

Supporting information

Carbon quantum dot serving as spectral converter through broadband upconversion of near-infrared photons for photoelectrochemical hydrogen generation

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Experimental

Materials

Graphite rod (99.99%, Alfa Aesar Co. Ltd.), ultrapure water ($18.4 \text{ M}\Omega \text{ cm}^{-1}$), hydrochloric acid (36.5~38wt%, Alfa Aesar Co. Ltd.), tetrabutyl titanate ($\geq 98\%$, Alfa Aesar Co. Ltd.), titanium tetrachloride (99.5%, Aldrich Chemicals), SeO_2 ($\geq 99\%$, Alfa Aesar Co. Ltd.), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99\%$, Alfa Aesar Co. Ltd.), NaBH_4 ($\geq 96\%$, Alfa Aesar Co. Ltd.).

Synthesis of carbon quantum dots (CQDs)

The CQDs were synthesized via an electrochemical etching method. The anode and cathode were two same graphite rods (99.99%, Alfa Aesar Co. Ltd., 13 cm in length and 0.6 cm in diameter) which were perpendicularly inserted in a 600ml beaker containing 550ml ultrapure water ($18.4 \text{ M}\Omega \text{ cm}$) with a separation of 7.5 cm. An external potential of 60 V was applied between the two electrodes through a direct current (DC) power for seven days combined with intensely magnetic stirring. Subsequently, the black solution was filtered with slow-speed quantitative filter paper and the filtrate was centrifugated at 22000 rpm for 30 minutes to wipe off the large graphite particles. Finally, a 0.1 mg/ml of CQDs solution was obtained by being concentrated with rotary evaporation at 80°C .

Preparation of TiO_2 nanorod arrays (NRs) on FTO

Highly ordered TiO_2 NRs were synthesized by hydrothermal growth method as reported by Liu et al.¹ FTO glasses ($1.2 \text{ cm} \times 2 \text{ cm}$) were cleaned by orderly ultrasonic cleaning in acetone, ethanol and deionized water and then dried in nitrogen gas. Prior to the growth of NRs, TiO_2 seed crystals were deposited on FTO current-conducting side by immersing the FTO in 25 mM TiCl_4 aqueous solution and keep for 30 min at 70°C , followed by annealing in air at 450°C for 1h. 15 ml of concentrated HCl solution and 15 ml deionized water were added to a Teflon-lined stainless steel autoclave (40ml) and stirred for 5 minutes. And then, 0.5 ml of tetrabutyl titanate was added to the 30 ml of aqueous HCl solution and continued to stir for another 5 minutes. Subsequently, the seeded FTO glass was immersed into the autoclave with an angle against the wall of the autoclave. The autoclave was sealed and heated to 160°C in an electric oven and kept for 6 h. After the autoclave naturally cooled to ambient temperature, the FTO substrate was taken out of the autoclave and thoroughly rinsed with ethanol and deionized water and finally annealed in air at 450°C for 1h.

Deposition of CdSe on TiO_2 NRs

CdSe quantum dots were deposited on TiO_2 NRs through successive ionic layer absorption and reaction process (SILAR) reported by Lee et al.² The whole process were performed in glove bag filled with nitrogen. 0.09986 g of SeO_2 is dissolved in 30mL ethanol (30mM) in a round-bottom flask and stirred for 5min and then 0.068g of NaBH_4 (60 mM) was added. In another round-bottom flask, 0.2777g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was added into 30mL ethanol (30mM). The TiO_2 NRs was dipped into the Cd^{2+} solution, rinsed with ethanol and then dried, the Se^{2-} solution, and then pure ethanol (then dried) successively for 30 second for deposition each and longer time for washing and dried. Such an immersion cycle was repeated 10 times.

Fabrication of the photoanode and the PEC measurements

The TiO_2 NRs were fashioned into photoanodes by securing a cooper wire onto the electric-conductive side of the FTO glass with double-side electric-conductive copper tape. The substrate was then sealed on all edges with epoxy resin except for a working area. The CQDs were deposited on CdSe/ TiO_2 NRs photoanode by a constant-voltage electro-deposition method which was performed in a two-electrode mode at an applied potential

of 0.5 V for 10 minutes with a coiled Pt wire as the counter electrode. The electrolyte was 0.1 mg/ml CQDs solution and the recorded current density was in the range of 20-40 μAcm^{-1} .

