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Supporting Information

Assembling metallic 1T-MoS_2 nanosheets with inorganic-ligand stabilized quantum dots for exceptional solar hydrogen evolution

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1. TEM image

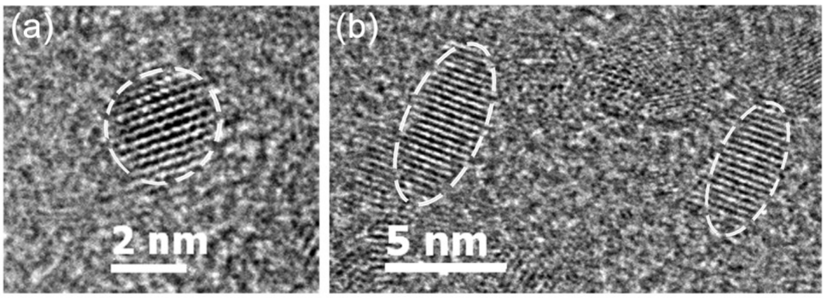

Figure S1. (a) High resolution TEM images of CdSe core and (b) corresponding inorganic-ligands stabilized CdSe/ZnS QDs.

2. XRD pattern

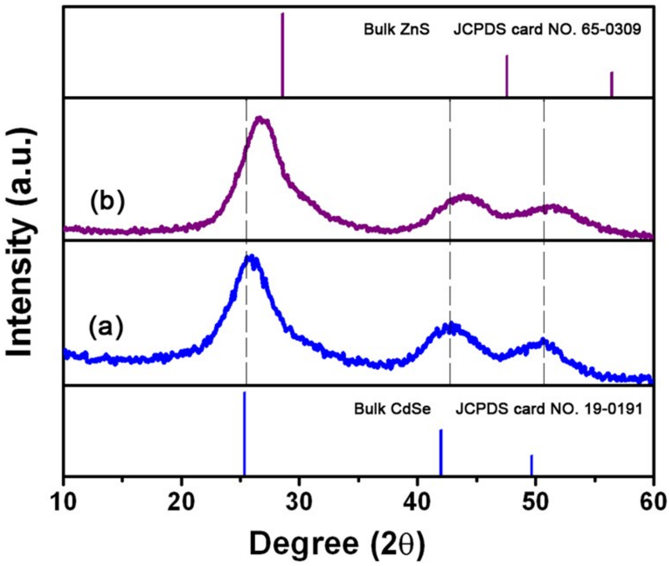

Figure S2. XRD diffractogram of CdSe cores (a) and the corresponding inorganic-ligands stabilized CdSe/ZnS QDs (b).

3. Raman spectra

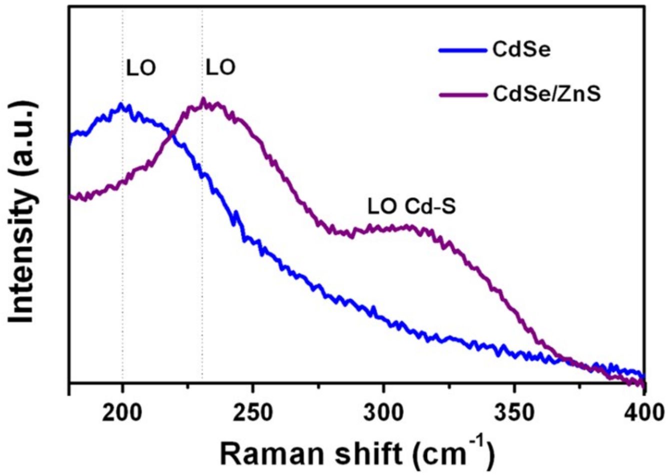

Figure S3. Room-temperature Raman spectra comparison of bare CdSe QDs and the obtained CdSe/ZnS QDs under 780 nm laser excitation.

As shown in Figure S1, high-resolution TEM was employed for characterizing the growth of ZnS shell on CdSe core. The sphere-like CdSe templates, with a size of ~2.0 nm, were transformed to ellipsoidal-shaped counterparts, which directly confirmed the growth of ZnS on CdSe. As presented in Figure S2, XRD pattern of CdSe cores is consistent with that of cubic CdSe structure (JCPDS Card NO. 19-0191), while the diffraction pattern of CdSe/ZnS QDs moves gradually toward higher angle, well catering to previous reports of forming ZnS shell on CdSe core.[1, 2] Figure S3 compares the room temperature Raman spectra of CdSe QDs and CdSe/ZnS QDs, from which we can find that besides the shift of Raman peak of CdSe QDs at ∼197 to 231 cm^{-1}, an additional peak (∼312 cm^{-1}) appears, which is due to the growth of ZnS shell on CdSe core.[3] All of these results confirm the successful introduction of ZnS shell on the surface of CdSe QDs. As no extra surface ligands were added into the solution, we thought that the obtained CdSe/ZnS QDs were stabilized by sulfide ions.

