

Supporting information for

One-pot preparation of Bi/Bi₂WO₆/reduced graphene oxide as a plasmonic photocatalyst with improved activity under visible light[†]

Yan Zhou, Sushan Ren, Qimei Dong, Yingying Li, Hanming Ding*

School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China

Synthesis of graphene oxide (GO)

Graphite oxide (GO) was synthesized via a modified Hummers' method.¹⁻² Briefly, 0.5 g previously oxidized graphite was reacted with a mixture of 2 g NaNO₃, 12 mL concentrated H₂SO₄ and 3 g KMnO₄, followed by addition of 40 mL H₂O and 10 mL H₂O₂ (30%). The product was filtered and washed with 5% HCl solution and deionized water to obtain a light yellow powder, and dried at 60 °C for 12 h.

Synthesis of Bi/Bi₂WO₆

For the synthesis of Bi/Bi₂WO₆, 1g PVP (K-30) and 3.5mmol Bi(NO₃)₃•5H₂O were dissolved in 20 mL of ethylene glycol under stirring. And then 0.5 mL Na₂WO₄ solution (2 mol/L) was dumped into the mixture and stirred for 30 min obtain a homogeneous suspension. After that, the suspension was transferred into a Teflon-lined autoclave

[†] Electronic supplementary information (ESI) available.

with a capacity of 25 mL, and kept at 180 °C for 24 h. For the Bi/Bi₂WO₆ composites with a controllable composition, the mass fractions of Bi can be tuned by adjusting the molar ratio of Bi(NO₃)₃ to Na₂WO₄ in the reaction. The molar ratios of Bi(NO₃)₃ to Na₂WO₄ were controlled at 1:1, 2:1, 2.5:1, 3:1, 3.5:1 and 4:1, and the resulting samples were denoted as Bi/Bi₂WO₆-1, Bi/Bi₂WO₆-2, Bi/Bi₂WO₆-2.5, Bi/Bi₂WO₆-3, Bi/Bi₂WO₆-3.5 and Bi/Bi₂WO₆-4, respectively.

Synthesis of Bi₂WO₆ and Bi₂WO₆/rGO

For the synthesis of Bi₂WO₆, 1g PVP (K-30) and 3.5mmol Bi(NO₃)₃•5H₂O were dissolved in 20 mL of water under stirring. And then 0.5 mL Na₂WO₄ solution (2 mol/L) was dumped into the mixture and stirred for 30 min obtain a homogeneous suspension. After that, the suspension was transferred into a Teflon-lined autoclave with a capacity of 25 mL, and kept at 180 °C for 24 h. Typically, rGO wrapped Bi₂WO₆ composite was obtained by the similar solvothermal method. As-prepared Bi₂WO₆, 1g PVP and 3mg GO were dispersed in 20 mL of ethylene glycol under stirring. Then the suspension was transferred into a Teflon-lined autoclave with a capacity of 25 mL, and kept at 180 °C for 24 h. After the autoclave was cooled naturally to room temperature, the product was separated, washed with absolute ethanol and distilled water for several cycles, and dried at 60 °C in vacuum.

As shown in Fig. S1, all of the diffraction peaks can be indexed to the orthorhombic phase of Bi₂WO₆ (marked with“•”) and the hexagonal phase of Bi

(marked with “ Δ ”), respectively. Two sets of XRD peaks of Bi_2WO_6 and Bi can be clearly observed in Figure S1b-f. Meanwhile, the diffraction peak intensity ratio ($I(\text{Bi})/I(\text{Bi}_2\text{WO}_6)$) between the two components increase gradually with increasing $n(\text{Bi}(\text{NO}_3)_3) / n(\text{Na}_2\text{WO}_4)$ molar ratio, indicating that the content of Bi nanoparticles can be adjusted by changing the precursor molar ratios of $n(\text{Bi}(\text{NO}_3)_3) : n(\text{Na}_2\text{WO}_4)$.

