Supporting Information

Ultrathin CdS shell sensitized hollow S-doped CeO₂ spheres for efficient

visible-light photocatalysis

Ning-Chao Zheng,^{a,b} Ting Ouyang,^a Yibo Chen,^a Zhu Wang, ^{*a,b} Di-Yun Chen,^b Zhao-Qing Liu,^{*a}

^aSchool of Chemistry and Chemical Engineering/Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China.

^bSchool of Environmental Science and Engineering/Guangdong Provincial Key Laboratory for Radionuclides Pollution Control and Resources, Guangzhou University, Guangzhou 510006, China.

Email: wangzhu@gzhu.edu.cn (Z. Wang); lzqgzu@gzhu.edu.cn (Z. Q. Liu)

Experimental section

1. Preparation of CdS nanoparticles

The CdS nanoparticles were synthesized by a simple hydrothermal method. In details, $0.66 \text{ g Cd}(Ac)_2 \cdot 2H_2O$ and 1.22 g CH_4N_2S were added into 40 mL distilled water to form a transparent solution with constant stirring. Then, the mixture was transferred into 25 mL stainless steel Teflon lined autoclave to undergo hydrothermal treatment at 140 °C for 24 h. After the reaction vessel was cooled down to 25 °C, the sample was collected by filtration and dried at 80 °C overnight, the SEM of CdS nanoparticles are presented in **Fig. S1f**.

2. Catalytic performance measurements

2.1. Photoelectrochemical performance evaluation

Photoelectrochemical performance was measured on an electrochemical workstation (CHI 760D, China Chenhua) equipped with a standard three-electrode cell. The as-prepared photoanodes, Ag/AgCl electrode and Pt sheet ($1 \times 1 \text{ cm}^2$) were used as working electrode, reference electrode, and counter electrode, respectively.

A mixture solution of 0.25 M Na₂S + 0.35 M Na₂SO₃ was employed as the electrolyte. A 300 W Xe lamp with a 420 nm cut-off optical filter was performed as visible-light source. The preparation of working electrode as followed: at first 2.5 mg the photocatalyst was evenly dispersed in the mixture of 0.5 mL ethanol and 20 μ L Nafion to form slurry. After that the slurry was coated onto a clean fluorine-doped tin oxide (FTO, 1.5 cm × 1.5 cm). Then, this working electrode was dried in an oven at 80 °C for 10 h.

2.2. Photocatalytic H₂ evolution activity evaluation

The photocatalytic H₂ evolution experiments were performed in a 250 mL quartz reactor at 5 °C. The reactor was connected to a low-temperature thermostat bath. A 300 W Xe lamp with a 420 nm cut-off optical filter was used as the visible-light source. In a typical photocatalytic experiment, 100 mg of photocatalyst powder was dispersed in 100 mL of aqueous solution containing 0.25 M of Na₂S + 0.35 M Na₂SO₃ solution. Before irradiation, the reactor was purged by Ar gas for 30 min in order to completely remove the air dissolved in the electrolyte and ensured the reaction system in an anaerobic condition. The obtained final products were analyzed by gas chromatograph (GC-14C, Shimadzu, Japan, high purity argon as a carrier gas, 99.99%) equipped with a thermal conductivity detector (TCD).

2.3. Photocatalytic dye degradation performance evaluation

The photocatalytic performance of the as-prepared photocatalyst was also evaluated by the photodegradation of rhodamine B (RhB) solution under visible-light illumination. Generally, 20 mg photocatalyst was dispersed in 50 mL of RhB solution (15 mg L⁻¹). Then, the mixture was stirred vigorously in dark for 20 min to reach the adsorption-desorption equilibrium. Next, the mixture was irradiated with visible-light. At different pre-set time interval, 4 mL of solution was taken out and centrifuged to separate solid particles. The concentration of the RhB solution (before and after degradation) was analyzed by a UV-vis absorption spectrometer at 554 nm. The degradation efficiency (%) of RhB solution was calculated by the following equation:

Degradation efficiency (%) = $(C_0 - C_t)/C_0 \times 100\%$

where C_0 is the initial concentration of RhB (15 mg L⁻¹), C_t is the concentration of RhB at different intervals during the degradation process.

