

Supporting information

Modulation of Interfacial Charge Transfer by Self-assembly of Single-layer Graphene Enwrapped One-dimensional Semiconductors Toward Photoredox Catalysis

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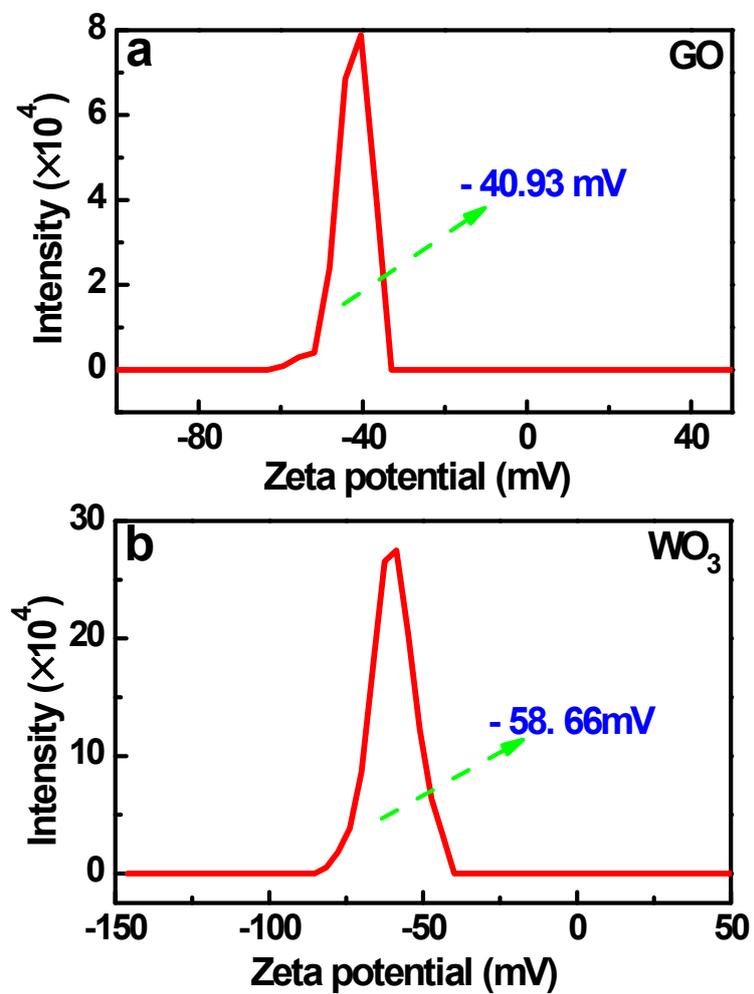


Fig. S1. Zeta potentials of (a) GO and (b) WO₃ NRs aqueous solutions.

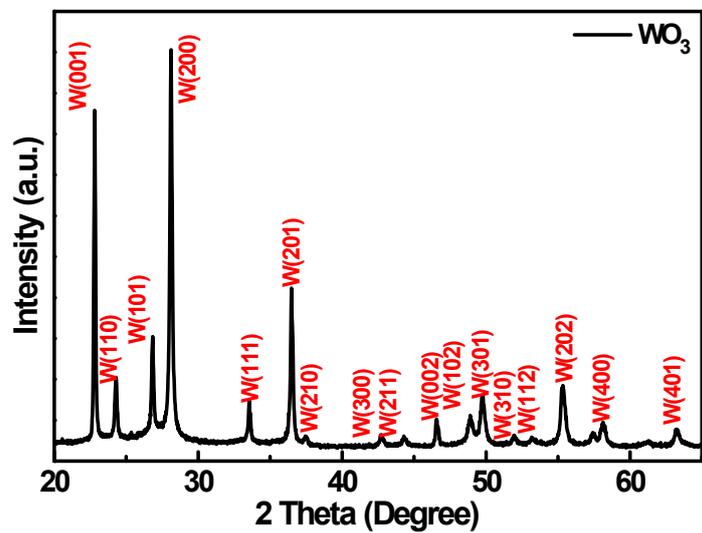


Fig. S2. XRD pattern of pristine WO₃ NRs.

