# **Electronic Supplementary Information for the manuscript**

# Morphology control, defect engineering and photoactivity tuning of ZnO

# crystals by graphene oxide-a unique 2D macromolecular surfactant

Xiaoyang Pan<sup>a,b</sup>, Min-Quan Yang<sup>a,b</sup>, and Yi-Jun Xu<sup>\*a,b</sup>

<sup>a</sup> State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, 350002, P.R. China

<sup>b</sup> College of Chemistry and Chemical Engineering, New Campus, Fuzhou University, Fuzhou,

350108, P. R. China

\* Corresponding author: Prof. Yi-Jun Xu; E-mail Address: <u>yjxu@fzu.edu.cn</u>; Tel. +86 591 83779326

## **Contents list:**

## **Experimental Details.**

Table S1. Summary of recently-reported synthesis of RGO-ZnO for photocatalytic applications.

Fig. S1. SEM images of 5wt% RGO-ZnO (a) and 10wt% RGO-ZnO nanocomposites (b).

Fig. S2. Additional typical SEM images of 3wt% RGO-ZnO nanocomposite.

**Fig. S3.** SEM image (a) and TEM images (b, c and d) of 3wt% RGO-ZnO nanocomposites; the inset of panel (b) is the HRTEM image of the ZnO nanocrystals of 3wt% RGO-ZnO.

**Fig. S4.** Zeta potentials of graphene oxide (GO) and GO mixing with Zn<sup>2+</sup>-HMT complex at pH 7.

**Fig. S5.**Schematic illustration of the ZnO crystallization process assisted by GO and HMT in the solution for the formation of RGO-ZnO nanocomposites.

**Table S2.** Summary of recently-reported synthesis of ZnO with oxygen vacancy for photocatalytic application.

**Scheme S1.** Schematic diagram illustrating thermally activated bridging lattice leaving behind a surface vacancy. The oxygen atom diffuses to the particle surface where it reacts with reductive oxygenation group of GO.

Fig. S6. SEM images of ZnO rod fabricated by a citrate-assisted method.

Fig. S7. Controlled experiment with and without  $K_2S_2O_8$  as quencher for photogenerated electrons in photocatalytic reduction of Cr (VI) aqueous solution over the 3wt% RGO-ZnO nanocomposite under visible light irradiation ( $\lambda$ >400 nm).

**Fig. S8.** Photoluminescence (PL) spectra of the blank ZnO DB rod and RGO-ZnO nanocomposites (a); scheme illustrating the transfer of charge carriers in RGO-ZnO nanocomposites under visible light irradiation (b).

Table S3. The BET surface areas of the blank ZnO DB rod, RGO-ZnO and GR-ZnO nanocomposites.

Fig. S9. Photoluminescence (PL) spectra of the blank ZnO DB rod and GR-ZnO nanocomposites.

**Fig. S10.** Electrochemical impedance spectroscopy Nyquist plot of the sample electrodes of ZnO DB rod, 3wt%GR-ZnO and 3wt%RGO-ZnO under visible light irradiation ( $\lambda$ >400 nm).

### Appendix

Fig. S11. SEM image of graphene oxide (GO).

**Fig. S12.** TEM image of graphene oxide (GO); inset is the high-resolution TEM (HRTEM) image of GO.

Fig. S13. XRD patterns of graphene oxide (GO) and graphene (GR).

Fig. S14. Additional typical TEM image of the 3wt% RGO-ZnO nanocomposite.

### **Experimental Details**

### Synthesis of graphene oxide (GO)

GO was synthesized from natural graphite powder by a modified Hummers method.<sup>1</sup> In detail, 2 g of graphite powder was put into a mixture of 12 mL of concentrated H<sub>2</sub>SO<sub>4</sub>, 2.5 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and 2.5 g of P<sub>2</sub>O<sub>5</sub>. 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<sub>2</sub>SO<sub>4</sub> and 30 mL of HNO<sub>3</sub> under vigorous stirring, and the solution was cold to 0 °C. Then, 15 g of KMnO<sub>4</sub> 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<sub>2</sub>O<sub>2</sub> 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.

