Electronic Supplementary Information

Metal-Semiconductor Double Shell Hollow Nanocubes for Highly Stable Hydrogen Generation Photocatalysts

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Experimental Section

Chemicals. Silver trifluoroacetate (CF_3COOAg, 99.99+%, Aldrich), sodium hydrosulfide hydrate ($NaSH{\cdot}xH_2O$, Aldrich), hydrochloric acid (HCl, 35.0%, Junsei), poly(vinylpyrrolidone) (PVP, M_w = 55000, Aldrich), ethylene glycol (EG, 99%, J. T. Baker), hexachloroplatinic(IV) acid hydrate ($H_2PtCl_6{\cdot}xH_2O$, 99.9+%, Aldrich), tetrachloroaurate(III) trihydrate ($HAuCl_4{\cdot}3H_2O$, 99.9+%, Aldrich), palladium(II) nitrate ($Pd(NO_3)_2$, 99.9+%, Aldrich), sodium chloride (NaCl, 99.999%, Aldrich), oleylamine (70%, Aldrich), oleic acid (99+%, Aldrich), sulfur (S, Aldrich), selenourea ($(NH_2)_2CSe$, 98%, Aldrich), cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$, 98%, Aldrich), and tributylphosphine (TBP, 97%, Aldrich) were used as received.

Synthesis of MAg Hollow Nanocubes (M = Pt, Au, and Pd). Ag nanocubes with an average edge length of 56 nm were synthesized according to the literature (Q. Zhang, W. Li, L.-P. Chen, Y. Xia, *Chem. Eur. J.* **2010**, *16*, 10234-10239). An aqueous dispersion of Ag nanocubes (350 μmol with respect to the Ag precursor concentration) was mixed with an aqueous solution of poly(vinylpyrrolidone) (PVP, 1.1 mmol, 120 mL). For the synthesis of PtAg hollow nanocubes, an aqueous solution of H_2PtCl_6 (18 mmol, 20 mL) was added to the reaction mixture at a rate of 1.0 $mL{\cdot}min^{-1}$ by a syringe pump under the reflux condition for 20 min. After stirring the reaction mixture for 30 min, the product was collected by centrifugation at 10,000 rpm for 30 min, washed once with a saturated NaCl solution to remove AgCl, and washed several times with deionized water. The particles were dispersed in deionized water (30 mL) for further uses. For the syntheses of AuAg and PdAg hollow nanocubes, $HAuCl_4$ (24 μmol) and $Pd(NO_3)_2$ (35 μmol) were used as metal precursors, otherwise the reaction conditions were identical to those of the PtAg hollow nanocubes, respectively.

Synthesis of MS-Ag_2S Double Shell Hollow Nanocubes. For the synthesis of PtS-Ag_2S double shell hollow nanocubes, the PtAg hollow nanocubes (40 μmol with respect to the Ag precursor concentration) were dispersed in the reaction mixture of sulfur (2.0 mmol), oleylamine (5.0 mL) and oleic acid (10 mL) by an aid of sonication for 30 min. The resulting mixture was allowed to stir at room temperature for additional 30 min. The product was collected by centrifugation, and washed with methanol several times. The particles were dispersed in methanol (5.0 mL) for further uses. For the syntheses of Au-Ag_2S and PdS-Ag_2S double shell hollow nanocubes, the AuAg and PdAg hollow nanocubes were used instead of the PtAg hollow nanocubes, otherwise the reaction conditions were identical to those of the PtS-Ag_2S double shell hollow nanocubes, respectively.

Synthesis of MS-CdS Double Shell Hollow Nanocubes. For the synthesis of PtS-CdS double shell hollow nanocubes, a methanol solution (0.11 mL) dissolving PVP (34 μmol) and $Cd(NO_3)_2$ (110 μmol) was added to the PtS-Ag_2S nanocube dispersion in methanol (1.1 mmol with respect to the Ag precursor concentration), and the mixture volume was fit to 1.0 mL by the addition of methanol. The mixture was vigorously stirred at 50 ^oC for 10 min. Then, TBP (25 μL) was added, and the reaction mixture was stirred at 50 ^oC for 1 d. The product was collected by centrifugation, and washed with methanol several times. The particles were finally dispersed in methanol (1.0 mL) for further uses. For the synthesis of Au-CdS and PdS-CdS double shell hollow nanocubes, the Au-Ag_2S and PdS-Ag_2S nanocube dispersions were used otherwise under the identical reaction conditions.

Synthesis of M-CdS Double Shell Hollow Nanocubes. For the reduction of PtS in PtS-CdS double shell hollow nanocubes, a methanol dispersion of PtS-CdS double shell hollow nanocubes (5.5 mmol with respect to the Ag precursor concentration) was dropped on the silicon wafer (1 cm x 1 cm), which was allowed to dry at 60 ^oC for 10 min. The resulting wafer was placed in a tube furnace and was treated at 300 ^oC for 30 min with a flow of the gas mixture of 4 % of hydrogen and 96 % of argon. After the hydrogen treatment, the sample was washed with methanol. The particles were dried at a vacuum oven at 70 ^oC for weighing, and then were dispersed in deionized water (1.0 mL) for the use as catalysts. Few ligands might be removed during the hydrogen treatment, but the residual PVP could stabilize the catalyst dispersion in water. PdS-CdS double shell hollow nanocubes were used for the reduction of PdS under the identical treatment conditions to those for the Pt-CdS hollows.

