

**Facile synthesis of CeO₂ nanoparticles sensitized CdS nanorods
photocatalyst with improved visible-light photocatalytic degradation
of Rhodamine B**

Shansi Gu ^{a, b}, Yaoning Chen ^{a, b, *}, Xingzhong Yuan ^{a, b, c, **}, Hou Wang ^{a, b}, Xiaohong
Chen ^c, Yang Liu ^{a, b}, Qian Jiang ^{a, b}, Zhibin Wu ^{a, b}, Guangming Zeng ^{a, b}

^a College of Environmental Science and Engineering, Hunan University, Changsha
410082, PR China

^b Key Laboratory of Environment Biology and Pollution Control, Hunan University,
Ministry of Education, Changsha 410082, PR China

^c Collaborative Innovation Center of Resource-conserving & Environment-friendly
Society and Ecological Civilization, Changsha 410083, PR China

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha
410082, PR China. Tel.: +86 73188821413; fax: +86 73188821413

E-mail address: cyn@hnu.edu.cn (Y.N. Chen)

** Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha
410082, PR China. Tel.: +86 73188821413; fax: +86 731 88823701.

E-mail address: yxz@hnu.edu.cn (X.Z. Yuan)

1. Materials and methods

1.1. Materials

RhB (Fig. 1) and ethylenediamine were obtained from Tianjin Hengxing Chemical Reagent Co. Ltd (Tianjin, China). Sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2 \cdot 3H_2O$) and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) were supplied by Tianjin Fengchuan Chemical Reagent Co. Ltd (Tianjin, China), Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) was from Shanghai Shanfu Chemical Co. Ltd (Shanghai, China). bisphenol A and salicylic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received without further purification. All solutions were diluted preparation using ultra-pure water. The pH value of the solution was adjusted with 0.1 M HCl and 0.1 M NaOH.

1.2. Catalyst Preparation

1.2.1. Synthesis of CdS nanorods

CdS NRs were synthesized according to the reported method ¹. In a typical run of synthesis, 2.248 g of cadmium diethyldithiocarbamate ($Cd(S_2CNEt_2)_2$), prepared by precipitation from a stoichiometric mixture of $C_5H_{10}NNaS_2 \cdot 3H_2O$ and $CdCl_2 \cdot 2.5H_2O$ in deionized water, was first dispersed in an appropriate amount of ethylenediamine to form 80 mL reaction solution and added to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 180°C for 24 h and then allowed to cool to room temperature. A yellowish precipitate was separated by centrifugation, washed

thoroughly with water and ethanol to remove any impurities and then dried in an oven at 70°C for 12 h.

1.2.2. Synthesis of 1D CdS-CeO₂ catalyst

CeO₂ NPs were attached on CdS NRs via a hydrothermal method with no need of extra polyelectrolytes. In a typical synthesis, 0.4 mol CdS NRs and a stoichiometric amount of Ce(NO₃)₃·6H₂O were dispersed in 50 mL of absolute ethanol by ultrasonication. Then, 30 mL of deionized water was added slowly with magnetic stirring. 12 h later, the yellow solution was poured into a 100 mL Teflon-lined stainless steel autoclave to perform the hydrothermal treatment at 180°C for 24 h. The obtained orange mixture was separated by centrifuging and washed several times with ethanol and distilled water. Finally, the composites were dried in an oven at 70°C for 24 h. In what followed, the value of R_C was used to describe the molar ratio of CdS to CeO₂; these were 5, 10, 20 and 30 nominal ratios.

