Electronic Supplementary Information for the Manuscript

Enhancing the visible light photocatalytic performance of ternary CdS-(graphene-Pd) nanocomposites *via* a facile interfacial mediator and co-catalyst strategy

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selective oxidation of benzyl alcohol under visible light irradiation (λ > 420 nm) for 2 h and (B) anaerobic selective reduction of 4-nitroaniline (4-NA) with the addition of ammonium oxalate as hole scavenger and N_2 purge under visible light irradiation (λ > 420 nm) for 80 min.

Experimental section for preparation of graphene oxide

Preparation of graphene oxide (GO): In detail, 2 g of graphite powder was put into a mixture of 12 mL of concentrated H_2SO_4, 2.5 g of $K_2S_2O_8$, and 2.5 g of P_2O_5. The solution was heated to 80 °C in an oil bath kept stirring for 24 h. The mixture was then carefully diluted with 500 mL of deionized (DI) water, filtered, and washed until the pH of rinse water became neutral. The product was dried under ambient condition overnight. This preoxidized graphite was then subjected to oxidation described as follows. In a typical procedure, preoxidized graphite powder was added to a mixture of 120 mL of concentrated H_2SO_4 and 30 mL of HNO_3 under vigorous stirring, and the solution was cold to 0 °C. Then, 15 g of $KMnO_4$ was added gradually under stirring, and the temperature of the mixture was kept to be below 20 °C by cooling. Successively, the mixture was stirred at room temperature for 96 h and then diluted with 1 L of DI water in an ice bath to keep the temperature below 50 °C for 2 h. Shortly after the further dilution with 1 L of DI water, 20 mL of 30% H_2O_2 was then added to the mixture, and a brilliant yellow product was formed along with bubbling. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. The filter cake was then dispersed in water by a mechanical agitation. Low-speed centrifugation was done at 1000 rpm for 2 min. The supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproduct. The final sediment was redispersed in water with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, giving a solution of exfoliated GO. The GO separated and dried is in the form of a brown powder.

Fig. S1 Photograph of the experimental setup for photocatalytic anaerobic selective reduction reaction.