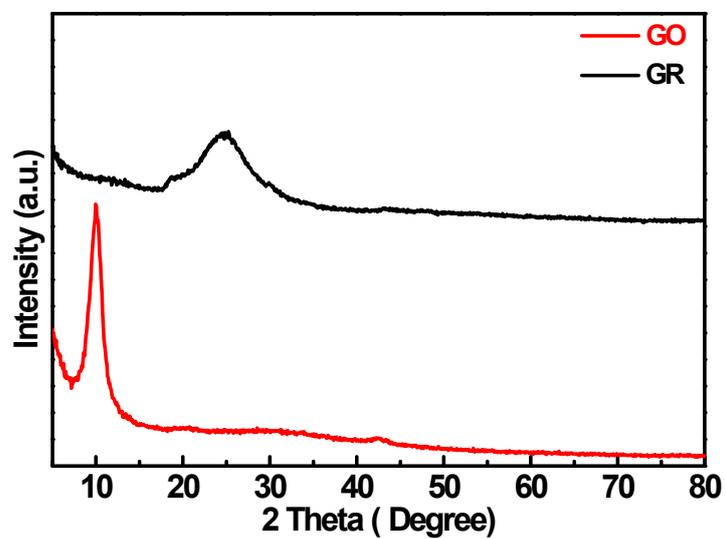


Fig. S3. XRD patterns of GO and GR.

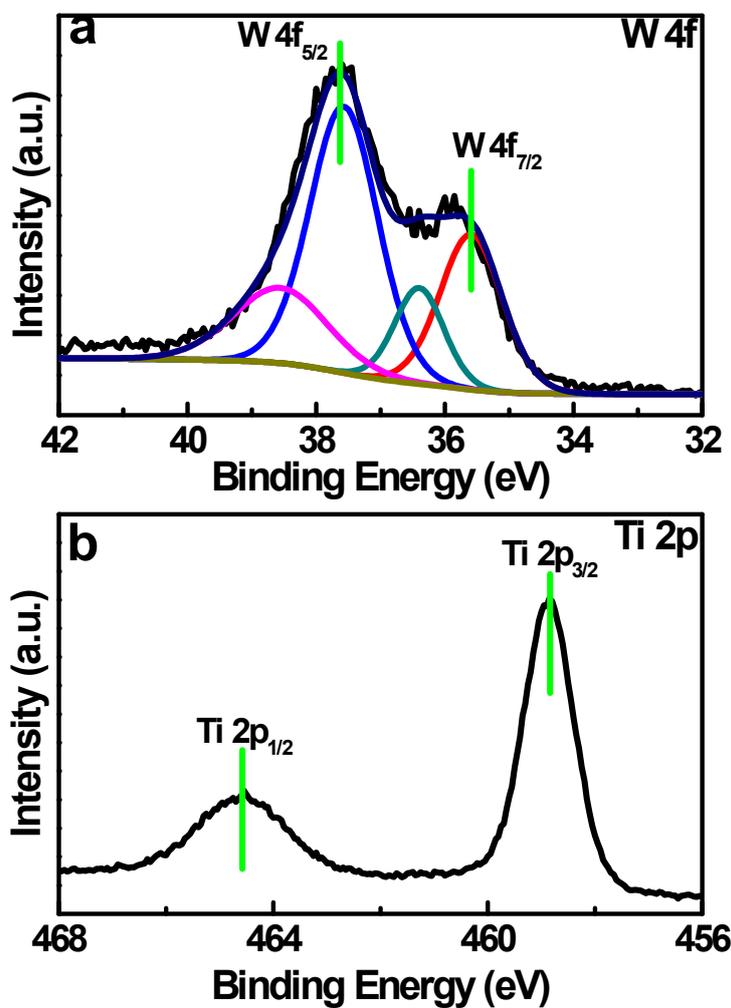


Fig. S4. High-resolution XPS spectra of (a) W 4f and (b) Ti 2p for pristine WO₃ NRs and TNBs, respectively.

