

Supporting Information

Remarkable photoelectrochemical performance of carbon dots sensitized TiO₂ under visible light irradiation

Shilei Xie,[‡] Hua Su,[‡] Wenjie Wei, Mingyang Li, Yexiang Tong* and Zongwan Mao*

Experimental Section

Synthesis of TiO₂ nanowire arrays:

All reagents used were of analytical grade and were used directly without any purification. TiO₂ nanowire arrays were synthesized on F-doped SnO₂-coated (FTO, NSG) glass substrate using a hydrothermal method reported elsewhere.^[1] In a typical synthesis process, fifteen milliliter of deionized water was mixed with 15 ml HCl (36~38 %) and followed by the addition of 0.45 ml titanium tetrabutoxide under strong stirring at ambient conditions. A piece of FTO substrates was placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The sealed autoclave was heated at 150 °C for 5 h. At last, sealed autoclave was cooled to room temperature in air and finally the as-prepared TiO₂ was annealed in air at 550 °C for 3 h.

CDs synthesis:

Carbon dots (CDs) was prepared according to pyrolysis method with minor modifications. ^[2] Briefly, a mixture of glycine (15 ml) and 4,7,10-Trioxa-1,13-tridecanediamine (1ml) was elevated to 220 °C with vigorously stirring under nitrogen atmosphere, followed by quick addition of citric acid pellet (1 g). The hot solution was then kept at 230 °C about 3.5 h and color change from pale yellow to dark brown can be observed. After cooling down to room temperature, the resultant mixture was centrifuged and filtered to remove insoluble black precipitate. The filtrate was diluted to 50 ml for subsequent use.

Characterizations:

The as-synthesized products were characterized by field emission scanning electron microscope (FE-SEM, JSM-6330F), X-Ray Diffractometer (XRD, D-MAX 2200 VPC), transmission electron microscopy (TEM, JEM2010-HR) and X-ray Photoelectron Spectroscopy (XPS, ESCALab250). The optical properties of the products were measured with a UV-Vis-NIR Spectrophotometer

(UV-Vis, Shimadzu UV-2450).

Photocatalytic and electrochemical measurements:

PEC measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. The electrolyte is 1.0 M KOH solution, and the working electrode is the bare TiO₂ and CDs/TiO₂ film, while a Pt wire was used as the counter electrode and a saturated Ag/AgCl electrode used as reference electrode. The illumination source was a 150W Xe arc lamp (Newport, 6255, 150W) directed at the quartz photoelectrochemical cell. Incident-photon-to-current-conversion efficiency (IPCE) measurements were conducted with a solar simulator (Newport 69911 300W xenon lamp), coupled to an aligned monochromator (Oriel Cornerstone 260 1/4m). IPCE can be expressed as:

$$\text{IPCE} = (1240 \times I) / (\lambda \times J_{\text{light}}) \quad (1)$$

[1] B. Liu and E. S. Aydil, *J. Am. Chem. Soc.*, 2009, **131**, 3985-3990.

[2] W. Shi, X. Li and H. Ma, *Angew. Chem. Int. Ed.*, 2012, **51**, 6432-6435.

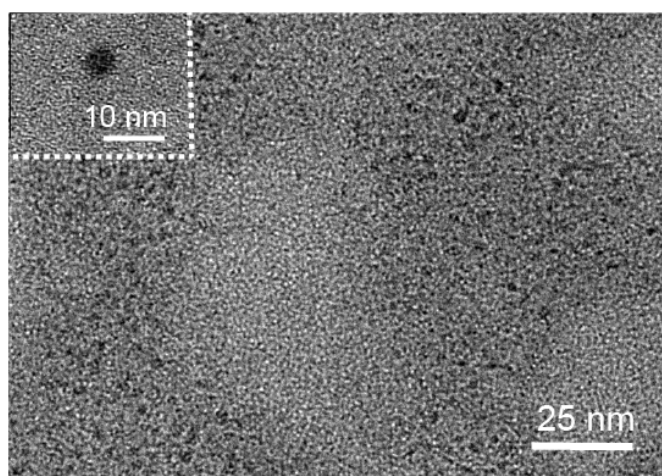


Figure S1 TEM and HRTEM images (inset) of the CDs.

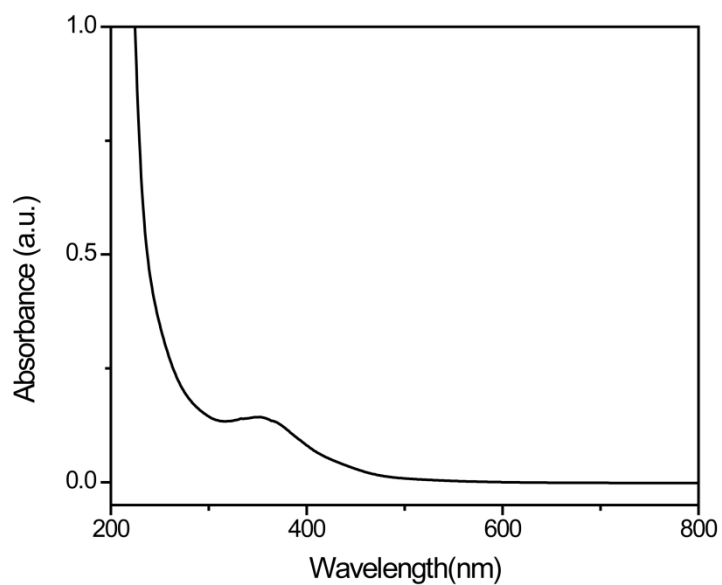


Figure S2 UV-Vis absorption spectra of CDs solution.

