Supporting Information

Cooperative Selective Benzyl Alcohol Oxidation and Hydrogen Production over Pd₆(SC₁₂H₂₅)₁₂ Cluster-Coupled CdS Nanorods: The Key Role of Water in Photocatalytic Benzyl Alcohol Splitting

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Experimental section

Reagents

Potassium palladium (II) chloride (K₂PdCl₄), 4-tert-butyltoluene, CdCl₂·2.5H₂O, thiourea, dodecanethiol and ethylenediamine (EDA) were purchased from Macklin. Deionized (DI) water with a resistivity of 18.25 M Ω ·cm was used in all experiments. All the reagents in this experiment were analytical grade and used directly without further purification.

Synthesis of Pd₆(SC₁₂H₂₅)₁₂ clusters

 $Pd_6(SC_{12}H_{25})_{12}$ clusters were synthesized according to a reported method with some modifications.¹ $Pd_6(SR)_{12}$ clusters were prepared under air-free conditions. Typically, K_2PdCl_4 (2 × 10⁻³ mol), 10 mL of 4-tert-butyltoluene, and dodecanethiol (4 × 10⁻³ mol) were added sequentially to a 50 mL tube. The mixture was degassed and then flushed with argon several times. Subsequently, it was refluxed at 192 °C in a preheated oil bath for 1 h under an atmosphere of

argon. After that, the tube was removed from the oil bath and cooled down to room temperature. The obtained orange-red solution was then dropped into 100 mL of 95% ethanol under vigorous stirring. Orange precipitates and a few red oil droplets formed immediately. The system was ceaselessly stirred overnight so that the droplets also formed orange precipitates. The final product was collected by centrifugation, washed with ethanol several times, and finally dried at 60 °C under vacuum overnight.

Synthesis of CdS nanorods

CdS nanorods were prepared according to the literature with some modifications.² Typically, $CdCl_2 \cdot 2.5H_2O$ (0.074 g), thiourea (0.051 g), dodecylthiol (8 g) and EDA (3 g) were put into a Teflon-lined stainless-steel autoclave with a volume of 25 mL. The autoclave was then filled with toluene up to 70% of its volume and maintained at 160 °C for 40 h. After cooling to room temperature naturally, the product was collected by centrifugation, washed with toluene and anhydrous ethanol several times, respectively. Finally, the product was dried at 60 °C in vacuum oven for 24 h. The powder was obtained for further use and characterization.

Synthesis of Pd₆(SR)₁₂/CdS

Typically, a calculated amount of $Pd_6(SR)_{12}$ clusters was dissolved in 2.0 mL of dichloromethane, and then added dropwise to an ethanol suspension containing 50 mg CdS nanorods. After stirring at room temperature for 5 h, $Pd_6(SR)_{12}$ /CdS composites were collected by evaporating solvent under vacuum, and dried overnight at 60 °C. Finally, the obtained powder was annealed in Ar atmosphere at a heating rate of 5 °C/min and maintained at 150 °C for 1 h. After cooling to room temperature naturally, the final product was obtained for further use and characterization.

Characterizations

Powder XRD patterns were recorded by using a Bruker D8 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) images of the products were taken on a Hitachi HT7700 transmission electron microscope operated at 120 kV. The lattice fringe and selected area electron diffraction (SAED) were obtained by high resolution transmission (HRTEM) in Tecnai G2 (Thermo Fisher Scientific). The high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) images and the corresponding EDS mapping analyses images were collected on FEI Talos F200X (Thermo Fisher Scientific). The valence state of the element was detected by X-ray photoelectron spectroscopy, which were carried out on an ESCALAB 250Xi instrument with a monochromatic Al K α (hv = 1486.6 eV), the X-ray beam spot was 500 µm with the transmittance of 30 eV. The FT-IR spectrum was recorded from KBr pellets in the range of 4000-400 cm⁻¹ on a Prestige-21 SHIMADZU FT-IR spectrometer. The photocurrent measurements were performed on electrochemical station (CHI660E, Shanghai Chenhua Limited, China) with simulated solar light irradiation. The working electrode was prepared by dropping a mixed solvent of 2 mL ethanol and 10 μ L Nafion containing 2 mg of catalysts onto indium tin oxide (ITO)-coated glass. The photocurrent signals of the samples were measured under chopped light. The measurements were also carried out on a conventional three-electrode cell in 0.5 M Na₂SO₄ solution.