Table S1. Summar	y of recently-reporte	d synthesis of RGO-ZnC	) for photocatalytic applications.
-		2	1 2 11

Pole of CO	Morphology	Light	Method for GO	Reference	
	Morphology	source	reduction		
Precursor	nonorod	UV light	Hydrazine	ACS Nano <b>2010</b> , 7,	
for GR	nanorod	UV light	reduction	4174-4180	
Precursor	. 1	UV light	Solvthermal	J. Mater. Chem. 2012,	
for GR	nanoparticle		treatment	22,11778–11784	
D	TT 11	UV light		J. Phys. Chem. C	
Precursor	Hollow		DMSO reduction	<b>2012</b> , 116,	
for GR	spheres	C C		8111-8117	
Precursor		UV light	Hydrazine	Appl. Catal., B 2011,	
for GR	nanoparticle		reduction	101, 382-387	
Precursor			Hydrothermal	Appl. Catal., B 2013,	
for GR	nanoparticle	UV light	treatment	140, 598-607	
Precursor			Hvdrothermal	CrystEngComm 2013.	
for GR	nanoparticle	UV light	treatment	15, 3022-3030	
Precursor			Microwave	Catal. Sci. Technol.	
for GR	nanorod	UV light	treatment	<b>2012</b> . 2. 2297-2301	
Precursor			Microwave	Catal. Sci. Technol.	
for GR	nanoparticle	UV light	treatment	<b>2011</b> .1. 1189-1193	
Precursor		UV light	Hvdrothermal	Powder Technol.	
for GR	microflower		treatment	<b>2013</b> , 235, 853-858	
Precursor		UV light	Hvdrothermal	Catal. Commun.	
for GR	nanoparticle		treatment	<b>2012</b> , 29, 29-34	
Precursor		Visible	Hydrothermal	J. Mater. Chem. 2011.	
for GR	nanoparticle	light	treatment	21, 3346-3349	
Precursor		8	Hydrothermal	J. Mater. Chem.	
for GR	nanoparticle	UV light	treatment	<b>2011</b> .21. 3346-3349	
Precursor		UV/Visibl	Hydrazine	Langmuir <b>2013</b> . 29.	
for GR	nanoparticle	e light	reduction	3097–3105	
Precursor			Hydrothermal	Appl. Catal., B 2013.	
for GR	nanorod	UV light	treatment	142, 442-449	
2D					
surfactant		Visible light			
for			One-step thermal		
morphology	Rod/tube		treatment in	This work	
tuning and			water		
defect					
engineering					

**Note:** The morphology control of semiconductor nanocrystals often requires the organic surfactant or organic solvent, which can strongly adsorb on the semiconductor surface and hamper their catalytic activity. More importantly, in most of the existing morphology control protocols, the employed surfactant works only as a regulator for a controllable shape but not as active species for function improvement. In our work, GO has been used as a novel macromolecular surfactant which

transforms the ZnO from 1D dumbbell-shaped prismatic hexagonal rod with pointed tip to tubular hexagonal nanoarchitecture with flattened tip. Our new findings suggest that GO could work not only as precursor for GR but also as an emergent macromolecular 2D surfactant for tuning the morphology of the semiconductor nanocrystals. During this preparation procedure, neither organic surfactant nor organic solvent is required for tuning the morphology of ZnO. In addition to its role as novel surfactant, graphene also act as functional components, improving the charge carriers separation process and contributing to the photoactivity enhancement of RGO-ZnO nanocomposites. This consequently offers a "system-materials-engineering" way for fabrication of the RGO-semiconductor nanocomposites with remarkable morphology control and tunable photoactivity. Notably, this prominent feature of GO has been remaining totally unclear for synthesis of RGO-ZnO nanocomposite photoactalysts in previous research works (Table S1)



Fig. S1. SEM images of 5wt% RGO-ZnO (a) and 10wt% RGO-ZnO nanocomposites (b).

**Note:** When the weight amount of GO is more than 3%, an intimate complexation between ZnO and RGO is formed, in which the polar facets of ZnO is completely covered by graphene, as can be seen from Figure 1e-f and Figure S2. The as-formed graphene shell on the polar facets of ZnO can inhibit the further erosion of ZnO polar facets to form tubular structure.



