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Supporting information

Revisiting the Constructing Graphene-CdS Nanocomposites as Efficient Visible-Light-Driven Photocatalyst for Selective Organic Transformation

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Experimental

1. Synthesis of CdS microspheres

CdS microspheres were prepared by a facile hydrothermal method.[1] In a typical synthesis, 3.5 mmol of cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5H_2O$), 3.5 mmol of thiourea (NH_2CSNH_2) and polyvinylpyrrolidone (PVP; MW~ 30 K, 0.389 g) were dissolved in 35 mL of ethylene glycol (EG) with the assistance of sonication to form a homogeneous solution. The solution was then transferred into a Teflon-lined stainless steel autoclave with 50 mL capacity and maintained at 160 °C for 12 h. The yellow precipitate was harvested by centrifugation and washed several times with DI H_2O and ethanol to remove possible remaining cations and anions before being dried in oven at 80 °C for 4 h.

2. Synthesis of graphene oxide (GO)

GO was synthesized from natural graphite powder by a modified Hummers method.[2-5] In a typical synthesis, 2 g of graphite powder (supplied from Sinopharm Chemical Reagent Co., Ltd., China) was put into a mixture consisting 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 and kept stirring for 24 h. The mixture was then carefully diluted with 500 mL of DI H_2O, filtered, and washed until the pH of rinse water became neutral. The product was dried under ambient condition overnight. This pre-oxidized graphite was subsequently subjected to oxidation described as follows: pre-oxidized graphite powder was added into a mixture of 120 mL of concentrated H_2SO_4 and 30 mL of HNO_3 under vigorous stirring, and cooled to 0 °C. Afterwards, 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 diluted with 1 L of DI H_2O in an ice bath to keep the temperature below 50 °C for 2 h. Shortly after diluting with 1 L of

DI H_2O, 20 mL of 30 % H_2O_2 was 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 and followed by DI H_2O to remove the acid. The filter cake was dispersed in DI H_2O by a mechanical agitation and then subjected to low-speed centrifugation at 1000 rpm for 2 min. The supernatant was underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproducts. The final sediment was redispersed in DI H_2O with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, thus producing aqueous solution of exfoliated GO. The GO was separated in the form of a dry and brown powder.

3. Synthesis of 5 % GR-CdS (5GC-E, 5GC-R, 5GC-I) nanocomposites

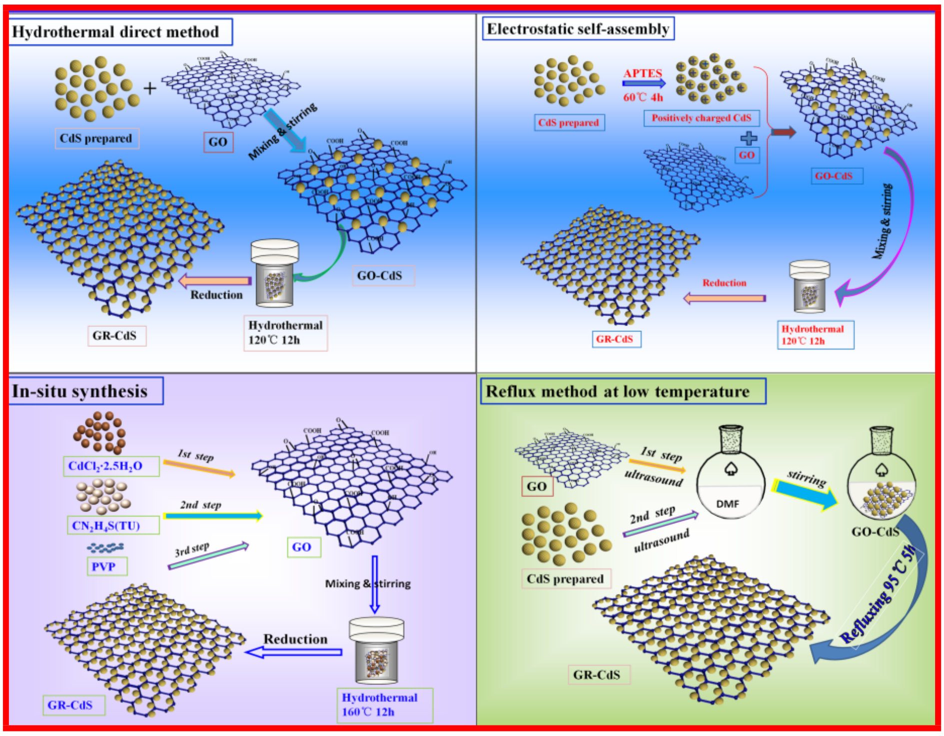
(I) Electrostatic self-assembly (5GC-E). 0.4 g of the as-prepared CdS microspheres was dispersed in 200 mL of ethanol by sonication for 30 min. Afterwards, ATPES (2 mL) was added to the above solution, heated and refluxed for 4 h. The ATPES-treated CdS solution was sufficiently rinsed with ethanol to wash away remaining ATPES moiety. Negatively charged GO aqueous solution (0.2 mg/mL) was then added into the positively charged amine-functionalized CdS dispersion at weight addition ratio of GO to CdS at 0.05 : 1 under vigorous stirring at pH = 6. After mixing for 30 min, the mixture was centrifuged and washed with DI H_2O. For reduction of GO to GR, 0.2 g of the GO–CdS was dispersed in DI H_2O (80 mL) and maintained in a Teflon-lined stainless steel vessel at 120°C for 12h. The dark green precipitates thus-obtained were collected, washed thoroughly with DI H_2O, and dried in oven at 60 °C for 6 h.

