Electronic Supplementary Information (ESI)

What is the better choice of Pd cocatalysts for photocatalytic reduction of CO₂ into renewable fuels: high-crystallinity or amorphous?

Qin Chen,^{ab} Shijie Wu,^b Shuxian Zhong,^{*a} Binjia Gao,^b Weijun Wang,^b Weihao Mo,^{ab} Hongjun Lin,^a Xiaoxuan Wei,^{*a} Song Bai^{*ab} and Jianrong Chen^{*ab}

^{*a*} College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, P. R. China.

^b Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, P. R. China

Additional experimental

Chemicals. $Pd(acac)_2$ (Aladdin, P101065), $Mo(CO)_6$ (Energy Chemical, E060813), n-octanoic acid (Aladdin, 0108279), trioctylphosphine oxide (TOPO, Sigma-Aldrich, 223301), $CdCl_2 \cdot 2.5H_2O$ (Aladdin, C118631) and oleylamine (OAm, Aladdin, O106967) were used in the synthesis. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water used in all experiments was de-ionized water prepared by passing through an ultra-pure purification system.

Synthesis of CdS quantum dots. In a typical procedure for the synthesis of CdS quantum dots,^{S1} 1 mmol of CdCl₂·2.5H₂O and 5 mL of oleylamine were kept in a three-necked round-bottom flask followed by degassing at 80 °C for 15 min under Ar. The temperature of the reaction flask was allowed to reach 100 °C, and Ar purging was continued for another 30 min. Thereafter the temperature was increased to 170 °C when the Cd-oleylamine complex was formed. The sulfur-oleylamine solution (1 mmol sulfur in 2.5 mL oleylamine) was then injected to the above solution at 170 °C and aged for 70 min, whereupon the flask was cooled down to room temperature. The product was precipitated with 10 mL isopropanol/ethanol (v/v = 1 : 1), and the product were separated by 10,000 rpm centrifugation for 5 min. The resulting precipitates were washed with ethanol for three times and dispersed in 10 mL of chloroform/ethanol mixture (v/v = 1 : 1.5).

Sample characterizations. Transmission electron microscopy (TEM), highresolution TEM (HRTEM) and scanning TEM (STEM) images were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. Powder X-ray powder diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer with Non-monochromated Cu-K α X-Ray. X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-K α X-ray as the excitation source. UV-vis-NIR diffuse reflectance data were recorded in the spectral region of 200-800 nm with a Shimadzu SolidSpec-3700 spectrophotometer. Photoluminescence (PL) spectra were recorded on a HITACHIF-7000 spectrofluorometer with the excitation wavelength of 370 nm. Isotope-labeling experiments were performed using ¹³CO₂, and the products were analyzed using gas chromatography-mass spectrometry (7890B/5977A, Agilent).



Fig. S1 TEM images of Pd nanosheets: (a) Pd-48, (b) Pd-60, (c) Pd-80 and (d) Pd-100.



Fig. S2 (a) TEM image of CdS quantum dots; (b) size distribution histograms and average size of CdS quantum dots.



Fig. S3 Low-magnified TEM images of CdS-Pd samples: (a) CdS-Pd-48, (b) CdS-Pd-60, (c) CdS-Pd-80 and (d) CdS-Pd-100.



Fig. S4 Survey XPS spectra of CdS-Pd samples.



Fig. S5 TEM images of CdS-Pd-48 after the photocatalytic cyclic process.



Fig. S6 (a) XRD patterns of CdS-Pd-48 before and after the photocatalytic cyclic process; (b-d) XPS spectra of CdS-Pd-48 before and after cyclic process: (b) Cd3d, (c) S2p and (d) Pd3d high-resolution spectra.



Fig. S7 TEM images of (a) CdS-Pd-60, (b) CdS-Pd-80 and (c) CdS-Pd-100 after the photocatalytic reactions.



Fig. S8 UV-vis absorption spectra of chloroform suspensions containing Pd-48, Pd-60, Pd-80 and Pd-100; inset is the photograph of chloroform suspensions containing Pd-48, Pd-60, Pd-80 and Pd-100.



Fig. S9 Relative energies of 10 possible interaction systems for the adsorption of CO_2 on the amorphous Pd (111) surface. The adsorption system with the lowest energy (No. 7) was set as a fiducial value.

Table S1 Optimized geometries for CO_2 and the supercells of high-crystallinity and amorphous Pd. q_C and q_O stands for the atomic charge on C and O. Peacock blue: Pd; Dark gray: C; Red: O.



Table S2 Optimized geometries and potential interaction sites on the (111) surface of high-crystallinity and amorphous Pd. Peacock blue: Pd; Red: potential interaction sites; Blue: structural unit.



Table S3 Optimized geometries of 10 possible interaction systems for the adsorption of CO₂ on the amorphous Pd(111) surface. L, \angle and q stands for the bond length, bond angle and atomic charge, respectively. Peacock blue: Pd; Dark gray: C; Red: O.



$$q_{\rm C} = 0.01 \ e; q_{\rm O} = -0.15 \ e, -0.15 \ e$$

CO₂-Pd_{amor} (111)-3

Table S3 (Continued) Optimized geometries of 10 possible interaction systems for the adsorption of CO_2 on the amorphous Pd (111) surface.



$$L_{\text{C-O}} = 1.29$$
 Å, 1.29 Å; $\angle_{\text{O-C-O}} = 124.89^{\circ}$
 $q_{\text{C}} = -0.01 \ e; \ q_{\text{O}} = -0.15 \ e, \ -0.15 \ e$
CO₂-Pd_{amor} (111)-6

Table S3 (Continued) Optimized geometries of 10 possible interaction systems for the adsorption of CO_2 on the amorphous Pd(111) surface.





Table S3 (Continued) Optimized geometries of 10 possible interaction systems for the adsorption of CO_2 on the amorphous Pd(111) surface.



Table S4 Comparison of the photocatalytic enhancement of Pd-48 in CO_2 reduction over CdS with those of previously reported cocatalysts.

Semiconductor	Cocatalyst	CO enhancement	CH ₄ enhancement	CO ₂ selectivity	Ref
CdS	Δσ	3 1		2 3	43
Cub	115	5.1		2.5	75
CdS	Reduced graphene		12.0	—	44
	oxide				
CdS	N-doped graphene	4.0	5.0	—	45
CdS	Reduced graphene	8.0	_	4.2	46
	oxide/Ag				
CdS	Pd-48	10.3	5.9	3.0	\star

*The photocatalytic enhancement of Pd-48 reported by us.

Reference

S1 G. Halder and S. Bhattacharyya, J. Phys. Chem. C, 2015, 119, 13404.