All PEC characterizations were performed in a three-electrode electrochemical cell in a stirred solution bubbled with nitrogen, with a coiled Pt wire as a counter electrode and Ag/AgCl electrode as a reference. The electrolyte is a mixture of 0.25 M Na_2S and 0.35 M Na_2SO_3 aqueous solution. A 300 W xenon arc lamp coupled with a long wavelength pass filter with central wavelength at 750 nm (Fig. S2) was perpendicularly illuminated at the front side of the all photoanodes. The detection of the produced hydrogen was carried out by a gas chromatograph with nitrogen as elegant gas.

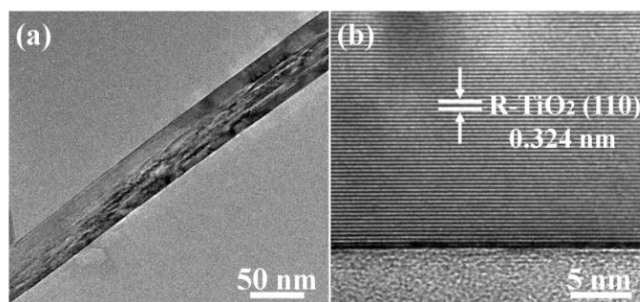


Fig. S1 TEM (a) and HRTEM (b) of the TiO₂ (Rutile) nanorod.

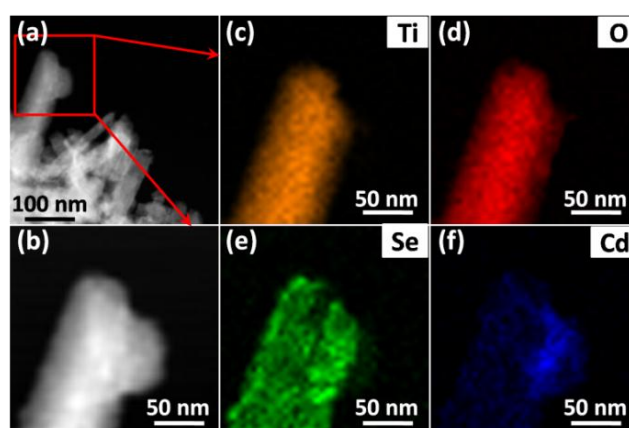


Fig. S2 (a) and (b) are the scanning transmission electron microscopy (STEM) images of TiO₂/CdSe core/shell nanorod. (c-f) EDS element mapping images from the same area as in (b).

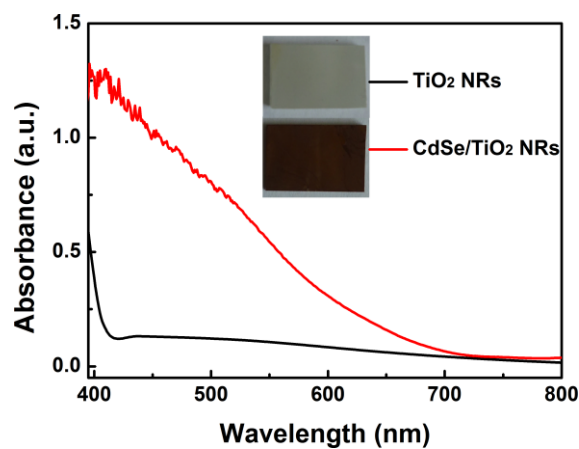


Fig. S3 The UV-VIS spectra of TiO₂ NRs and CdSe/TiO₂ NRs. The insets were the corresponding digital image of the two test samples.