Ultrafast transient absorption (TA) spectroscopy characterizations

The femtosecond transient absorption (TA) spectra were acquired with a typical transmission pump-probe (UV/vis pump-broadband supercontinuum probe) instrument. A Ti:sapphaire

regenerative amplifier (Spitfire Ace, Spectra Physics, Inc.) produced laser pulses (6 mJ, 1 kHz) with a pulse width of 80 fs and center wavelength at 800 nm. The laser output was then split into several beams, one of which was used to generate wavelength-tunable light serving as the pump laser for TAS via a downstream optical parametric amplifier (TOPAS-Prime). In the current work, 400 nm was chosen as the center wavelength of the TOPAS-Prime output. The pump laser was attenuated to 160 nJ and chopped with a 500 Hz mechanical chopper. Another laser beam propagated through an optical delay line (0-8 ns) and was then focused into a CaF_2 crystal to produce white light continuum, which serves as the probe light in the fs-TA. The pump and probe light overlap in the sample cell with an optical path of 2 mm. All experiments were conducted at room temperature.

Computational methods

Density functional theory (DFT) calculations have been performed based on the Vienna ab initio simulation Package (VASP)^{3,4} with the projected augmented wave (PAW) method.⁵ The PBE functional⁶ is chosen and related plane wave basis set cut-off energy is set at the 420 eV based on a Monkhost-Pack k-point mesh of $3\times3\times1.^7$ The convergence criteria for electronic structure iteration and forces on each atom were set to 10^{-5} eV and 0.02 eV/Å, respectively. Grimme's DFT-D3 scheme of dispersion correction was adopted to describe van der Waals (vdW) interactions in the systems.⁸ To avoid the interlayer interaction introduced by the periodic boundary condition, a sufficient 40 Å vacuum was applied in the z direction. Charge transfer and quantitative descriptions are effective approaches to investigate the interaction mechanism. Bader charge analysis was carried out to obtain the quantitative description of charge transfer.⁹ All the visualization of the charge density difference distribution was performed in the VESTA software.¹⁰

In the periodic calculation, we constructed a supercell model of $4 \times 4 \times 2$ CdS. To simplify our models and improve the computational efficiency, for model of $Pd_6(SR)_{12}$ cluster, the SR (R = CH₃) group was used as a substitute of 1-dodecanethiol ligand to form the model clusters. According to our test calculations, the simplified cluster does not affect the binding strength of the benzyl alcohol molecule, so only the result of R = CH₃ is shown here.

Photocatalytic hydrogen production coupled with selective benzyl alcohol oxidation measurements

The photocatalytic experiments were performed in a 100 mL reaction cell connected to a gasclosed glass vacuum system. Typically, 5 mg of the photocatalyst was suspended in a mixed solvent containing 8 mL of CH₃CN, 8 mL of H₂O and 2 mL benzyl alcohol. A 300 W Xe lamp with a 400 nm cutoff filter and full solar spectral band reflector was used as the light source. **The light intensity during the photocatalytic H₂ production was 35 mW cm⁻².** During the photocatalytic process, the reaction system was vigorously stirred with a magnetic stirrer, and the reaction temperature was controlled at 6 °C by circulating cooling water. The amount of hydrogen produced from the photocatalytic reaction was sampled and quantified by gas chromatography with Ar as the carrier gas.

