

Supporting information for the manuscript

Toward enhanced photoactivity and photostability of ZnO nanospheres via intimate surface coating with reduced graphene oxide

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1. Synthesis of ZnO nanospheres (NSs)

The ZnO NSs used in this work were prepared by hydrolyzing of zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) in diethylene glycol ($\text{C}_4\text{H}_{10}\text{O}_3$, DEG). It is a modified method as described by Seelig *et al*^{S1}. In a typical reaction, 2.1951 g $\text{Zn}(\text{CH}_3\text{COO})_2$ was added to 100 ml diethylene glycol (DEG). The reaction occurred when the mixed solution was heated under reflux to 160 °C for 12 h and the product was placed in a centrifuge. The supernatant (DEG, dissolved reaction products, and unreacted $\text{Zn}(\text{CH}_3\text{COO})_2$ and water) was decanted off and saved, and the precipitation segregated to the bottom of the tube was discarded. The secondary reaction began in the same way as a primary reaction: 2.1951 g $\text{Zn}(\text{CH}_3\text{COO})_2$ was added to 100 ml DEG and the reaction solution was heated under reflux. Prior to reaching the working temperature, however, typically at 150°C, 10 mL of the primary reaction supernatant was added to the solution. After reaching 160 °C, the reaction was stirred for one hour, after which the heat source was removed, and the flask cooled to room temperature. The colloidal spheres produced by this method have been reported to be monodispersed with a diameter size of 300 nm, and consist of many primary nanoparticles with a diameter of 20 nm.

2. Synthesis of Graphene Oxide (GO)

GO was synthesized from natural graphite powder by a modified Hummers method.^{S2-S5} In detail, 2 g of graphite powder (supplied from Sinopharm Chemical Reagent Co., Ltd., China) was put in to a mixture of 12 mL of concentrated H_2SO_4 , 2.5 g of $\text{K}_2\text{S}_2\text{O}_8$, 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 pre-oxidized graphite was then subjected to oxidation described as follows. In a typical procedure, pre-oxidized graphite powder was added to a mixture of 120 mL of concentrated H_2SO_4 and 30 mL 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 diluted 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 in the form of a dry, brown powder.



Fig. S1. Photograph of the experimental setup for photocatalytic activity testing.

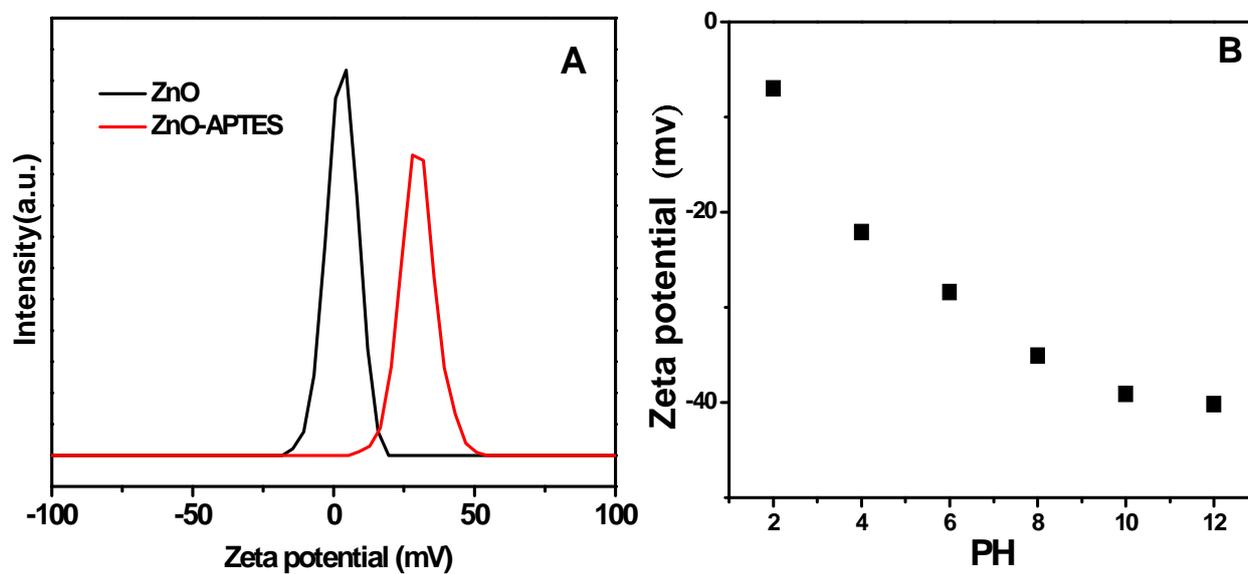


Fig. S2. The zeta potentials of blank ZnO NSs and the (3-aminopropyl) triethoxysilane (APTES)-modified ZnO NSs in water (pH = 6.5) (A) and the zeta potentials of GO as a function of pH in deionized water (B).