Photocatalytic H_2 Generation Experiments. The catalyst particles were dispersed in a 0.35 M Na_2SO_3/0.25 M Na_2S aqueous solution (20 mL). The amount of the catalysts was fixed to 1.0 mg, which were precisely weighed by elemental analysis using ICP-AES (inductively coupled plasma-atomic emission spectroscopy) and micro-balance. The reaction mixture was purged with N_2 gas for 40 min prior to the reaction. The H_2 generation experiments were conducted using each sample with the light irradiation of a Xe lamp (300 W, Oriel), equipped with a 10 cm IR filter. The reactor was a homemade quartz flask with a total volume of 40.5 mL, sealed with a rubber septum. An aliquot of the reaction mixture was periodically collected by the syringe from the head space. The amount of H_2 generation was measured by a gas chromatograph (GC, YL6100) with a thermal conductivity detector (TCD) using argon as a carrier gas.

Photoelectrochemical Characterization. The M-CdS hollow cubes were drop-casted on a SnO_2/ITO electrode (5 mm × 5 mm) functionalized with mercaptopropionic acid. Photoelectrochemical (PEC) characterization was performed in a three electrode configuration with the M-CdS/SnO_2/ITO as the working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The working electrode area exposed to the electrolyte was 0.28 cm^2. A 150 W Xe lamp (Abet Technologies) was used as a light. The PEC measurements were performed in a 0.35 M Na_2SO_3/0.25 M Na_2S aqueous solution. In all tests, the intensity of the lamp on the sample was measured to be 100 mW/cm^2. A monochromator (Oriel) was used to obtain action spectra (-0.5 V vs Ag/AgCl). Chopped light linear sweep voltammetry (LSV) was performed to obtain photocurrent responses using a DY2321 potentiostat (Digi-Ivy).

Characterization. Scanning electron microscopy (SEM) images and energy dispersive X-ray diffraction (EDX) spectra were obtained using a Nova 230 operated at 10 kV at KAIST and KBSI. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were acquired on Philips using JEOL JEM-ARM200 operated at 300 kV at NNFC. The elemental composition of each samples was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, iCPA-6300 Duo ICP-OES). The X-ray photoelectron spectrum (XPS) analysis was carried out with a Sigma Probe (Thermo VG Scientific) spectrometer. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 (18 kW) diffractometer using Cu Kα radiation. The samples were prepared by the deposition of nanoparticle dispersions on small pieces (5 mm × 5 mm) of silicon wafer (P-100) for SEM, on slide glasses for XRD, or on copper grids coated with a lacey carbon film (Ted Pella, Inc) for TEM measurements, followed by the solvent evaporation in air.

Calculation of Quantum Efficiencies. Quantum efficiencies (QEs) of the metal-CdS double shell hollow nanocubes were calculated according to the literature (R. Sasikala *et al. Int. J. Hydrogen Energy* **2008**, *33*, 4966–4973). QE is calculated as

$$QE(\%) = \frac{2 \cdot N_{hydrogen}}{N_{photon}} \times 100$$

where N_{photon} is the total number of incident photons, and $N_{hydrogen}$ is the total number of produced hydrogen gas during the H_2 generation for 1 h. $N_{hydrogen}$ was measured using a gas chromatography. For N_{photon}, the UV-Vis illumination source was used for the photocatalytic reaction. According to the action spectra (Figure 3c), the metal-CdS double shell hollow nanocubes exhibited typical light absorptions of CdS (> 2.4 eV). The average photon energy is derived by the emission profile of the lamp (Figure S10) in the range of 300-500 nm as

$$\bar{E} = \sum_{\lambda_i = 300}^{500} \frac{I_i}{I} \times \frac{hc}{\lambda_i}$$

where I is the sum of intensities of all photons, I_i is the intensity at λ_i. The incident light power E in the range of 300-500 nm was measured by a power meter (Newport 848-R), and the total number of photons is given by

