

## Electronic Supporting Information

### Upconversion Fluorescent Carbon Nanodots Enriched with Nitrogen for Light Harvesting

Chuanfu Wang<sup>b</sup>, Xia Wu<sup>c</sup>, Xiangping Li<sup>d</sup>, Wentai Wang<sup>a</sup>, Lianzhou Wang<sup>c\*</sup>, Min Gu<sup>d\*</sup>, Qin Li<sup>a,b\*</sup>

- a. Environmental Engineering & Queensland Micro- and Nanotechnology Centre,  
Griffith University, Brisbane, QLD 4111, Australia
- b. Department of Chemical Engineering, Curtin University of Technology, Perth,  
Western Australia 6845, Australia
- c. School of Chemical Engineering, The University of Queensland, Brisbane,  
Queensland 4072, Australia
- d. Centre for Micro-Photonics, Swinburne University of Technology, Hawthorn VIC  
3122, Australia

**Chemicals.** Glycerol, citric acid, melamine and H<sub>2</sub>SO<sub>4</sub> were purchased from Sigma-Aldrich and used without further purification. Dialysis tubing was purchased from Spectra/Por.

**CNPs purification.** The viscous as prepared carbon nanoparticles (CNPs) were first diluted with 50ml MillQ water, followed by filter by sterilized 0.5µm syringe filters (Supelco). Then 10ml sample was put into the dialysis tubing for purification. The dialysis was repeated 3 times and 2.5L MillQ water was used each time. CNPs penetrated the tubing was collected and concentrated by evaporation for further dialysis with smaller MWCO tubing or column chromatography.

**AFM imaging.** 1µL CNPs aqueous solution was drop onto the clean surface of a mica tablet. Then the mica was spin-coated (WS-400BZ-6NNP, Laurell Inc.) at 3000 rpm for 1min. CNPs were imaged in air by tapping-mode.

**FTIR.** CNPs solution was spotted onto an aluminium foil and dried at 60 °C to form thick film. Then the film was attached onto the diamond window of Perkin-Elmer 2000 FTIR for the spectrum analysis. An air baseline correction was applied.

**UV-VIS spectroscopy.** UV-VIS spectroscopy was conducted on a JASCO V670 spectrometer. MillQ water was used as a background.

**Fluorescence spectra measurement.** Fluorescence spectra were measured on a Perkin-Elmer fluorescence spectrometer.

**Quantum yield determination.** Reference on quantum yield measurements: Lakowicz, J. R. Principles of Fluorescence Spectroscopy, 3<sup>rd</sup> Ed., 2006, Springer Publishers. Quinine sulfate in 0.1 M H<sub>2</sub>SO<sub>4</sub> (quantum yield 0.577 under 350 nm excitation) was chose as a reference. Absolute values are calculated using the following equation:

$$Q = Q_r \times \frac{I_s}{I_r} \times \frac{A_r}{A_s}$$

Where  $Q$  is the quantum yield,  $I$  is the measured integrated fluorescence emission intensity, and  $A$  is the absorbance. The subscript “r” refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects, absorbencies in the 10 mm fluorescence cuvette were kept under 0.05 at the excitation wavelength (350 nm).

**Two-photon cross section measurements and two photon imaging:** The two-photon (2P) cross section measurement and 2P imaging were performed on a homebuilt microscope. A Ti:sapphire ultrashort pulsed laser (pulse width of 100 fs, repetition rate of 80 MHz), operating in the wavelength range of 700–1000 nm was employed as a 2P excitation source. The two-photon fluorescence is collected by a high numerical aperture (NA) objective of NA=1.4 and detected by a photomultiplier tube (Hamamatsu H7422P40). A charge coupled device (CCD) is employed to acquire the two-photon fluorescence spectrum in the 400-600 nm wavelength range. Using the 2P-induced fluorescence data the 2P absorption cross-sections can be expressed as [1,2]

$$F \sim \eta\phi\sigma_2NI^2,$$

where  $F$  is the fluorescence counts,  $\eta$  is the fluorescence quantum yield,  $\phi$  is the system collection efficiency,  $N$  is the number of particles inside the focus and  $I$  is the incident intensity.