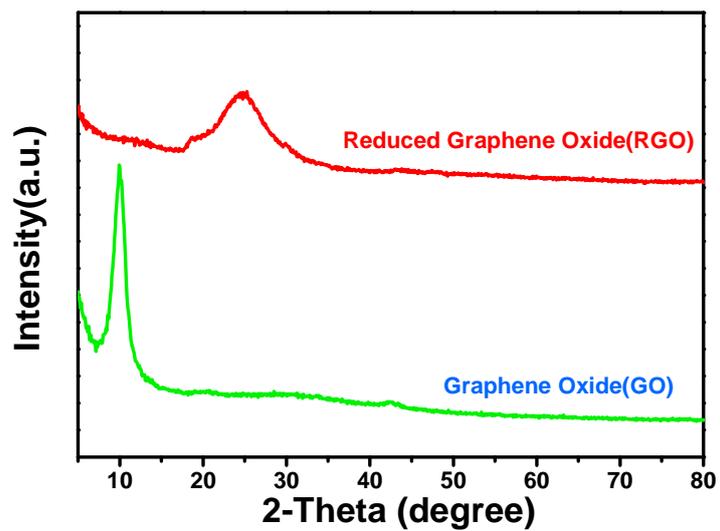


Fig. S3. XRD patterns of the samples of GO and RGO.

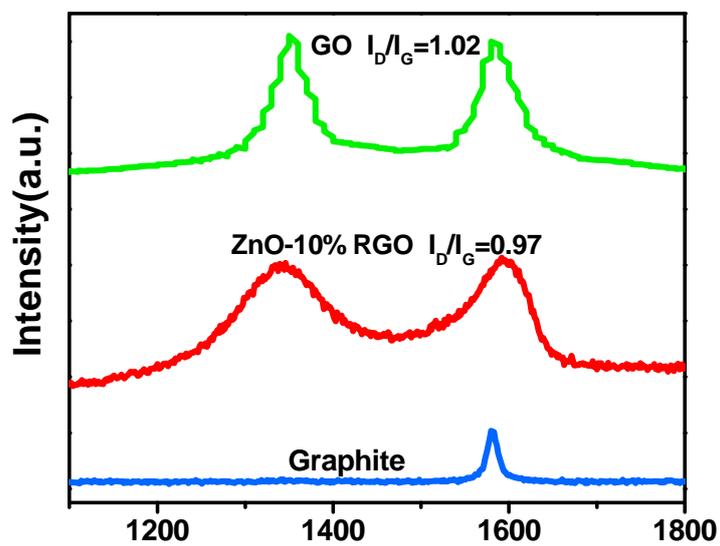


Fig. S4. The Raman spectra of the original GO and ZnO-10%RGO NCs and graphite.

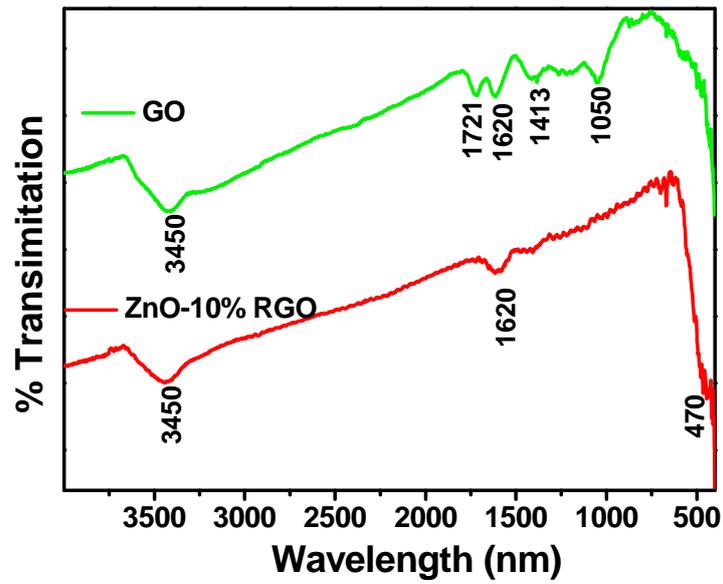


Fig. S5. FT-IR spectra of the original GO and ZnO-10%RGO NCs.