Equation S1:

$$[Ce^{3+}] = \frac{S_{v'} + S_{u'}}{\sum (S_v + S_u)}$$

where S is the integrated area corresponding to peak v' or u'.

Photocatalytic degradation evaluation

The photocatalytic activity of the as-prepared photocatalyst was further conducted by the degradation of RhB under visible-light irradiation. The photodegradation efficiency of RhB was found to be 99.8% within 25 min (Fig. S8). The CeO₂ hollow spheres exhibited only about 14.9% degradation efficiency of RhB. The trend of degradation efficiency is $CeO_{2-x}S_x@CdS > CdS > CeO_{2-x}S_x > CeO_2$. The photocatalytic activity of the $CeO_{2-x}S_x@CdS$ nanocomposites is apparently higher than that of the other samples. The enhanced photocatalytic activity is in accordance with the photocatalytic H₂ evolution activity, which is induced by the successful doping of sulfur and coating of CdS shell.



Fig. S1 SEM images of as-synthesized samples: (a) SiO_2 , (b) $SiO_2@CeO_2$, (c) Hollow CeO_2 , (d) Hollow $CeO_{2-x}S_x$, (e) Hollow $CeO_{2-x}S_x@CdS$ and (f) CdS spheres.



Fig. S2 EDX spectrum of the $CeO_{2-x}S_x@CdS$ photocatalyst.



Fig. S3 Nitrogen adsorption-desorption isotherm of the CeO_2 , $CeO_{2-x}S_x$, CdS and $CeO_{2-x}S_x$ @CdS photocatalysts (the inset shows their BET surface areas).



Fig. S4 XPS survey spectrum of the CeO₂, CeO_{2-x}S_x and CeO_{2-x}S_x@CdS photocatalysts.



Fig. S5 ESR spectra of CeO₂, CeO_{2-x}S_x, and CeO_{2-x}S_x@CdS.



Fig. S6 (a) UV-visible diffuse absorption spectra, (b) EIS Nyquist plots, (c) Photocatalytic degradation of RhB solution (20 mg samples; 50 mL, 15 mg L^{-1} RhB solution) and (d) Hydrogen evolution rates of the as-prepared samples.



Fig. S7 (a) UV-visible diffuse absorption spectra, (b) EIS Nyquist plots, (c) Photocatalytic degradation of RhB solution (20 mg samples; 50 mL, 15 mg L^{-1} RhB solution) and (d) Hydrogen evolution rates of the as-prepared samples.

In order to investigate the influence of sulfur content in $CeO_{2-x}S_{x}$, various mass of (2, 4, 6 and 8 g) CH₄N₂S was transferred to the square combustion boat and heated under a nitrogen flow at 500 °C for 2 h. The as-prepared samples were denoted as $CeO_{2-x}S_x$ -2, $CeO_{2-x}S_x$ -4, $CeO_{2-x}S_x$ -6 and $CeO_{2-x}S_x$ -8, respectively. It could be observed that the gradually enhanced visible light absorption range with the various content of S-doping (**Fig. S6a**). In all the samples, $CeO_{2-x}S_x$ -8 possessed the mostly widely spectral response in visible light wavelength. However, the EIS Nyquist plots revel that the lowest R_{ct} of the $CeO_{2-x}S_x$ -6, illustrating that the optimal mass of CH₄N₂S is 6.0 g (**Fig. S6b**). This result was further demonstrated by the degradation of RhB and photocatalytic H₂ generation under visible light irradiation. As shown in **Fig. S6c** and **d**, it can be seen that the $CeO_{2-x}S_x$ -6 sample possessed the fastest degradation efficiency and the highest hydrogen production activity.

