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

Hui Luo,<sup>a,g</sup> Stoichko Dimitrov,<sup>b,c</sup> Matyas Daboczi,<sup>d</sup> Ji-Seon Kim,<sup>d</sup> Qian Guo,<sup>a</sup> Yuanxing Fang,<sup>e</sup> Marc-Antoine Stoeckel,<sup>f</sup> Paolo Samorì,<sup>f</sup> Oliver Fenwick,<sup>a</sup> Ana Belen Jorge Sobrido,<sup>a</sup> Xinchen Wang <sup>e</sup> and Maria-Magdalena Titirici<sup>a,g</sup> \*

Corresponding author e-mail: m.titirici@imperial.ac.uk

### **Experimental section**

#### Reagents

Chitosan (medium molecular weight), transparent titania paste, sodium sulfate, sodium sulfide and sodium sulfite are purchased from Sigma-Aldrich without further purification. Fluorinedoped tin oxide (FTO) coated glasses were purchased from Solaronix.

#### The synthesis of NCDs

NCDs were synthesised by a facile one-step solvothermal carbonization as we reported before.<sup>[1]</sup> Typically, 1.4 g chitosan was dispersed in ethanol (4% w/v) and then the mixture was transferred into a 50 mL Teflon-sealed autoclave and maintained at 200°C for 12 hours. The dark brown liquid that contains NCDs was centrifuged at 20,000 rpm for 10 min to separate from the solid carbonaceous microspheres, followed by filteringusing standard 0.2  $\mu$ m pore size syringe filters.

#### The decoration of NCDs on mesoporous TiO<sub>2</sub> films

The films were fabricated by a spin coating method with titania paste dispersed in ethanol with concentration 0.125 g/mL. 100  $\mu$ L solution was added for each spin, with a spin rate at 3000 rpm for 45s. 5 layers were coated for each film. The films were then undergone slow calcination

at 500 °C/2 h by using 2 °C/min ramp with 1 h of continuous heating step at 200 °C. After naturally cooling down, the films were immersed in NCDs solution for 24 hours. The NCDs are uniformly decorated on  $TiO_2$  and the white colour  $TiO_2$  electrode turned light brown. Finally the electrode was washed with ethanol and dried in vacuum oven at 80 °C overnight.

### Characterization

The morphology of TiO<sub>2</sub> films were studied by Scanning electron microscope (SEM, FEI Inspect F). Transmission electron microscopic (TEM) and high resolution TEM (HRTEM) images were obtained on a Jeol JEM 2010. HAADF-STEM images and EDX mapping was done with a probe aberration-corrected analytical electron microscope JEOL ARM200F under STEM mode with operation voltage set at 200kV. Imaging condition: 12 cm condenser lens, 40 µm C12 aperture with 3 mm bright field aperture. The X-ray diffraction (XRD) patterns were performed using Panalytical Xpert Pro diffractometer with Cu-Ka radiation. UV-Vis absorption spectra of NCDs in ethanol were recorded by using Perkin Elmer Lambda LS 35 UV-visible spectrometer, and UV-Vis of TiO<sub>2</sub> films were performed on a Perkin Elmer Lambda LS 950 UV-visible spectrometer equipped with an integrating sphere under absorption mode. X-ray photoelectron spectroscopic (XPS) measurements on NCDs were performed using an AXIS Ultra DLD (Kratos Surface Analysis) setup equipped with an 180° hemispherical analyser, using Al  $K_{\alpha 1}$  (1486.74 eV) radiation from a monochromatized X-Ray source at operating power of 300W (15 kV  $\times$  20 mA). The XPS and ultra-violet photoelectron spectroscopic (UPS) measurements on NCDs/TiO<sub>2</sub> films were conducted on a ThermalFisher Nexsa using Al  $K_{\alpha l}$  X-ray source and UV source, respectively. Continuous-wave EPR measurements were performed on a Bruker E-scan benchtop spectrometer at room temperature. Experimental parameters were as follow: microwave frequency ~9.773 GHz, 2 mW microwave power, 0.15 mT modulation amplitude, 86 kHz modulation frequency, 81.92 ms conversion time and 20.48 ms time constant. Brunauer-Emmett-Teller (BET) surface area of as-prepared TiO<sub>2</sub> powder and commercial P25 was measured using a Micromeritics' Gemini VII 2390a BET instrument. TCSPC experiments were carried with LifeSpec II (Edinburgh Instruments Ltd.) using 405 nm 60 ps pulsed laser diode for excitation in an ambient atmosphere, and the emission was detected at 520 nm. The PL quenching was performed in a 5 ml cuvette with electrolyte containing 50 mM Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>. Photoelectron spectroscopy in air (PESA) measurements were performed using an AC-2 Photoelectron Spectrometer (Riken Keiki), using a UV intensity of 600 nW. The Fermi level of the samples was measured by an APS04 (KP Technology) applying a vibrating tip (2 mm, gold alloy) Kelvin probe. The controlled average temperature in the lab we measure is 22 °C ( $\pm$ 1 °C) and the relative humidity is 36.3% ( $\pm$  8%). The difference of contact potential between the sample and the tip was measured until the signal saturated. The final equilibrium value was added to the tip's work function in order to get the absolute Fermi level. The tip work function was determined against a cleaned silver reference before the samples were measured.