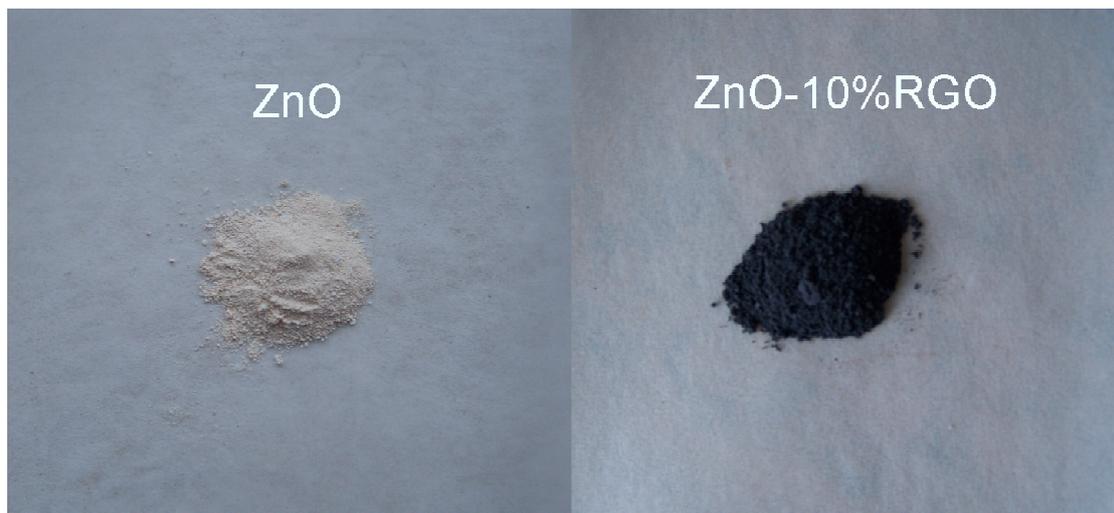


Fig. S6. The photographs of the sample ZnO NSs (A) and ZnO-10%RGO NCs (B).

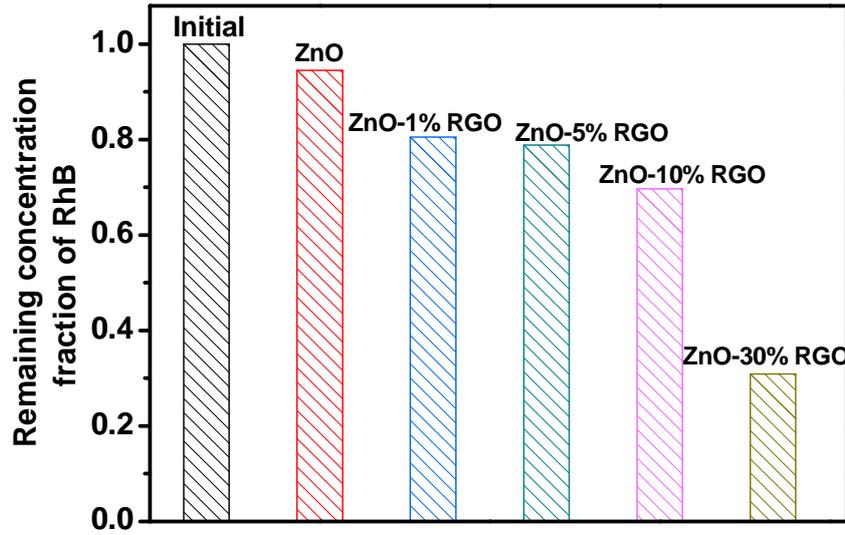


Fig. S7. Bar plot showing the remaining RhB after reaching the adsorption-desorption equilibrium in the dark over the ZnO-RGO nanocomposites for the degradation of RhB.