In order to estimate the influence of CdS content in the $CeO_{2-x}S_x@CdS$, various

mole of (0.01, 0.03, 0.05 and 0.07 M) (CH₄N₂S + CdN₂O₆·4H₂O) was dissolved in the solution (100 mL distilled water + 100 mg CeO_{2-x}S_x-6 sample) and undergo reflux condensation at 90 °C with stirring for 1 h. The as-prepared samples were denoted as CeO_{2-x}S_x@CdS-1, CeO_{2-x}S_x@CdS-3, CeO_{2-x}S_x@CdS-5, CeO_{2-x}S_x@CdS-7, respectively. It is clearly observed that all samples show a wide optical adsorption range at about 560 nm and without distinct red shift occurred (**Fig. S7a**). However, the EIS Nyquist plots revel that the lowest R_{ct} of the CeO_{2-x}S_x@CdS-5 (**Fig. S7b**). Meanwhile, the CeO_{2-x}S_x@CdS-5 exhibits the fastest degradation efficiency and the highest hydrogen evolution rate under visible light irradiation (**Fig. S7c** and **S7d**). These results illustrate that the optimal mole of CH₄N₂S and CdN₂O₆·4H₂O is 0.05 M.



Fig. S8 (a) Photocatalytic degradation of RhB solution, (b) degradation efficiency of the asprepared four photocatalysts under visible-light illumination, (c) Plot of In (C_0/C_t) vs. illumination time (min) for RhB degradation and (d) degradation rate constant of the four photocatalysts (20 mg samples; 50 mL, 15 mg L⁻¹ RhB solution).

In order to investigate the main active species contributed to the photocatalytic degradation activity, a series of radicals and holes trapping experiments were designed on $CeO_{2-x}S_x@CdS$ photocatalyst. Isopropanol (IPA), p-benzoquinone (BQ), ammonium oxalate (AO) and AgNO₃ scavengers were used to study the roles of \cdot OH, O_2^- , h⁺ and e⁻ radicals, respectively.^{1,2} It can be observed that the addition of IPA, AO and AgNO₃ in the RbB solution respectively has little effect on the photocatalytic activity of CeO_{2-x}S_x@CdS photocatalyst (Fig. S9a), indicating that \cdot OH, h⁺ and e⁻ cannot play a vital role for the degradation of RhB. On the contrary, the photocatalytic activity of RhB is obviously restrained after the addition of BQ, demonstrating that the O_2^- is actually the reactive species. Fig. S9b shows the degradation rate of different organic pollutants on the $CeO_{2-x}S_x@CdS$ photocatalyst. It can be clearly seen that the $CeO_{2-x}S_x@CdS$ has an excellent photocatalytic degradation of rhodamine B (RhB) and methylene blue (MB) under visible-light irradiation, but has little effect on the degradation of methyl orange (MO) and amaranth (AR27), indicating that the $CeO_{2-x}S_x@CdS$ photocatalyst has a selective degradation of organic pollutants.



Fig. S9 (a) Time course of the photodegradation of RhB over $CeO_{2-x}S_x@CdS$ in the presence of various radical scavengers, and (b) photocatalytic degradation of different organic pollutants by $CeO_{2-x}S_x@CdS$ photocatalysts (20 mg samples; 50 mL, 15 mg L⁻¹ RhB solution).



Fig. S10 (a) Adsorption spectra of RhB solution in the presence of $CeO_{2-x}S_x@CdS$ photocatalysts at different intervals, and (b) Cycling runs of the $CeO_{2-x}S_x@CdS$ photocatalysts for the degradation of RhB solution under visible-light illumination (20 mg samples; 50 mL, 15 mg L⁻¹ RhB solution).