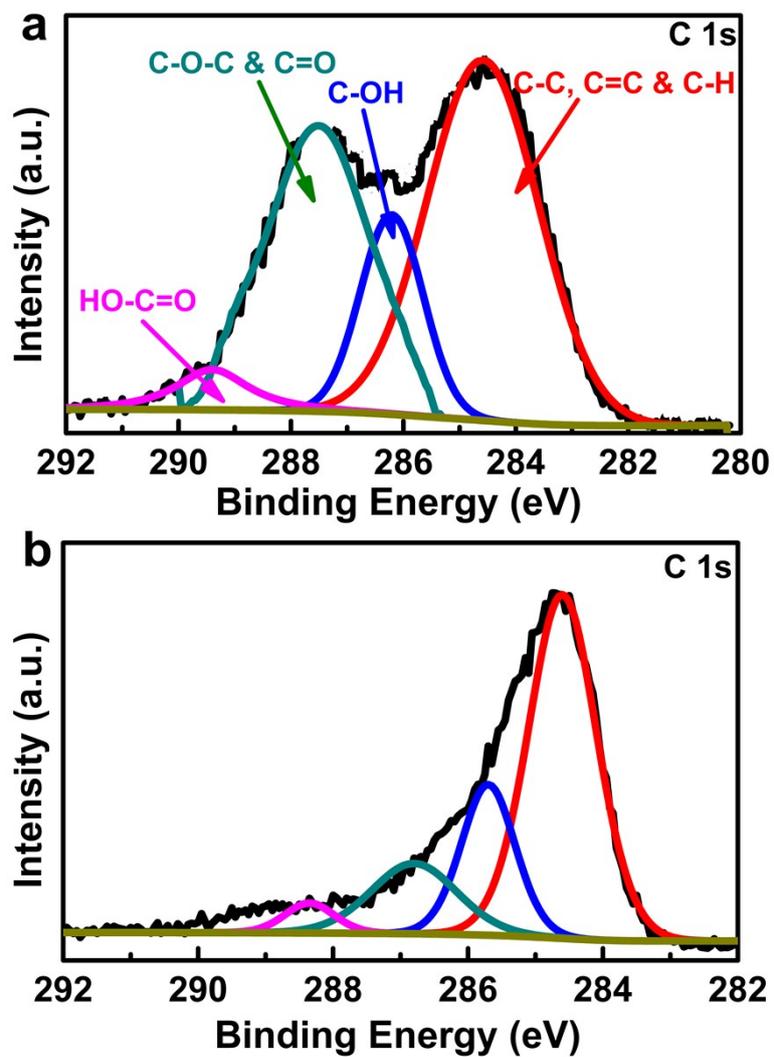


Fig. S5. High-resolution C 1s spectra of (a) GO and (b) TNBs/WO₃ NRs/GR ternary heterostructure.

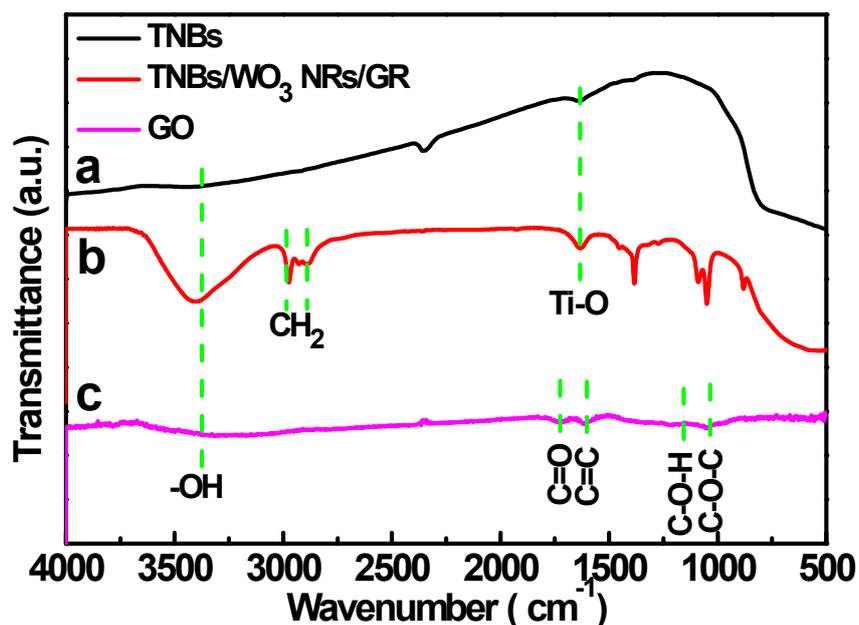


Fig. S6. FTIR spectra of (a) TNBs, (b) TNBs/WO₃ NRs/GR and (c) GO.