$$N_{photon} = \frac{E}{\bar{E}}$$

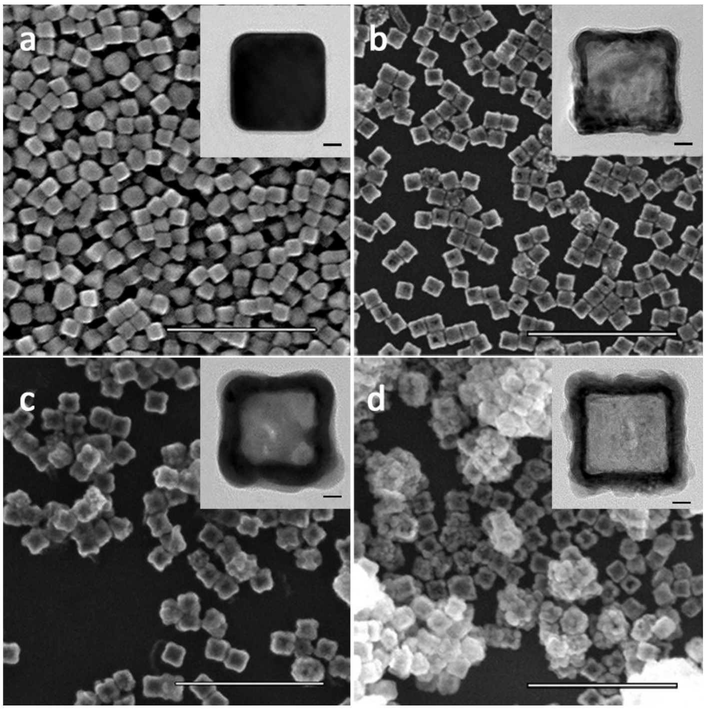
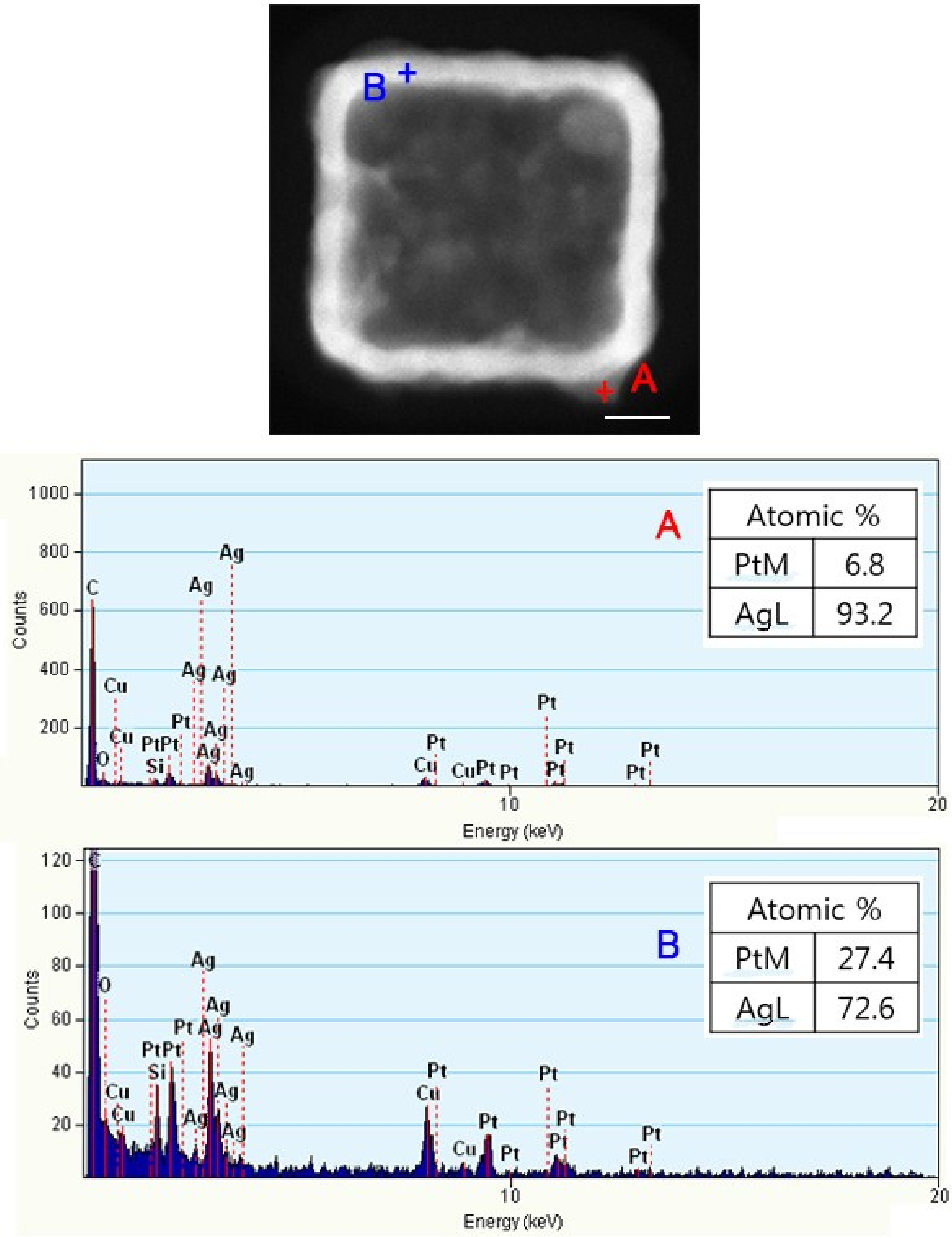


Fig. S1 Scanning electron microscopy (SEM) and inset) transmission electron microscopy (TEM) images of a) Ag nanocubes, b) PtAg hollow nanocubes, and c) PtS-Ag_2S and d) PtS-CdS double shell hollow nanocubes. The bars represent 500 nm and inset) 10 nm.



A

Atomic %	
PtM	6.8
AgL	93.2

B

Atomic %	
PtM	27.4
AgL	72.6

Fig. S2 Point EDX analysis of a single PtAg hollow nanocube.

