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Shape-Controlled Synthesis of Pd Nanoparticles for Effective Photocatalytic Hydrogen Production

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Supporting Information

Experimental

Chemicals and Materials

All the chemicals listed here were used as received, without further purification: Sodium tetrachloropalladate (Na_2PdCl_4, Aladdin, ⩾ 99.9%), Potassium bromide (KBr, Aladdin, ⩾ 99.5%), Sodium chloride (NaCl, Aladdin, ⩾ 99.5%), , Poly(vinylpyrrolidone) (PVP, K30， MW = 30,000) and N,N-dimethylformamide (DMF, Aladdin, ⩾ 99.9%), Cadmium sulfide (CdS, Energy Chemical, ⩾ 98%), Ammonium sulfite monohydrate Ammonium sulfite monohydrate ((($(NH_4)_2SO_3•H_2O$, Aladdin, ⩾ 94%), Perchloric acid ($HClO_4$, Perchloric acid ($HClO_4$, Aladdin, ⩾ 72%) and, 5% Nafion solution (Alpha). 5% Nafion solution (Alpha). Water used for all experiments was prepared using an ultra-pure purification system with resistivity conductivity of 18.20 MΩ*cm.

Catalyst preparation

Preparation of Pd NCs/CdS and Pd NOTs/CdS composite photocatalysts: 0.25 mg as-prepared Pd nanoparticles was dispersed in 100 mL water containing 0.05 g CdS photocatalysts (commercial product), and stirred for 2 h at room temperature. The resulting Pd/CdS composite was collected by centrifugation, washed and dried under vacuum at 60 °C.

Preparation of Pd nanospheres loaded CdS composite photocatalysts (Pd NSPs/CdS): For comparison, the third Pd/CdS composite photocatalyst was prepared using the photodeposition method. The photodeposited Pd metal particles formed irregular spherical nanoparticles (Pd NSPs) because they grew on the surface of CdS photocatalyst. In detail, 250 µL 1.0 mg/mL aqueous Na_2PdCl_4 solution containing 0.25 mg Pd was added into 100 mL water containing 0.05 g CdS photocatalyst (commercial product) and 0.125 mol of $(NH_4)_2SO_3$. The mixed solution was then transferred to a Pyrex glass reactor cell (Perfectlight Co., Labsolar-I). The system was vacuum-degassed and irradiated using a 300W Xe lamp (PLS-SXE300/300UV, Perfectlight Co.) equipped with a water filter to remove infrared light and an optical cutoff filter to eliminate the UV radiation (> 420 nm).).

Calculation of average sizes of Pd nanoparticles: The average particle sizes of Pd nanocubes and nanooctahedrons can be calculated based on Scherrer: $D = k\lambda/\beta\cos\theta$, where k is the Scherrer constant (= 0.89); D is the average particle diameter; β is the half width of a peak. θ is the diffraction angle of XRD. Finally, λ is the wavelength of X-ray (λ = 0.15418 nm). In order to achieve more accurate results, five XRD peaks were used for the calculation as shown in Table S1.

Table S1. Determination of Pd nanoparticle sizes for nanocubes and nanooctahedrons

	Particle Diameters from Five Peaks (nm)					Average D (nm)
	(111)	(100)	(220)	(311)	(222)	
Pd nanocube	9.33	9.80	9.95	10.09	11.01	10.04
Pd nanooctahedron	6.53	7.47	7.59	8.10	8.81	7.70

UV-Visible light absorption spectra of Pd colloidal solution:

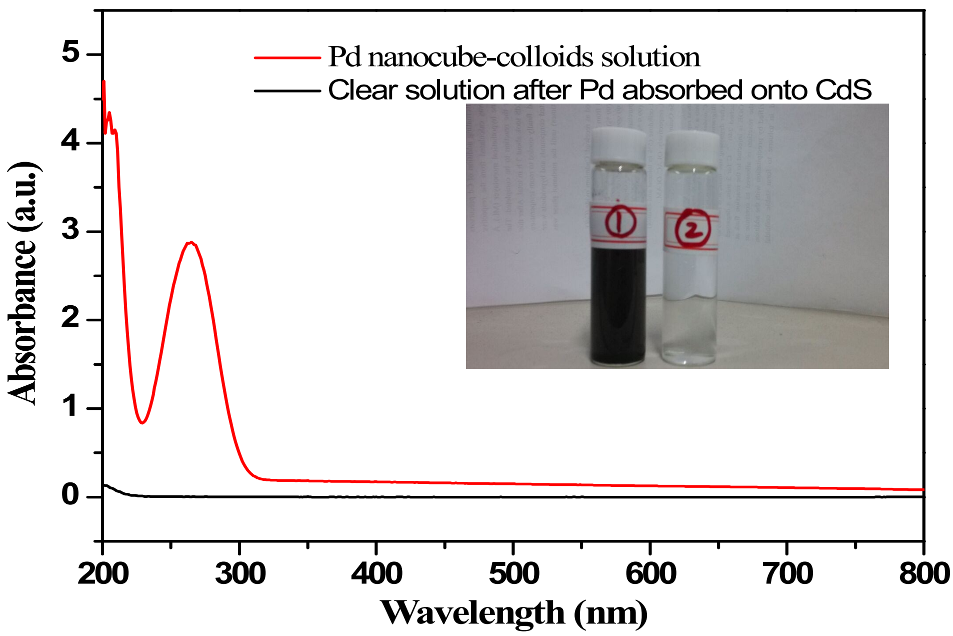

Figure S1. UV-visible absorption spectra of Pd colloidal solution and the clear solution after Pd nanoparticles were loaded onto CdS. Insert photo: Pd colloidal solution (1) and the clear solution after Pd nanoparticles were loaded onto CdS (2).

As shown in Figure S1, the prepared Pd colloidal solution is dark black in color. The A very strong UV-Vis absorption peak is shown at 264 nm. When CdS powder was mixed with the Pd colloidal solution Pd nanoparticles were absorbed onto the surface of CdS. After filtration, the remaining solution became clear and no featured UV-Vis absorption peak was observed. Comparing to the UV-Vis spectrum of pure water, this result indicates that Pd nanoparticles were completely deposited onto the surface of CdS particles using the technology reported in this research. Therefore, the Pd contents of Pd NCs/CdS, Pd NOTs/CdS can be calculated based on the mass of Pd nanoparticles suspended in the colloidal solution.