Note: GO displays several characteristic bands at 1730, 1633, 1401, 1226, and 1058 cm⁻¹. Specifically, the carboxyl group appears at 1730 cm⁻¹ (*i.e.*, C=O stretching vibration)¹ along with the presence of C-O vibration of epoxy groups at 1058 and 857 cm⁻¹.² The hydroxyl group (-OH) is located at ca. 3400 and 1401 cm⁻¹, the epoxy group (C-O-C) at 1226 cm⁻¹, and the alkoxy group (C-OH & C-O) at 1050 cm⁻¹.³ The peak located at 1633 cm⁻¹ is associated with the aromatic C=C bond in GO.⁴⁻⁵

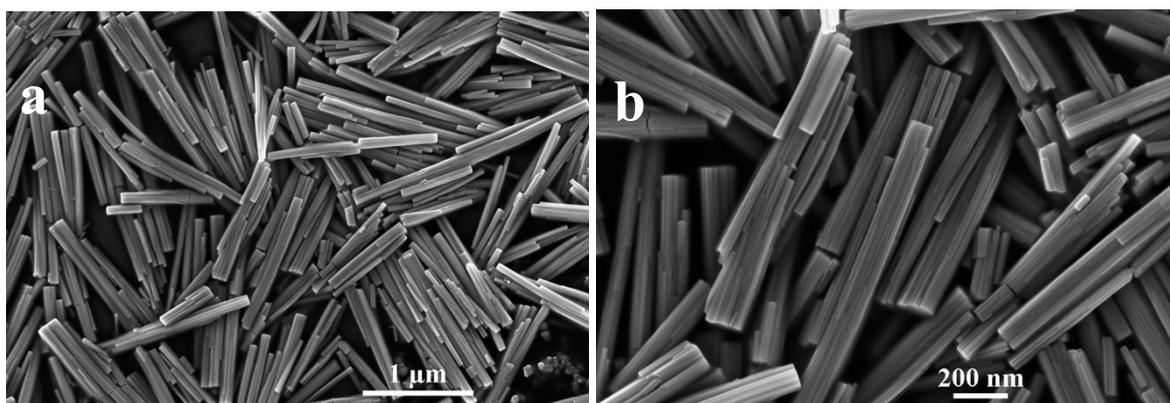


Fig. S7. (a) High and (b) low-magnified FESEM images of WO₃ NRs.