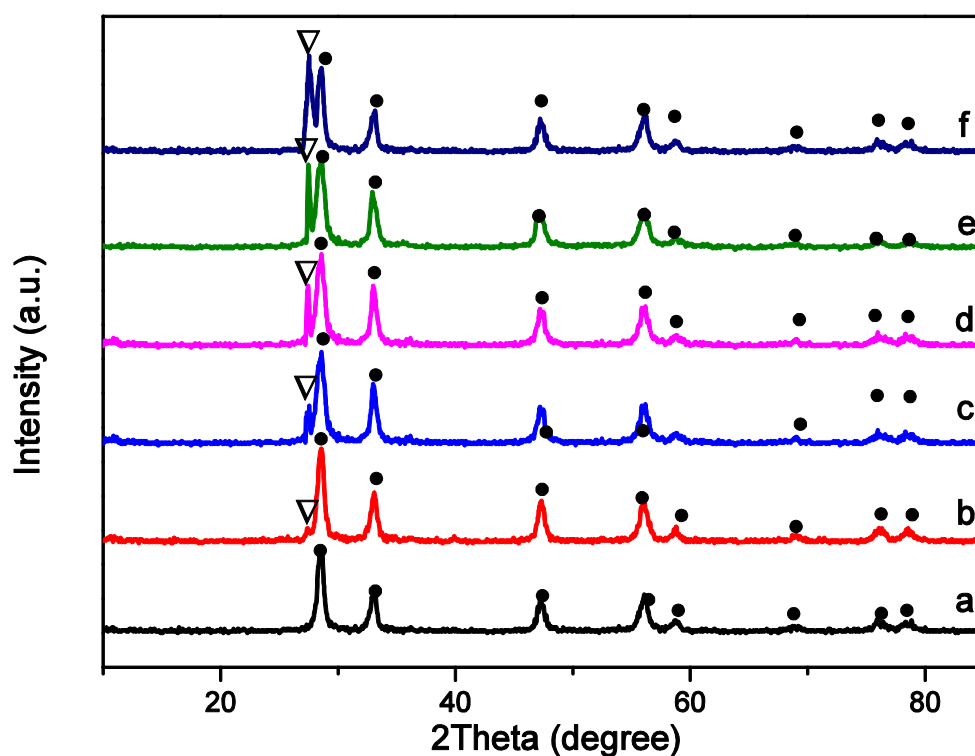


Fig. S1 Power X-ray diffraction patterns of (a) $\text{Bi}/\text{Bi}_2\text{WO}_6$ -1, (b) $\text{Bi}/\text{Bi}_2\text{WO}_6$ -2, (c) $\text{Bi}/\text{Bi}_2\text{WO}_6$ -2.5, (d) $\text{Bi}/\text{Bi}_2\text{WO}_6$ -3 (e) BB-3.5, and (f) $\text{Bi}/\text{Bi}_2\text{WO}_6$ -4.

Fig. S2 shows the XRD patterns of the $\text{Bi}/\text{Bi}_2\text{WO}_6/\text{rGO}$ nanocomposites prepared with different amounts of GO. The results indicating that the presence of rGO in the reaction mixture does not influence the structure of Bi and Bi_2WO_6 . No diffractions peaks corresponding to either GO or rGO has been observed in the XRD patterns of the

resultant products, probably due to its low amount and relatively low diffraction intensity.³