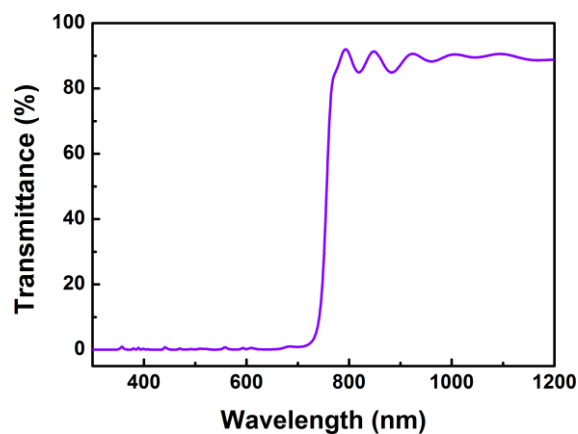


Fig. S4 The tested UV-VIS spectrum of the long wavelength pass filter with central wavelength at 750 nm.

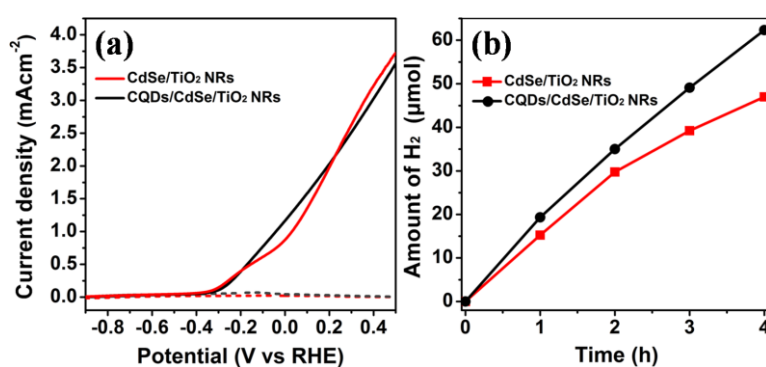


Fig. S5 (a) Linear sweep voltammetric (J-t) curves of two representative CdSe/TiO₂ NRs (0.98 cm²) and CQDs/CdSe/TiO₂ NRs (0.95 cm²) photoanodes at a scan rate of 30 mV/s under simulated sunlight illumination. The corresponding dotted lines are the dark scan (J-t) curves. (b) Comparison of the PEC hydrogen generation rate of the two photoanodes under simulated sunlight illumination.

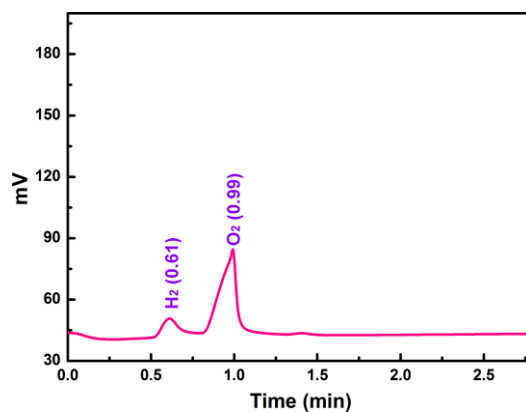


Fig. S6 The detection of produced hydrogen by the gas chromatograph measurement after a 24h hydrogen generation experiment.

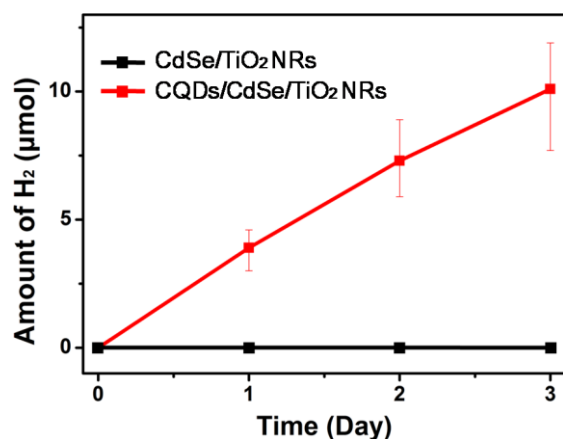


Fig. S7 Comparison of PEC hydrogen generation rate of CdSe/TiO₂ NRs and CQDs/CdSe/TiO₂ NRs photoanodes illuminated with 300 W xenon lamp coupled with a 750 nm long wavelength pass filter. The hydrogen generation data of CQDs/CdSe/TiO₂ NRs photoanode were obtained by measuring three photoanodes (active areas are 0.93, 0.96, 0.97 cm², respectively) to give an error distribution.