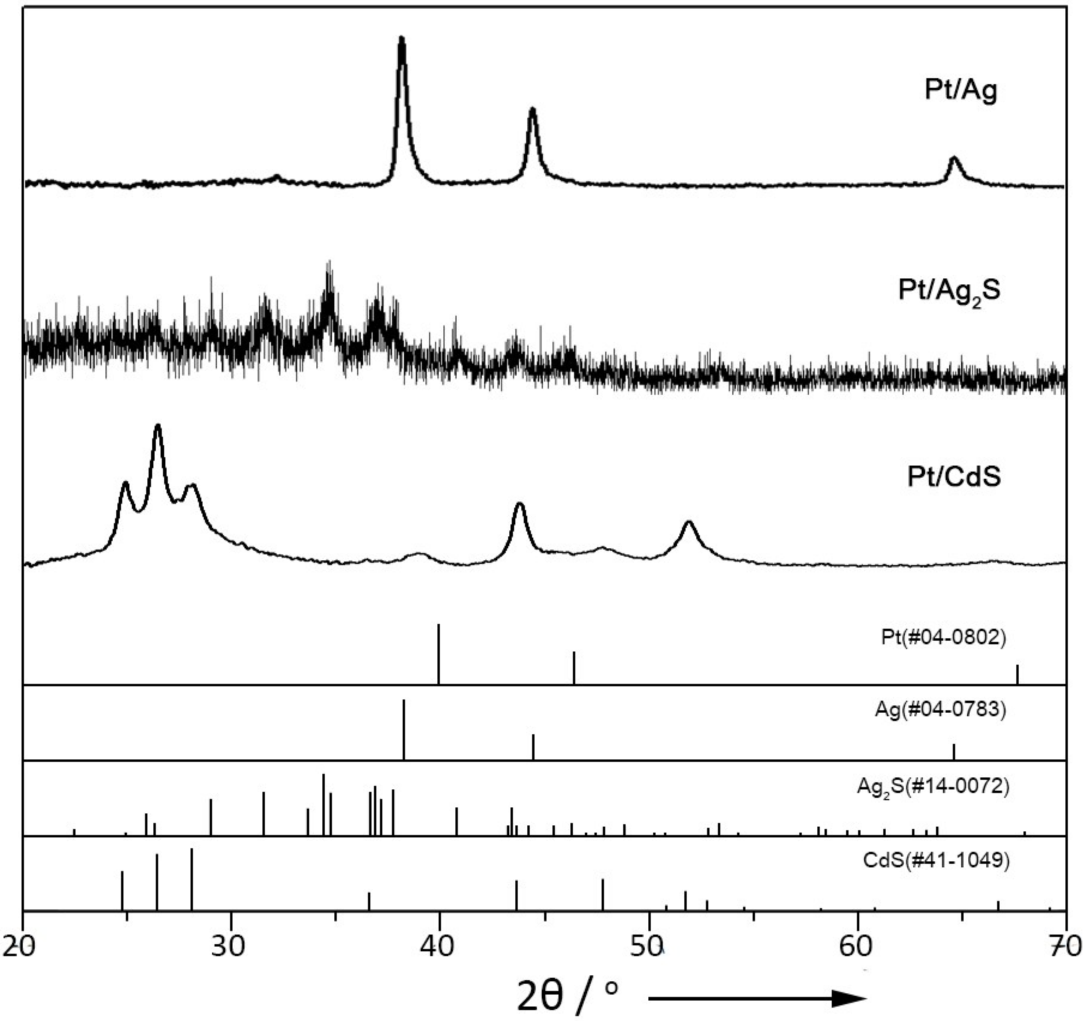


Fig. S3 XRD spectra of PtAg hollow nanocubes and PtS-Ag$_2$S, PtS-CdS, and Pt-CdS double shell hollow nanocubes

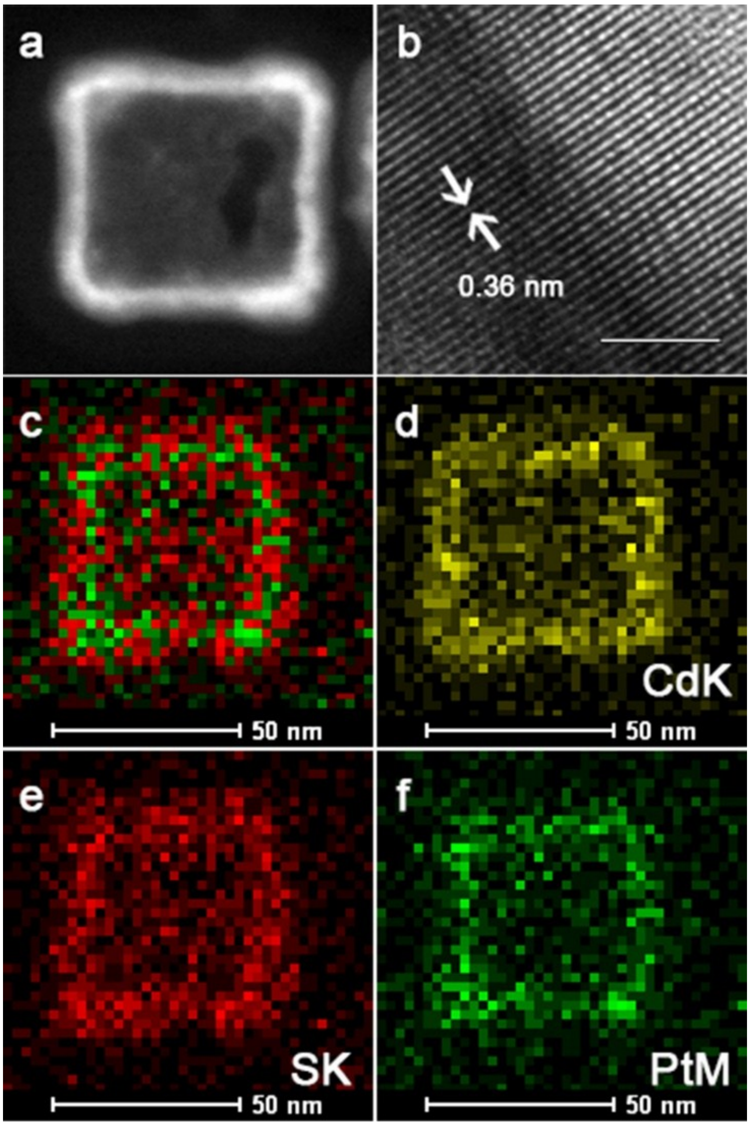


Fig. S4 a) HAADF-STEM and b) HRTEM images, and c-f) EDX elemental mapping of a PtS-CdS double shell hollow nanocube. The bar in b) represents 4 nm.