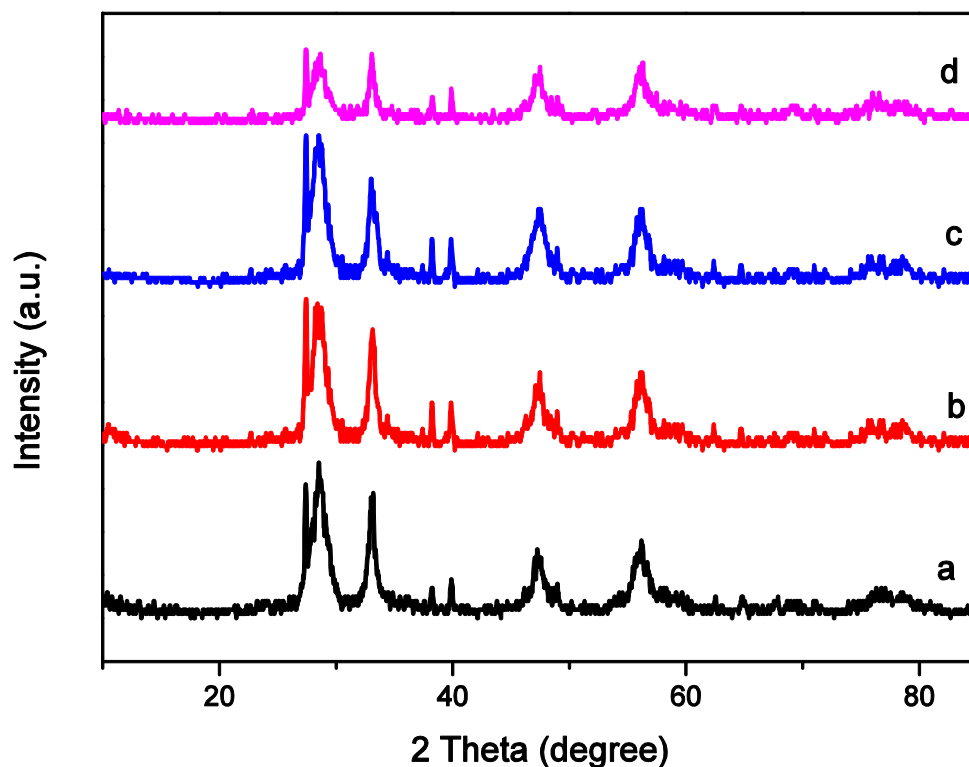


Fig. S2 Power X-ray diffraction patterns of (a) Bi/Bi₂WO₆/rGO-1, (b) Bi/Bi₂WO₆/rGO-2, (c) Bi/Bi₂WO₆/rGO-3, and (d) Bi/Bi₂WO₆/rGO-4.

The DRS of the as-prepared Bi/Bi₂WO₆ composites are shown in Fig. S3. The Bi/Bi₂WO₆ composites exhibit an enhanced absorption in the visible region than Bi₂WO₆. Furthermore, the absorbance of the Bi/Bi₂WO₆ composites increases especially in the visible region with increasing the molar ratio of Bi(NO₃)₃ to Na₂WO₄ in the precursor solutions, which is due to more Bi reduced in the Bi/Bi₂WO₆ composites.⁴ These results imply that the visible light response of the composites is improved by introducing Bi to the Bi₂WO₆ nanosheets, and the phase junction is

beneficial to the separation of the photogenerated charge carriers, which subsequently results in an enhanced photocatalytic activity.