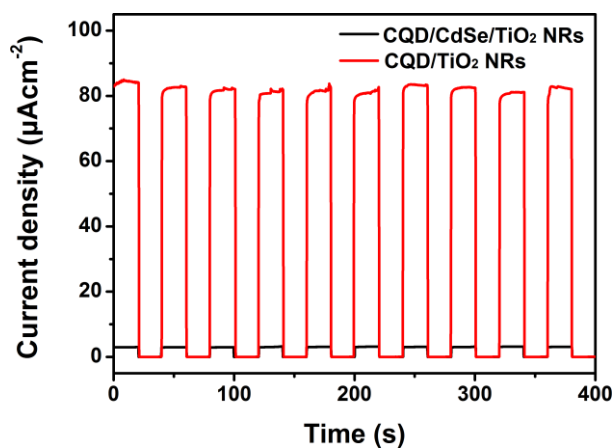


Fig. S8 Chopped light current-time curves of CQD/TiO₂ NRs and CQD/CdSe/TiO₂ NRs photoanodes under illumination of 300 W xenon lamp coupled with a 750 nm long wavelength pass filter and a 850 nm short wavelength pass filter. The results is a good proof that the CdSe shell can prohibit the direct electron transfer between TiO₂ and CQDs and the photocurrent density of 3 mA cm⁻² of CQD/CdSe/TiO₂ NRs photoanode was due to upconversion effect of CQDs.

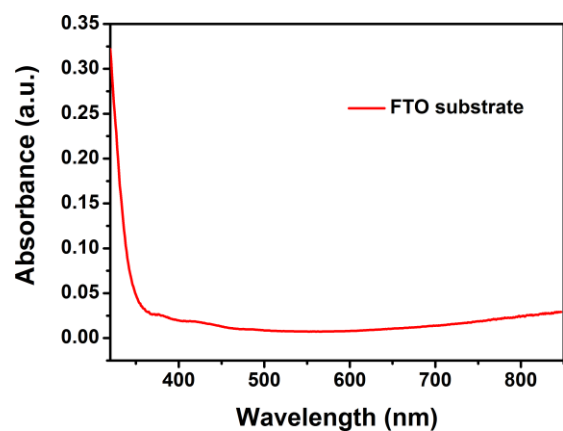


Fig. S9 Diffused reflectance UV-VIS absorption spectrum of FTO substrate.

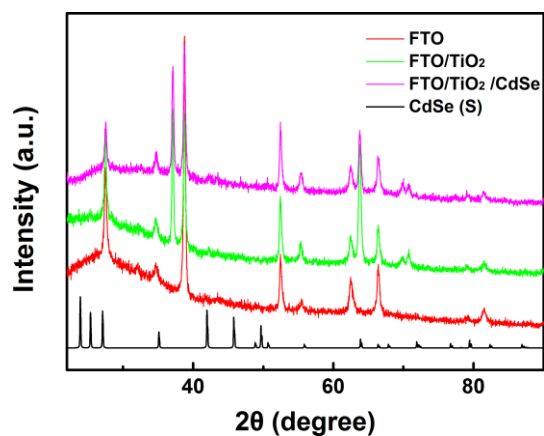


Fig. S10 The XRD spectra of FTO, FTO/TiO₂, FTO/TiO₂/CdSe and CdSe (standard cards JCPDS No. 8-459).

Reference

- 1 B. Liu and E. S. Aydil. *J. Am. Chem. Soc.* 2009, **131**, 3985.
- 2 H. Lee, M. K. Wang, P. Chen, D. R. Gamelin, S. M. Zakeeruddin, M. Gratzel, and M. K. Nazeeruddin. *Nano Lett.*, 2009, **9**, 4221.