Supporting information



Fig S1. Emission spectra of CdTe QD with different particle size. Emission spectra were recorded with 450 nm excitation.



Fig S2: Photocurrent response of CdTe QD sensitized TiO_2 nanotube array photoelectrodes after CBD CdS deposition cycles of: one (red); three (green); five (blue); black (seven).



Fig S3: I-V characteristics of a core/shell CdS/CdTe QD TiO_2 nanotube array photoelectrode after four months storage. The three curves are obtained every two hours. The green curve is the first measurement, the blue curve is the second measurement, and the red curve is the third measurement.



Fig S4. Schematic diagram of the home-made gas collection device.

The reaction mechanism in the presence of S^{2-}/SO_3^{-2} as sacrificial reagent is described by

eqs 1-6:

photocatalyst + hv $h^{+} + e^{-}$ (1) $2e^{-} + 2H_2O$ $H_2 + 2OH^{-}$ (2) $SO_3^{2^{-}} + 2OH^{-} + 2h^{+}$ $SO_4^{2^{-}} + 2H^{+}$ (3) $2S^{2^{-}} + 2h^{+}$ $S_2^{2^{-}}$ (4) $S_2^{2^{-}} + SO_3^{2^{-}}$ $S_2O_3^{2^{-}} + S^{2^{-}}$ (5) $SO_3^{2^{-}} + S^{2^{-}} + 2h^{+}$ $S_2O_3^{2^{-}}$ (6)

When a photon is absorbed by photocatalyst, an e^{-}/h^+ pair is generated. Then, the e^- and h^+ may migrate to the surface and react with the adsorbed reactants, or they may undergo undesired recombination. The photogenerated electrons in the conductive band reduce the water to form hydrogen, as described by eq 2. Meanwhile, the photogenerated holes in the valence band oxidize $SO_3^{2^-}$ and S^{2^-} to form $SO_4^{2^-}$ and $S_2^{2^-}$ directly, according to eqs 3 and 4, respectively. The production of $S_2^{2^-}$ ions, which act as an optical filter and compete with the reduction of protons, was efficiently suppressed by mixing with $SO_3^{2^-}$ ions, according to eq 5. The presence of excess S^{2^-} ions in the reaction solution also stabilizes the photocatalyst surface because the formation of sulfur defects could be suppressed. Furthermore, thiosulfate ions do not interfere significantly with protons in the reduction process. However, the hydrogen formation can drop due to the excess consumption of $SO_3^{2^-}$ and S^{2^-} ions present through eq 6

The redox reaction of TiO2 in electrolyte:

TiO2 + 4H+4e $Ti + 2H_2O$