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Supporting Information

Uniform Decoration of Pt Nanoparticles on Well-Defined CdSe Tetrapods and Their Effect of Pt Cluster Size on the Photocatalytic H_2 Generation

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1. Chemicals

Cadmium oxide (CdO, 99.95%) was purchased from Alfa Aesar. Selenium (99.99%, powder), *n*-triocytylphosphine (TOP, 90%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), 1,2-hexadecanediol (90%), oleylamine (70%), platinum(II) acetylacetonate ($Pt(acac)_2$, 97%), 1,2-dicholrobenzene (anhydrous, 99%), 11-mercaptoundecanoit acid (MUA, 95%), tetramethylammonium hydroxidepentahydrate salt (>97%) and cetyltrimethylammonium bromide (CTAB, 99+ %) were all purchased from Sigma Aldrich. Phenyl ether (90%) was purchased from TCI. Toluene, methanol and ethanol were purchased from Samchun Chemicals. All chemicals were used as purchased.

2. Preparation of Injection Solution

For the preparation of cadmium oleate ($Cd(OA)_2$) solution, 12 mmol CdO, 10.8 mL OA and 6 mL ODE were placed in an 100 mL 3-neck round flask equipped with a condenser. The reaction mixture was degassed under vacuum at 100 °C for degassing, followed by heating to 280 °C under Ar for 20 min to form an optically clear solution. The mixture was then cooled down to room temperature for further use. Separately, 12 mmol Se and 6 ml TOP were mixed in a 50 mL 3-neck round flask with a condenser and heated to 200 °C until powdered Se fully dissolved. After SeTOP was cooled down to room temperature, 6 mL SeTOP solution was mixed with 14 mL $Cd(OA)_2$ solution for further injection.

3. Synthesis of Zincblende CdSe Seeds

Procedure for the synthesis of zincblende CdSe quantum dot seeds was adopted with a slight modification from the literature. First, to a 100 mL 3-neck round flask equipped with a condenser, 1 mmol Se and 10 mL ODE were loaded and heated to 100 °C for degassing under vacuum. Under Ar, the reaction mixture was heated to 300°C for the injection of as-prepared $Cd(OA)_2$. At 300 °C, 2.8 mL $Cd(OA)_2$ and 7.2 mL ODE were injected to make the total volume of 20 mL and the reaction solution was reacted at 270 °C for 15 min. In common, spherical zincblende CdSe quantum dot seeds with ~5

nm diameter (1st exciton peak ~630 nm) were obtained, and this crude solution was used without further purification.

4. Synthesis of CdSe Tetrapods by the CPI Approach

To a 100 mL 3-neck round flask equipped with a condenser, 5 mL zincblende CdSe seed solution, 2.25 mL OA, 1.5 mL TOP, 21.25 mL ODE and 0.21 mmol CTAB were loaded and heated to 100 °C under vacuum for degassing. Under Ar, the reaction mixture was heated to 270 °C for the injection of as-prepared $Cd(OA)_2$ and SeTOP injection solution, with the injection rate of 0.4 mL/min for 50 min by syringe pump. After the reaction, the crude mixture were loaded to centrifuge tube and equal amount of toluene and ethanol were added repeatedly for the precipitation of the products by centrifugation at 4000 rpm.

5. Decoration of Pt Nanoparticles onto CdSe Tetrapods

Synthetic procedure for the decoration of Pt nanoparticles onto CdSe tetrapod side walls were adopted from the literature. To a 100 mL 3-neck round flask equipped with a condenser, 43 mg 1,2-hexadecanediol, 0.2 mL OA, 0.2 mL oleylamine and 10 mL phenyl ether were loaded and heated to 80 °C under vacuum for degassing. Under Ar, the reaction mixture were heated to 225 °C for further injection. Meanwhile, 25 mg as-synthesized CdSe tetrapods along with a controlled amount of platinum precursors, which were platinum acetylacetonate, were dissolved in 1 mL 1,2-dichlorobenzene for the injection solution. At 225 °C, the injection solution was injected into the reaction mixture and reacted for 8 min, followed by cooling down to room temperature and 5 mL toluene were injected under 100 °C to prevent further solidification of the products. The crude product solution was then transferred to a centrifuge tube, and a relative amount of ethanol and toluene was added to selectively remove free Pt nanoparticles with centrifugation at 2500 rpm.

6. Photocatalytic H_2 Generation Reactions of Pt-Decorated CdSe Tetrapods

First, as-prepared Pt-decorated CdSe tetrapods were precipitated by adding an excess amount of methanol. Next, 250 mg 11-mercaptoundecanoic acid (MUA) were dissolved in 20 g methanol. Tetramethylaamonium hydroxidepentahydrate salt was added until the solution pH of 11 was obtained. This solution was added to the precipitates of Pt-decorated CdSe tetrapods and sonicated for a few seconds, followed by adding toluene and centrifugation at 4000 rpm for the precipitation of the products. Finally, Pt-decorated CdSe tetrapods passivated with MUA were dispersed in water.