In order to obtain a visualized observation for photocatalytic degradation of RhB, UV-vis absorption spectra of the RhB up to 25 min irradiation using $CeO_{2-x}S_x@CdS$ photocatalyst was provided, and the characteristic absorption peak of RhB at 554 nm was selected to monitor the photocatalytic degradation process (**Fig. S10a**). It is clear that the curves have one absorption peak and the peak intensity decrease rapidly with a distinct blue shift, indicating the RhB have been decomposed to small molecule species. This result is consistent with the color change of the reaction solution (**Fig. S10a** inset). Moreover, the cycling stability of the $CeO_{2-x}S_x@CdS$ photocatalyst was also studied (**Fig. S10b**). It is evident from the data that the $CeO_{2-x}S_x@CdS$ retains high photocatalytic activity after four cycles, indicating good stability for practical applications.



Fig. S11 Kubelka-Munk plots converted from the absorption spectrum of (a) $CeO_{2-x}S_x$ hollow sphere and (b) CdS nanosphere. Mott-Schottky plots of (c) $CeO_{2-x}S_x$ hollow sphere and (d) CdS nanosphere.

Peak position (eV)								
	Ce 3d _{5/2}				Ce 3d _{3/2}			
Catalyst	V	V^{I}	V^{II}	V^{III}	U	U^{I}	U^{II}	U^{III}
CeO ₂	883.9	/	888.5	899.5	902.8	/	907.8	916.6
$CeO_{2-x}S_x$	882.5	885.0	886.9	900.3	902.7	904.4	906.4	916.2
CeO _{2-x} S _x @CdS	882.3	885.1	886.8	899.7	902.5	904.1	906.2	916.2

Table S1. The XPS analysis results for the CeO₂, CeO_{2-x}S_x and CeO_{2-x}S_x@CdS samples.

Sample	Short lifetime	Long lifetime			Average lifetime
	$\text{component}\tau_1$	component	A1(%)	A ₂ (%)	component τ
	(ns)	τ_2 (ns)			(ns)
CeO ₂	0.867	18.298	54.29	45.71	17.369
$CeO_{2-x}S_x$	0.695	15.950	54.90	45.10	15.182
CeO _{2-x} S _x @CdS	0.486	9.203	74.62	25.38	8.031

Table S2. Fitting results of time-resolved PL spectra for as-prepared samples.

Table S3. Comparison of photocatalytic H_2 evolution for various photocatalysts.

Photocatalyst Light source		Sacrifical	H_2 generation	Ref. (year)
		reagent	(µmol h ⁻¹ g ⁻¹)	
	300 W Xe-	0.25 M Na ₂ S		
CeO _{2-x} S _x @CdS	lamp $\lambda \ge 420 \text{ nm}$	$0.35 \text{ M} \text{ Na}_2 \text{SO}_3$	1147.2	This work
	300 W Xe-	10 vol.%		
$c-CeO_2/g-C_3N_4$		TEOA	860	3 (2017)
	<i>λ</i> ≥ 420 nm			
	300 W Xe-	10 vol.%		
0.5% Au-CNSs	$\lambda \ge 420 \text{ nm}$	lactic acid	601.2	4 (2016)
	300 W Xe-	$0.1 \text{ M} \text{ Na}_2\text{S}$		
Au@CdS	lamp $\lambda \ge$ 420 nm	$0.1 \text{ M} \text{ Na}_2 \text{SO}_3$	180	5 (2014)
CdSODs-AuNps-	500 W Xe-	$0.1 \text{ M} \text{ Na}_2\text{S}$		
	lamp λ > 420 nm	0.1 M Na ₂ SO ₃	550	6 (2013)
6%@PW12	λ≥ 420 mm			
	500 W Xe-	lactic acid	369	7 (2014)
CdS/WO ₃ -20	$\lambda > 400 \text{ nm}$			/ (===:)
	300 W Xe-	0.5 M Na ₂ S		
CdS-3% Co ₃ O ₄	lamp		236	8 (2015)
	$\lambda \ge$ 420 nm	0.5 IVI Na ₂ SO ₃		- ·
6.8% mol	500 W/ Xo	25 vol.%		
	lamp		61	9 (2014)