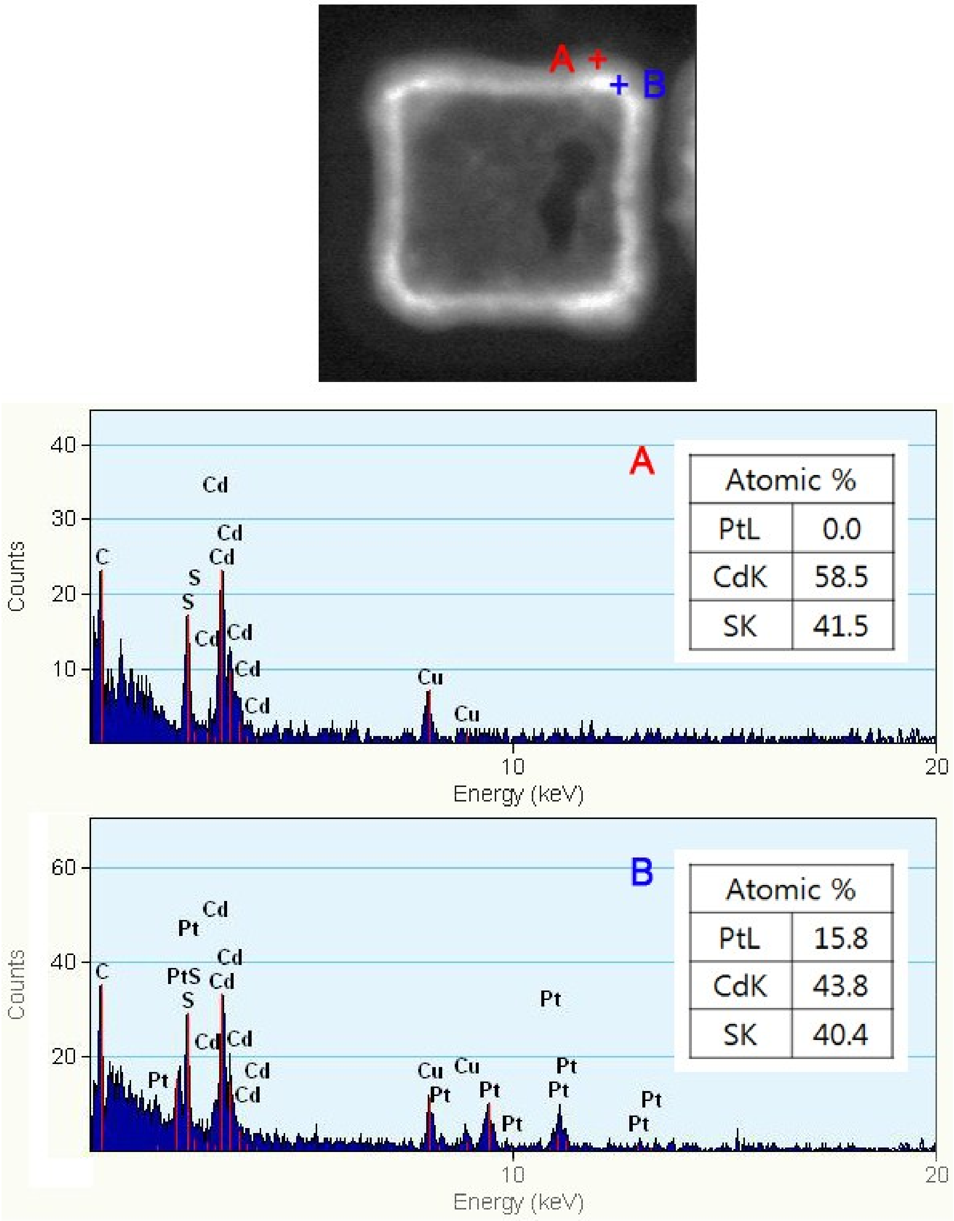


Fig. S5 Point EDX analysis of an individual PtS-CdS double shell hollow nanocube.