1.3. Characterization.

The morphology and structure of the samples were determined by a field emission scanning electron microscopy (SEM) (JSM-7001F, Japan) and transmission electron microscopy (TEM) (H-800, Japan). The X-ray diffraction (XRD) patterns were obtained with Bruker AXS D8 Advance diffractometer using Cu-K α source ($\lambda = 1.541 \text{ \AA}$). The surface elemental composition analyses were conducted based on the X-ray Photoelectron Spectroscopy spectra (XPS) (Thermo Fisher Scientific, UK). UV-visible diffuse-reflectance spectra (UV-vis DRS) of the samples were recorded using a Varian Cary 300 spectrometer outfitted with an integrating sphere. The Brunauer-Emmett-Teller (BET) specific surface area and pore size were measured with an automatic instrument (ASAP2020, Micromeritics, USA). The RhB and

intermediates generated in the photooxidative process were analyzed using Agilent 1100 HPLC instrument system equipped with UV-VIS detector and C₁₈ inverted phase column in the mixed eluent (methanol: H₂O = 7: 3 by volume, flow rate = 1 mL/min, temperature = 30°C). The total organic carbon (TOC) assays were carried out using a Shimadzu TOC-VCPH analyzer. Cd content in solution was detected via a Perkin-Elmer Analyst 700 atomic absorption spectrophotometer.

1.4. Photocatalytic Activity.

The photocatalytic activities of the as-prepared samples were evaluated through the experiments of photocatalytic degradation of RhB under visible light irradiation. The photodegradation reaction was conducted on a CEL-HXF300 photochemical reactor (Jinyuan Science and technology Co. Ltd, Beijing, China) with a 300 W xenon lamp as the light source. The experiments were performed at room temperature as follows: 40 mg of the as-synthesized photocatalyst was added to 100 ml of 40 mg/L dye aqueous solution. The suspension was stirred thoroughly for 1h in the dark to reach the adsorption–desorption equilibrium. The dispersion was then irradiated under visible-light ($\lambda \geq 420$ nm). During the reaction process, 4 ml of the suspension was withdrawn at regular time intervals of 8 min and was centrifuged to remove the particles. The filtrates were analyzed using a UV-vis spectrophotometer at 554 nm. The efficiency of the degradation reaction was calculated from the following equation:

$$X = (1 - C/C_0) \times 100\% \quad (1)$$

Where X is the efficiency of degradation, C_0 is the concentration of RhB after desorption–adsorption equilibrium and C is residue concentration of RhB.

1.5. The effect of pH

Fig. S8 showed the effects of different initial pH on the degradation of RhB. A variation in pH from 2 to 10 greatly influenced the photo-assisted degradation of RhB in CdS/CeO₂ dispersions. Results showed that the RhB photoreaction efficiency decreased with increasing pH values. Upon visible light irradiation for 48 min, the percent of RhB decoloration was 100.0%, 97.0%, 87.5%, 87.2% and 51.4% at pH of 2, 4, 6, 8 and 10, respectively. This might be attributed to the lower concentration of hydroxyl radicals at higher pH². More important, increased pH led to a dissociation of RhB at -COOH sites³, which inhibited it to diffuse into the reactive zone (bubble-liquid interface). While under strong acidic condition, RhB gathered in higher concentrations at the bubble interface and thus facilitated the attack of free radicals (like O₂^{•-})⁴.