Co(OH) ₂ /CdS	300 W Xe-	ethanol		
	lamp	10 vol.%	447.7	10 (2014)
g-C ₃ N ₄ /NiS-1.5	$\lambda \ge 420$ IIII	TEOA		
$a \in \mathbb{N}$ (7nS 20 wt%)	lamp	0.25 M Na ₂ S	713.6	11 (2018)
g C3N4/2113 20 Wt/0/	$\lambda \ge 420 \text{ nm}$	$0.35 \text{ M} \text{ Na}_2 \text{SO}_3$		
CdS/Au/ZnO	lamp	0.1 M Na ₂ S	608	12 (2013)
	λ ≥ 420 mm 300 W Xe-	$0.1 \text{ M} \text{ Na}_2 \text{SO}_3$		
Δu-Pt-CdS	lamp	0.25 M Na ₂ S	778	13 (2016)
	$\lambda \ge 420 \text{ nm}$	$0.35 \text{ M} \text{ Na}_2 \text{SO}_3$		

References

- 1 C. J. Zhou, J. Yan, B. H. Chen, P. R. Li, X. P. Dong, F. N. Xi, J. Y. Liu, *RSC Adv.*, 2016, **6**, 108955–108963.
- 2 G. Rajender, J. Kumar, P. K. Giri, Appl. Catal., B, 2018, 224, 960–972.
- 3 W. X. Zou, Y. Shao, Y. Pu, Y. D. Luo, J. F. Sun, K. L. Ma, C. J. Tang, F. Gao, L. Dong, *Appl. Catal., B*, 2017, **218**, 51–59.
- 4 P. Y. Kuang, P. X. Zheng, Z. Q. Liu, J. L. Lei, H. Wu, N. Li, T. Y. Ma, *Small*, 2016, **12**, 6735–6744.
- 5 X. Ma, K. Zhao, H. Tang, Y. Chen, C. Lu, W. Liu, Y. Gao, H. Zhao, Z. Tang, *Small*, 2014, **10**, 4664–4670.
- 6 X. L. Xing, R. J. Liu, X. L. Yu, G. J. Zhang, H. B. Cao, J. N. Yao, B. Z. Ren, Z. X. Jiang, H. Zhao, J. Mater. Chem. A, 2013, 1, 1488–1494.
- 7 L. J. Zhang, S. Li, B. K. Liu, D. J. Wang, T. F. Xie, ACS Catal., 2014, 4, 3724–3729.
- 8 J. Yuan, J. Wen, Q. Gao, S. Chen, J. Li, X. Li, Y. Fang, *Dalton Trans.*, 2015, **44**, 1680–1689.
- 9 L. J. Zhang, R. Zheng, S. Li, B. K. Liu, D. J. Wang, L. L. Wang, T. F. Xie, ACS Appl. Mater. Interfaces, 2014, 6, 13406–13412.
- 10 Z. H. Chen, P. Sun, B. Fan, Z. G. Zhang, X. M. Fang, J. Phys. Chem. C, 2014, 118,

7801-7807.

- 11 X. Q. Hao, J. Zhou, Z. W. Cui, Y. C. Wang, Y. Wang, Z. G. Zou, *Appl. Catal., B*, 2018, **229**, 41–51.
- 12 Z. B. Yu, Y. P. Xie, G. Liu, G .Q. Lu, X. L. Ma, H. M. Cheng, *J. Mater. Chem. A*, 2013, **1**, 2773–2776
- 13 L. Ma, K. Chen, F. Nan, J. H. Wang, D. J. Yang, L. Zhou, Q. Q. Wang, *Adv. Funct. Mater.*, 2016, **26**, 6076–6083.