Electronic Supplementary Information (ESI)

Graphene–metal–oxide composites for the degradation of dyes under visible light irradiation

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Preparation of Chemically Exfoliated Graphene Oxide. The graphene oxide used in this work was prepared from natural graphite (Alfa Aesar) by using a modified Hummers method.[1] 5 g of graphite and 2.5 g of sodium nitrate ($NaNO_3$) were mixed with 160 mL of concentrated sulfuric acid (H_2SO_4, 95%, Sigma–Aldrich) in a 500 mL flask. After the mixture was stirred for 30 min in an ice bath, 18 g of potassium permanganate ($KMnO_4$) was added under vigorous stirring. The rate of addition was carefully controlled to keep the reaction temperature lower than 20 °C. After the mixture was continuously stirred at room temperature overnight, 150 mL of deionized (DI) water was slowly added under vigorous agitation. After the diluted suspension was stirred for one day, 50 mL of 30 wt.% H_2O_2 was added to the mixture. Finally, the mixture was washed by rinsing and centrifugation with 5 wt.% HCl and then DI water for several times. Chemical exfoliation of thus-obtained graphite oxide was carried out in an ultrasonic bath. After ultrasonication, a GO colloid was obtained.

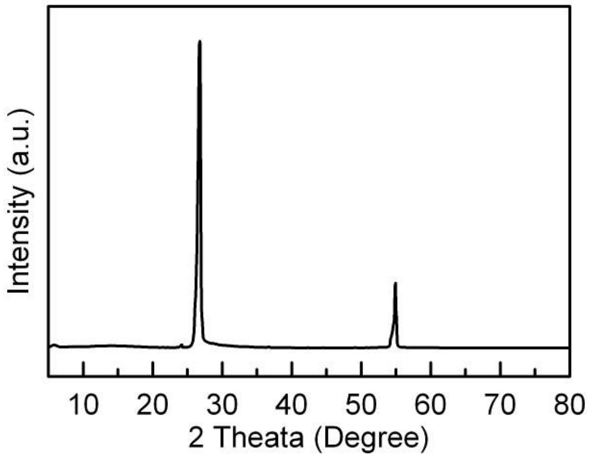

Figure S1. XRD pattern of the graphite used in this study.