**Fabrication of C-dots sensitized TiO<sub>2</sub> solar cell.** Standard Dyesol<sup>TM</sup> TiO<sub>2</sub>-coated test cell glass plates (with TEC 15 FTO and 18NR-T TiO<sub>2</sub> coating layer) were employed and loaded with C-dots by soaking overnight. Then the TiO<sub>2</sub> films were dried by N<sub>2</sub> gas thoroughly instead of high temperature calcination to protect the C-dots. Subsequently, the C-dots sensitized TiO<sub>2</sub> electrode and Pt-counter electrode (Dyesol<sup>TM</sup>) were assembled into a sandwich type cell and sealed with a spacer of 30 μm thickness (Surlyn, DuPont) with a drop of electrolyte solution (EL-HPE, Dyesol<sup>TM</sup>) introduced via vacuum back-filling. Blank TiO<sub>2</sub> solar cells without the sensitization of C-dots were also prepared for comparison.

**Photocurrent density–voltage ( $J - V$ ) and incident photon-to-current conversion efficiency IPCE measurements.** An AM 1.5 solar simulator (Oriel) equipped with a 150 W xenon light source, an AM 1.5G type filter (Newport, 81094) and a Keithley model 2420 digital source meter were employed to perform the  $J - V$  measurement. The IPCE was recorded on a Newport 1918-c power meter under the irradiation of a 300 W xenon light source (Oriel) with an Oriel Cornerstone 260 1/4 m monochromator in DC mode. A reference scan with the Si detector was taken prior to the sample measurement where the background can be subtracted.

### 1. Quantum yield determination

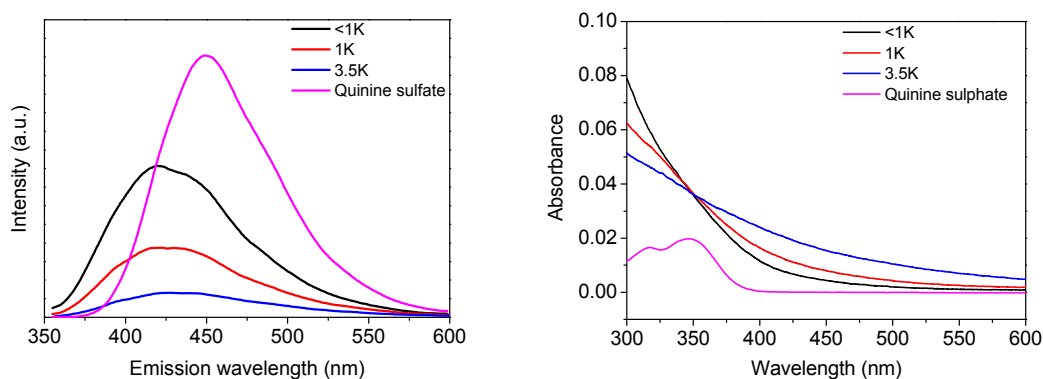


Figure S1. (a) Photoluminescence (PL, excited at 350nm) and (b) corresponding UV-vis absorption spectra of samples of <1K, 1K and 3.5K and quinine sulphate.

### 2. Photos of the three fractions C-dots.

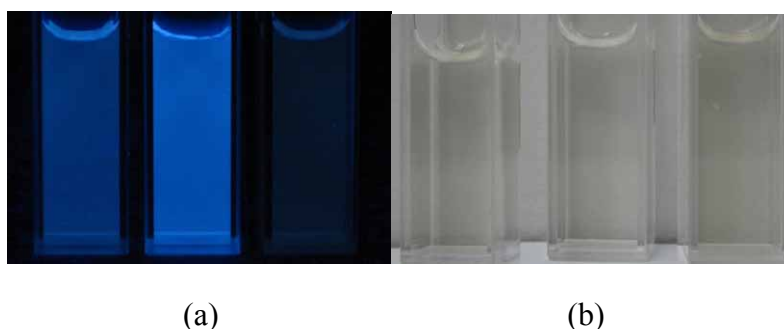


Figure S2. Images of with (a) and without (b) 360nm UV lamp irradiation. Samples from left to right, 1K, <1K and 3.5K.