Photocatalytic hydrogen production with TEOA as hole sacrificial reagent

The photocatalytic experiments were performed in a 100 mL reaction cell connected to a gasclosed glass vacuum system. Typically, 5 mg of the photocatalyst was suspended in a mixed solvent containing 2 mL of triethanolamine (TEOA) and 8 mL of H_2O . A 300 W Xe lamp with a 400 nm cutoff filter and full solar spectral band reflector was used as the light source. **The light** intensity during the photocatalytic H₂ production was 35 mW cm⁻². During the photocatalytic process, the reaction system was vigorously stirred with a magnetic stirrer, and the reaction temperature was controlled at 6 °C by circulating cooling water. The amount of hydrogen produced from the photocatalytic reaction was sampled and quantified by gas chromatography with Ar as the carrier gas.

Photocatalytic splitting of alcohols into hydrogen and corresponding aldehyde compounds over a $Pd_6(SR)_{12}/CdS$ Photocatalyst

The photocatalytic experiments were performed in a 100 mL reaction cell connected to a gasclosed glass vacuum system. Typically, 5 mg of the photocatalyst was suspended in a mixed solvent containing 2 mL of benzyl alcohol and 8 mL of CH_3CN . A 300 W Xe lamp with a 400 nm cutoff filter and full solar spectral band reflector was used as the light source. **The light intensity during the photocatalytic H₂ production was 35 mW cm⁻²**. During the photocatalytic process, the reaction system was vigorously stirred with a magnetic stirrer, and the reaction temperature was controlled at 6 °C by circulating cooling water. The amount of hydrogen produced from the photocatalytic reaction was sampled and quantified by gas chromatography with Ar as the carrier gas.

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Figure S1. (a) Total molecular structure and (b) Tiara-like Pd_6S_{12} kernel of $Pd_6(SC_{12}H_{25})_{12}$ clusters.



Figure S2. FTIR spectra of 1-dodecanethiol ligands and $Pd_6(SC_{12}H_{25})_{12}$ clusters: (a) survey spectra and (b) enlarged spectra. (c) UV-Vis absorption spectrum of as-prepared $Pd_6(SC_{12}H_{25})_{12}$ clusters.



Figure S3. (a) ¹H NMR of 1-dodecanethiol ligands and $Pd_6(SR)_{12}$ clusters. the NMR peak of the protons from C are significantly broadened and shift to downfield in the rectangle area, confirming the formation of Pd-S bond. (b) ESI-MS profile of the clusters.



Figure S4. (a) XRD patterns and (b) UV-vis absorption spectra of pristine CdS and $Pd_6(SR)_{12}/CdS$.



Figure S5. XPS analyses of the as-obtained $Pd_6(SR)_{12}/CdS$: (a) survey spectrum, (b) Cd 3d, (c) S 2p and (d) Pd 3d.



Figure S6. FTIR spectra of the as-obtained Pd₆(SR)₁₂/CdS and Pd₆(SR)₁₂.



Figure S7. Mass spectra of the obtained liquid-products in acetonitrile solution of benzyl alcohol using $Pd_6(SR)_{12}/CdS$ as catalyst: (a) with water and (b) without water. (c) Mass spectrum of the obtained liquid-products in acetonitrile solution of benzyl alcohol using CdS as catalyst.



Figure S8. BA relative conversion ratios in the photocatalytic H₂ evolution coupled to highly selective oxidation of benzyl alcohol without and with water. Reaction conditions: 5.0 mg of the Pd₆(SR)₁₂/CdS, 2 mL of benzyl alcohol, 8 mL of CH₃CN; or 2 mL of benzyl alcohol, 8 mL of CH₃CN and 8 mL of water. Visible light ($\lambda > 400$ nm) irradiation for 6 h at room temperature.



Figure S9. The photocurrent responses of CdS and $Pd_6(SR)_{12}/CdS$ in aqueous solution of triethanolamine.



Figure S10. TA mapping of $Pd_6(SR)_{12}/CdS$ nanorods in glycol solution of triethanolamine (a) and corresponding representative time delays spectra (b).