For the photocatalytic H_2 generation reaction, the as-prepared Pt-decorated CdSe tetrapod photocatalyst solution was mixed with 0.35 M Na_2SO_3/0.25 M Na_2S aqueous solution (10 mL). The amount of the photocatalysts was set at 2.5 mg considering the concentration of solution and head space. The reaction mixture was loaded to a homemade quartz tube with a total volume of 19 mL and sealed with a rubber septum, and purged with Ar for 30 min prior to the reaction, followed by illumination with AM 1 SUN condition by a solar simulator (ABET Technologies). The aliquot of the reaction mixture was collected by a syringe from the head space in every 30 min. The amount of H_2 generated was measured by a gas chromatograph (GC, YL6100).

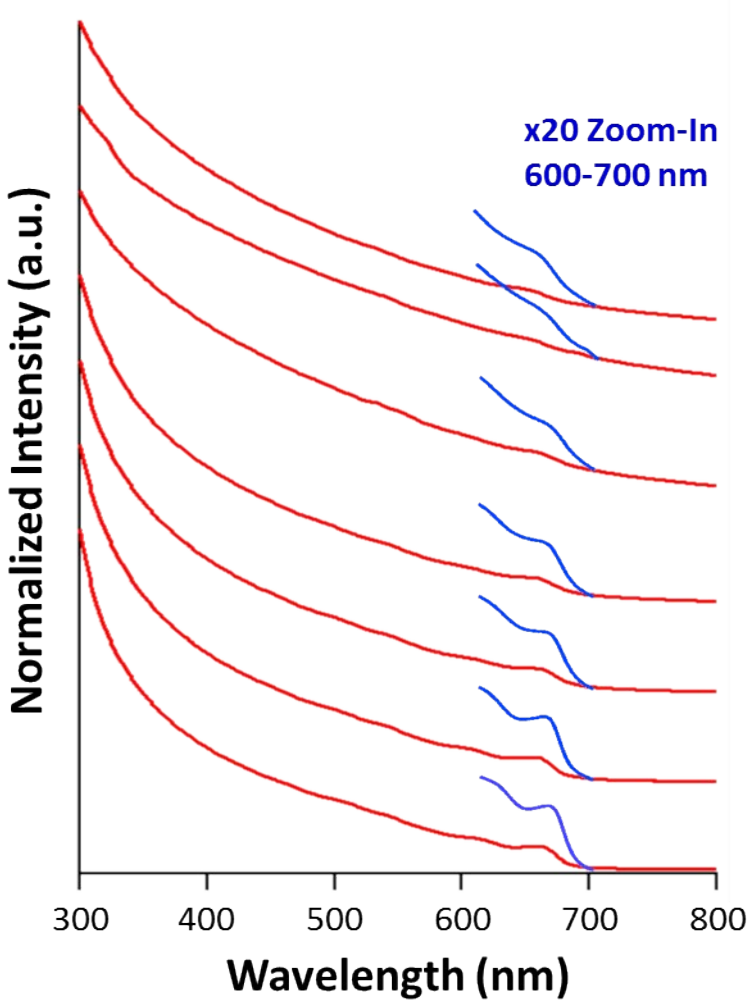

Figure S1. UV/Vis absorption spectra of Pt-decorated CdSe tetrapods from bare CdSe tetrapods to 1/5/15/25/35/45 mg of Pt precursors (from bottom).

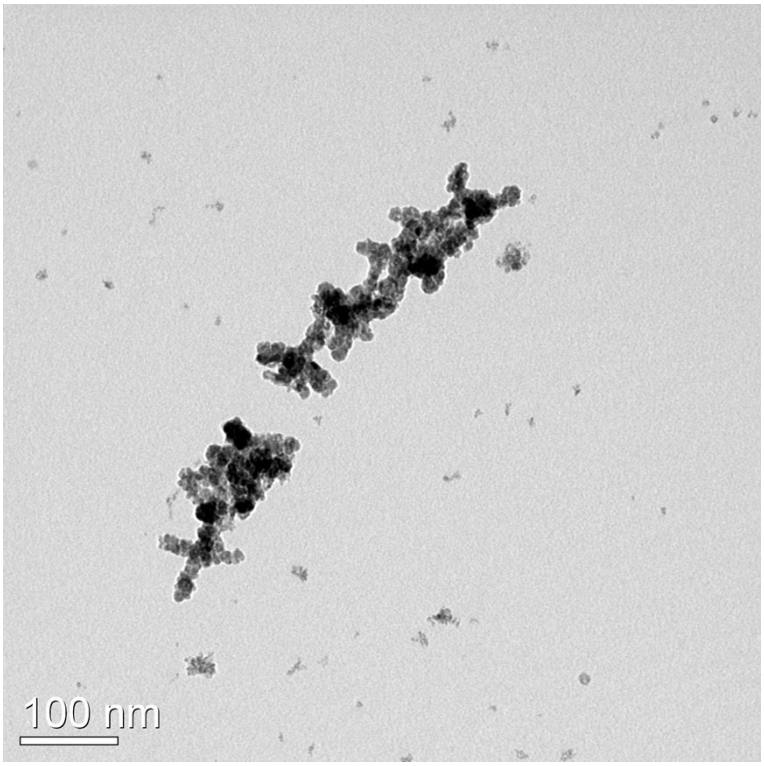

Figure S2. Control experiment of the growth of cobalt nanoparticles onto Pt-decorated CdSe tetrapods prepared with 1 mg of Pt precursors.