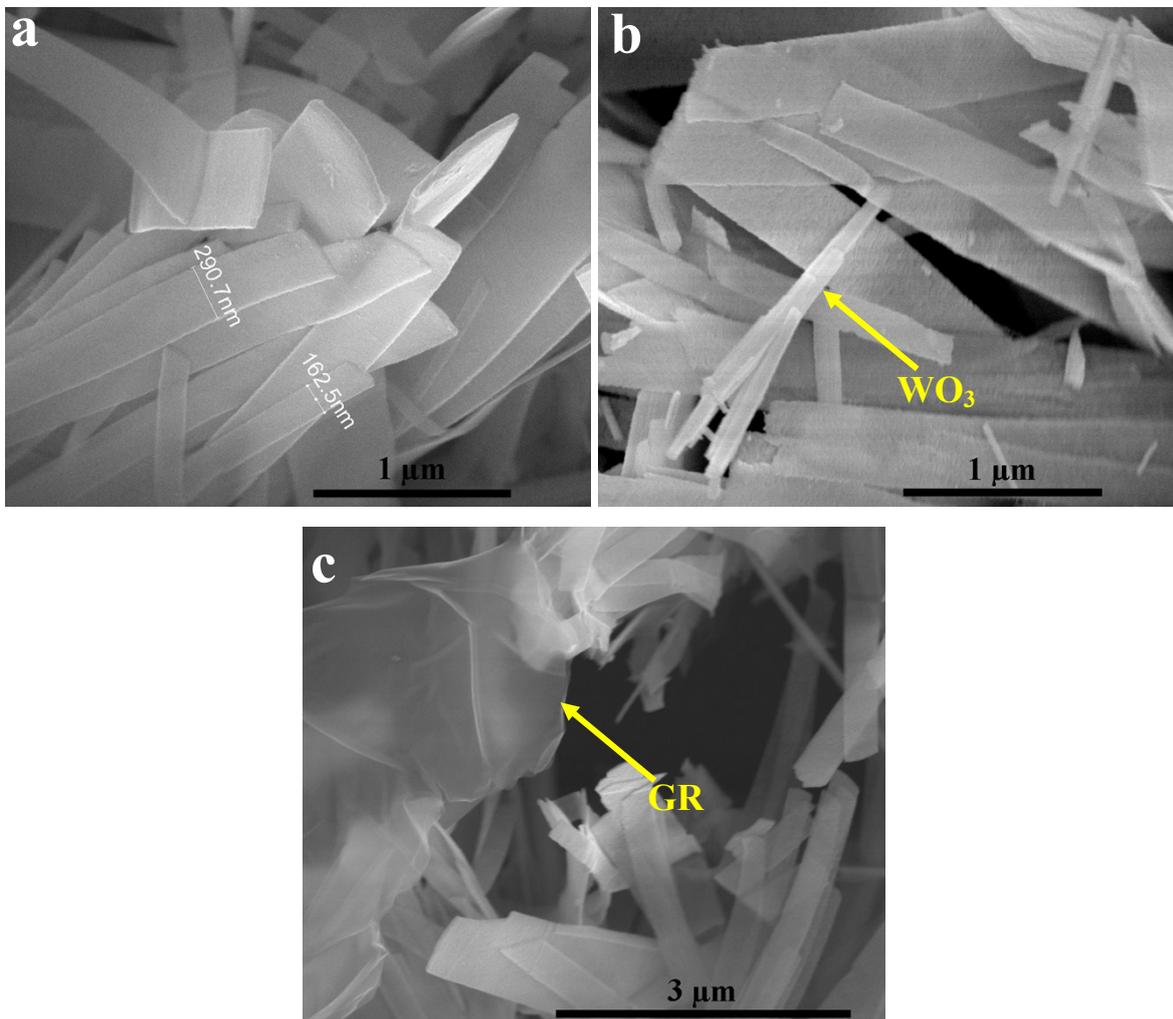


Fig. S8. High-magnified FESEM images of (a) TNBs matrix, (b) TNBs/ WO_3 NRs and (c) TNBs/GR binary heterostructures.

