Supplementary Information

Crystal defects-mediated band-gap engineering: A new strategy for tuning optical properties of Ag_2Se quantum dots toward enhanced hydrogen evolution performance

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Experimental details and supplementary Figures S1–S2.

Experimental details

Materials and chemicals. Silver nitrate ($AgNO_3$, 99.98%), Na_2SO_3 (> 97%), n-hexane (AR), absolute ethanol (GR), methanol (AR) and dichloromethane (AR) were purchased from Sinopharm Chemical Reagent Company. 3-mercaptopropionic acid (3-MPA, 99%) was purchased from Alfa-Aesar Company. Selenium powder (Se, 99.99%) and octadecylamine (ODA, > 97%) were obtained from Sigma-Aldrich Company. Toluene (> 99.85%, Extra Dry) was obtained from Arcos Organics Company. P25-TiO_2 powder (a mixed phase of 70% anatase and 30% rutile) was bought from Evonik-Degussa and 3-aminopropyltriethoxysilane (APTES, 98%) from Fluka. All chemicals were used just as received without further purification, and in all experiments, extremely pure deionized water (DI water, Millipore) with the resistivity greater than 18.0 MΩ·cm was used.

Synthesis of defects-rich silver nanocrystals. Silver nanocrystals were prepared according to a published report (*J. Am. Chem. Soc.*, 2008, **130**, 4016-4022.). Briefly, $AgNO_3$ (0.5 g) was added to the solvent ODA (10 mL) at 180 °C and stirred for 10 min in air. In order to generate considerable amount of crystal defects in silver nanocrystals, thermal vibrations between 170 °C to 190 °C were introduced during synthesis and kept for 1, 3, 5 and 7 min respectively during the 10 min reaction. After the reaction finished and cooled down to room temperature, the resulting products were collected at the bottom of the flask (50 mL) and washed by addition of ethanol and n-hexane accompanied by centrifugation for several times.

Synthesis of defects-rich Ag_2Se QDs and ligand exchange. Na_2SeSO_3 aqueous solution (0.1 M) was prepared at first using a published method (*Chem. Eur. J.*, 2006, **12**, 3672-3677.). In a typical process, the obtained silver nanocrystals (1 mmol), 3-MPA (5 mmol) and deionized water (10 mL) were mixed in a 50 mL three-necked flask and heated under continuous stirring to 90 °C for 15 min in air. Then 5 mL of the Na_2SeSO_3 solution (heated and maintained at 95 °C in advance) was quickly injected into the flask and kept for another 30 min. During the 30 min selenylation reaction, thermal vibrations between 80 °C to 98 °C were introduced again and kept for 5, 10, 15 and 20 min respectively. After the reaction finished and cooled down naturally to room temperature, the resulting products were washed

and collected by addition of ethanol and deionized water accompanied by centrifugation for several times.

Estimation of the percentage of defects in as-obtained Ag_2Se QDs. Basically, based on the imaging mechanism of diffraction contrast by transmission electron microscope (TEM), crystal defects in as-synthesized Ag_2Se QDs can be identified. Generally, the crystal defect acts as a strain center for scattering the incident electron beam, therefore contributes different contrast compared to defect-free region. Around the defective region, atoms deviate away from their original positions somehow, thus form a strain field locally. And when the incident beam propagates such a strained region, various diffraction contrast might be formed due to the strained crystal planes. As a result, defective structures like twins and stacking faults could be observed clearly in TEM images. Particularly in our experiments, we chose appropriate magnifications which were neither too high nor too low and approximated to 100k – 200k, to record TEM patterns. In this way, both easy identification of crystal defects and a considerable amount of particles in one image could be achieved at the same time. Afterward, for each sample, we statistically examined five TEM patterns (each image contains at least 20 QDs, thus at least 100 QDs in total) to know the approximate percentage of the Ag_2Se QDs containing crystal defects.

Surface modification of as-purchased P25-TiO_2. The surface amination of as-purchased P25-TiO_2 powder with APTES was first conducted *via* a post-synthesis grafting method (*Catal. Today*, 2015, **250**, 218-225.). Typically, 0.005 mmol of APTES was dissolved in dry toluene to form a clear solution. Next, 1.5 g of P25-TiO_2 was dispersed in 25 mL of APTES solution within a Teflon reactor and stirred for 15 min. The suspension was then sealed and heated at 100 °C for 8 h. After the reaction finished, the resulting powders were filtered, washed with dry toluene and dichloromethane for several times, and dried in the oven at 110 °C for 12 h.