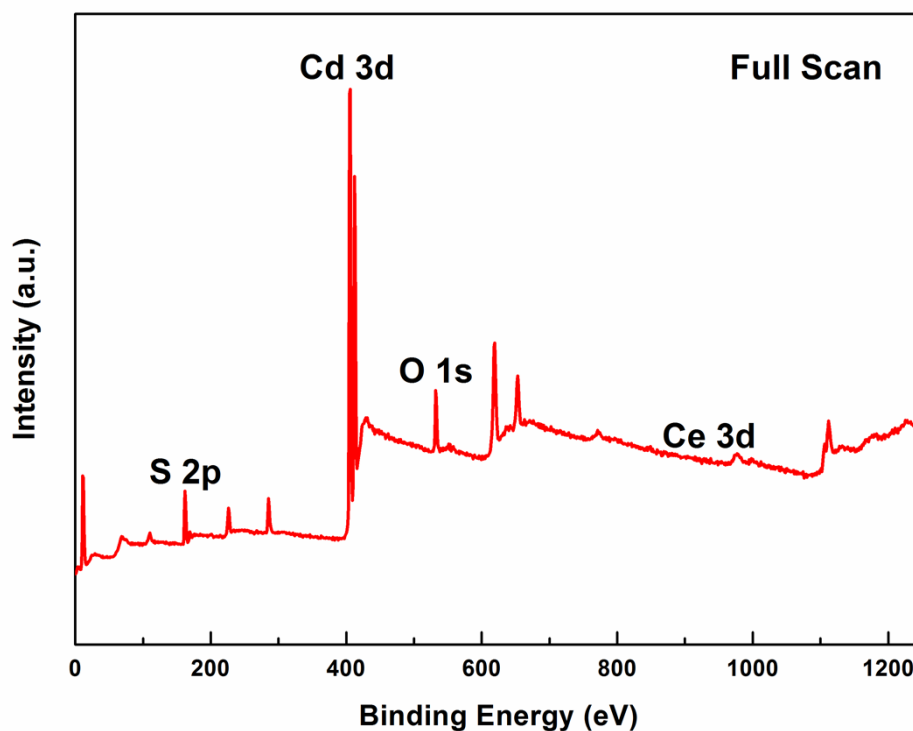


Fig. S1. Full XPS spectra of CdS/CeO₂ catalysts (R_C = 20).

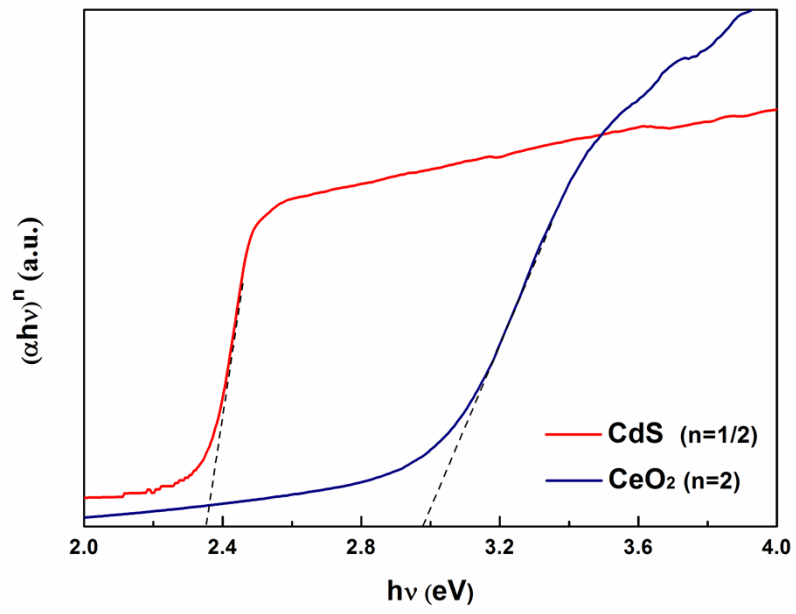


Fig. S2. Estimated band gap of CdS (the red line) and CeO₂ (the blue line).