4. Control experiments

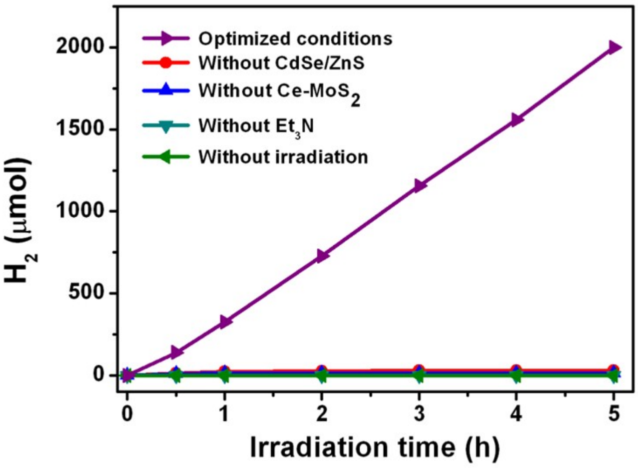

Figure S4. Control experiments: time courses of H_2 evolution by eliminating any component of the system under visible-light irradiation (λ = 410 nm).

5. Long-time irradiation

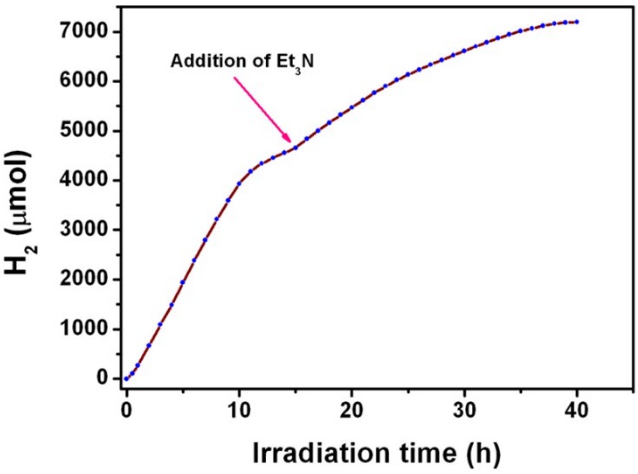

Figure S5. The time course of H_2 evolution under the optimal conditions and the effect of addition of sacrificial reagent (Et_3N) to the system.

6. UV-vis spectra

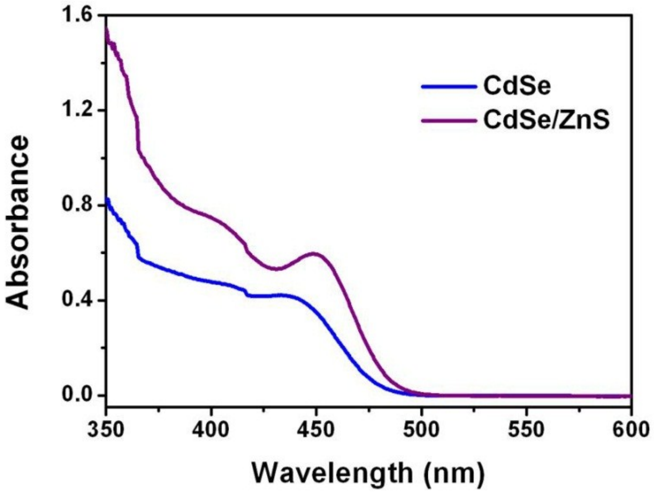

Figure S6. UV-vis absorption spectra of bare CdSe QDs and CdSe/ZnS QDs under the same conditions.