Deposition of Ag_2Se QDs on surfaces of TiO_2. Briefly, 0.02 g of 3-MPA capped crystal defects-rich Ag_2Se QDs (2 wt%) and 0.98 g of APTES-functionalized P25-TiO_2 were dispersed in 200 mL of deionized water and magnetically stirred for about 24 h under room

temperature. Afterwards, the resulting product was washed and centrifugated with deionized water for several times, and dried in the oven overnight.

Photocatalytic hydrogen evolution from water splitting. The evaluation of photocatalytic hydrogen evolution performance was carried out utilizing a photocatalytic evaluation system (Labsolar-IIIAG, Perfect-Light Company, Beijing) with the Xe lamp irradiation ($\lambda > 420$ nm, 300 W) and a gas chromatograph (GC-7900, Techcomp, Shanghai) at room temperature. The GC-7900 system exploits a thermal conductivity detector (TCD) and the ultrahigh-purity N_2 as the carrier gas. In a typical procedure, 0.1 g of the Ag_2Se-TiO_2 photocatalysts were dispersed in mixed solution of methanol (50 mL) and deionized water (150 mL) under continuous visible light irradiation and magnetically stirring. Besides, reference experiments were also performed without photocatalysts in the presence of light and with photocatalysts in the dark. Nevertheless in both cases, no production of hydrogen gas was observed.

Characterization. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded with a field-emission transmission electron microscope (FE-TEM, JEOL JEM-2100F, Japan) equipped with a post-column Gatan imaging filter system (GIF, Tridium 863, United States) working at 200 kV of the acceleration voltage. The off-axis electron holography analysis and geometric phase analysis (GPA) were carried out using Gatan-DigitalMicrograph® software (version 1.71.38). Powder X-ray diffraction (XRD) patterns were collected with a powder X-ray diffractometer (D8-Advance, Bruker, Germany) working with Cu-Kα radiation (1.5406 Å) at 40 mA and 40 kV. The near-infrared (NIR) photoluminescent spectra were recorded using a homemade device with a Prinston NIR-CCD as the detector and an 808 nm laser as the excitation source.

