Supplementary Information for

ZnO@graphene Composite with Enhanced Performance in Removal of Dye from Water

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Experimental Section

Synthesis. Graphene oxide (GO) was prepared from purified natural graphite according to the Hummers method.[1] In detail, graphite powder (1.0 g), $NaNO_3$ (0.5 g) and $KMnO_4$ (3.0 g) were slowly added into concentrated H_2SO_4 (23 ml) cooled by ice bath and the mixture was vigorously stirred at 35±3 °C for 30 min. On completion of the reaction, water (46 ml) was added, and the temperature was kept at 98 °C for 15 min. Then the temperature was reduced to 60 °C with the addition of warm water (140 ml), H_2O_2 (30%, 10 ml) was added and the reaction was further stirred for 2 h. The above mixture was filtrated to collect the solid product and washed with 4% HCl solution (5 times), and then washed repeatedly with distilled water (three times). Finally the material was dried in vacuum to obtain a loose brown powder.

GO (10 mg) and water (20 ml) was ultrasonicated in a flask for 2 h. A aqueous solution (10 ml) of $Zn(AcO)_2{\cdot}2H_2O$ added to the flask. The mixture was stirred for 4 h to complete ion exchange. Aqueous solution (10 mL) of NaOH was added dropwise. The mixture was kept stirring for a further 1 h. The solid was obtained by centrifuge and washed with water, dried in vacuum at room temperature and then heated in air at 150 °C for 2 h. In the absence of GO, pure ZnO was obtained via similar process. The powder was suspended into water (10 ml). After stirring and ultrasonication for 30 min, $NaBH_4$ (24.8 mg, 6.4 mmol) was added and the mixture was transferred into a Teflon lined autoclave and heated to 120 °C for 4 h. The resulted solid products were washed with water (3×10 ml) and ethanol (3×10 ml) and ZnO@graphene composites were obtained. Graphene was obtained from GO by reduction with $NaBH_4$ via similar process. The designated amount of ZnO on graphene is 90 mg. In the absence of GO, ZnO was obtained via similar process.

Characterization. Fourier transform infrared (FTIR) spectra measurements were carried out on a NICOLET 560 Fourier transform infrared spectrophotometer. Raman spectrum was recorded on a Renishaw RM–1000 with excitation from the 514 nm line of an Ar–ion laser with a power of about 5 mW. The phase structures of as–prepared products were characterized with X–ray diffraction (XRD, Bruker D8 advance) with Cu Kα λ=1.5418 Å). X–ray photoelectron spectrum (XPS) were recorded on a PHI quantera SXM spectrometer with an Al Kα=280.00 eV excitation source, where binding energies were calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect. The morphology of as–prepared products was studied by using transmission electron microscope (TEM, JEOL JEM–2100, operating at 100 kV) and high resolution TEM (HRTEM, JEOL JEM–2010F electron microscope, operating at 200 kV). For atom force microscopy (AFM) measurement, the samples were coated on Si surface and AFM studies were performed using a Digital Instruments Dimension 3100 microscope in the tapping mode.

The ZnO@graphene composite dispersions were prepared by mixing composite (0.5 mg) in aqueous solution (100 μL) containing 2–propanol (20 μL) and a Nafion® solution (5wt%, 5 μL) (V_{water}:$V_{2\text{–}propanol}$:$V_{5\%\ Nafion}$=0.8:0.2:0.05), followed by ultrasonication for 10 min. A designed amount (20 μL) of dispersion was drop–cast onto the gold electrode (2.1 mm in diameter) and dried for 8 h before the cyclic–voltammogram (CV) measurements. The CV measurement is carried out at the CHI660B type Electrochemical Working Station with classical three electrode system. The Ag/AgCl/KCl (sat.)

electrode and Pt wire were used as reference and counter electrode respectively. The electrode capacitance value (C°) was obtained from CV at 0.25 V versus Ag/AgCl in saturated aqueous solution of KCl.

The photocatalytic activities of catalysts were evaluated in terms of the degradation of Rh B and MB in an aqueous solution. A 300 W high-pressure mercury lamp (λ>365 nm, Beijing Huiyixin Electric Forces Technology Development Co. LTD) was used as ultraviolet light source and cooled by circulating water jacket for keeping room temperature. The catalyst (50 mg) was suspended in an aqueous solution of Rh B (1.0×10^{-5} M, 50 ml) with a magnetic stirring bar in a glass baker, which was positioned at place with a 10 cm distance from light source. After stirring for 30 min to homogenize the mixture, the light source was turn on. The concentration of Rh B and MB was monitored by using a UV–VIS recording spectrophotometer (UNIC Corp. UV–2102PC). The 300 W high-pressure mercury lamp with a filter (λ>400 nm) was used as visible light source.

The ZGC was pressed into a 13 mm round plate and pressed into membrane, then the membrane was fixed in a filter. Solution of RhB (1.0×10^{-5} M) was impelled to pass through the membrane under a constant rate of 0.1 mL min^{-1}. The concentration of RhB in the filtrate was measured with a UV–VIS recording spectrophotometer (UNIC Corp. UV–2102PC).

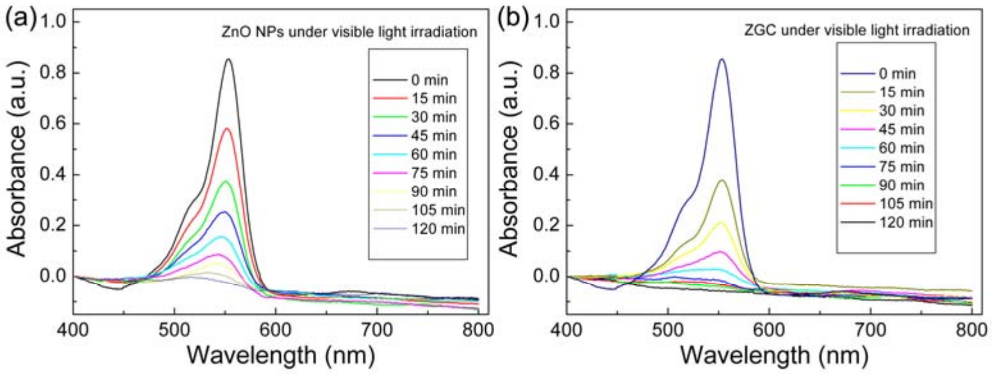

Figure S1. Evolution of RhB during the photocatalytic degradation reaction for (a) ZnO NPs, and (b) ZnO@graphene composite catalysts under visible light irradiation.

References

(1) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339.