7. Emission spectra

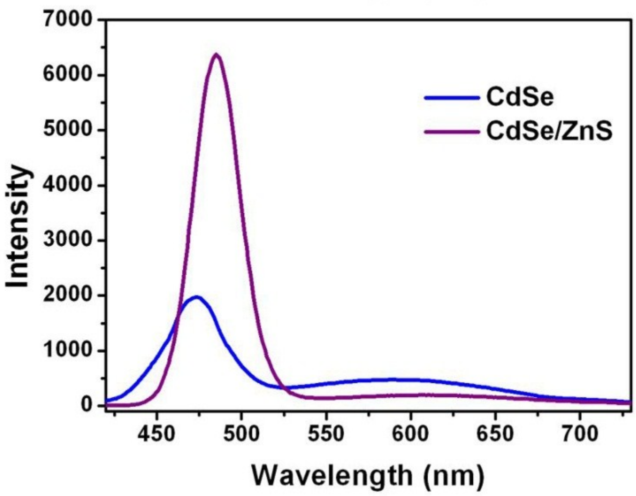

Figure S7. Emissive spectra of bare CdSe QDs and CdSe/ZnS QDs under the same conditions (400 nm excitation).

8. Gibbs free energy analysis

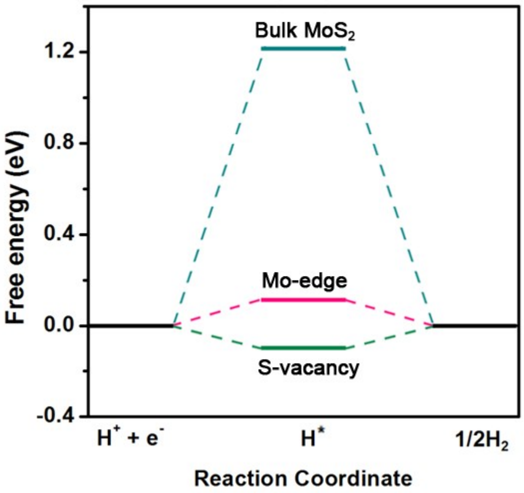

Figure S8. Analysis of adsorption Free Energies of H Atoms at different sites of MoS_2.[4]

9. Experiments

(1) Synthesis of the magic sized MPA-CdSe QDs template: the water-soluble CdSe QDs were synthesized by reported methods.[5, 6] Briefly, 40 mg selenium powder was transferred to 100 mL of Na_2SO_3 (189 mg) aqueous solution. The resulting mixture was then refluxed until the selenium powder dissolved completely to obtain transparent Na_2SeSO_3 solution. The water-soluble magic sized MPA-CdSe QDs were prepared by mixing a solution of $CdCl_2 \bullet 5/2H_2O$ and 3-mercaptopropionic acid (MPA), then adjusting the pH to 11 with 1.0 M NaOH, and finally adding a measured volume of synthesized Na_2SeSO_3 solution. This mixture was placed in a three-necked flask and deaerated with N_2 bubbling for 30 min. Then, the transparent solution was refluxed for about 3 h to promote the growth of CdSe nanocrystals. Aliquots of the reaction solution were taken out at regular intervals for characterization by UV-Vis absorption and emission. And the obtained CdSe QDs were also characterized by the high resolution TEM and XRD.

(2) Synthesis of inorganic ligands (S^{2-}) stabilized CdSe/ZnS QDs[7]: a volume of 200 mL the above synthesized magic sized MPA-CdSe QDs was condensed to 20 mL through rotary evaporation, and precipitated from aqueous solution by adding isopropanol. The precipitates were separated by centrifugation (7000 rpm, 6 min) and washed with ultrapure water three times to remove any residual ligands not bound to the surface of the QDs. The precipitate was re-dispersed in 200 mL ultrapure water, placed in a three-necked flask and deaerated with nitrogen for 30 min. Then, the solution was heated and kept at 55 degree under inert atmosphere. Sodium sulfide (60 mL; 5.0×10^{-3} mol/L) and zinc nitrate (40 mL; 5.0×10^{-3} mol/L) aqueous solutions were in turn pumped into the flask with a speed of 5.0 mL/20 min and 3.6 mL/10 min, respectively. Finishing adding of both precursors, the reaction mixture was kept at 55 degree for another 2.0 h for the growth of the heterogeneous nanocrystals. The obtained CdSe/ZnS QDs were purified by precipitation and centrifugation process, removing any unreacted precursors, S^{2-} or Zn^{2+}, before any characterization and hydrogen evolution utilization.