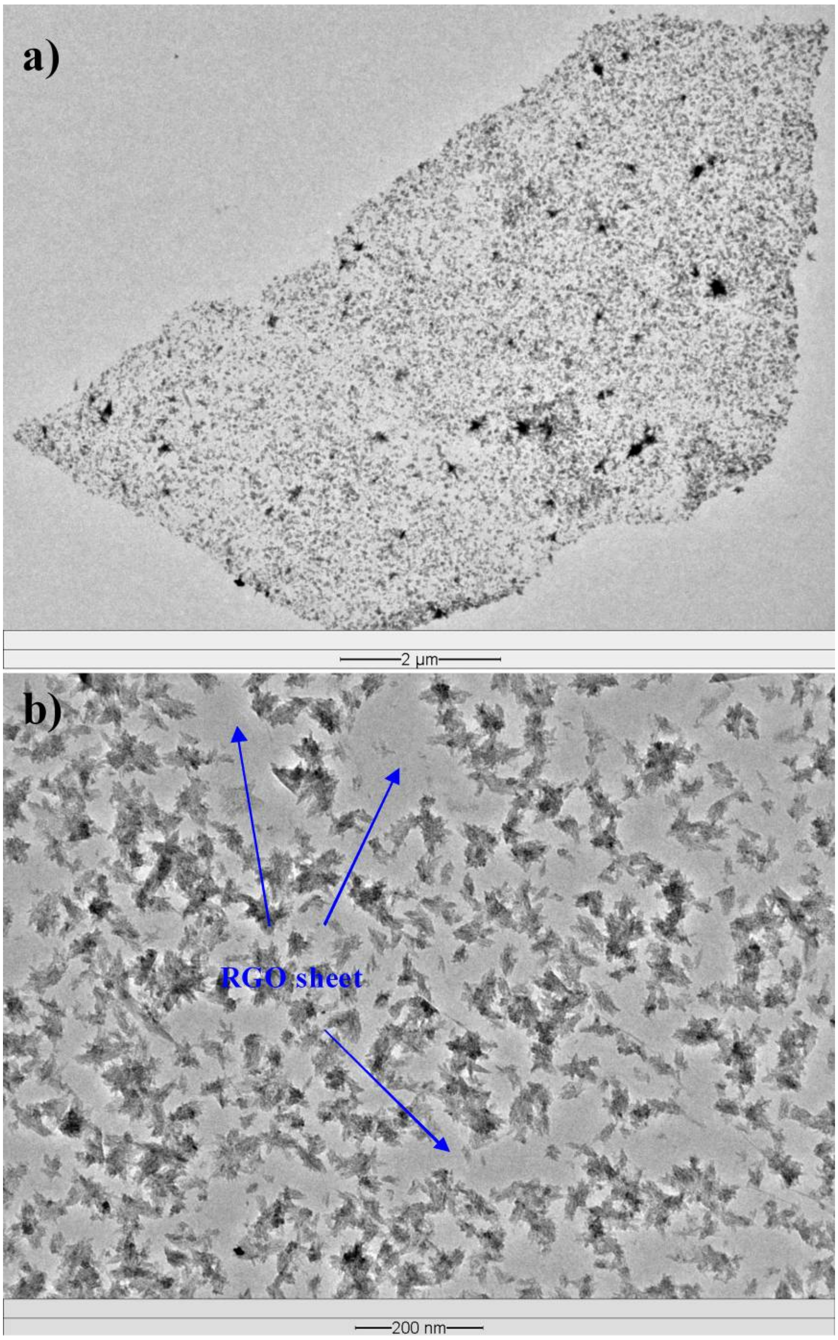

Figure S2. TEM images of sample RGO–TiO_2 at different magnifications.