(II) Refluxing method at low temperature (5GC-R). 0.2 g of CdS and 2 mL of GO (5 mg/mL) were first dispersed in 50 mL of DMF by sonication for 30 min. Subsequently, the mixed solution

was heated to 95°C and maintained at that temperature for 5 h by refluxing. The product was subjected to repeated washing with ethanol by centrifugation and finally with DI H_2O. The as-prepared GR-CdS nanocomposite was dried in oven at 55°C for 6 h.

(III) In-situ synthesis (5GC-I). 3.5 mmol of cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5H_2O$), 3.5 mmol of thiourea (NH_2CSNH_2) and polyvinylpyrrolidone (PVP; MW~ 30K, 0.389 g) were dissolved with a certain amount of GO (5 mL, 0.5mg/mL) in 35 mL of ethylene glycol (EG) with the assistance of sonication to form a homogeneous solution. The solution was then transferred into a Teflon-lined stainless steel autoclave with 50 mL capacity and maintained at 160 °C for 12 h. The yellow precipitate was harvested by centrifugation and washed several times with DI H_2O and ethanol to remove possible remaining cations and anions before being dried in oven at 80 °C for 4 h.

The detailed synthetic processes for preparation of above different GR-CdS nanocomposites were vividly delineated in **Scheme S1**.



Scheme S1. Schematic illustration for preparation of GR-CdS nanocomposites by different synthetic methods.

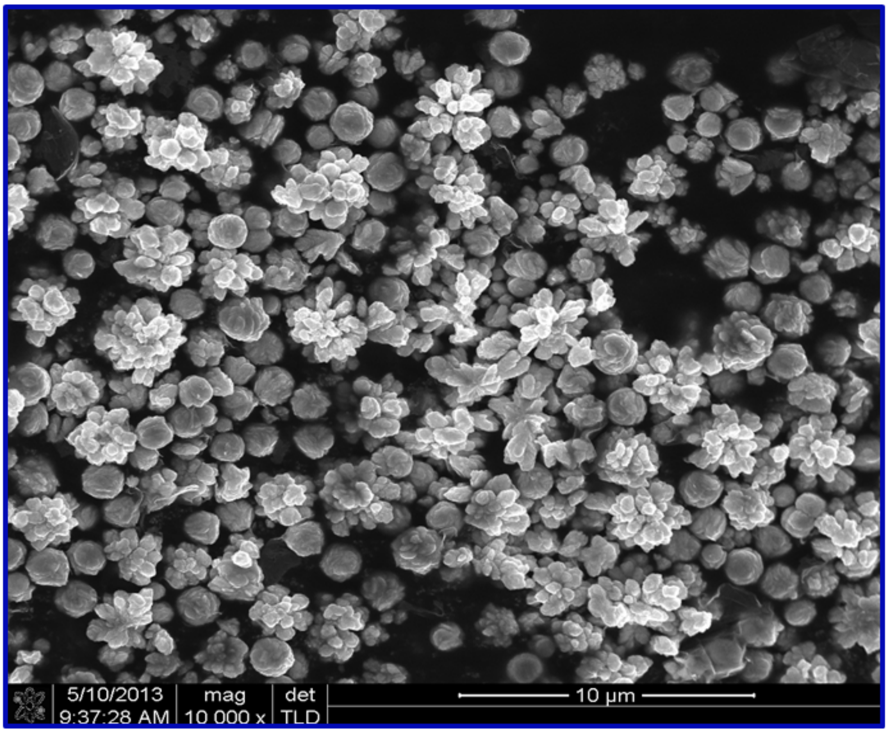


Figure S1. FESEM image of the as-prepared CdS microsphere by hydrothermal method.