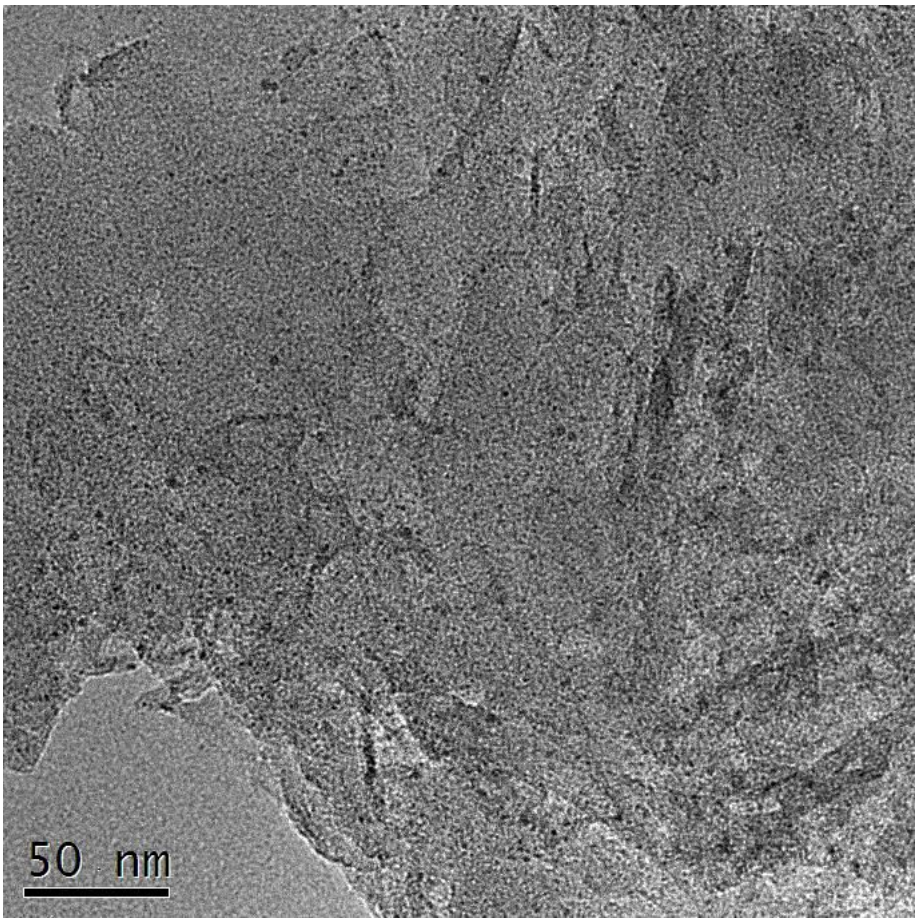


Fig. S2 TEM image of the GO-Pd composite.

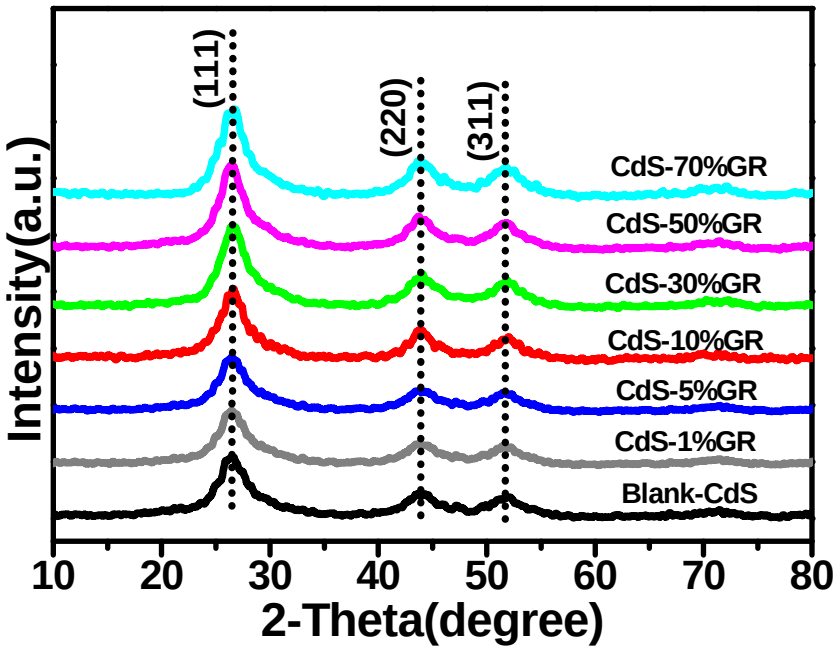


Fig. S3 XRD patterns of blank-CdS and CdS-GR nanocomposites with different weight addition ratios of GR.

Table S1 The average crystallite sizes of CdS nanoparticles in blank-CdS and GR-CdS nanocomposites calculated from the (111), (220) and (311) facet diffraction peaks of cubic CdS on the basis of Scherrer formula.[a]

GR content (wt. %)	Average crystallite sizes (nm)
0%	2.0
1%	2.4
5%	2.7
10%	2.7
30%	2.9
50%	3.8
70%	4.6

[a] Scherrer equation: $D=K\lambda/\beta\cos\theta$, where D is the mean size of the ordered crystalline domains, K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

Table S2 The photocatalytic performance of blank-CdS, CdS-5%GR and CdS-30%(GR-Pd) for selective oxidation of benzylic alcohols under visible light irradiation (λ > 420 nm).