#### Photoelectrochemical measurements

For the TiO<sub>2</sub> films, the measurement of photocurrent was carried out using the same custom made electrochemical cell with 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution as electrolyte using a potentiostat (Gamry Interface 1000).A platinum wire was used as counter electrode and an Ag/AgCl electrode as reference electrodes. The photoanode was irradiated with full spectrum by a Sciencetech SLB-150B solar simulator and visible light by blocking the light with a 420 nm cut-off filter. The light intensity was adjusted to 100 mW/cm<sup>2</sup> (1 sun). The scan rate was 5 mV/s. The electrochemical impedance spectroscopy (EIS) was measured by applying 0.3 V vs RHE under dark/1 sun illumination and recorded over the frequency range of 100 kHz-100 mHz with ac amplitude of 10 mV, and Mott-Schottky plots were obtained at an AC frequency of 1, 3 and10 kHz with an amplitude of 5mV from -0.8 V to 0.8 V (vs Ag/AgCl).

## **Supporting Figures**

Chitosan hydrolysis to glucosamine



Glucosamine dehydration/deamination



#### HMF reaction with ammonia



Figure S1. Potential chemical reactions involved in the formation of CDs from chitosan precursor to form three different nitrogen functionalities.



Figure S2. XRD (a) and Raman (b) spectra of NCDs.



Figure S3. Optical properties of NCDs: (a) UV-Vis absorption; (b) excitation-dependent PL.



Figure S4. EPR signal of NCDs powder at room temperature.



Figure S5. SEM (a) top-view and (b) cross-section images showing the morphology and thickness of the NCDs/TiO<sub>2</sub> film.



Figure S6. XRD patterns of TiO<sub>2</sub> and NCDs/TiO<sub>2</sub>



Figure S7. Thermogravimetric analysis patterns of TiO<sub>2</sub> and NCDs/TiO<sub>2</sub> showing the NCDs loading.



Figure S8. Bar graph profile showing the composition of UV and visible light induced photocurrent proportion.



Figure S9. Stability test of NCDs/TiO<sub>2</sub> at 1.23 V vs. RHE under simulated solar light illumination.



Figure S10. Mott-Schottky plots of  $TiO_2$  (a) and NCDs/ $TiO_2$  (b) measured at different frequencies; the comparison of the two electrodes at (c) 1 kHz and (d) 3 kHz.



Figure S11. TCSPC decay profile of  $TiO_2$  without (a) and with (b) hole scavengers.



Figure S12. (a) PESA spectra of NCDs showing the ionization energy; (b) UPS spectra of TiO<sub>2</sub> (onset: 2.43 eV, cut-off: 15.98 eV) and NCDs/TiO<sub>2</sub> (onset: 2.43 eV, cut off: 16.04 eV)