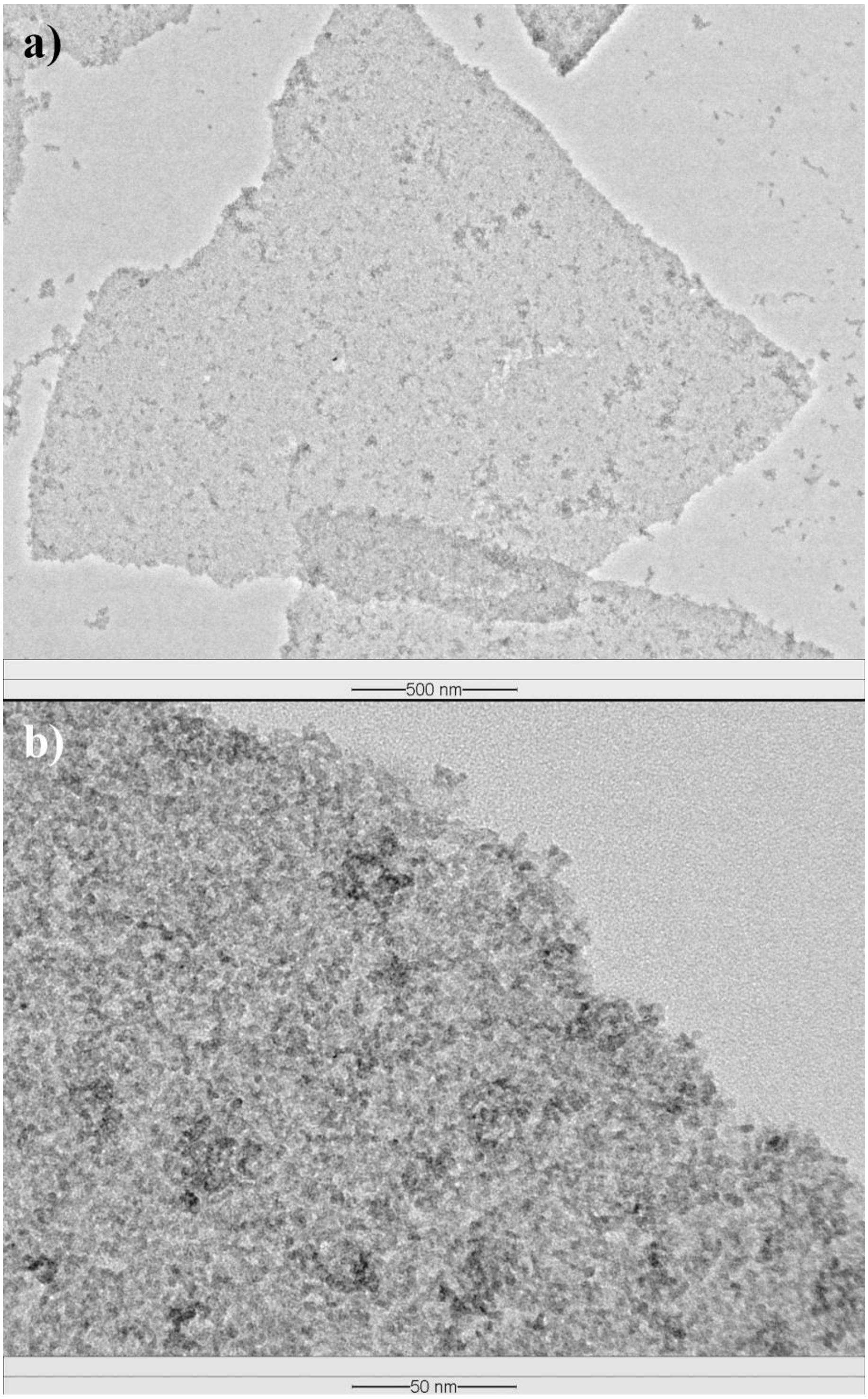

Figure S3. TEM images of sample RGO–SnO_2 at different magnifications.

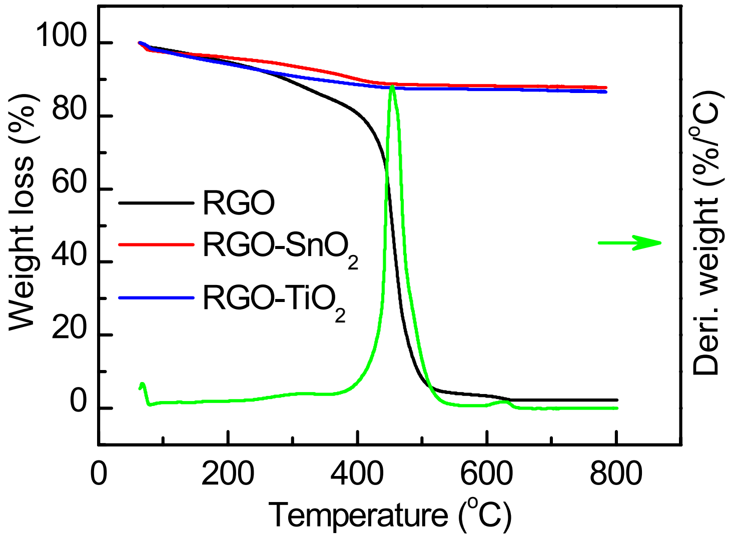

Figure S4. TGA and derivative TG curves of RGO, RGO–SnO_2, and RGO–TiO_2.