Fig. S2. Additional typical SEM images of the 3wt% RGO-ZnO nanocomposite.



**Fig. S3**. SEM image (a) and TEM images (b, c and d) of 3wt% RGO-ZnO nanocomposites; the inset panel (b) is the HRTEM image of the ZnO nanocrystals of 3wt% RGO-ZnO.



**Fig. S4**. Zeta potentials of GO and GO mixing with  $Zn^{2+}$ -HMT complex at pH 7.

**Note:** The zeta potential of GO is measured to be -38.3 mV. After mixing with  $Zn^{2+}$ -HMT complex, it shows a positive zeta potential around +29.8 mV, suggesting the conjugation of  $Zn^{2+}$ -HMT complex and GO.<sup>2</sup> The strong association of the respective components due to the coordination and multidentate electrostatic interaction between  $Zn^{2+}$ , HMT, and GO induces changes in the kinetics of nucleation and growth of ZnO crystals.<sup>2</sup>



**Fig. S5**. Schematic illustration of the ZnO crystallization process assisted by GO and HMT in the solution for the formation of RGO-ZnO nanocomposites.

**Note:** At the fist step,  $Zn^{2+}$  ions, formed by the dissolution of  $Zn(CH_3COO)_2 \cdot 2H_2O$  in water, favorably bind with the oxygen atoms of the negative charged oxygenation functional groups on

GO sheets via electronic force.<sup>2-3</sup> When the mixture of GO,  $Zn^{2+}$  and HMT was heated to 90 °C, the HMT decomposes and releases OH<sup>-,4</sup> OH<sup>-</sup> subsequently reacts with  $Zn^{2+}$  to form  $ZnO_2^{2^-,4}$  Finally, a large number of nuclei of ZnO nanocrystals are formed in a short time via homogeneous precipitation under mild conditions.<sup>4</sup>

In the case of formation of 1D hexagonal ZnO crystals, previous studies provide a reasonable interpretation for this phenomenon.<sup>5</sup> Structurally, ZnO can be described as a number of alternate planes stacked by tetrahedrally coordinated  $O^{2-}$  and  $Zn^{2+}$  ions along the c-axis.<sup>6</sup> ZnO has positively charged (0001) and negatively charged (000-1) polar surfaces, while the (0001)-Zn terminated surface is chemically active and the (000-1)-O terminated surface is inert.<sup>7</sup> This structure makes ZnO a kind of polar crystal, and there is a divergence in the surface energy. Thus, the growth rate along the c-axis direction is much faster than along other crystallographic directions, usually resulting in a 1D structure of ZnO nanowires or nanorods.



**Fig. S6**. SEM images of ZnO rod fabricated by a citrate-assisted method. **Note:** The ZnO rod was fabricated using the same synthesis procedures as that for the above RGO-ZnO nanocomposites except that GO was replaced by the sodium citrate.

Method	Light source	Synthesized temperature	Reference	
Doping of Ag ions	UV light	1100 °C (1h)	Appl. Sur. Sci. <b>2004</b> , 227, 312-317	
Doping of Cu ions	UV light	800 °C (1h)	<i>Solid State Commun.</i> <b>2012</b> , 152, 375-380	
Doping of S ions	Solar light	600 °C (1h)	<i>J. Hazard. Mater.</i> <b>2010</b> , 183, 315-323	
ZnO <sub>2</sub> decomposition	Visible light	400 °C (2h)	ACS Appl. Mater. Interface 2012, 4, 4024-4030	
Hydrogen reduction (RGO-ZnO)	UV/Visible light	465 °C (5h)	Langmuir <b>2013</b> , 29, 3097-3105	
Vacuum deoxidation	visible light	200 °C (2h)	Appl. Catal., B <b>2013</b> , 138-139, 26-32	
Doping of Sn ions	UV light	160 °C (12h)	<i>Mater. Res. Bull.</i> <b>2011</b> , 46, 1107-1112	
Doping of La ions	UV light	150 °C (20h)	J. Alloys Compd. <b>2009</b> , 484, 410-415	
Ethanol as reductant	UV light	160 °C (24h)	Inorg. Chem. <b>2007</b> , 46, 6675-6682	
Ethanol as reductant (RGO-ZnO)	UV light	180 °C (15h)	Appl. Catal., B <b>2013</b> , 142-143, 442-449	
Ethanol as reductant	UV light	160 °C (24h)	Inorg. Chem. <b>2007</b> , 46, 6980-6986	
GO as reductant	Visible light	90 °C (3h)	This work	