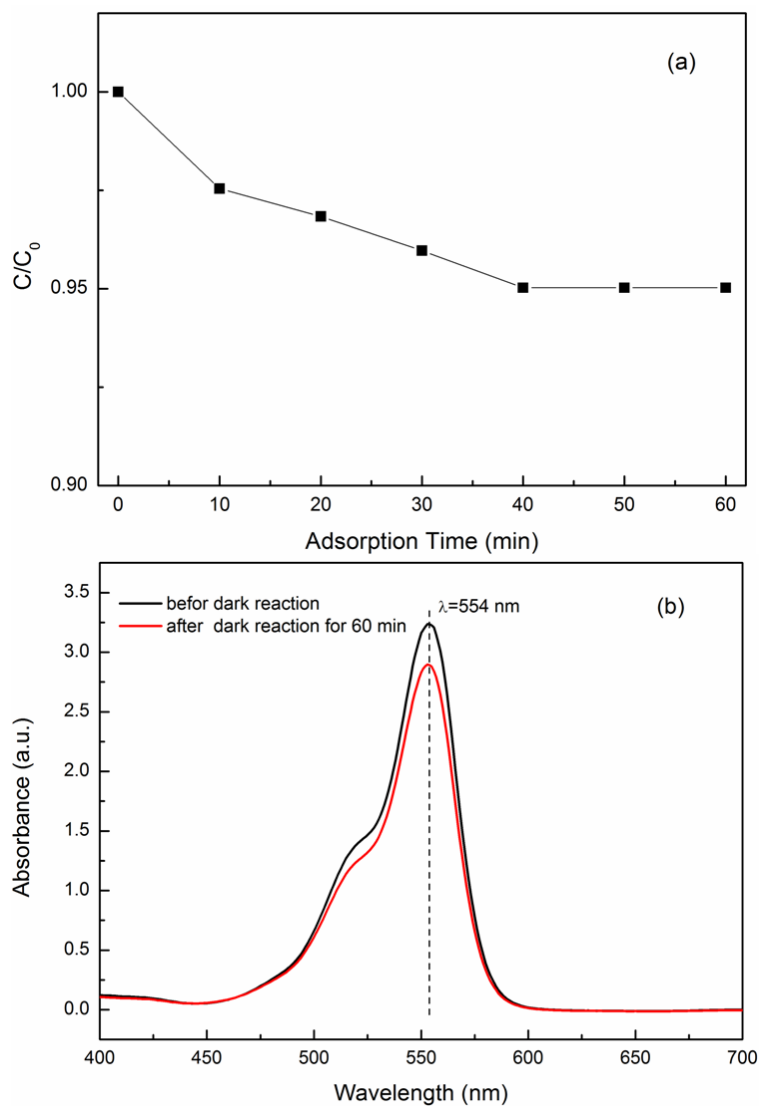


Fig. S3. (a) Adsorption of Rhodamine B in the CdS/CeO₂ (R_c = 20) kept in the dark; (b) UV-vis spectral of RhB/CdS-CeO₂ (R_c = 20) dispersion before (the black line) and after (the red line) 60 min adsorption in the dark.

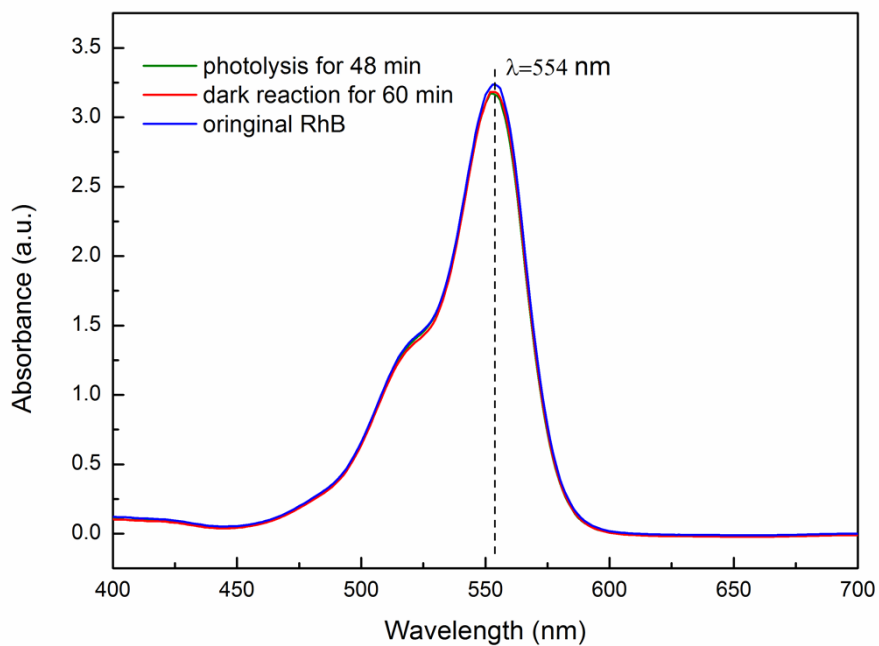


Fig. S4. UV-vis spectral comparison among the initial RhB solution, RhB solution photolyzed for 48 min and RhB solution after dark reaction for 60 min.