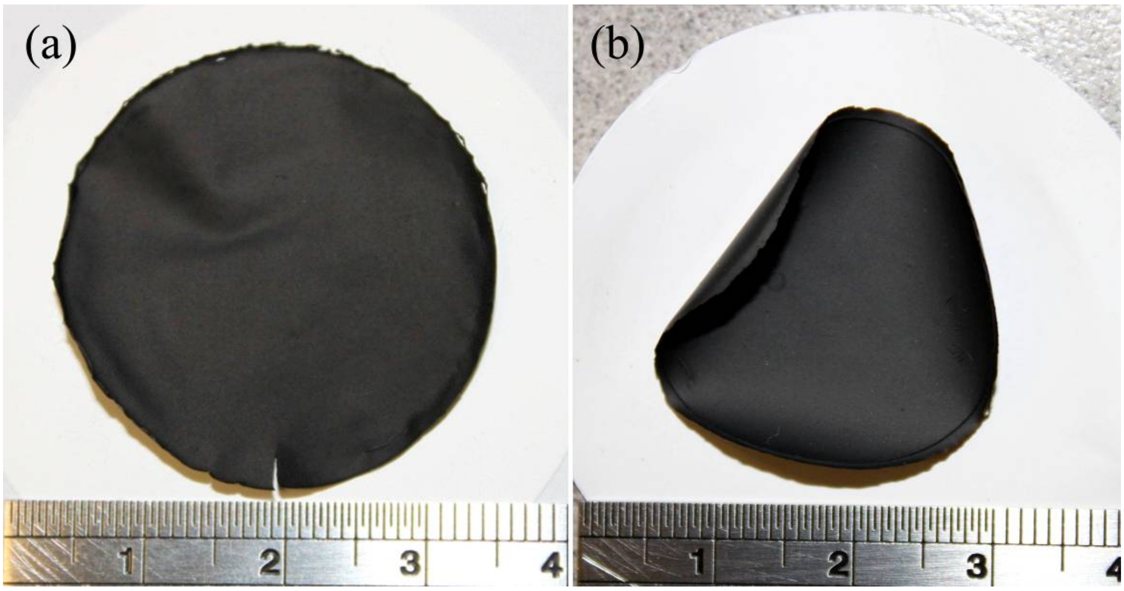

Figure S5. Photographs of free-standing RGO–SnO_2 (a) and RGO–TiO_2 films (b).

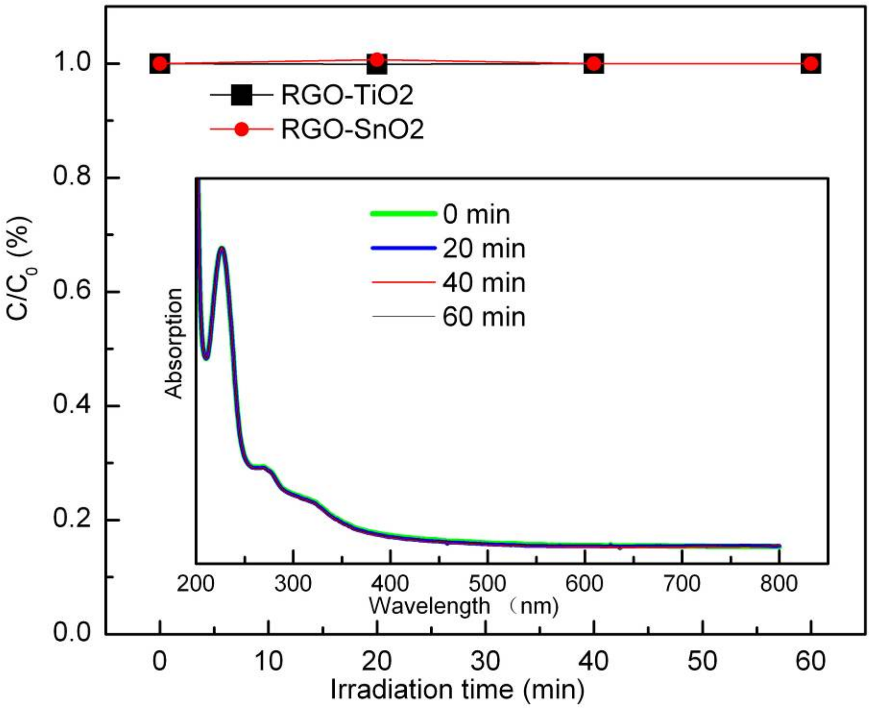

Figure S6. Photocatalytic activity of catalysts RGO-TiO_2 and RGO-SnO_2 in the degradation of benzoic acid under visible light irradiation. The inset shows the absorption profiles of benzoic acid against irradiation time in the presence of catalyst RGO-TiO_2, showing no red shift.