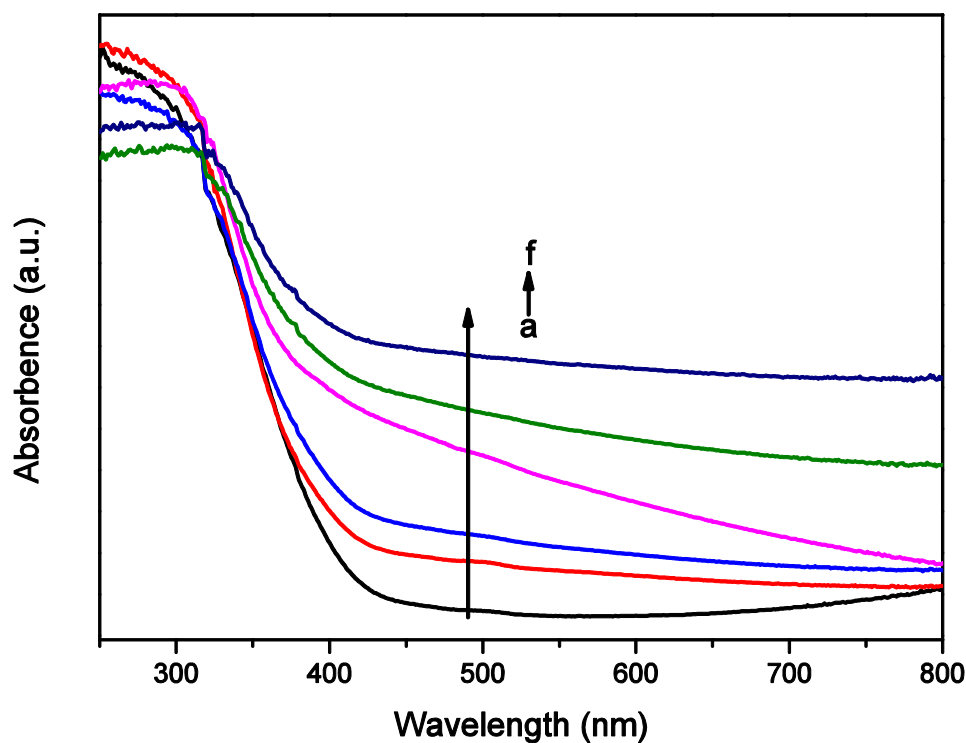


Fig. S3 UV-vis diffuse reflectance adsorption spectra of (a) Bi/Bi₂WO₆-1, (b) Bi/Bi₂WO₆-2, (c) Bi/Bi₂WO₆-2.5, (d) Bi/Bi₂WO₆-3 (e) Bi/Bi₂WO₆-3.5, and (f) Bi/Bi₂WO₆-4.

Fig. S4 shows the photocatalytic properties of the as-prepared Bi/Bi₂WO₆ nanocomposites under visible light irradiation. The photocatalytic activity was enhanced when $n(\text{Bi}(\text{NO}_3)_3) / n(\text{Na}_2\text{WO}_4)$ increased from 1 to 3.5 and decreased when the molar ratio was 4. The BB-1.4 composite has the highest photocatalytic activity.