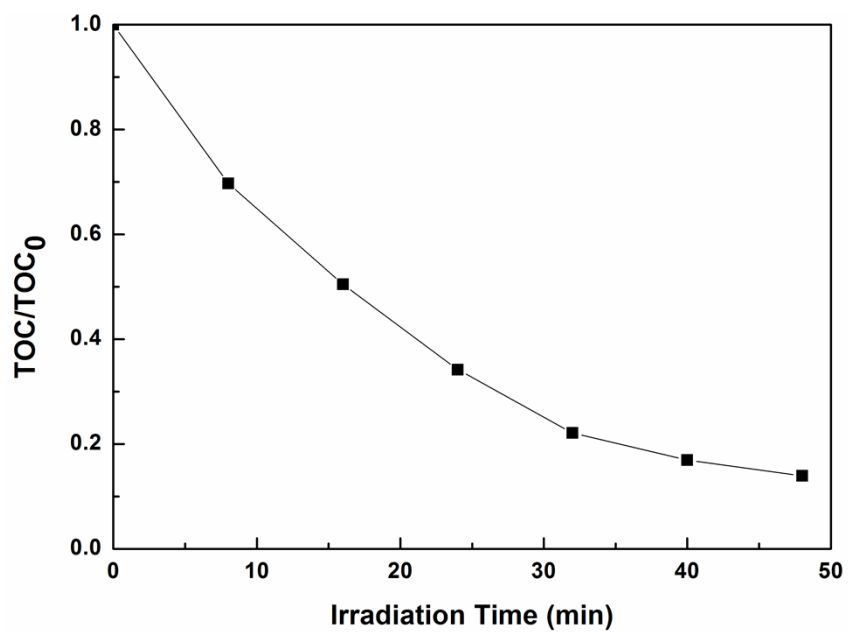


Fig. S5. TOC removal during RhB degradation over CdS/CeO₂ (R_c = 20).

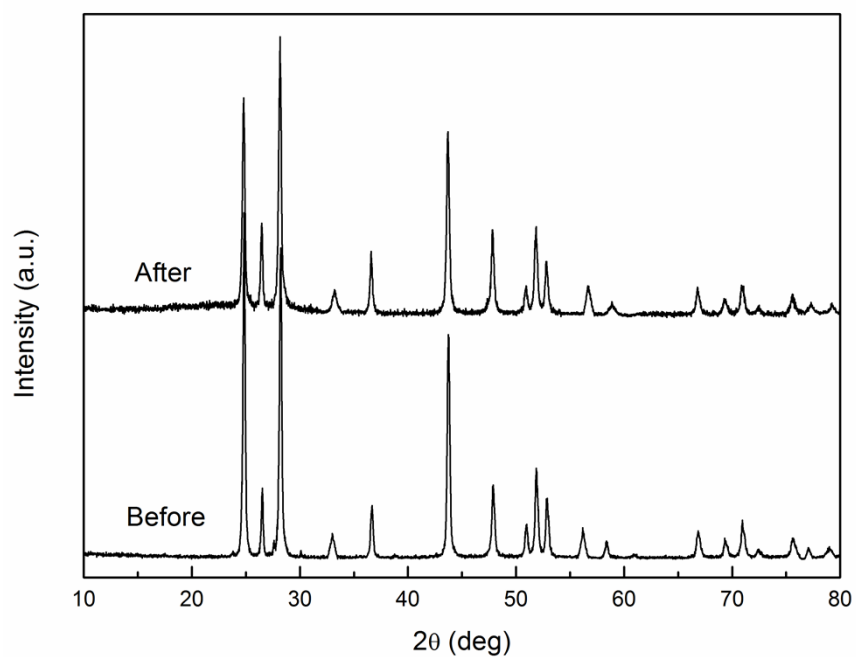


Fig. S6. XRD pattern of CdS/CeO₂ nanocomposites before (bottom) and after (top) photocatalytic reaction.

