Supporting information

Carbon quantum dots sensitized TiO_2 nanotube arrays for photoelectrochemical hydrogen generation under visible light

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Experimental

Materials

Titanium foil (Ti, 0.25 mm thickness, 99.6% purity; Sigma-Aldrich), ammonium fluoride (NH_4F, Sigma–Aldrich, 98+%), ethylene glycol (Junsei Chemical Co, 99.0%), graphite rod (99.99%, Alfa Aesar Co. Ltd.), ultrapure water (18.4 MΩ cm^{-1}).

Preparation of TiO_2 nanotube arrays

Highly ordered TiO_2 NTs were fabricated by the electrochemically anodizing Ti foils in the fluorine-contained ethylene electrolyte with further optimazation[27]. Ti foils (2.5 × 1.5 cm in size) was firstly purified by orderly ultrasonic cleaning in acetone, ethanol and deionized water and then dried in nitrogen gas. The treated Ti foil was first anodized in an electrolyte solution containing 98 mL ethylene, 0.33 g NH_4F (0.3 wt%) and 2 mL deionized water (~2 vol%) with a graphite plate as the counter electrode in a two-electrode cells. The first anodization process was performed at an applied voltage of 60 V for 4 h and then the Ti foil was taken out and rinsed with large amount of distilled water and ethanol. After dried in the ambient atmosphere, the TiO_2 NTs film was peeled off by an adhesive tape and then the Ti foil was secondly anodized at an external voltage of 50 V for 1.5 h in the used Fluorine-contained electrolyte. Afterward, the Ti foil with a high quality TiO_2 NTs film was thoroughly rinsed and then annealed at 450 ℃ for 2 h in air to transform the amorphous TiO_2 into crystalline photoactive anatase form.

Photoelectrochemical hydrogen generation and measurement

Photoelectrochemical hydrogen evolution was performed in a two-electrode mode with a coiled Pt wire as the counter electrode. The electrolyte is a mixture of 0.25 M Na_2S and 0.35 M Na_2SO_3 aqueous solution which had a PH of ~9.5. The potential between the two electrodes were controlled by a potentiostat and were reported against the reversible hydrogen electrode (RHE) following the equation below:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E°_{Ag/AgCl}$$

The $E°_{Ag/AgCl}$ is 0.1976 V vs RHE at 25 °C. Therefore, an external potential of 0.758 V vs RHE was used to assist the hydrogen production. The two electrodes were sealed into a 300 mL container with 250 mL electrolyte solution by leading the electrode cables through a rubber plug. A 300 W xenon arc lamp coupled with an AM 1.5G filter was perpendicularly illuminated at the front side of the CQDs/TiO_2 NTs electrode. The detection of the produced hydrogen was completed by a gas chromatograph with nitrogen as elegant gas.

The Faradaic efficiency

The Faradaic efficiency was calculated based on the following equation:

$$\text{Faradaic efficiency} = \frac{\text{Evolved hydrogen [mol]} \times 2\ \times N_A}{\text{current density } [\text{Acm}^{-2}] \times \text{Time [S]}\ \times \text{Active Area of photoanode } [\text{cm}^2] \div e} \times 100\%$$

N_A is avogadro's number, e is the electron charge.

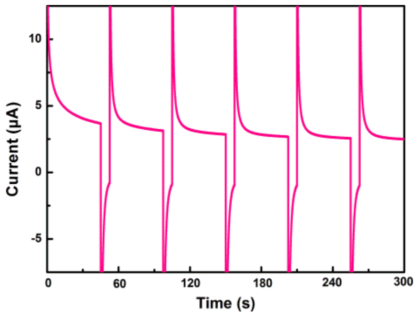
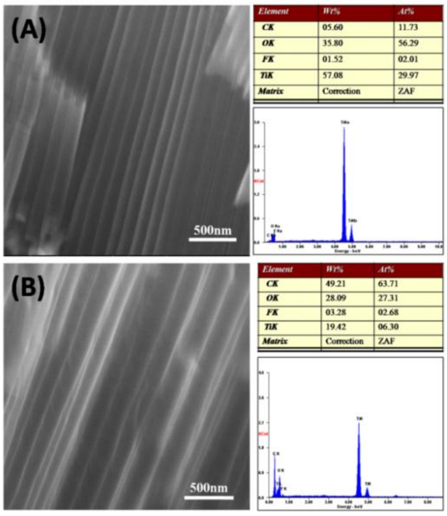


Figure S1. The recording I-t curve of the electrodeposition of CQDs on the TiO_2 NTs photoanode.