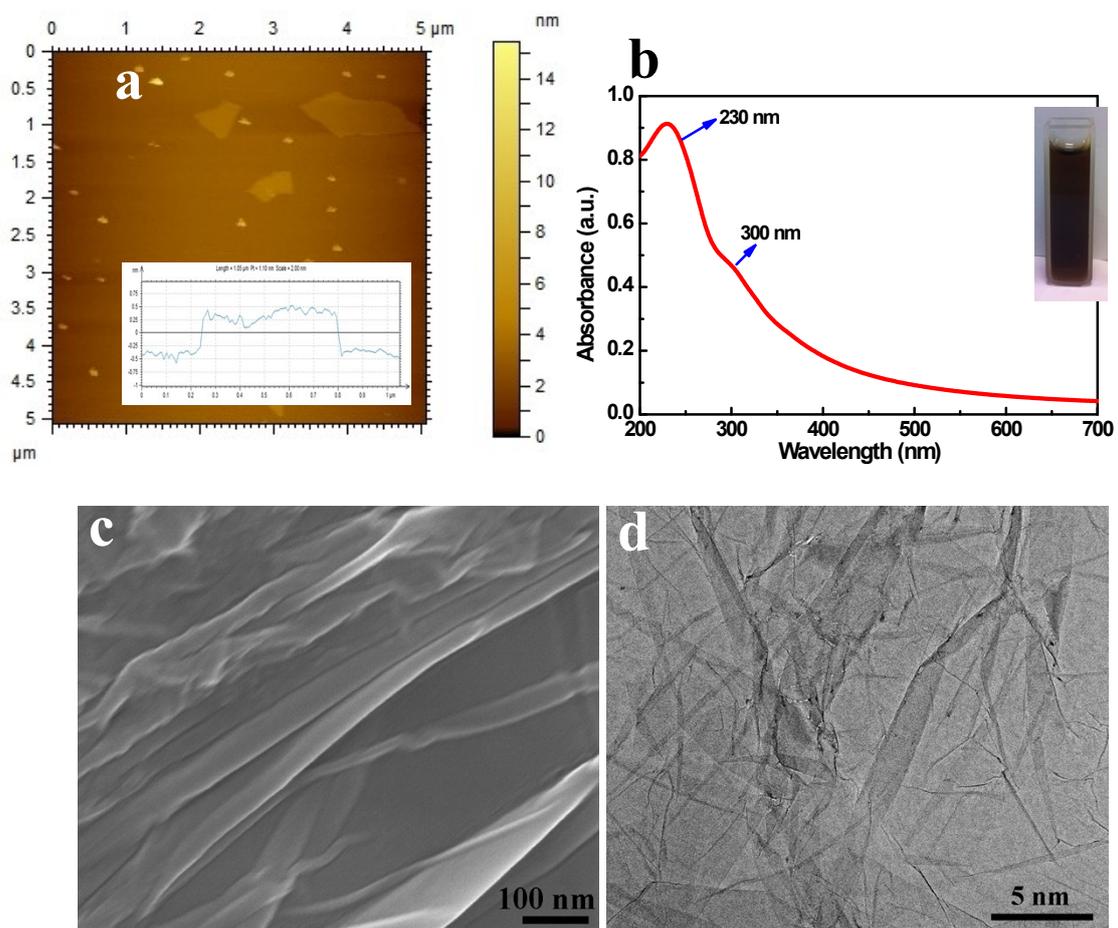


Fig. S9. (a) AFM image of GO with corresponding height profile in the inset and (b) UV-absorption spectrum of GO aqueous solution with photograph in the inset, (c) FESEM and (d) TEM images of GO.

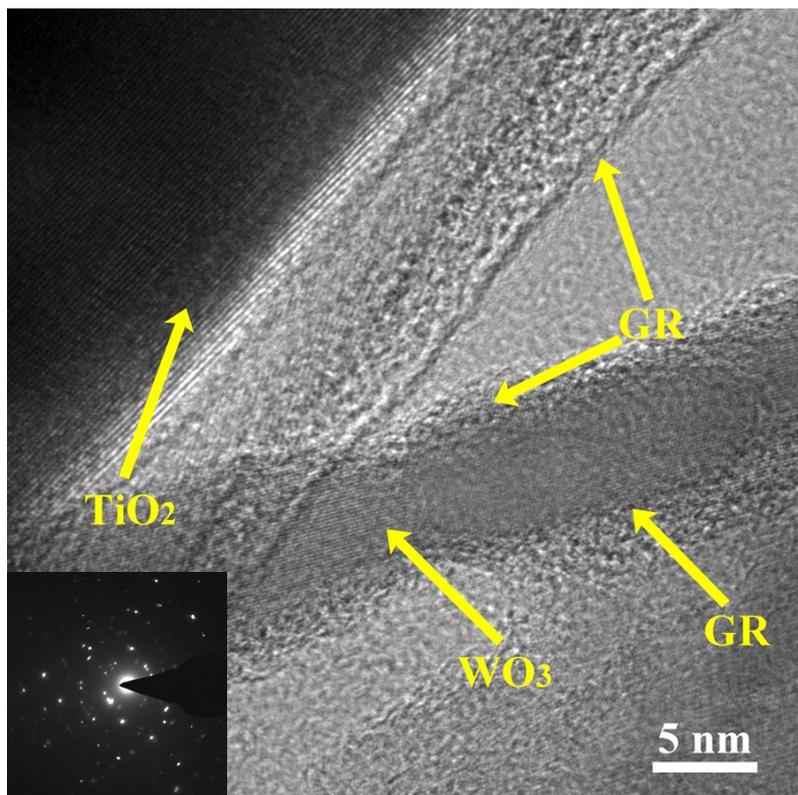


Fig. S10. HRTEM image of TNBs/ WO_3 NRs/GR ternary heterostructure with corresponding SAED pattern in the inset.