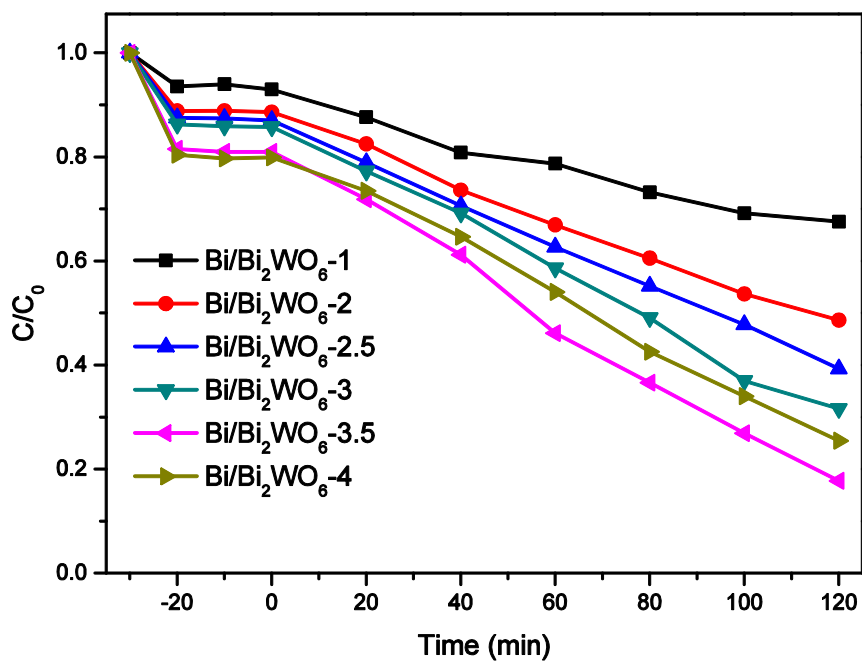
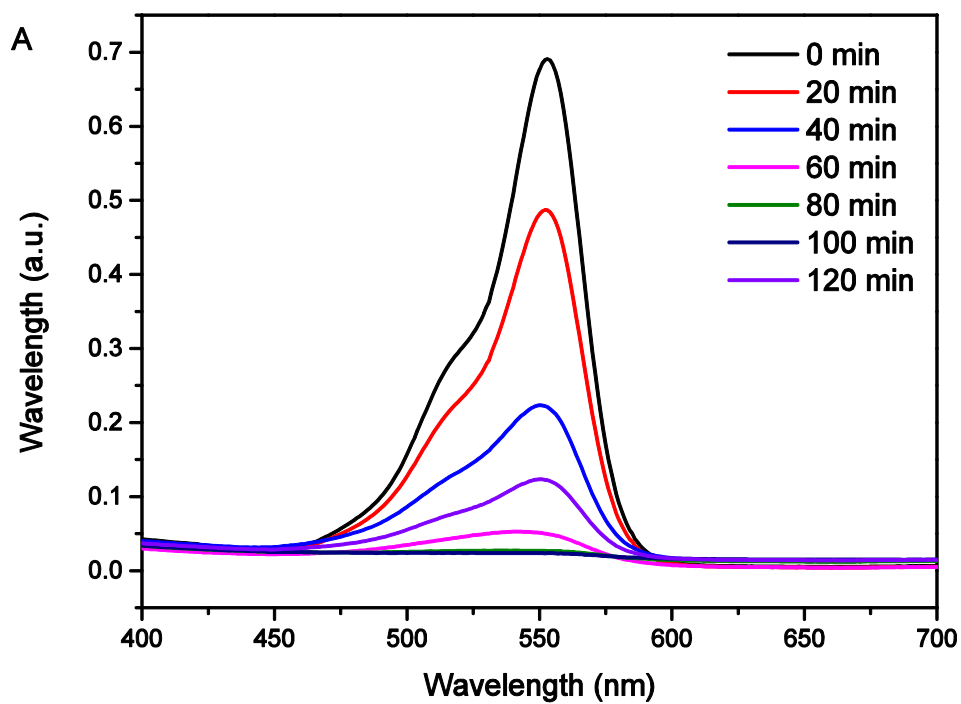


Fig. S4 Photocatalytic degradation of RhB under visible light irradiation with different photocatalysts.