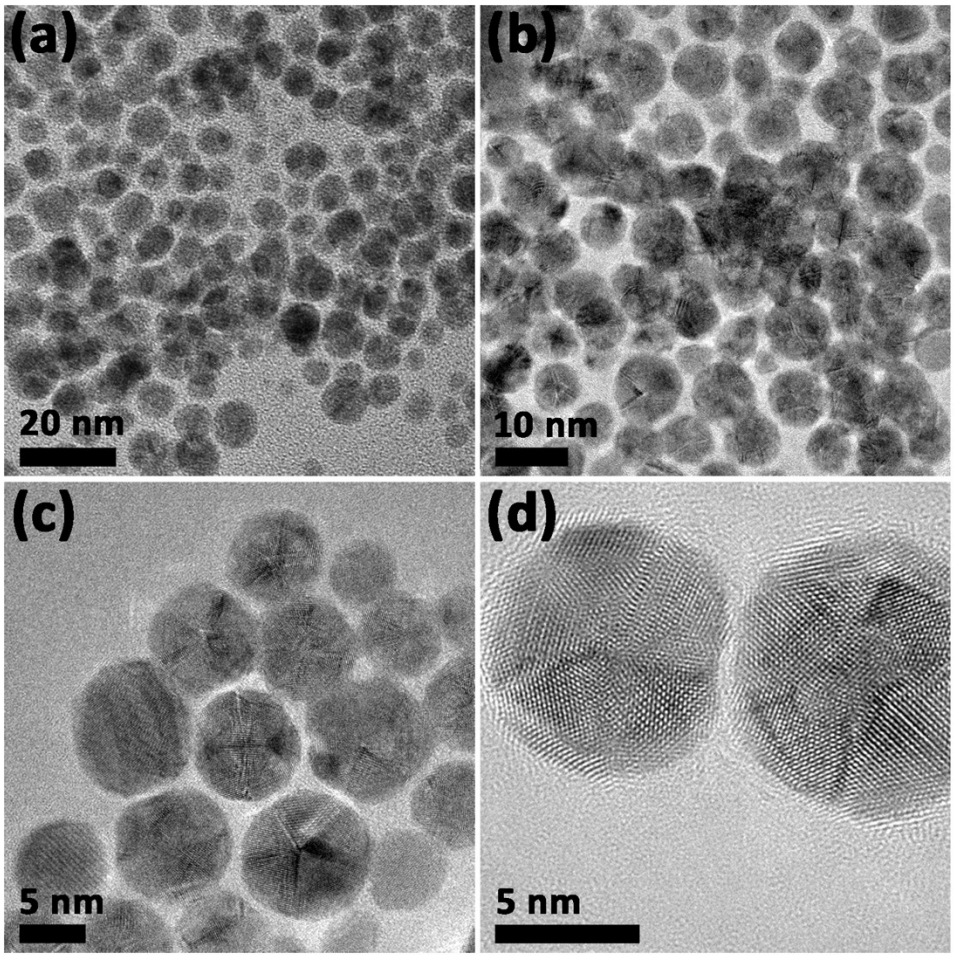

Figure S1. Representative (a-c) TEM and (d) HRTEM images of the crystal defects-rich Ag_2Se nanocrystals recorded under different magnifications.

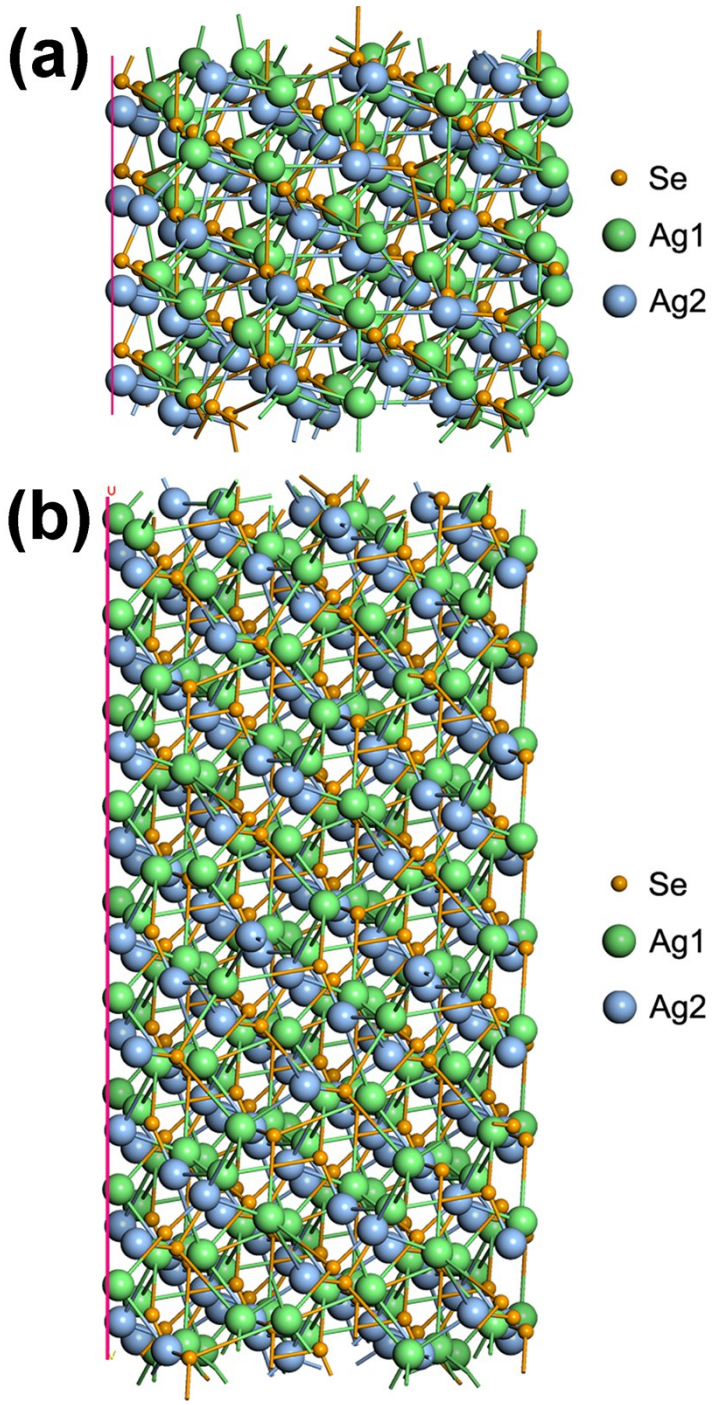

Figure S2. Two representative crystal-structure projections along the [**Error! Error!** 4] zone axis. The red lines on the left in panel (a) and (b) represent the projections of (**Error!** 2 2) and (2 0 1) twin planes observed in the HRTEM images of Figure 2a–b of the manuscript, respectively.