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Supplementary information

Effect of electron transfer on the photocatalytic hydrogen evolution efficiency of faceted TiO_2/CdSe QDs under visible light

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Contents

1. Preparation of CdSe QDs, {001}-TiO_2 and {101}-TiO_2

1.1 Synthesis of water soluble CdSe QDs

Water soluble CdSe QDs was synthesized according to literature.[1-3] Firstly Na_2SeSO_3 stock solution was prepared as the selenium source. Typically, 189 mg Na_2SO_3 were dissolved in 100 mL deionized water, and then 40 mg selenium powder was added. After deoxygenated with Ar for 30 min, the system was refluxed for 3-4 h until all the selenium powder was dissolved.

46 mg of $CdCl_2\cdot2.5H_2O$ were dissolved in 190 mL deionized water, and 3-mercaptopropionic acid (26 μL) was added in a 500 mL round-bottom flask. Then the pH value of system was adjusted to 11 by NaOH aqueous solution (10 M). After deoxygenated with argon gas for 30 min, the freshly prepared Na_2SeSO_3 aqueous solution (10 mL) was added into the system. Afterwards, the system was deoxygenated with Ar for 30 min again and then refluxed for 4 h at 130 °C. Finally, the light green-yellow aqueous solution of CdSe QDs was obtained.

1.2 Synthesis of TiO_2 Nanocrystals with Different Facets

1.2.1 Synthesis of $Ti(OH)_4$ precursor

The synthesis of $Ti(OH)_4$ precursor was accomplished by sol-gel process.[4] 6.6 mL of $TiCl_4$ were dispersed into 20 mL aqueous HCl solution (0.43 M) in an ice bath to yield the clear solution. The solution was then slowly dropped to 5.5 wt% aqueous $NH_3\cdot H_2O$ in an ice bath with stirring, which yield the white suspension. 4 wt% aqueous $NH_3\cdot H_2O$ were dropped into it to adjust the pH value to 6.85. After aging at room temperature (25 °C) for 2 h, the precipitate was filtrated and washed with absolute ethanol and deionized water for at least 3 times, and $AgNO_3$ aqueous solution (0.05 M) was then used to detect the existence of chloride in the system. Eventually, the products were dried at 60 °C in air for 12 h.

1.2.2 Synthesis of {101}-TiO_2

{101}-TiO_2 were prepared by hydrothermal method.[4] In detail, 2 g newly prepared $Ti(OH)_4$ and 0.2 g NH_4Cl were dispersed in a mixed solution of isopropyl alcohol and water (30 mL, 1:1 v/v) and stirred for 30 min. Then the system was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated for 24 h at 180 °C. After that, the suspension were separated by filtration and then washed with ethanol and deionized water for at least 3 times. Finally, the samples were dried for 12 h at 60 °C.

1.3 Synthesis of {001}-TiO_2

In a typical procedure according to the references,[5-6] 3.75 mL of $Ti(OC_4H_9)_4$ was added into a dried Teflon-lined stainless steel autoclave with a capacity of 15 mL. Then 0.6 mL of HF solution was slowly dropped into the above liquid. The mixture was heated to 200 °C and kept for 24 h in oven. After reaction, the white precipitate was separated by centrifugation. Then the products were washed thoroughly with absolute ethanol, 1 M NaOH aqueous solution and deionized water for at least 3 times to remove the residual fluoride. After dried at 60 °C in air for 12 h and cooled down to room temperature, {001}-TiO_2 with clean surface were obtained.

2. Absorption spectra of supernatant of CdSe QDs with or without TiO_2

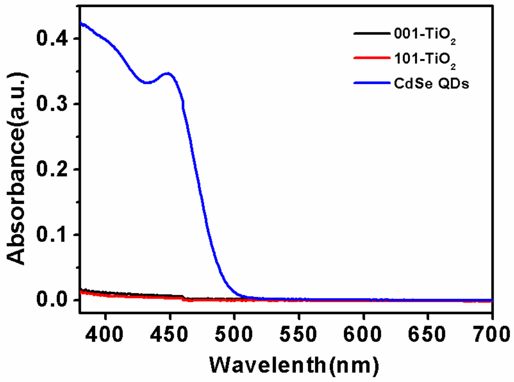

Fig. S1 The absorption spectra of the aqueous solution of QDs before and after interaction with {001}-TiO_2 and {101}-TiO_2.

3. The photocatalytic hydrogen evolution activity of different TiO_2/CdSe QDs

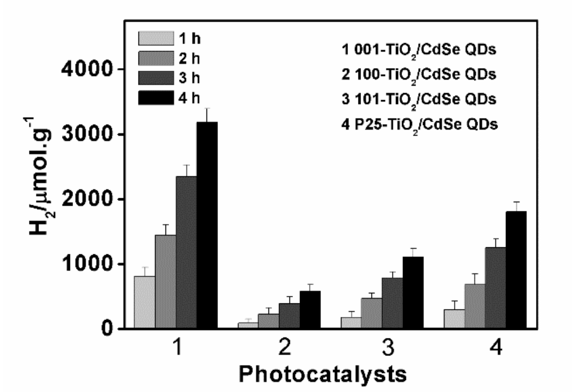

Fig. S2 The evolution hydrogen amount of 5 mg of different CdSe QDs/TiO_2 composite containing with 0.4 mg Ni^{2+} in 10 mL of isopropanol /H_2O (1:1 v/v) under visible-light (λ ≥ 420 nm) 500 W high-pressure mercury lamp (I = 15.56 mW cm^{-2}) at pH = 11.

4. Stability test of of {001}-TiO_2/CdSe QDs

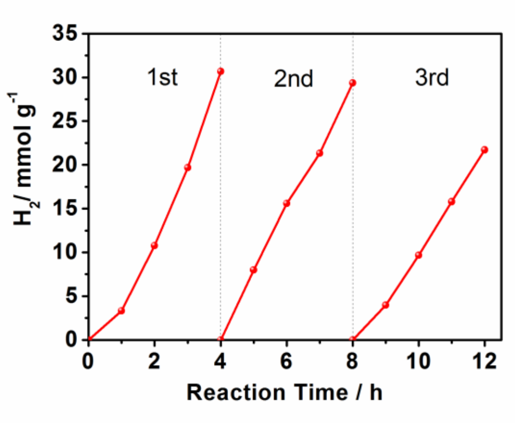

Fig. S3 Stability test of {001}-TiO_2/CdSe QDs for photocatalytic hydrogen evolution. Reaction conditions: 2 mg of {001}-TiO_2/ CdSe QDs; sacrificial donor: isopropanol (1:1, v/v) in 7 mL of aqueous solution; cocatalyst: 0.2 mg Ni^{2+} at pH 11; λ = 410 nm, I = 150 mW/cm^2, LED light.)

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