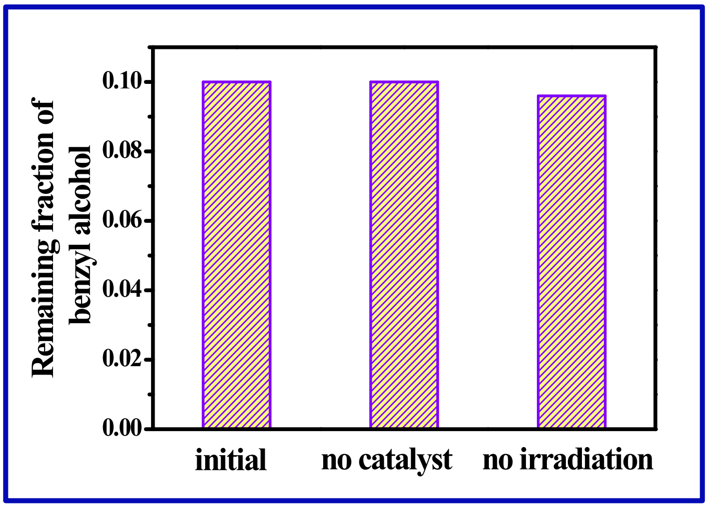


Figure S2. Photocatalytic performances of 5 % GR-CdS nanocomposite toward selective oxidation of benzyl alcohol to benzaldehyde under visible light irradiation without catalyst and in the dark with catalyst for 2 h.

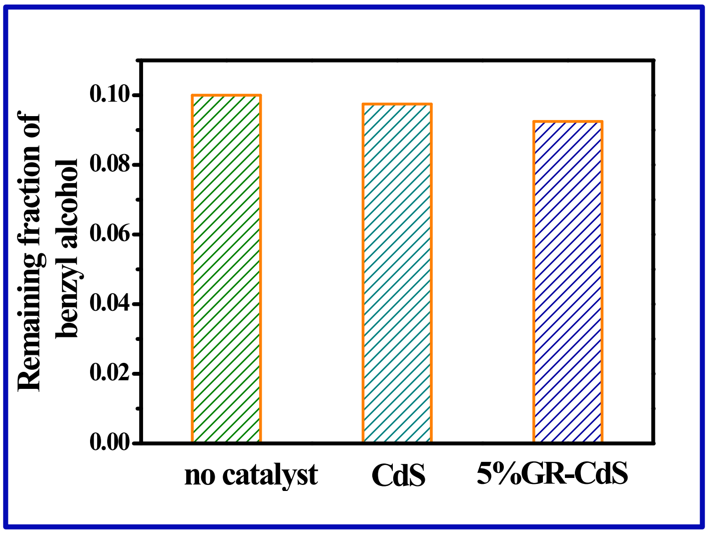


Figure S3. Remaining fraction of benzyl alcohol after adsorption–desorption equilibrium in the dark over CdS and 5 % GR-CdS nanocomposite.

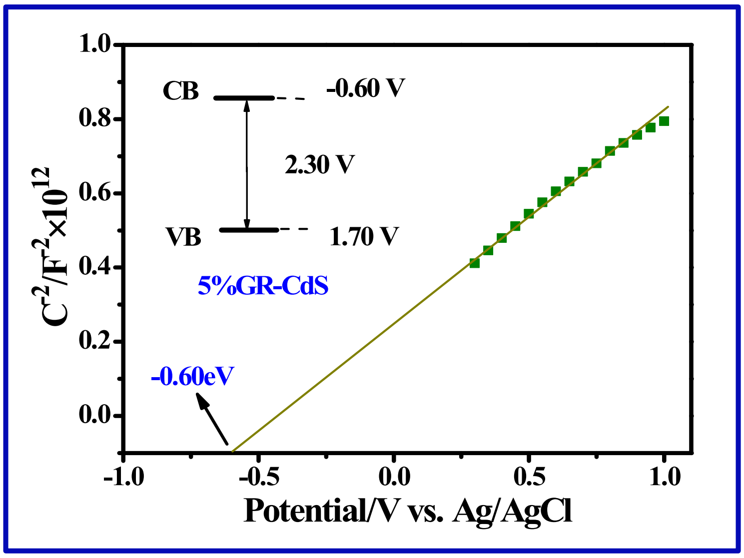


Figure S4. Mott-Schottky plot for the 5 % GR-CdS nanocomposite in 0.2 M Na_2SO_4 aqueous solution (pH = 6.8).

