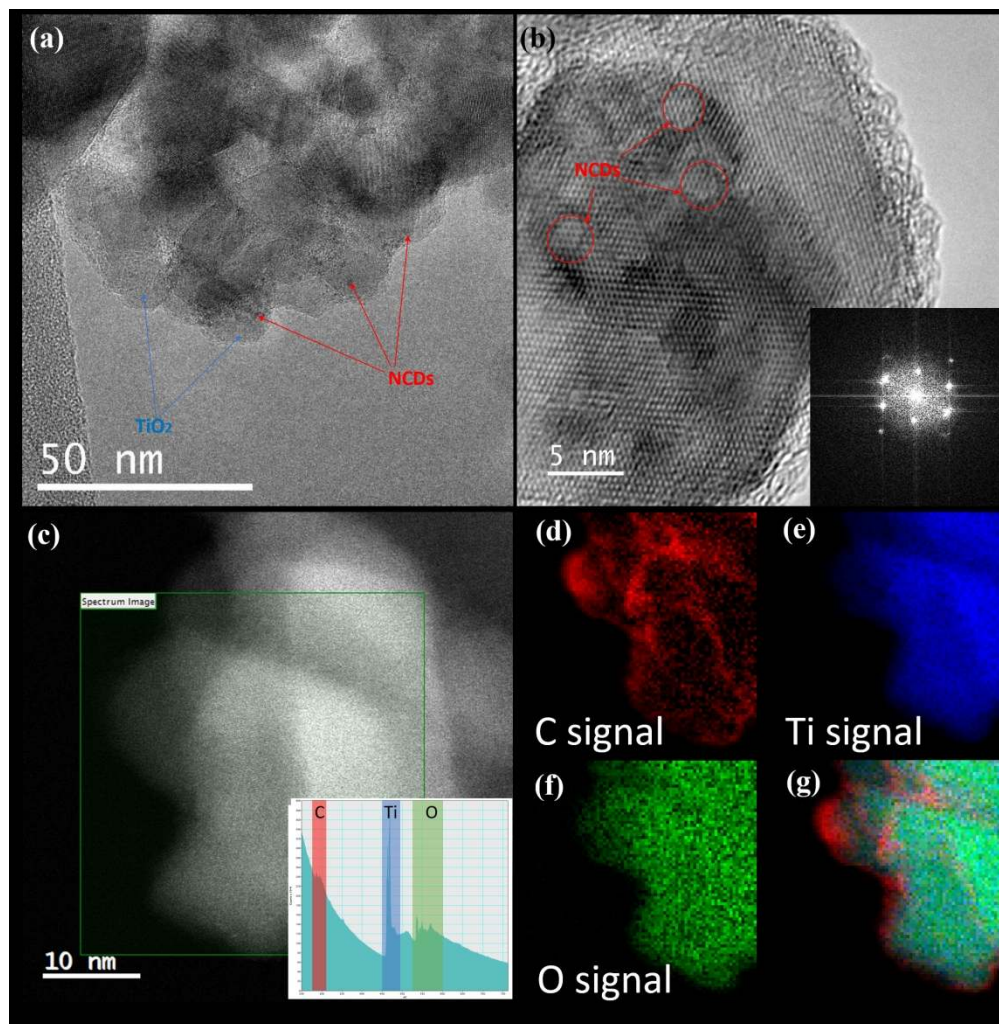


Figure 2 TEM (a) and HR-TEM (b) of NCDs/TiO<sub>2</sub> (insert is the FFT patterns); (c) HAADF image of NCDs/TiO<sub>2</sub> and corresponding EELS spectra (inserted). The single element maps derived from the spectra: (d) C signal, (e) Ti signal, (f) O signal and (g) colour mix (red: C, blue: Ti, green: O).