**Table S2.** Summary of recently-reported synthesis of ZnO with oxygen vacancy for photocatalytic application.

**Note:** From **Table S2**, we can clearly see that the creation of oxygen vacancy on ZnO often requires metal or non-metal ions doping under high temperature treatment. It should be noted that the foreign ions incorporated into ZnO lattice often serve as charge recombination center, which would hamper the charge carriers separation process. Compared with the conventional doping method, the creation of oxygen vacancy without introducing impurity elements in the lattice of ZnO is more favorable on preserving the intrinsic crystal structures of ZnO and leads to enhanced photocatalytic performances under visible light irradiation. On the synthesis of oxygen vacancy rich ZnO samples, there is still a great challenge. The conventional methods often require high temperature annealing treatment, which can result in increase of particle size and damage of morphology on ZnO. Additionally, the concentrations of oxygen vacancies are usually low, which would not be adequate to expand the visible light absorption obviously. Therefore, although ZnO with oxygen vacancy has been successfully fabricated by several methods, most of these catalysts are only used as UV-light-driven photocatalyst. In our work, the creation of oxygen vacancies on ZnO is achieved under mild conditions by utilizing the unique property of GO. The creation of oxygen vacancy coupled with the decoration of graphene effectively narrows the band gap of ZnO and increases the visible light absorption on the resulting RGO-ZnO nanocomposites. Therefore, the RGO-ZnO nanocomposites exhibit significantly enhanced visible light photocatalytic activity, as compared to the bare ZnO.



**Scheme S1.** Schematic diagram illustrating thermally activated bridging lattice leaving behind a surface vacancy. The oxygen atom diffuses to the particle surface where it reacts with reductive oxygenation group of GO.

**Note:** The detailed mechanism for the formation of oxygen vacancy with addition of GO can be explained by the well known Mars and Van Krevelen mechanism as schematically displayed in Scheme S1.<sup>8</sup> In a typical process, the lattice oxygen in ZnO is activated under thermal treatment in the synthesized procedure. Then the reductive oxygenation groups on GO are involved in a redox reaction with the lattice oxygen. During this process, the lattice oxygen is extracted by these reductive organic species and results in the formation of an oxygen vacancy. This result is in good accordance with the previous reports using ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) as reducing agent for oxygen vacancy creation on ZnO (see **Table S2**).



Fig. S7. Controlled experiment with and without  $K_2S_2O_8$  as quencher for photogenerated electrons in photocatalytic reduction of Cr (VI) aqueous solution over the 3wt% RGO-ZnO nanocomposite under visible light irradiation ( $\lambda$ >400 nm).



**Fig. S8**. Photoluminescence (PL) spectra of the blank ZnO DB rod and RGO-ZnO nanocomposites (a); scheme illustrating the transfer of charge carriers in RGO-ZnO nanocomposites under visible light irradiation (b).

Note: It is widely accepted that the GR (or RGO) can act as an electron acceptor, promoting interfacial electron-transfer processes from the attached semiconductor metal oxide to the RGO under light irradiation.<sup>9</sup> For the RGO-ZnO system, charge transfer from the ZnO conduction band to RGO is energetically favorable, since the conduction band of ZnO is more negative than that of RGO.<sup>10</sup> Therefore, the presence of RGO in the RGO-ZnO nanocomposites is able to improve the lifetime of photoexcited electron-hole pairs generated from ZnO and boost the efficient transfer of charge separation.<sup>11</sup> This statement is supported by the analysis of photoluminescence (PL) spectra. Fig. S7a shows the PL spectra of the bare ZnO DB rod and RGO-ZnO nanocomposites, and a broad visible PL band at 450-800 nm can be seen for the bare ZnO DB rod and RGO-ZnO nanocomposites. According to the literature,<sup>11-12</sup> this visible emission is able to serve as a probe to monitor the interfacial electron-transfer processes. As shown in Fig. S7a, the presence of RGO in RGO-ZnO nanocomposites obviously reduces the intensity of the PL emission of ZnO. The decrease in the PL emission intensity reveals that an additional pathway for the transfer of the charge carriers, because of the interactions between the excited ZnO and the RGO sheets.<sup>11-12</sup> As demonstrated earlier, such emission quenching represents electron transfer from the excited ZnO to the RGO,<sup>11-12</sup> indicating that the RGO-ZnO nanocomposites have a lower recombination rate of electrons and holes. This is mainly due to the facts that photogenerated electrons are transferred to the RGO and photoexcited holes are trapped by the electrons located on the oxygen vacancy states, preventing a direct recombination of electrons and holes (Fig. S7b).<sup>13</sup>