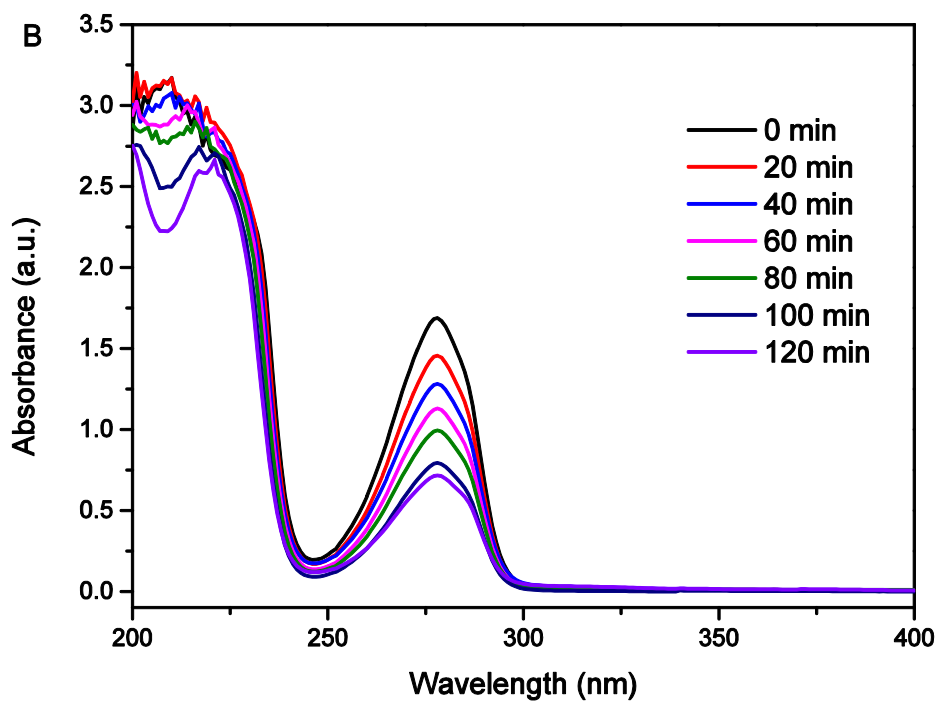
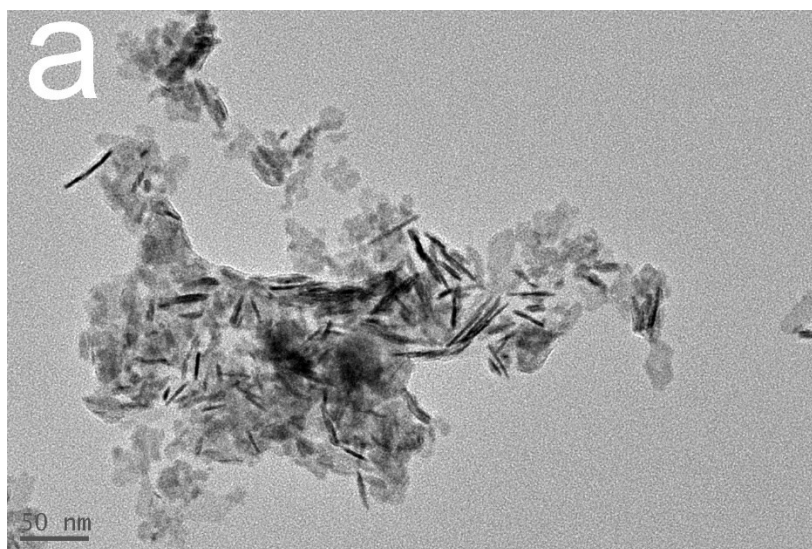


Fig. S5 The evolution of UV-Vis spectra for RhB and 4-CP aqueous solution in the presence of Bi/Bi₂WO₆/rGO-3 as a function of visible light irradiation time (20 min interval between t = 0 min and t = 120 min)