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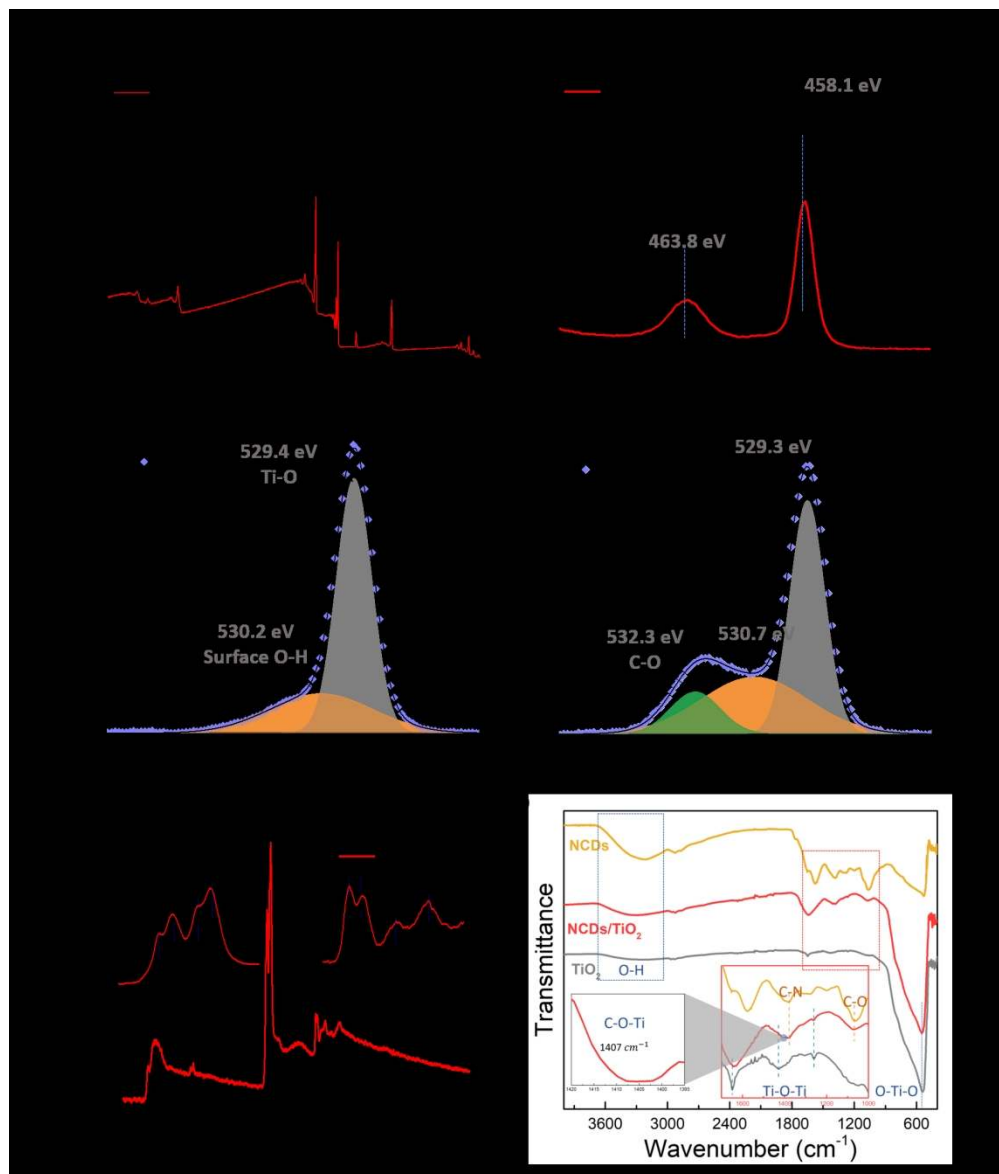


Figure 3 Comparison of XPS survey spectra (a) and corresponding core level spectra (b) Ti 2p of the TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> films; O 1s spectra of (c) TiO<sub>2</sub> and (d) NCDs/TiO<sub>2</sub>. (e) EELS spectra of TiO<sub>2</sub> (black) and NCDs/TiO<sub>2</sub> (red) and (f) FTIR signals.

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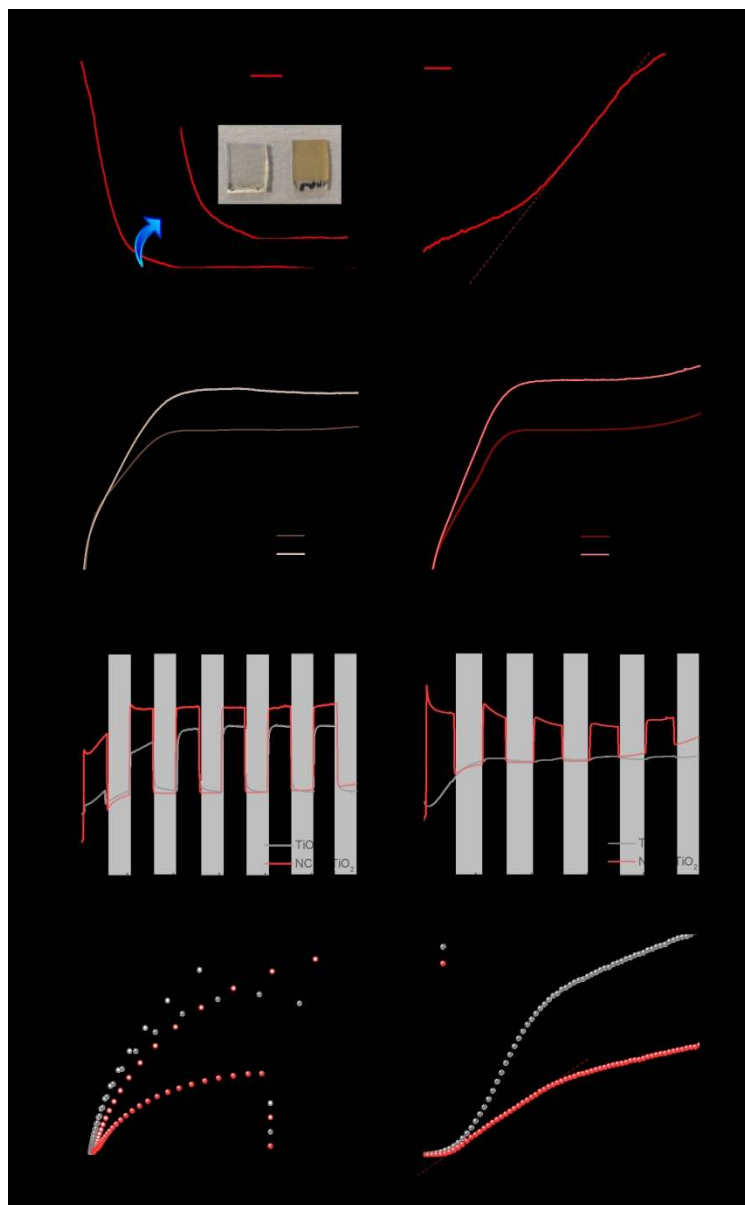