In addition, as can be seen from **Fig. S7**, the peak position of the photoluminescence (PL) emission of the RGO-ZnO nanocomposites exhibits an obvious blue-shift, as compared to blank ZnO DB rod. The variation in the position of the PL emission in various ZnO nanostructures is often attributed to the different concentration of native defects.<sup>14</sup> It has been found that the presence of oxygen vacancies in ZnO can induce the blue shift of the PL emission.<sup>15</sup> Since the adding of GO into the synthesis system can create oxygen vacancies in the lattice of RGO-ZnO nanocomposites, the blue-shift of the PL emission as observed in the RGO-ZnO nanocomposites can be attributed to the creation of oxygen vacancy in ZnO crystals.

Sample	$S_{BET} (m^2/g)$	Sample	$S_{BET} (m^2/g)$
ZnO DB rod	8.3	1wt%GR-ZnO	6.8
1wt%RGO-ZnO	6.8	3wt%GR-ZnO	6.5
3wt%RGO-ZnO	6.4	5wt%GR-ZnO	6.1
5wt%RGO-ZnO	5.9	10wt%GR-ZnO	5.7
10wt%RGO-ZnO	5.2		

**Table S3.** The BET surface areas of the blank ZnO DB rod, RGO-ZnO and GR-ZnO nanocomposites.



**Fig. S9**. Photoluminescence (PL) spectra of the blank ZnO DB rod and GR-ZnO nanocomposites. **Note:** Graphene (GR) is obtained by the hydrothermal reduction of GO in a solvent of ethanol-water at 180 °C for 12 h, by which the significant amount loss of oxygenated functional groups of GO is obtained.<sup>2,3</sup> The GR-ZnO nanocomposite is prepared using the same procedure as that for preparing the RGO-ZnO nanocomposites. It is clearly seen from **Fig. S8** that, similar to the case for RGO-ZnO, the presence of GR can also inhibit the photogenerated electron-hole pairs recombination. But, no variation in the position of PL emission is observed in GR-ZnO as compared to the blank ZnO DB rod, which is remarkably different from the RGO-ZnO composites. In addition, **the PL intensity of 3wt% GR-ZnO is much higher than the 3wt% RGO-ZnO than 3wt% GR-ZnO**.



**Fig. S10.** Electrochemical impedance spectroscopy Nyquist plot of the sample electrodes of ZnO DB rod, 3wt%GR-ZnO and 3wt%RGO-ZnO under visible light irradiation ( $\lambda$ >400 nm).

**Note:** To further confirm the more efficient charge separation in the RGO-ZnO nanocomposites, electrochemical impedance spectroscopy (EIS) Nyquist plots have also been carried out. As displayed in **Fig. S10**, the Nyquist plots of ZnO DB rod, 3wt%RGO-ZnO and 3wt%GR-ZnO all show semicycles at high frequency, which corresponds to the charge transfer limiting process and is attributed to the double-layer capacitance ( $C_{dI}$ ) in parallel with the charge-transfer resistance ( $R_{ct}$ ) at the contact interface between electrode and electrolyte solution.<sup>1a</sup> As shown in **Fig. S10**, the introduction of GR (RGO) leads to obvious decrease of the arc as compared to blank ZnO DB rod, indicating that GR (RGO) can facilitate the interfacial charge transfer.<sup>1a</sup> In addition, the 3wt%RGO-ZnO sample show smaller arc than that of 3wt%GR-ZnO, indicating that the 3wt%RGO-ZnO has smaller Rct than the 3wt%GR-ZnO, which suggests more efficient transfer of charge carriers over 3wt%RGO-ZnO than that over 3wt%GR-ZnO.<sup>1a</sup>