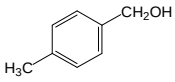
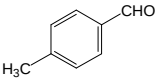
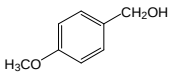
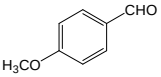
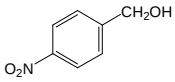
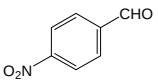
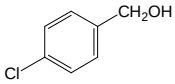
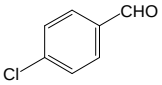
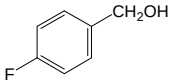
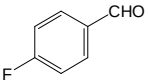
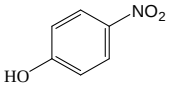
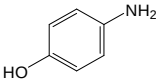
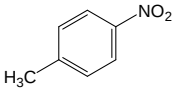
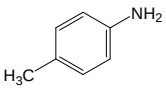
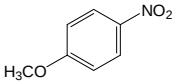
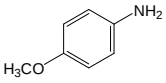
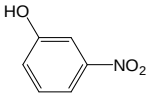
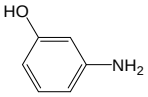
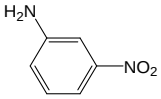
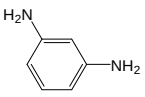
Entry	Substrate	Product	Time (h)	blank-CdS		CdS-5%GR		CdS-30%(GR-Pd)	
				Conv. (%)	Yield (%)	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)
1			2	22	21	27	27	40	40
2			2	43	39	56	56	67	67
3			2	19	15	20	20	32	32
4			2	30	20	41	29	52	52
5			2	29	27	30	29	41	37

Table S3 The photocatalytic performance of blank-CdS, CdS-5%GR and CdS-30%(GR-Pd) for selective reduction of aromatic nitro compounds under visible light irradiation (λ > 420 nm) with N_2 purge and the addition of hole scavenger, ammonium oxalate.

Entry	Substrate	Product	Time (min)	blank-CdS		CdS-5%GR		CdS-30%(GR-Pd)	
				Conv. (%)	Yield (%)	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)
1			30	36	30	46	38	55	48
2			20	46	40	58	53	71	65
3			20	50	43	75	68	84	79
4			30	15	12	22	18	32	26
5			30	34	28	41	38	52	47

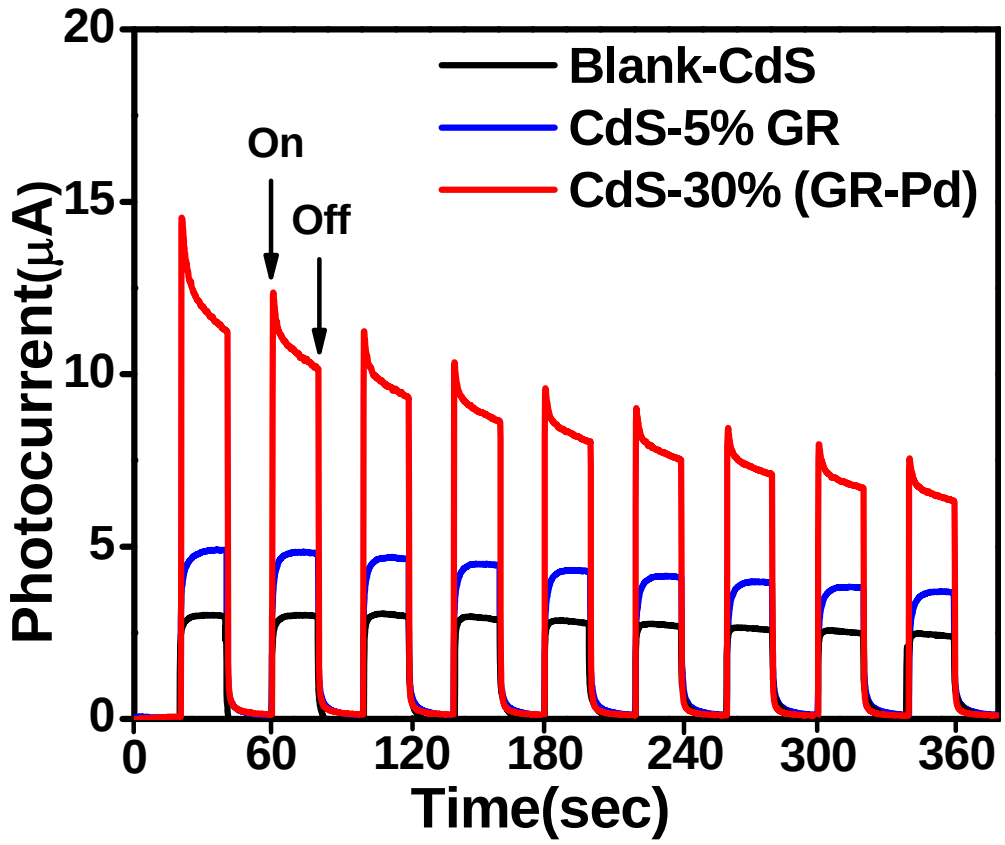


Fig. S4 Transient photocurrent response of blank-CdS, the optimal binary CdS-5%GR and ternary CdS-30%(GR-Pd) electrodes in the electrolyte of 0.2 M Na_2SO_4 aqueous solution versus Ag/AgCl under visible light irradiation ($\lambda > 420$ nm).