(3) Synthesis of MPA stabilized CdSe/ZnS QDs: 3-Mercaptopropionic acid stabilized CdSe/ZnS QDs were obtained through a ligand-exchange experiment[8, 9]. A certain volume of as-synthesized sulfide stabilized CdSe/ZnS NCs (100 mL) was precipitated by adding 0.1 M hydrochloric acid. The precipitates were separated by centrifugation (7000 rpm, 6 min) and washed with ultrapure water three times to remove the sulfide ions not bound to the nanocrystal surfaces. 3-Mercaptopropionic acid (MPA, 100 mg) was placed into 20 mL methanol in a three-neck flask. The pH was adjusted to about 11 with the addition of tetramethylammonium hydroxide pentahydrate. Above obtained CdSe/ZnS precipitates (50 mg) were added into the reaction vessel under nitrogen. The vessel was reflux at 65 degree for 6 h. After reflux, the reaction was cooled to room temperature, removed from nitrogen, and stored in the dark. Nanocrystals were precipitated with ethyl acetate and re-dissolved in methanol and precipitated with ethyl acetate 2 more times. After the final precipitation, the obtained QDs were dissolved in ultra-pure water.

(4) Synthesis of 1T-MoS_2 nanosheets: all materials were obtained from Alfa Aesar, unless otherwise indicated. Procedures were adapted from the reported literature.[10, 11] In a nitrogen environment, 2.0 g of MoS_2 powder (~325 mesh) was immersed in 20 mL *n*-butyl lithium (2.5 M in hexane), stirred for one week at room temperature. The obtained suspension was centrifuged and washed with dry hexane to remove the excess *n*-butyl lithium, and then the substrates were sonicated for 4.0 h in excess 18 MΩ deionized water to achieve exfoliation. The obtained nanosheets were then collected and dialyzed against di-H_2O for 7 days. Solid 1T-MoS_2 nanosheets were obtained through lyophilisation for further characterizations and applications.

(5) Inductively coupled plasma atomic emission spectrometry (ICP-AES): ICP-AES specimens were prepared by adding fixed aliquots (2.5 to 50 μL) of QDs/1T-MoS_2 solution to 100 μL of 1:1 $HCl:HNO_3$ (trace grade). Mixture was then placed in 75 degree water bath for digestion (6.0 h). 25 μL of ICP-AES internal standard solution was then added, and solution was diluted to 5.0 ml using di-H_2O. External standards were prepared accordingly using Mo standard solution from Sigma Aldrich. Each external standard is made with varying quantities of Mo standard, 100 μL of 1:1 $HCl:HNO_3$ (trace grade) and 25 μL of internal standard. Each external standard solution was then diluted to 5 mL, as with the case of specimens. Accuracy of external standard preparation was checked by linear regression of ICP-AES signal. Mo concentration of undiluted specimen was then determined by using dilution factor described above. Mass of MoS_2 in solution was estimated by taking formula weight ratios of MoS_2 versus Mo.

(6) Photoelectrochemical measurements: all experiments were performed on a Zennium electrochemical workstation (Germany, Zahner Company) in a conventional three-electrode system.

The resultant electrode served as the working electrode, platinum as the counter electrode and Ag/AgCl (3.0 M KCl) electrode as the reference electrode. A 300 W Xe-lamp with a UV-cut-off filter was used as the light source. A 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. The working electrodes were prepared by dispersing 30 mg of QDs/1T-MoS_2 in a mixture of 50 μL a Nafion (5%) aqueous solution and 100 μL of ethanol. The obtained slurry was then spread on a FTO glass substrate with an active area of about 0.64 cm^2. The film was dried under inert atmosphere.

(7) Solar hydrogen production: first of all, 2.5 mg the obtained photocatalysts were dispersed in a 5.0 mL mixture of water and Et_3N (v:v = 4:1). Then, the solution was degassed by bubbling nitrogen for 30 min before irradiation. Then 600 μL ultrapure CH_4 was injected into the system to work as the internal standard for quantitative GC analysis. For short time irradiation (below 1 h), the generated molecular H_2 in the reaction headspace was performed by using a gas chromatograph (TianMei-7890 II) equipped with a thermal conductivity detector and a 5Å molecular sieves GC column. Nitrogen was used as a carrier gas. The response factor for H_2/CH_4 was about 5.15 under the experimental condition, which was established by calibration with known amounts of H_2 and CH_4, and determined before and after measurements. As the activity of solar H_2 evolution is very fast, the amount of H_2 gas was determined by using a home-made drainage gas-collecting method using a gas-tight acid burette. Error bars on H_2 were calculated from at least three independent experiments.

10. Reference

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