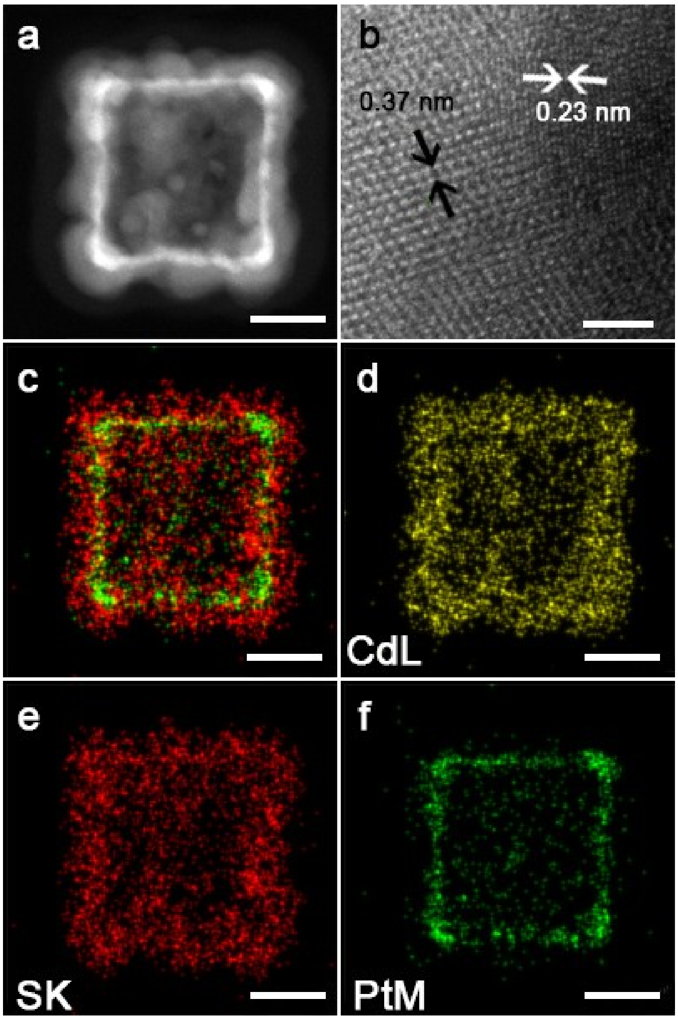


Fig. S6 a) HAADF-STEM and b) HRTEM images, and c-f) EDX elemental mapping of Pt-CdS double shell hollow nanocubes. The bars represent 20 nm and b) 2 nm.

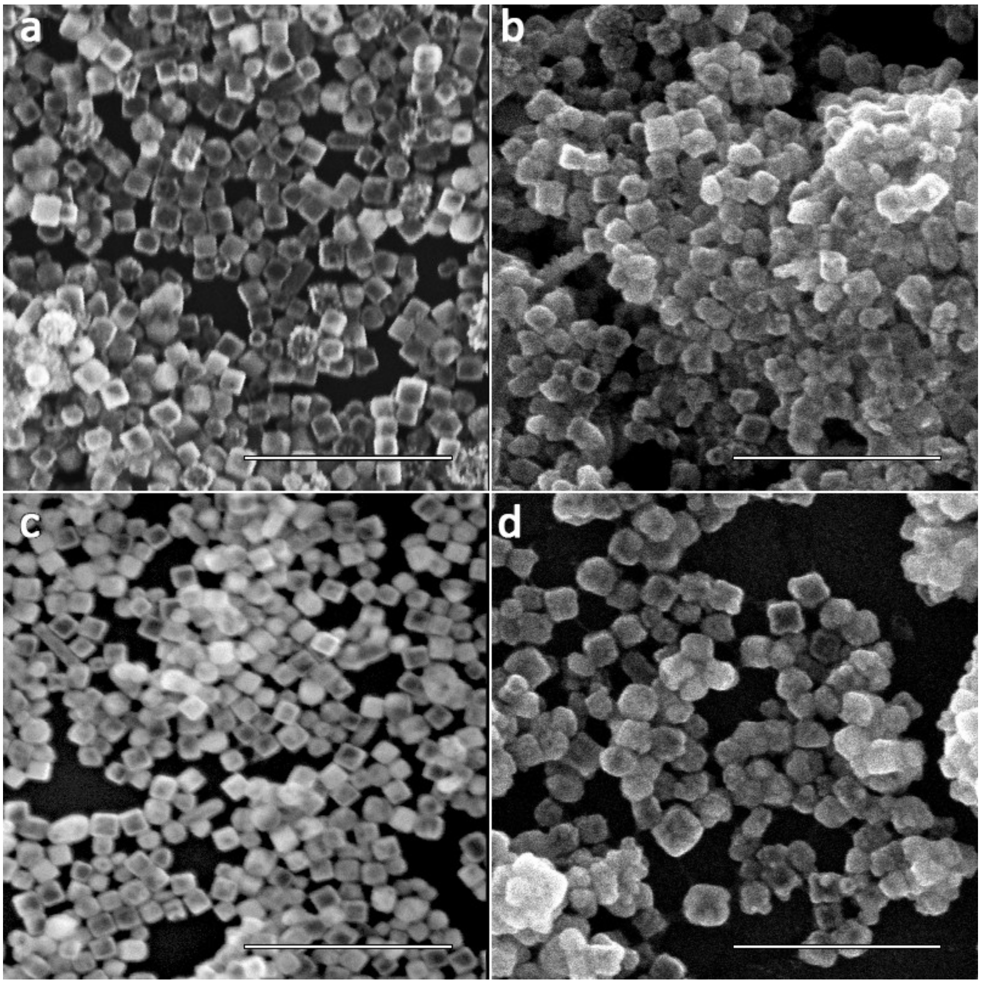


Fig. S7 SEM images of a) Au-Ag hollow nanocubes, b) Au-Ag_2S double shell hollow nanocubes, c) Pd-Ag hollow nanocubes, and d) PdS-Ag_2S double shell hollow nanocubes. The bars represent 500 nm.