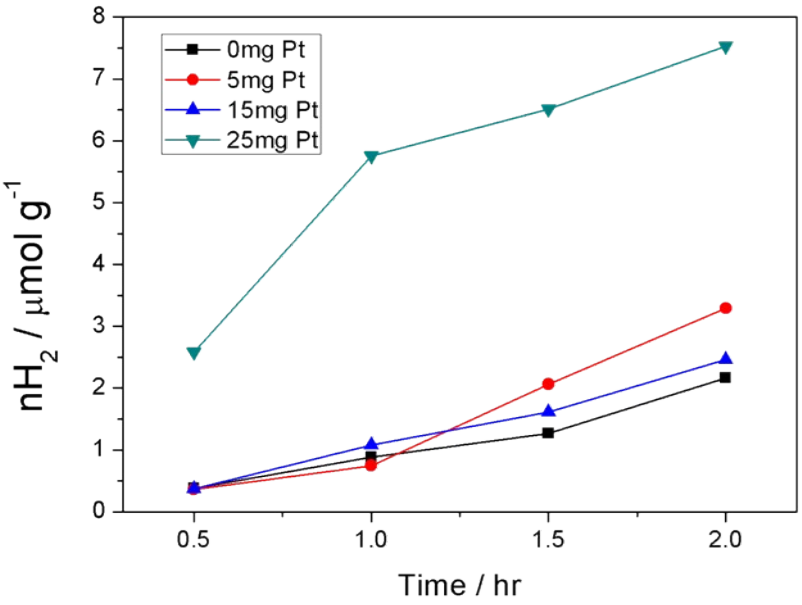

Figure S3. Photocatalytic H_2 generation from the Pt-CdSe hybrid nanocrystals prepared with different amount of Pt precursors (except 1 mg of Pt precursors).

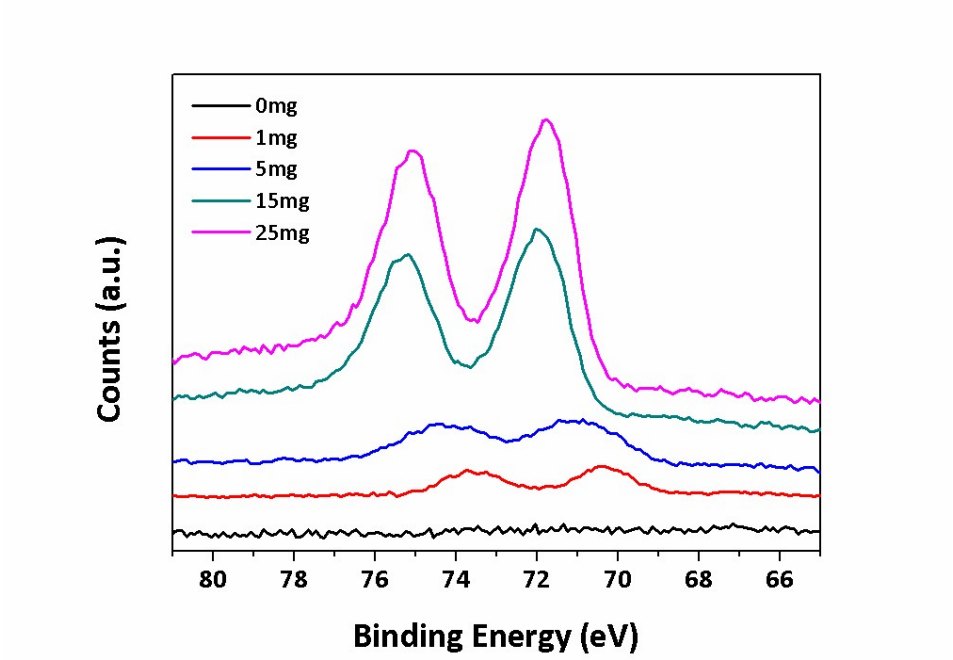

Figure S4. X-ray Photoemission Spectra showing the binding energies of Pt 4f electrons from Pt-decorated CdSe tetrapods with different amounts of Pt precursors.

Amount of CdSe Tetrapods	25 mg				
Amount of Pt Precursor	0 mg	1 mg	5 mg	15 mg	25 mg
Pt (mol.%)	0 %	1.61 %	8.73 %	15.59 %	41.62 %

Table S1. ICP-AES analysis of Pt-decorated CdSe tetrapods with different amounts of Pt precursors