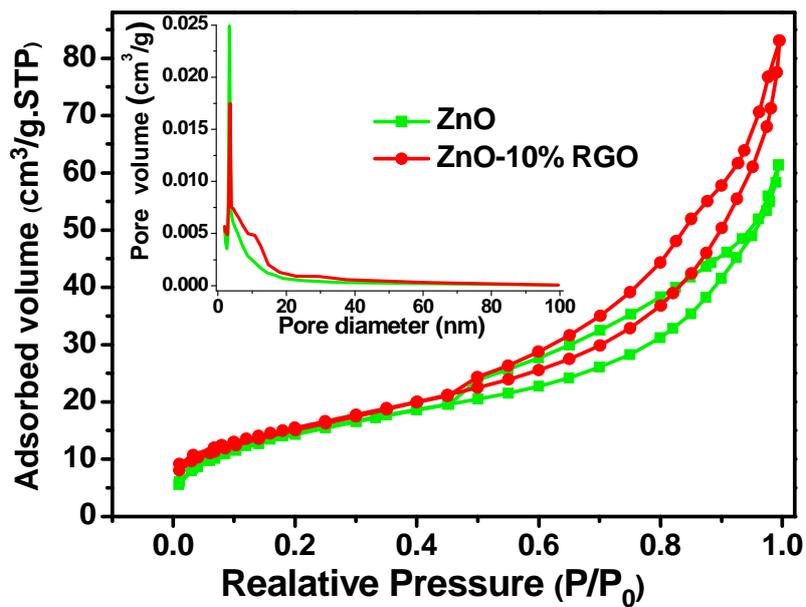


Fig. S8. Nitrogen adsorption-desorption isotherms of the ZnO NSs and the ZnO-10%RGO NCs; the inset is the corresponding pore size distribution.

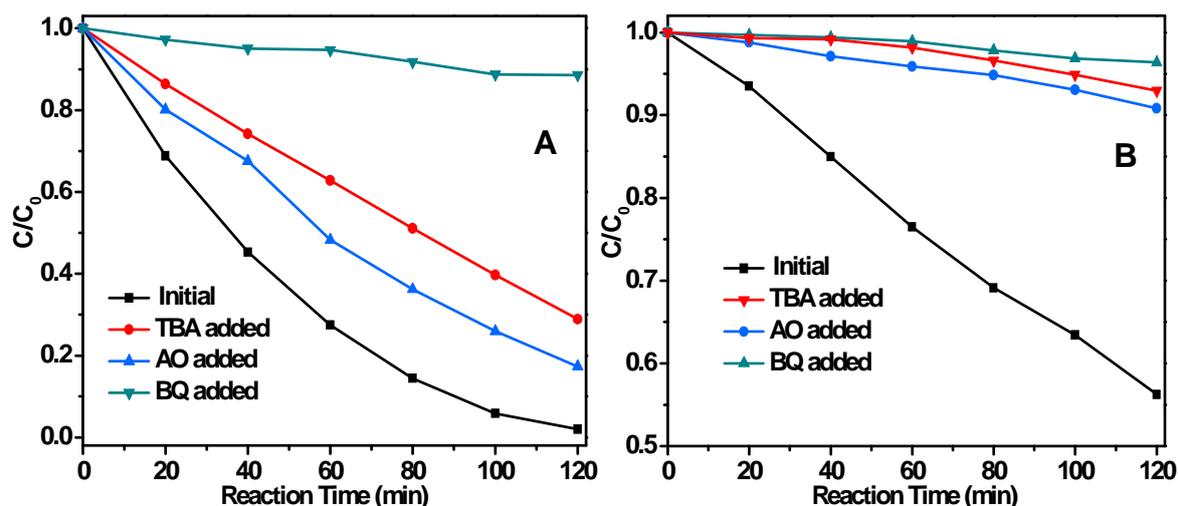


Fig. S9. Controlled experiments of photocatalytic degradation of RhB over ZnO-10%RGO NCs (A) and ZnO NSs (B) in the presence of tert-butyl alcohol (TBA, scavenger for hydroxyl radicals), benzoquinone (BQ, scavenger for superoxide radicals), ammonium oxalate (AO, scavenger for holes) under UV light irradiation.