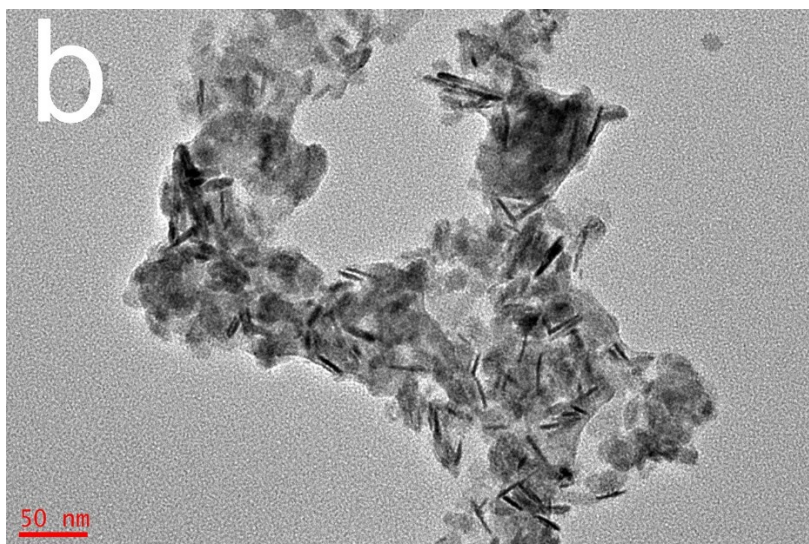
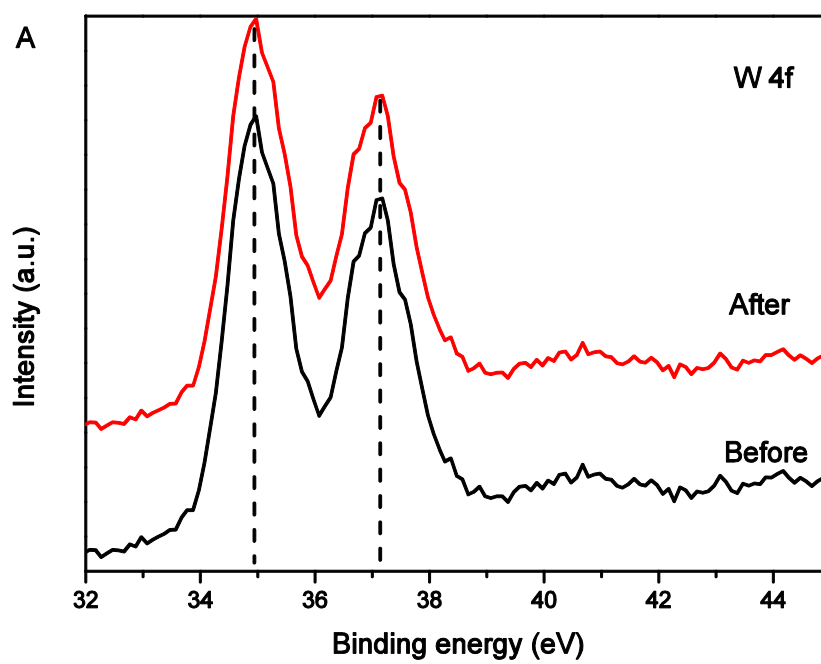
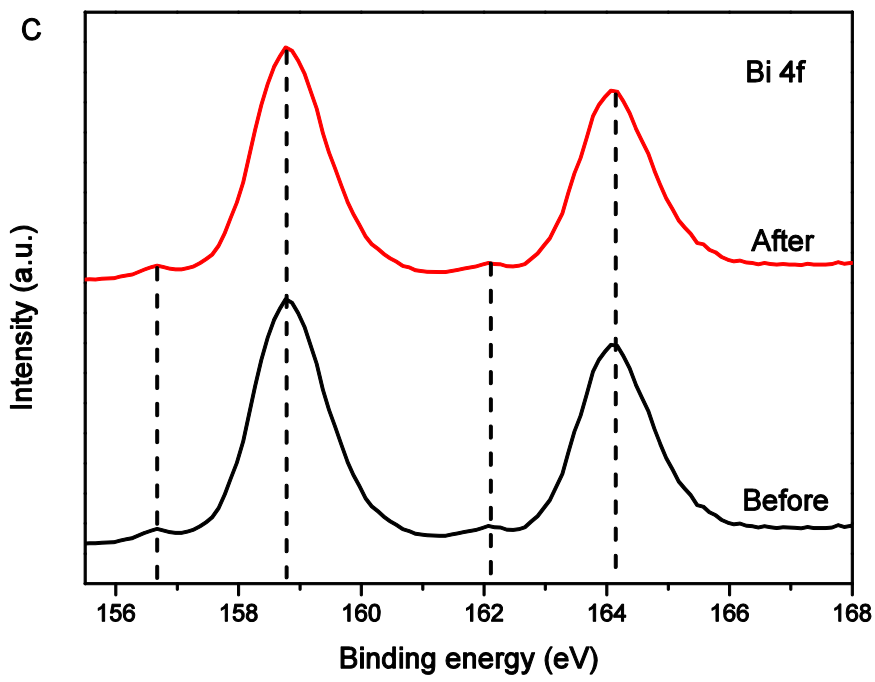
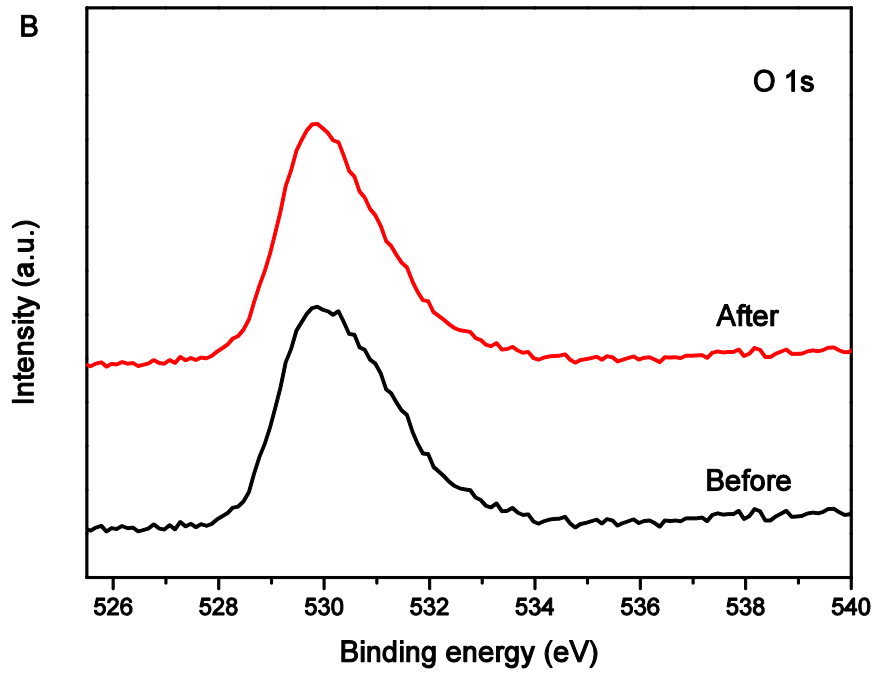