Figure S11. Reaction pathways for benzyl alcohol decomposition using $Pd_6(SR)_{12}/CdS$ as catalyst with and without water.



Figure S12. (a) XRD pattern and (b) TEM image of the as-obtained $Pd_6(SR)_{12}/CdS$ photocatalyst after long-term stability test.

Catalysts	Reaction Conditions	Hydrogen generation rate (µmol h ⁻¹ g ⁻¹)	Light Source	Refs.
Pd ₆ (SR) ₁₂ /CdS	Benzyl alcohol	51667	$\lambda > 400 \text{ nm}$	This work
CdS/SiO ₂	benzyl alcohol	17900	300 W Xe	ACS Catal. 2020,
			lamp	10, 14327–14335.
Au@Pt@CdS	benzyl alcohol	160	$\lambda > 420 \text{ nm}$	Chem. Sci. 2019, 10, 3514-3522.
$CdS@ZnS_x@CoS_x\\$	Na2S(0.25M)/Na2SO3(0.35	3920	300 W Xe	Angew. Chem. Int.
	M)		lamp	<i>Ed.</i> 2020 , <i>59</i> , 3287 –
				3293.
CdS@Au/MXene	Lactic acid	5371	$\lambda > 420 \text{ nm}$	ACS Catal. 2021,
				<i>11</i> , 8510–8520.
CdS/UiO-66	lactic acid	14047	$\lambda > 380 \text{ nm}$	ACS Catal. 2018, 8,
C10/C-0	N- C/N- CO	20200	1 > 420	11615-11621
CdS/CoS _x	Na_2S/Na_2SO_3	39200	$\lambda > 420 \text{ nm}$	Angew. Chem. Int.
UT-9-C-N	Glucose	12160	$\lambda > 420 \text{ nm}$	Ed. 2020. 39. 3287. Adv. Mater. 2021
01 5 0314	Glucose	12100	<i>R</i> + 120 mm	2101751.
Co/NGC@ZIS	TEOA	11270	$\lambda > 420 \text{ nm}$	Adv. Mater. 2019,
				1903404.
Sv-ZnIn ₂ S ₄ /MoSe ₂	ascorbic acid	63210	$\lambda > 420 \text{ nm}$	Nat. Commun. 2021,
				<i>12</i> , 4112.
RhPx/g-C-N-5%	τεοα	3055	$\lambda > 420 \text{ nm}$	ACS Catal 2020
	ILON	5055	<i>R</i> + 120 mm	10. 458–462.
TpDTz COF	TEOA	941	AM 1.5	J. Am. Chem. Soc.
				2019 , <i>141</i> , 11082.
CTF-BT/Th-1	TEOA	6600	$\lambda > 420 \text{ nm}$	Angew. Chem. Int.
				Ed. 2019, 131, 8768.
Pt-PVPTP-COF	ascorbic acid	8420	300 W Xe	Angew Chem Int
11-1 11 11-001		0420	lamp	Ed 2019 58 18290
			imith	2012 2012, 200, 102,01
ter-CTF-0.7	TEOA	19300	$\lambda > 420 \text{ nm}$	ACS Catal. 2019, 9,
				9438.
CTF-HUST-A1	TEOA	9200	$\lambda > 420 \text{ nm}$	Angew. Chem. Int.
				Ed. 2020, 59, 6007.
ACN14	benzyl alcohol	820	AM 1 5	Angew Chem Int
1101111		020	111111.0	<i>Ed.</i> 2021 . <i>60</i> . 4815
				,,,,,

Table S1. Comparison of photocatalytic H_2 production performances of $Pd_6(SR)_{12}/CdS$ with various photocatalysts reported in the literatures.

PA-Ni@PCN	MeOH	2560	AM 1.5	Angew. Chem. Int.
				<i>Ed.</i> 2021 , <i>133</i> , 5305.