Table 1. Summary of surface area, pore volume and pore size of the as-prepared ZnO NSs and ZnO NSs-10%RGO for comparison

Samples	S_{BET} (m^2/g) ^a	Total pore volume (cm^3/g) ^b	Average pore size (nm) ^c
ZnO NSs	55	0.095	6.96
ZnO NSs-10%RGO	56	0.128	9.16

^a BET surface area is calculated from the linear part of the BET plot.

^b Single point total pore volume of the pores at $P/P_0 = 0.99$.

^c Adsorption average pore width ($4 V/A$ by BET).

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Appendix:

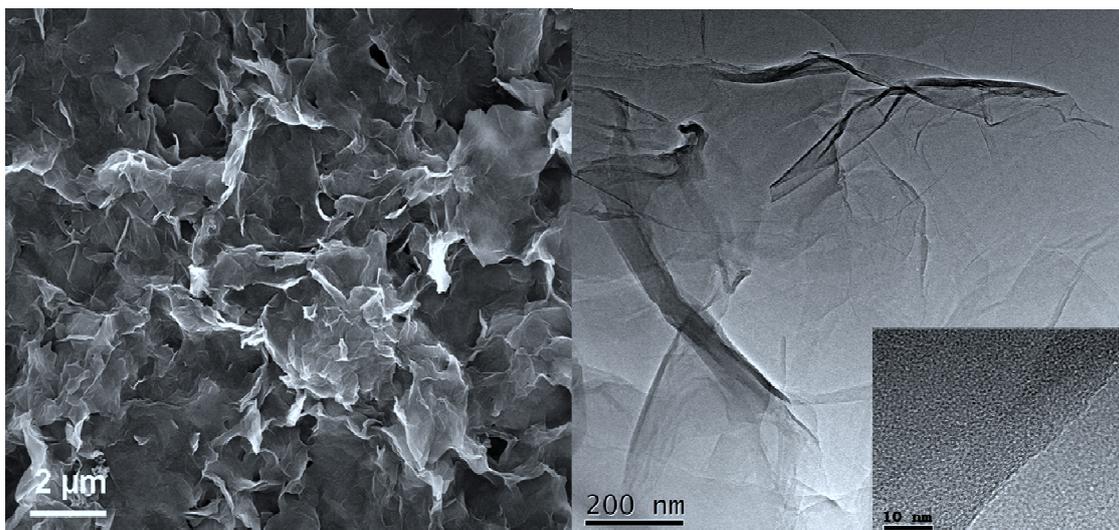


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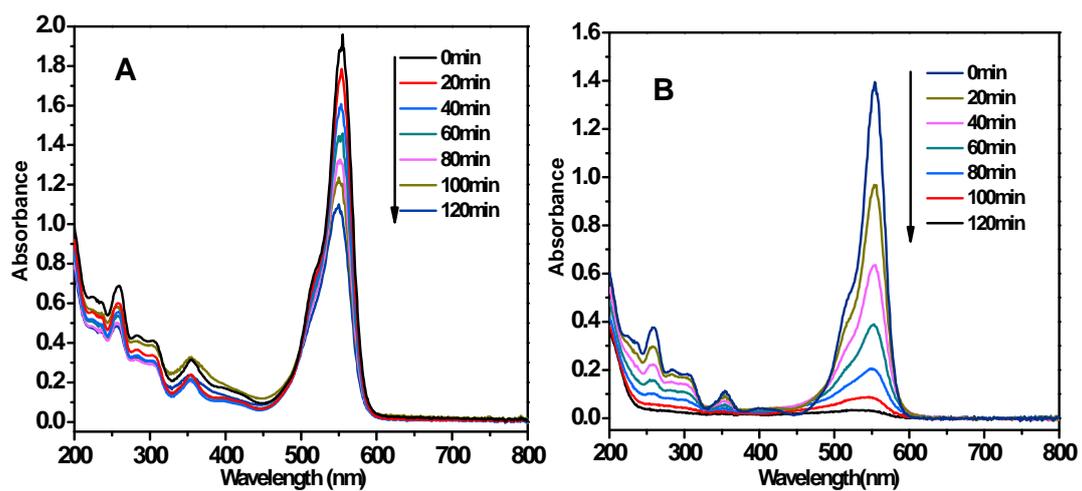


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