Element	*Wt%*	*At%*
CK	05.60	11.73
OK	35.80	56.29
FK	01.52	02.01
TiK	57.08	29.97
Matrix	Correction	ZAF

Element	*Wt%*	*At%*
CK	49.21	63.71
OK	28.09	27.31
FK	03.28	02.68
TiK	19.42	06.30
Matrix	Correction	ZAF

Figure S2. (a) and (b) is the energy-dispersive spectra (EDS) of the TiO_2 NTs without and with CQDs deposition, respectively.

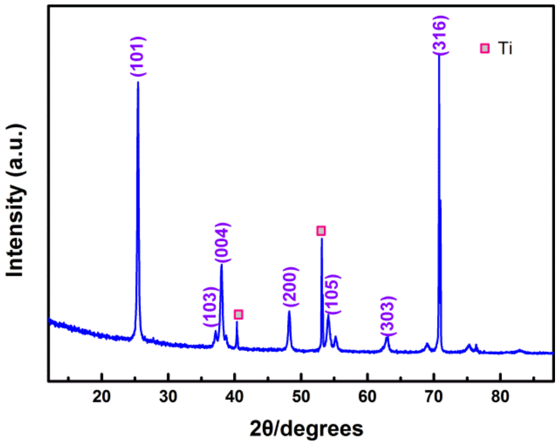


Figure S3. The XRD spectrum of the TiO_2 NTs on the Titanium substrate.

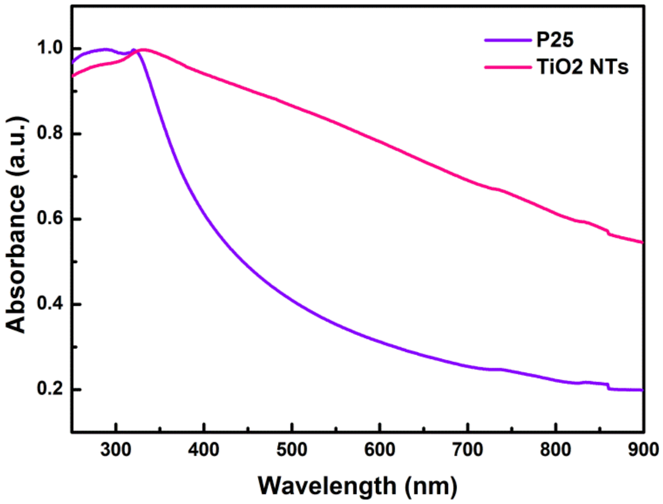


Figure S4. The UV-VIS spectra of P25 and TiO_2 NTs (peeled off from the Titanium sustrate) aqueous solution.

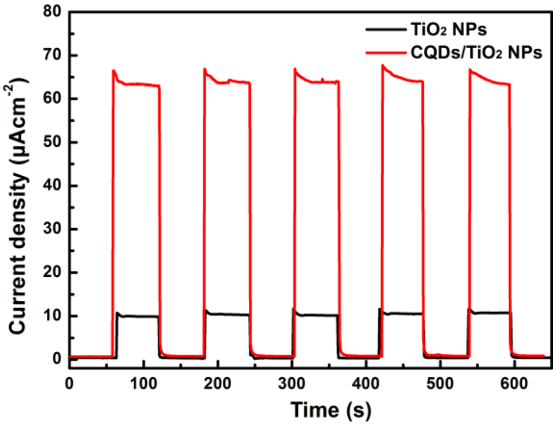


Fig. S5. The of the TiO2 NPs and the CQDs/TiO2 NPs photoanodes with repeated on/off cycles of simulated sunlight (AM 1.5 G, 100 mWcm-2) at 0 V vs Ag/AgCl.

The TiO2 nanoparticles (TiO2 NPs) films were fabricated by spin-coating TiO2 pastes on FTO glass.1The thickness of the TiO2 NPs films were controlled to be similar to the TiO2 NTs films (~13μm) by tuning the parameters and numbers of the spin-coating process. All the PEC measurement conditions of the TiO2 NPs and CQDs/TiO2 NPs photoanodes are the same as the TiO2 NTs and CQDs/TiO2 NTs photoanodes. And also, the TiO2 NPs photoanodes were sensitized with CQDs by a pulsed electrodeposition method which is the same as described for the fabrication of CQDs/ TiO2 NTs photoanodes. Seen from Fig. S5, a time-dependent current curves six times enhancement of photocurrent density can be obtained by the TiO2 NPs photoanode with CQDs' sensitization. However, the photocurrent densities of both TiO2 NPs and CQDs/TiO2 NPs photoanodes are much lower than that of TiO2 NTs and CQDs/TiO2 NTs photoanodes respectively. The reason may be that the electrons transfer in the disordered TiO2 NPs film is inefficient compared with that in the ordered TiO2 NTs film because vectorial charge transport perpendicularly to the charge collecting substrate can be achieved in TiO2 NTs film.

Reference

1. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, M. Gratzel, Prog. Photovolt: Res. Appl., 2007, 15, 603.