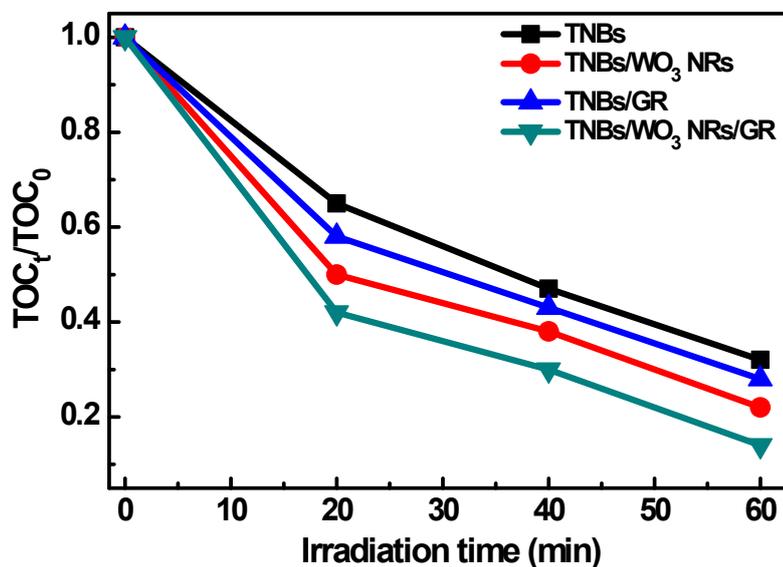


Fig. S11. Variations of TOC percentage as function of irradiation time over different catalysts.

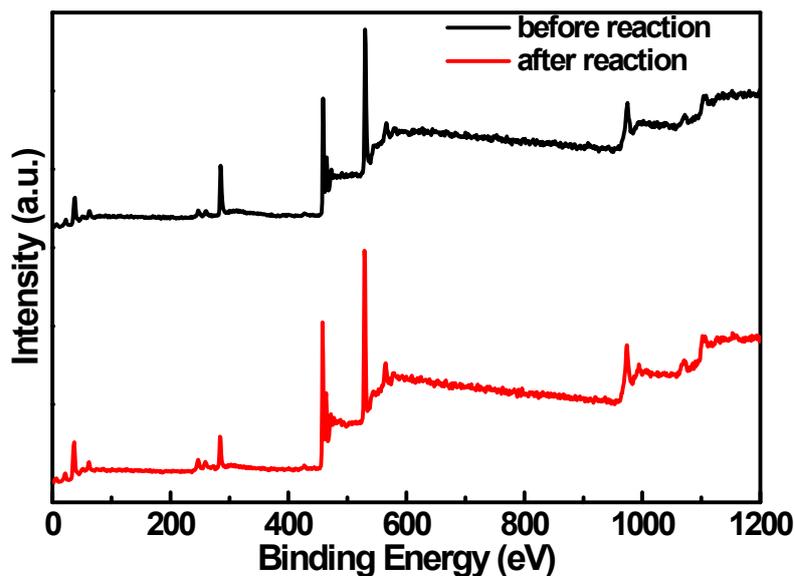


Fig. S12. Survey XPS spectra of TNBs/WO₃ NRs/GR ternary heterostructure before and after cyclic reactions.

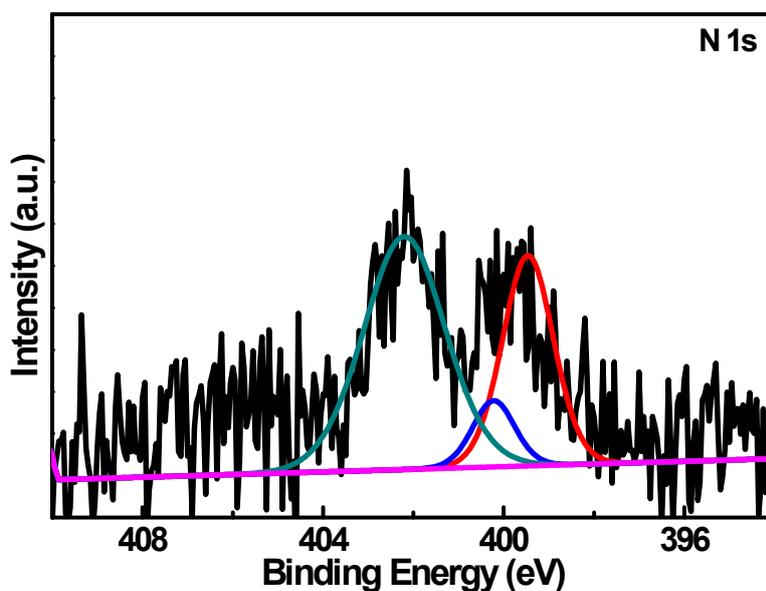


Fig. S13. High-resolution N 1s spectrum of TNBs/WO₃ NRs/GR ternary heterostructure after cyclic reactions.