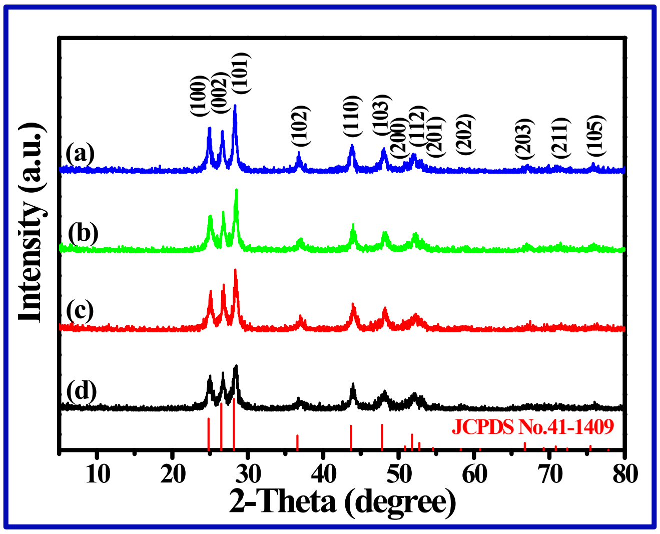


Figure S5. XRD patterns of 5 % GR-CdS nanocomposites prepared by different methods, *i.e.* (a) hydrothermal reduction (5GC-H), (b) refluxing reduction (5GC-R), (c) electrostatic self-assembly (5GC-E), and (d) *in-situ* hydrothermal synthesis (5GC-I).

Note: *A series of 5 % GR-CdS nanocomposites samples were synthesized by different methods. The crystallographic structure and phase purity of these samples were examined by X-ray powder diffraction (XRD). All the diffraction peaks can be consistently indexed to the hexagonal CdS with lattice constants of a = 4.140 Å and c = 6.719 Å (JCPDS card no. 41-1409). No cubic phase or impurity peaks was detected.*

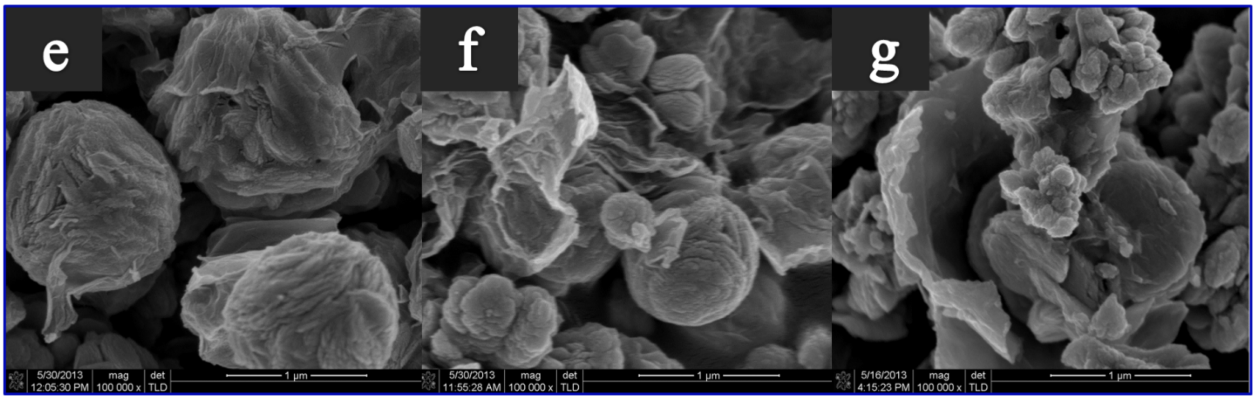


Figure S6. FESEM images of 5 % GR-CdS nanocomposites prepared by different methods, *i.e.* (e) 5GC-E, (f) 5GC-R and (g) 5GC-I.

Table S1. Specific surface area and pore size of CdS and 5 % GR-CdS nanocomposite (5GC-H)

Samples	**S_{BET} (m^2/g)**[a]	**Total pore volume (cm^3/g)**[b]	**Average pore size (nm)**[c]
blank-CdS	**12**	**0.14**	**29**
5 % GR-CdS	**19**	**0.19**	**35**

[a] *BET specific surface area is calculated from the linear part of the BET plot.*
[b] *Single point total pore volume at $P/P_0 = 0.99$.*
[c] *Adsorption average pore width (4V/A by BET).*

References

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