Figure 4 optoelectronic properties of TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> films: (a) UV-Vis absorption (inserted are the digital pictures of the films: left: TiO<sub>2</sub>, right: NCDs/TiO<sub>2</sub>); (b) tauc plot of TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> with indirect band gap; LSV curves of (c) TiO<sub>2</sub> and (d) NCDs/TiO<sub>2</sub> under dark and light conditions; the chopped photocurrent response of the two samples under (e) full spectrum and (f) visible light ( $\lambda > 420$  nm) illumination; (g) EIS Nyquist plots under simulated solar light illumination (100 kHz – 0.1 Hz, 0.3V vs. RHE, 100 mW cm<sup>-2</sup>) and (h) Mott-Schottky plots with 10 kHz frequency under dark condition at equilibrium.

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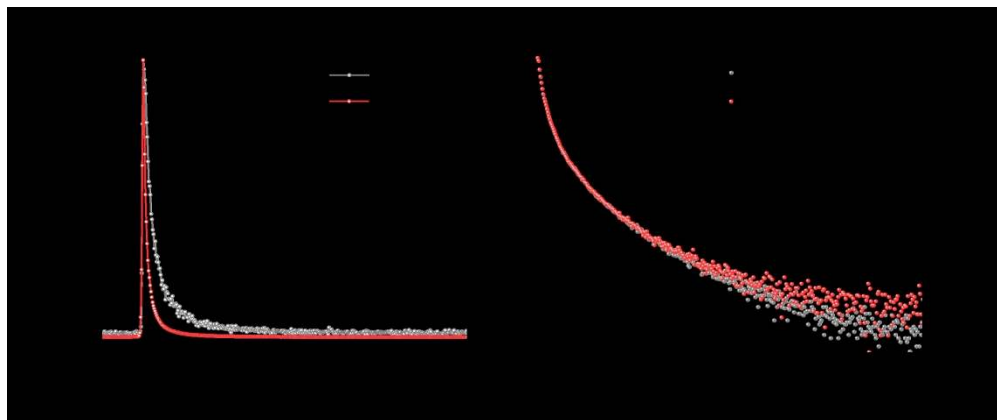


Figure 5 (a) TCSPC decay profile of TiO<sub>2</sub> (grey) and NCDs/TiO<sub>2</sub> (red); (b) decay profiles of NCDs/TiO<sub>2</sub> with (red) and without (grey) the presence of hole scavenger Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>. The excitation wavelength for all the experiments is 405 nm,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

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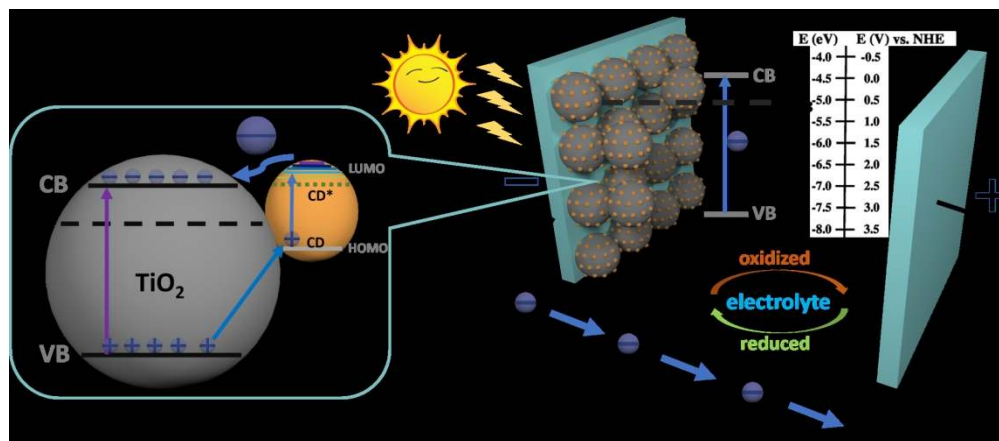


Figure 6 Proposed formation of the heterostructure with band alignments and charge transfer at the surface of TiO<sub>2</sub> and NCDs under light irradiation.

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