Fig. S6 TEM images of Bi/Bi₂WO₆/rGO-3 measured before (a) and after a photocatalytic reaction (b)

under visible light irradiation.





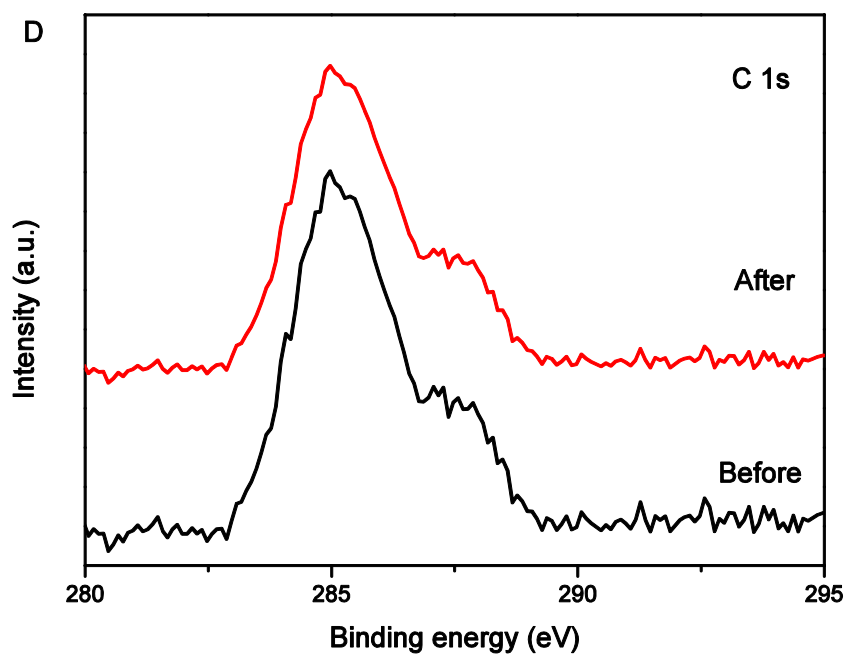


Fig. S7 XPS of Bi/Bi₂WO₆/rGO-3 measured before and after a photocatalytic reaction under visible light irradiation.

Notes and references

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