3. Optical spectra of N-rich C-dots formed when citric acid was substituted by H<sub>2</sub>SO<sub>4</sub> or H-ZSM-5.

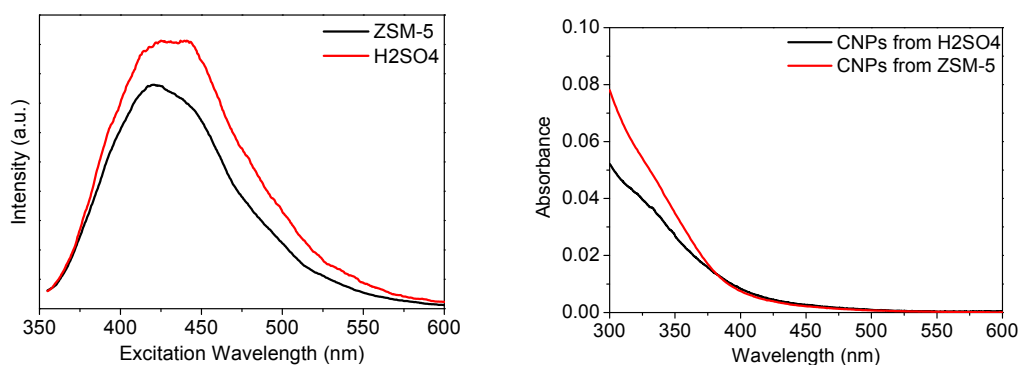


Figure S3. PL spectra of C-dots derived by adding H<sub>2</sub>SO<sub>4</sub> and H-ZSM-5 under 350nm excitation (left), and corresponding UV-vis absorption spectra (right).

4. FT-IR spectra

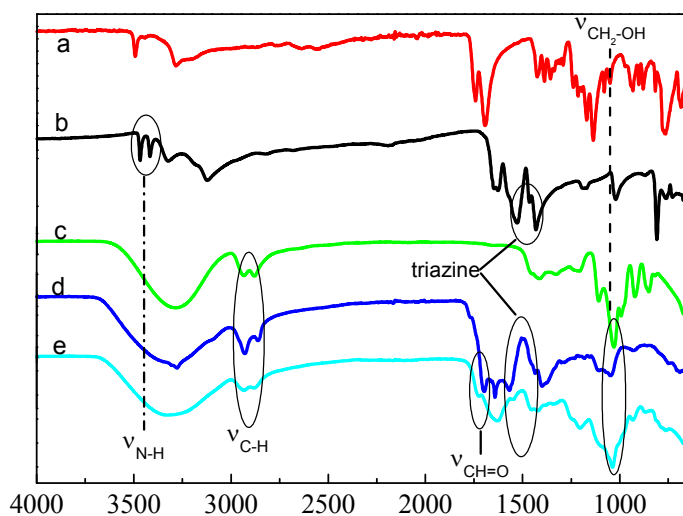
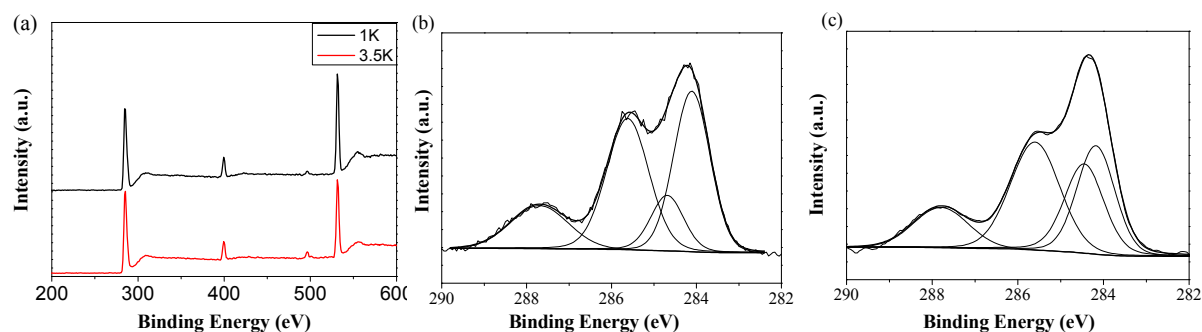


Figure S4. FT-IR spectra of (a) citric acid; (b) melamine; (c) glycerin; (d) N-rich C-dots synthesised from citric acid and melamine in glycerol; (e) N-rich C-dots synthesised from sulphuric acid and melamine in glycerol.

## 5. XPS



**Figure S5.** XPS analysis of sample 1K and 3.5K. (a) full spectra, (b) C1s of 1K and (c) C1s of 3.5K.

Further chemical structure information is obtained by performing C1s analysis. Figure 4b and 4c shows that C1s of the two samples can be fitted to 4 peaks centred at 284.1eV, 284.5eV, 285.5 eV and 287.8 eV, corresponding to C-C, C-N, C-O and C=N respectively. As the C=N bond in triazine is relatively constant, the quantity changes of other three C bonds can be calculated relative to C=N bonding, as shown in Supporting Information Table 1. Compared with 3.5K fraction, a higher amount of C-O and C-C bonds are found in sample 1K, which suggests the 3.5K fraction contains more triazine rings derived from melamine. The ratio between C=N and C-N bonds as of 1:2 in both fractions shows that all the -NH<sub>2</sub> groups on melamine molecule have reacted with carbonyl groups, which were converted from glycerol under high temperature in the presence of acid catalysts.