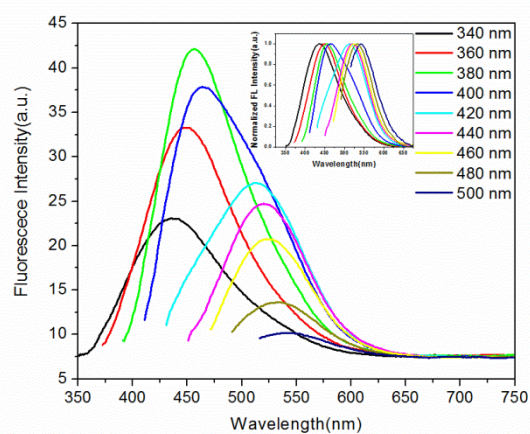


Figure S3. PL emission spectra of CDs in the excitation wavelength from 340 nm to 500 nm.

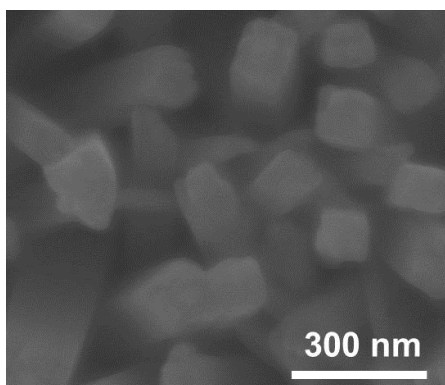


Figure S4 SEM image of C₁₀/TiO₂.

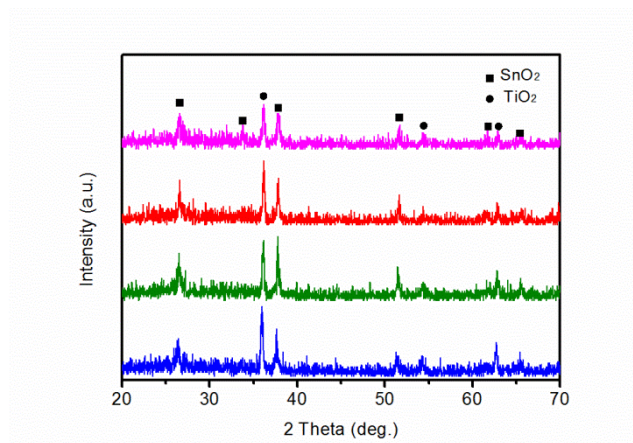


Figure S5 XRD spectra of bare TiO_2 , C_1/TiO_2 and C_5/TiO_2 and $\text{C}_{10}/\text{TiO}_2$ electrodes.

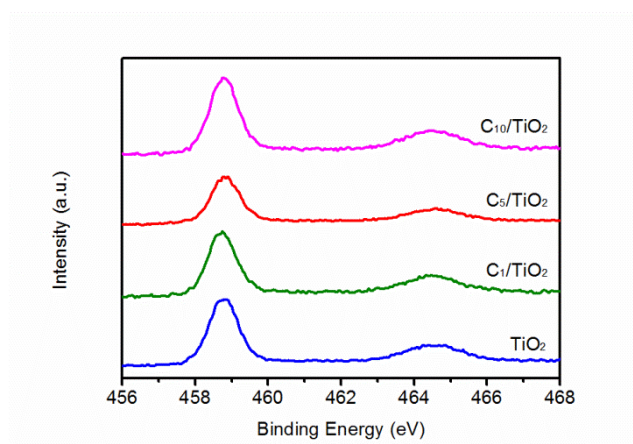


Figure S6 Ti 2p core level XPS spectra of bare TiO_2 , C_1/TiO_2 , C_5/TiO_2 and $\text{C}_{10}/\text{TiO}_2$.

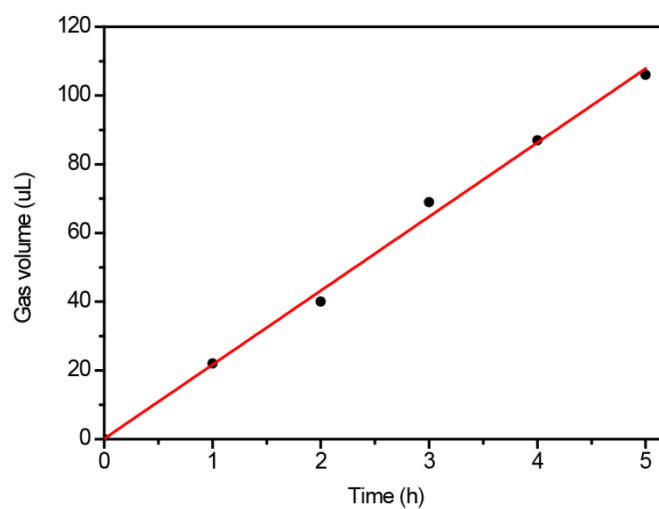


Figure S7 Measured gas production of the C_1/TiO_2 photoelectrode at + 0.4 V vs. Ag/AgCl as a function of time under visible light illumination.