Note: The decrease of photocurrent density should be attributed to the competitive separation and recombination of photogenerated electron-hole pairs under light irradiation, which often occurs on the photoelectrode in the absence of external potential.[S1] As for the photocurrent response of CdS-30%(GR-Pd), there is an obvious anodic photocurrent spike, *i.e.*, overshooting behavior at the initial illumination. This initial anodic photocurrent spike is caused by the separation of photogenerated electron-hole pairs within the photoelectrode.[S2] More specifically, upon visible light irradiation, electron-hole pairs are generated from CdS; the holes move to CdS surface where they are trapped or captured by reduced species in the electrolyte, while the electrons are transported to the back contact.[S2] After the spike current has been attained, a continuous decrease in the photocurrent with time can be observed, which is due to that holes accumulated at the CdS surface competitively recombine with electrons from the CdS conduction band, instead of being trapped or captured by reduced species in the electrolyte. Therefore, the overshooting behavior of photocurrent is observed. In the light of the above statements on the formation of anodic photocurrent spike, the large overshooting behavior of photocurrent at ternary CdS-30%(GR-Pd) electrode should be ascribed to the rapid transfer of photogenerated electrons from CdS to graphene and/or Pd nanoparticles.

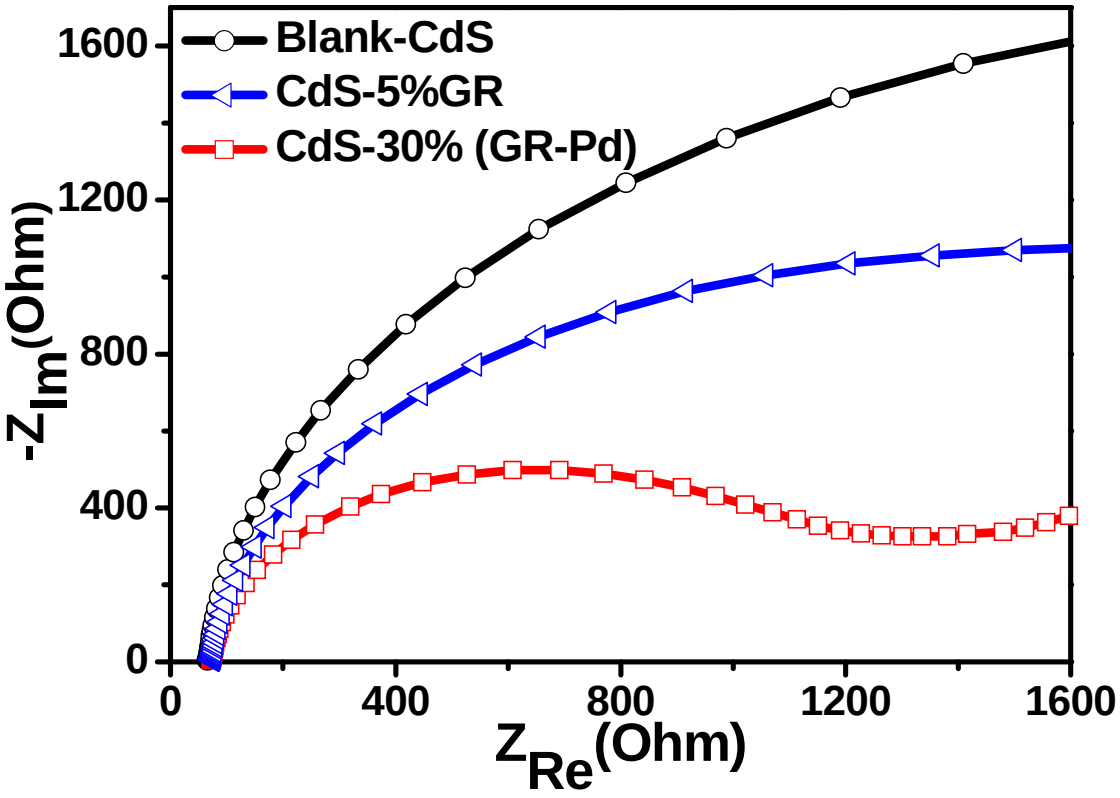


Fig. S5 Nyquist impedance plots of blank-CdS, the optimal binary CdS-5%GR and ternary CdS-30%(GR-Pd) electrodes in 0.5 M KCl aqueous solution containing 0.01 M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1).

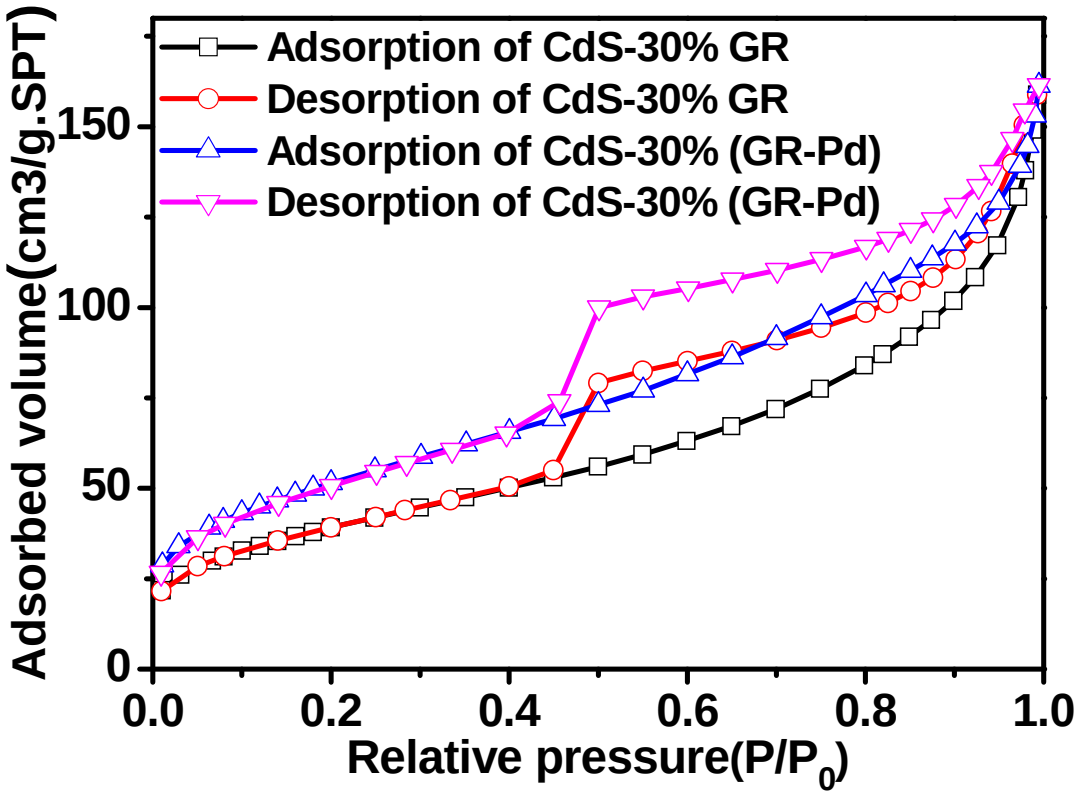


Fig. S6 The nitrogen adsorption-desorption isotherms of CdS-30%GR and CdS-30%(GR-Pd) nanocomposites.