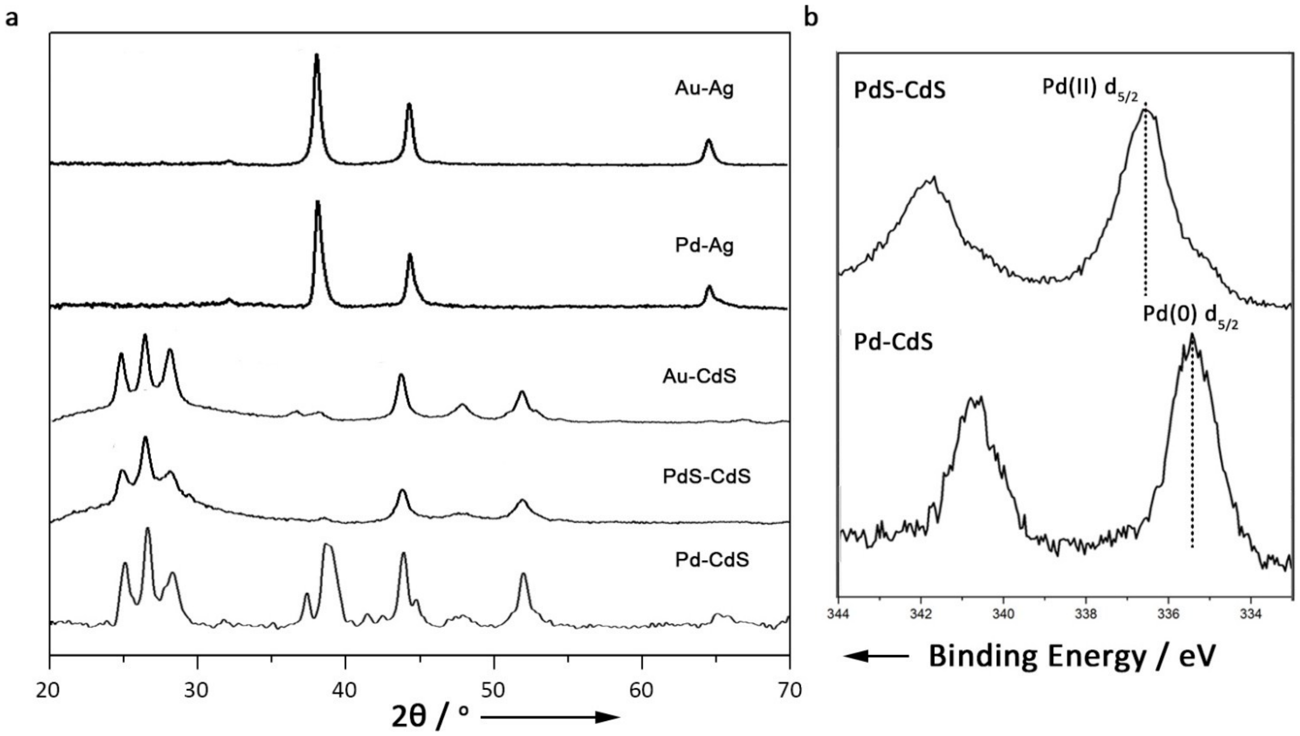


Fig. S8 a) XRD spectra of M-Ag hollow nanocubes, and PdS-CdS and M-CdS double shell hollow nanocubes (M = Au, Pd). b) XPS spectra of PdS-CdS and Pd-CdS double shell hollow nanocubes.

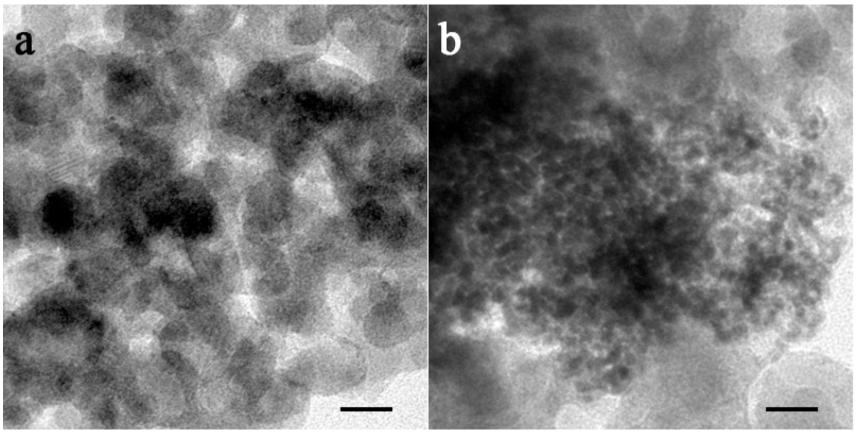


Fig. S9 TEM image of commercial CdS platinized by photodeposition a) before, and b) after 10 cycles of H_2 generation reactions. The bars represent 10 nm.