#### Reference

- (a) N. Zhang, Y. Zhang, X. Pan, X. Fu, S. Liu and Y.-J. Xu, *J. Phys. Chem. C*, 2011, **115**, 23501; (b)
   Y. Zhang, Z.-R. Tang, X. Fu and Y.-J. Xu, *ACS Nano*, 2010, **4**, 7303; (c)
   Y. Zhang, Z.-R. Tang, X. Fu and Y.-J. Xu, *ACS Nano*, 2011, **5**, 7426.
- S. Deng, V. Tjoa, H. M. Fan, H. R. Tan, D. C. Sayle, M. Olivo, S. Mhaisalkar, J. Wei and C. H. Sow, J. Am. Chem. Soc., 2012, 134, 4905.
- 3. S. Chen, J. Zhu, X. Wu, Q. Han and X. Wang, ACS Nano, 2010, 4, 2822.
- Q. Yu, W. Fu, C. Yu, H. Yang, R. Wei, M. Li, S. Liu, Y. Sui, Z. Liu, M. Yuan, G. Zou, G. Wang, C. Shao and Y. Liu, *J. Phys. Chem. C*, 2007, **111**, 17521.
- 5. A. McLaren, T. Valdes-Solis, G. Li and S. C. Tsang, J. Am. Chem. Soc., 2009, 131, 12540.
- 6. J. Elias, R. Tena-Zaera, G.-Y. Wang and C. Lévy-Clément, Chem. Mater., 2008, 20, 6633.
- X. Cao, H. Zeng, M. Wang, X. Xu, M. Fang, S. Ji and L. Zhang, J. Phys. Chem. C, 2008, 112, 5267.
- 8. D. A. Panayotov and J. R. Morris, J. Phys. Chem. C 2009, 113, 15684.

- 9. X. An and J. C. Yu, *RSC Advances*, 2011, 1, 1426.
- 10. Z. Liang, X. Cai, S. Tan, P. Yang, L. Zhang, X. Yu, K. Chen, H. Zhu, P. Liu and W. Mai, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16111.
- 11. Z. Chen, N. Zhang and Y.-J. Xu, CrystEngComm, 2013, 15, 3022.
- 12. G. Williams and P. V. Kamat, Langmuir, 2009, 25, 13869.
- 13. (a) X. Bai, L. Wang, R. Zong, Y. Lv, Y. Sun and Y. Zhu, *Langmuir*, 2013, 29, 3097; (b) J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang and Y. Dai, *ACS Appl. Mater. Interfaces*, 2012, 4, 4024; (c) A. Janotti and C. G. Van de Walle, *Appl. Phys. Lett.*, 2005, 87, 122102.
- 14. A. B. Djurišić and Y. H. Leung, Small, 2006, 2, 944.
- 15. G. R. Li, T. Hu, G. L. Pan, T. Y. Yan, X. P. Gao and H. Y. Zhu, J. Phys. Chem. C, 2008, 112,

11859.

### Appendix:



Fig. S11. SEM image of graphene oxide (GO).



**Fig. S12.** TEM image of graphene oxide (GO); inset is the high-resolution TEM (HRTEM) image of GO.



Fig. S13. XRD patterns of graphene oxide (GO) and graphene (GR).

**Note:** Graphene is obtained by the hydrothermal reduction of GO in a solvent of ethanol-water at 180 °C for 12 h.<sup>2,3</sup> As can be seen from Figure S14, GO has a characteristic peak at  $2\theta$ = 10.2°. After hydrothermal reduction, the peak at  $2\theta$ = 10.2° disappears and a weak and broad peak appears at around 24.6°, which is the characteristic peak of GR.



Fig. S14. Additional typical TEM image of the 3wt% RGO-ZnO nanocomposite.