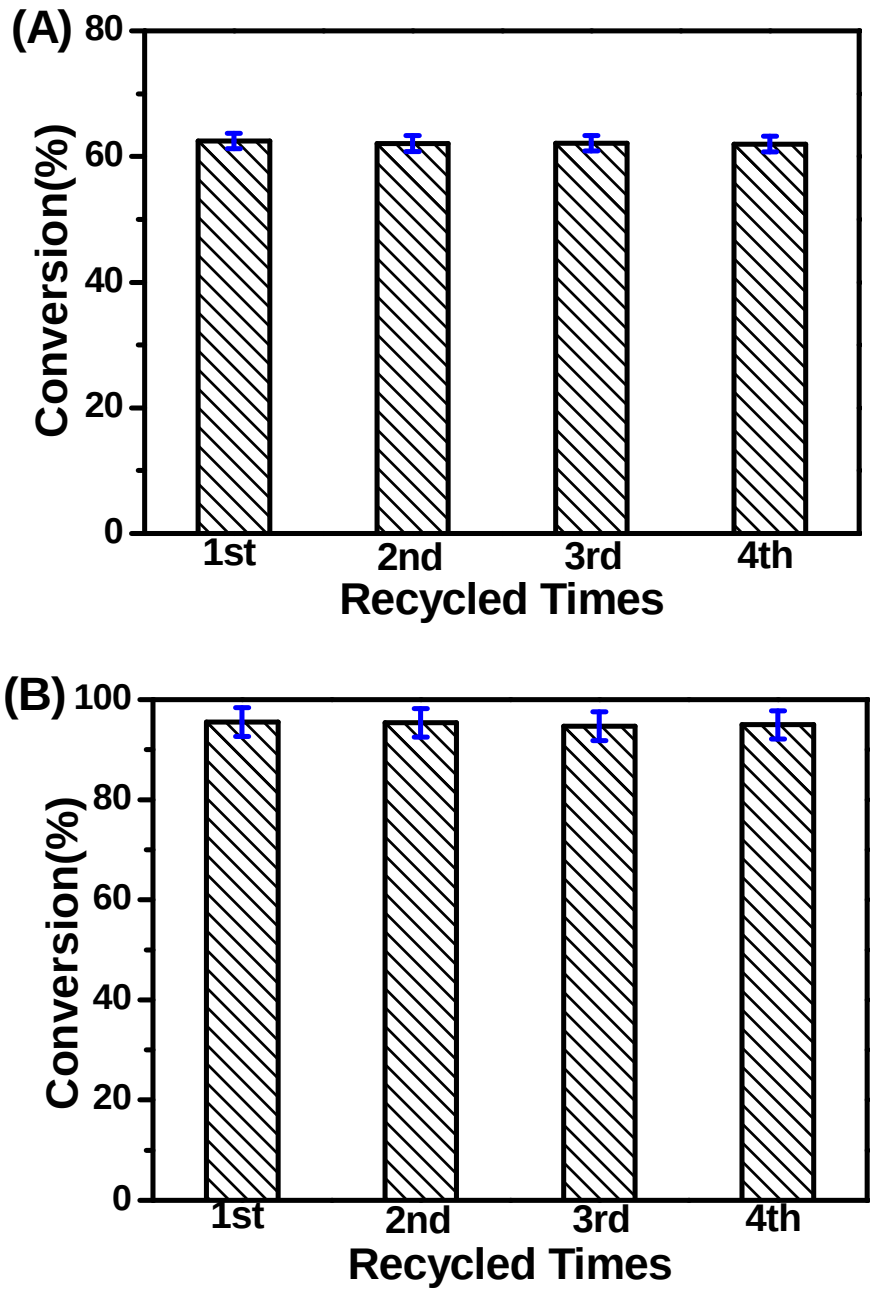


Fig. S7 Recycled testing of photocatalytic activity of CdS-30%(GR-Pd) toward (A) aerobic selective oxidation of benzyl alcohol under visible light irradiation (λ > 420 nm) for 2 h and (B) anaerobic selective reduction of 4-nitroaniline (4-NA) with the addition of ammonium oxalate as hole scavenger and N_2 purge under visible light irradiation (λ > 420 nm) for 80 min.

References

S1 Y. Zhang, Z.-R. Tang, X. Fu and Y.-J. Xu, *ACS Nano*, 2011, **5**, 7426-7435.

S2 J. Yu, T. Ma, G. Liu and B. Cheng, *Dalton Trans.*, 2011, **40**, 6635-6644.