Note: It is apparent that peak intensity of high-resolution N 1s spectrum of TNBs/WO₃ NRs/GR ternary heterostructure is still rather weak and comparable to that of before cyclic reaction, indicating PDDA layer intercalated within the interfacial region of TNBs and WO₃ NRs was not removed during the photocatalytic reaction and this is beneficial for retaining the structural integrity of the ternary heterostructure.

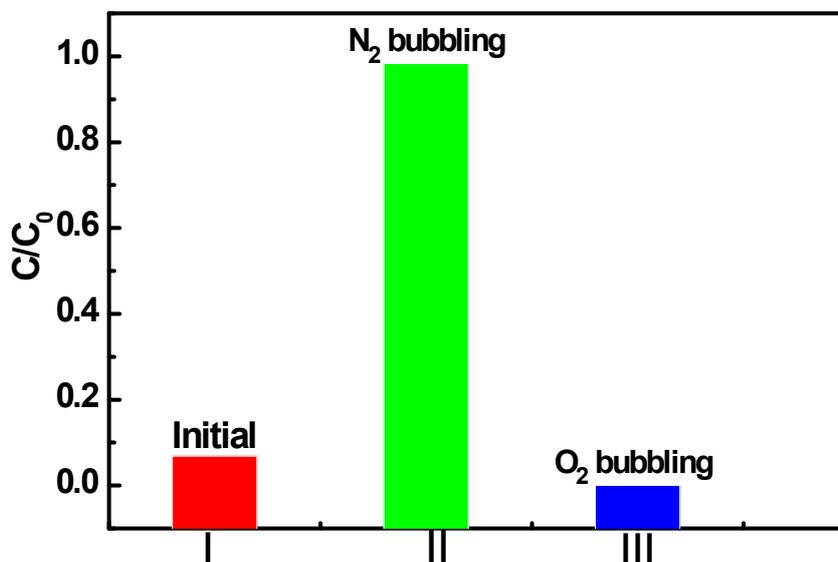


Fig. S14. Control experiments by bubbling N₂ and O₂ gas into the reaction system toward the photocatalytic degradation of RhB over TNBs/WO₃ NRs/GR ternary heterostructure with the same irradiation time of 60 min.

Experimental section

Synthesis of Graphene Oxide (GO)

GO nanosheets were synthesized from crystalline graphite nanosheets powder (99.5 %) using a modified Hummers method.^{6,7} In a typical synthesis, 10 g of graphite powder was added to 230 mL of concentrated H₂SO₄ (98 %) which was cooled in an ice bath. Following, 30 g of KMnO₄ was added slowly to the above solution with gentle stirring for 10 min. Temperature of the mixed solution was then raised to 35 °C and kept for 2 h to completely oxidize graphite. Afterwards, the mixture was diluted with 460 mL of DI H₂O and further diluted by 1.4 L of DI H₂O 5 min later under vigorous stirring. 50 mL of H₂O₂ was then added to the mixture and a brilliant yellow product was formed along with bubbling. The mixture was filtered and washed by 1 : 10 HCl aqueous solution to remove metal ions and by DI H₂O to remove residual acid. The filter cake thus-obtained was dispersed in DI H₂O with a mechanical agitation and centrifuged at 4500 rpm for 2 min and 5 cycles to remove small GO pieces and water-soluble byproducts. The final sediment was dialyzed for two-

weeks to remove impurity atoms and then re-dispersed in DI H₂O with mechanical agitation or mild sonication to result in exfoliated GO aqueous solution.

References

- 1 D. Yu and L. Dai, *J. Phys. Chem. Lett.*, 2010, **1**, 467-470.
- 2 H. Yang, F. Li, C. Shan, D. Han, Q. Zhang, L. Niu and A. Ivaska *J. Mater. Chem.*, 2009, **19**, 4632-4638.
- 3 J. L. Zhang, H. J. Yang, G. X. Shen, P. Cheng, J. Y. Zhang and S. W. Guo, *Chem. Commun.*, 2010, **46**, 1112-1114.
- 4 H. P. Cong, X. C. Ren, P. Wang and S. H. Yu, *ACS Nano*, 2012, **6**, 2693-2703.
- 5 G. I. Titelman, V. Gelman,; S. Bron, R. L. Khalfin, Y. Cohen and H. Bianco-Peled, *Carbon*, 2005, **43**, 641-649.
- 6 F. -X. Xiao, J. Miao and B. Liu, *J. Am. Chem. Soc.* 2014, **136**, 1559-1569.
- 7 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.