Table 1. Fine XPS structure analysis of 1K and 3.5K

	1K	3.5K
C=N, 287.7eV	1	1
C-O, 285.5 eV	2.4	2.0
C-N, 284.5 eV	2.0	2.0
C-C, 284.1 eV	2.4	1.5

## 6. Other solar cell testing data:

- Dyesol™ cells impregnated with **non** N-doped C-dots do not show IPCE peaks in the NIR range, confirming that it is the incorporation of nitrogen atoms in the carbon nanoparticles that increased the two photon absorption cross section.

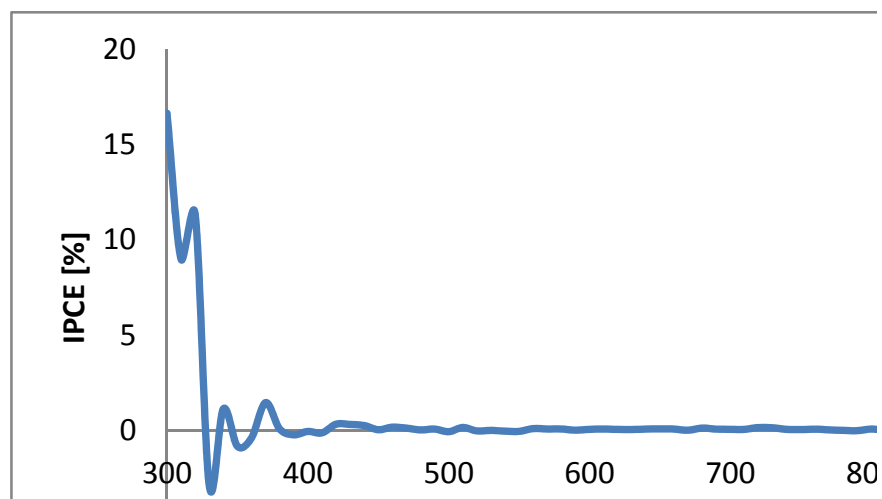


Figure S6. IPCE spectra of solar cells based on **non** N-rich C-dots sensitized TiO<sub>2</sub> film.

- b. The input light intensity around 700 nm was varied and the corresponding photocurrent was obtained. The photocurrent is of clear quadratic dependence on light intensity as shown in the plot below. This confirms the origin of the IPCE peak at 700 nm is due to the two photon absorption of N-doped C-dots.

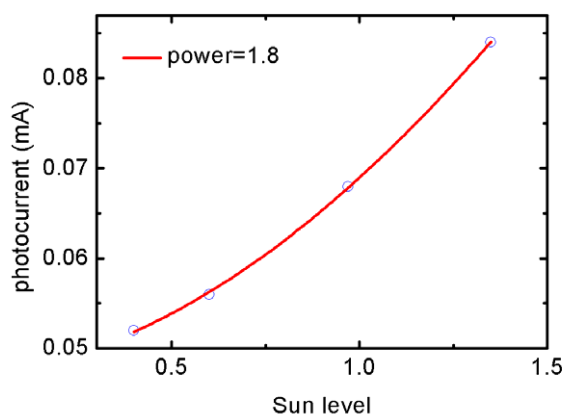


Figure S7. Photocurrent versus light intensity.

## References

1. Xu, C. and Webb, W. W., "Measurement of two-photon excitation cross sections of molecular fluorophores with data from 690 to 1050 nm," *J. Opt. Soc. Am. B: Opt. Phys.* **13**, 481-491 (1996).
2. Li, X., Embden, J., Chon, J. W. M., and Gu, M., "Enhanced two-photon absorption of CdS nanocrystal rods," *Appl. Phys. Lett.* **94**, 103117 (2009).
3. Wang, F., Pang, S., Wang, L., Li, Q., Kreiter, M., Liu, C-Y, "One Step Synthesis of Highly Luminescent Carbon Dots in Noncoordinating Solvents", *Chemistry of Materials*, **22**: 4528-4530, (2010).