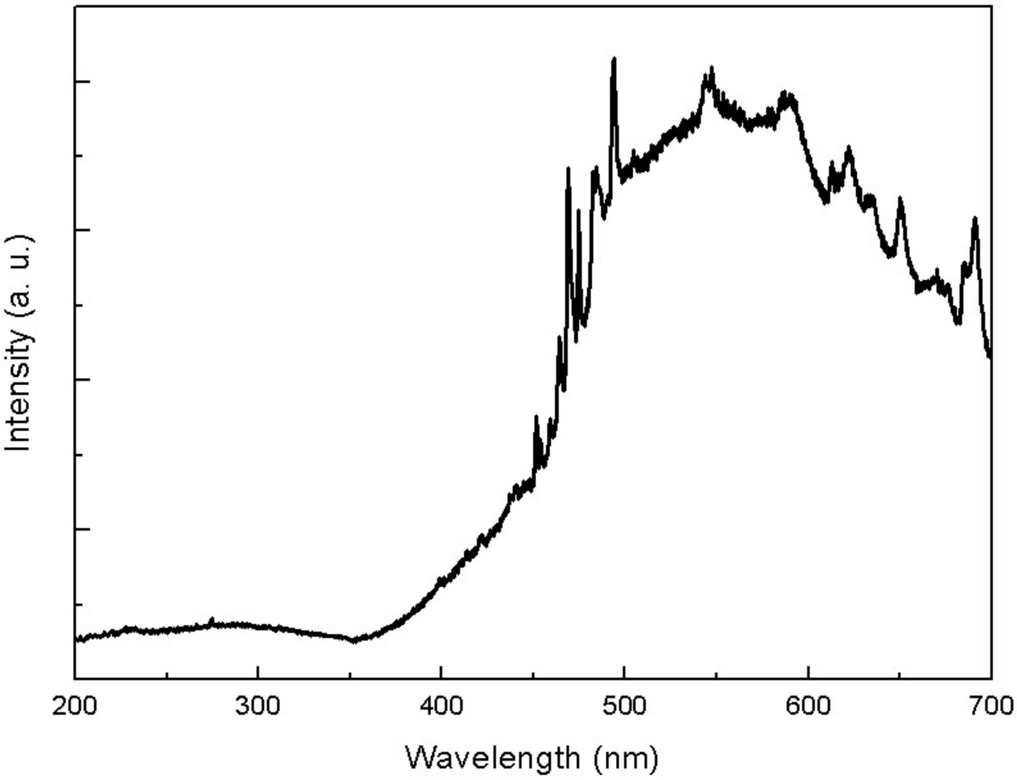
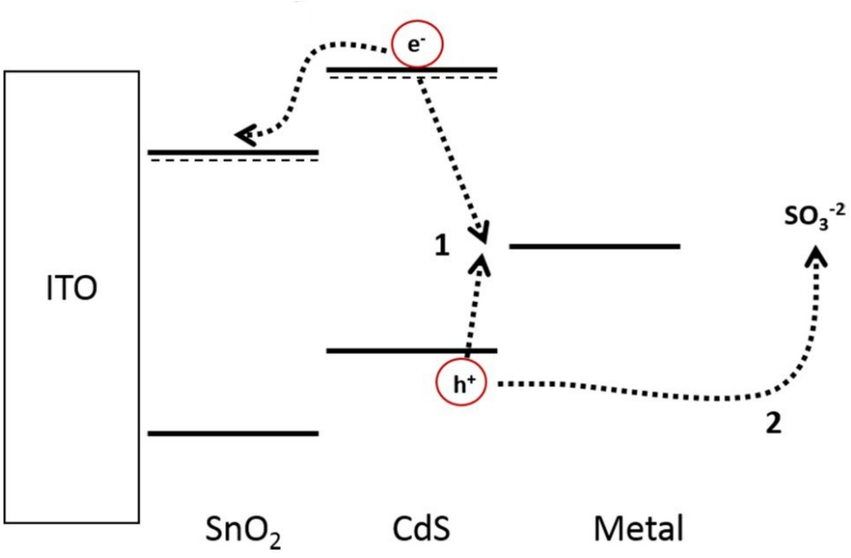


Fig. S10 Emission profile of the UV-Vis light source for photocatalytic reactions.



Scheme S1 Pathways of photogenerated electrons and holes at the junctions of CdS, metal, and an electrode surface in a 0.35 M Na_2SO_3/0.25 M Na_2S aqueous solution.

Table S1 Comparison of H_2 generation rates using CdS-based photocatalysts

Catalyst	Co-catalyst	Light Source	Hole Scavenger	H_2 generation ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	Q.Y. (%)	Ref
CdS	**Pt**	**300 W Xe**	**Na_2SO_3+Na_2S**	**80000**	**2.84***	**present**
CdS	Pt	300 W Xe	Na_2SO_3	5000	3.9*	1
CdS	Pt, CdSe	300 W Xe	Isopropyl alcohol	40000	20	2
CdS	Pd_4S	40 mW laser (405 nm)	Na_2SO_3+Na_2S	-	3.25	3
CdS	Au	40 mW laser (405 nm)	Na_2SO_3+Na_2S	-	6.3	4
CdS	Pt	300 W Xe	Na_2SO_3	-	1.7*	5
CdS	Pt	300 W Xe	Na_2SO_3+Na_2S	27333	60	6
CdS	$Ni(OH)_2$	300 W Xe	Na_2SO_3+Na_2S	5084	28	7
CdS	Pt	300 W Xe	Na_2SO_3+Na_2S	9357	22	8
CdS	Au	300 W Xe	Na_2SO_3+Na_2S	4000	-	9
CdS	Pt, Graphene	300 W Xe	Lactic acid	56000	22.5	10
CdS	Pt, CdSe	50 mW LED (455 nm)	Isopropyl alcohol	142000	99	11
CdS	Pt	400 W Hg	Formic acid	4460	13.9*	12
CdS	Pt, PdS	300 W Xe	Na_2SO_3+Na_2S	29230	93	13

* Quantum yield was calculated using a broad illumination source.

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