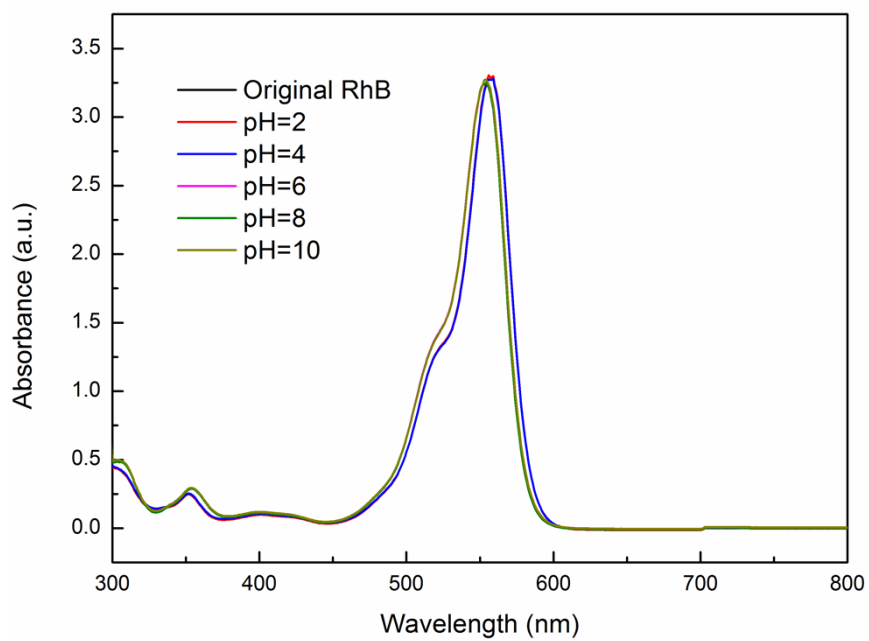


Fig. S7. UV-vis spectral of RhB solution with different pH values (pH = 2, 4, 6, 8, 10).

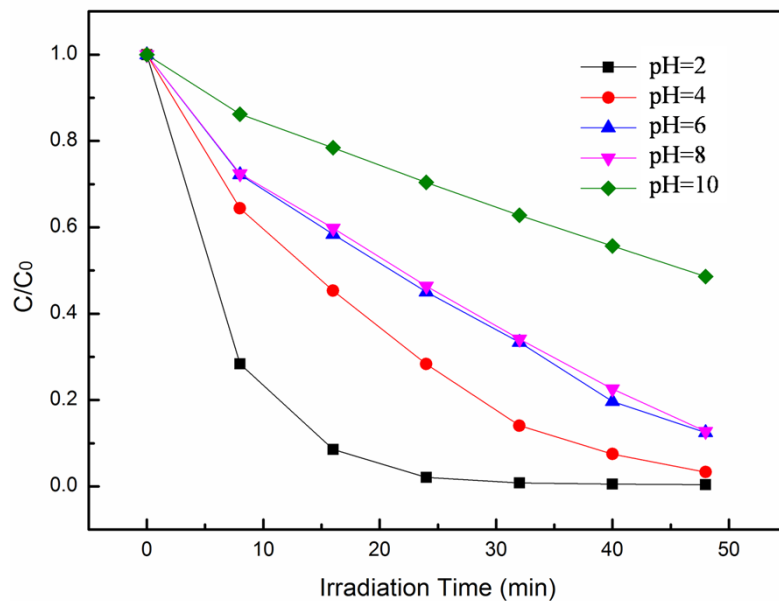


Fig. S8. Effect of initial pH on photocatalytic degradation of RhB.

References:

1. L. Wang, H.W. Wei, Y.J Fan, X. Gu, J.H. Zhan, One-Dimensional CdS/ α -Fe₂O₃ and CdS/Fe₃O₄ Heterostructures: Epitaxial and Nonepitaxial Growth and Photocatalytic Activity, *J. Phys. Chem. C* 113 (2009) 14119-14125.
2. B. Zhou, X. Zhao, H. Liu, J. Qu and C. P. Huang, *Appl. Catal. B: Environ.*, 2010, **99**, 214-221.
3. M. A. Behnajady, N. Modirshahla, S. B. Tabrizi and S. Molanee, *J. Hazard. Mater.*, 2008, **152**, 381-386.
4. S. Merouani, O. Hamdaoui, F. Saoudi and M. Chiha, *Chem. Eng. J.*, 2010, **158**, 550-557.