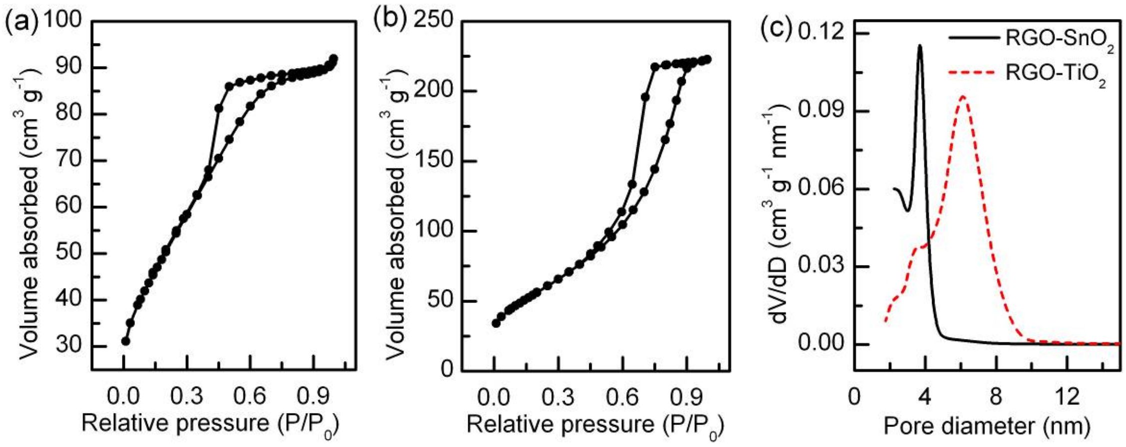

Figure S7. N_2 adsorption-desorption isotherms of a) RGO–SnO_2–400 and b) RGO–TiO_2–400. c) The corresponding pore size distributions.

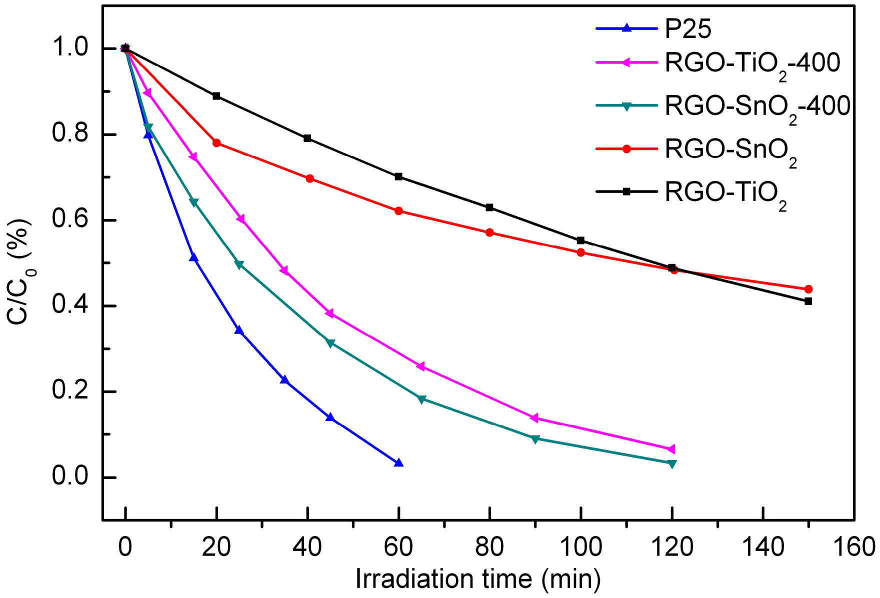

Figure S8. Degradation of RhB over various catalysts under UV light irradiation.

The degradation of RhB over various catalysts prepared in this work together with that of P25 under UV light irradiation has been investigated. The results are shown in Figure S8. As can be seen, RGO–TiO_2 and RGO–SnO_2 the analogous activity trend for photocatalytic degradation of RhB under UV light irradiation. After being calcined at 400 °C, , the photocatalytic activities of both samples were enhanced as can be seen catalysts RGO–TiO_2–400 and RGO–SnO_2–400. The degradation rate constants for catalysts RGO–SnO_2–400, RGO–TiO_2–400, RGO–SnO_2–400, and RGO–TiO_2 were calculated to be about 2.7×10^{-2} min^{-1}, 2.3×10^{-2} min^{-1}, 5.2×10^{-3} min^{-1}, and 5.9×10^{-3} min^{-1}, respectively. However, these rate constants are all lower than that of P25 (4.3×10^{-2} min^{-1}), showing a lower photocatalytic activity of the composite materials than that of P25 under UV irradiation.

Under UV light irradiation both the catalysts and the dye can be excited, it is thus difficult to distinguish the contributions of semiconductor photocatalysis and photosensitized dye degradation.[2,3] This makes it impossible to evaluate the relationship between the dye degradation and the redox potentials of the conduction bands of TiO_2, graphene and SnO_2. Thus, in this work, we employed visible light to exclude the effect of semiconductor photocatalysis to ensure the degradation was merely due to the photosensitized dye degradation.

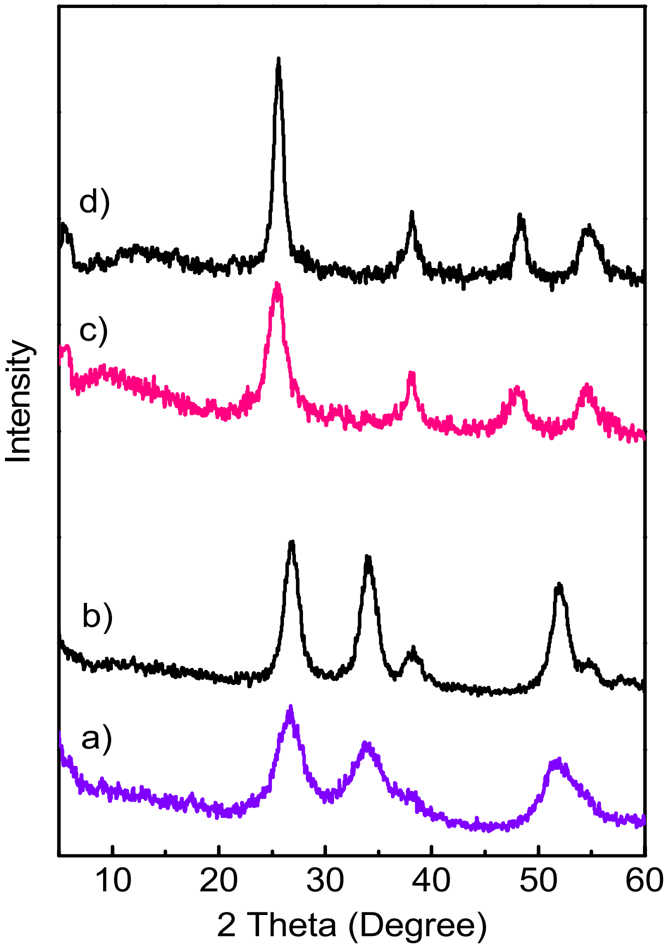

Figure S9. XRD patterns of a) RGO–SnO_2, b) RGO–SnO_2–400, c) RGO–TiO_2, and d) RGO–TiO_2–400.

References :

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

2. P.V. Kamat, *Chem. Rev.* **1993**, *93*, 267.

3. T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone *J. Phys. Chem. B* **1998**, *102*, 5845.