

Supporting information for

Enhanced photocatalytic activity of g-C₃N₄-ZnO/HNTs composite heterostructure photocatalysts for degradation of tetracycline under visible light irradiation

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1. Photoelectrochemical Measurements

Incident-photon-to-current conversion efficiencies (IPCE) were calibrated with an electrochemical system (CHI 660B, Shanghai, China) using a standard three-electrode quartz cell with 0.5 M Na₂SO₄ electrolyte solution, a Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrodes. The process of preparing the working electrode is as follows. 30 milligrams of as-prepared sample was suspended in 5 mL of the mixed solution of ethanol and ethanediol with a volume ratio of 1:1, 0.5 mM polyvinyl pyrrolidone⁴⁰ and 0.1 mmol oleic acid were added into the solution. The mixture was dip-coated on a 20 mm × 10 mm indium-tin oxide (ITO) glass electrode after ultrasound for 20 minutes. The electrode was then heated in a tubular furnace at 200 °C for 3 hours. Visible irradiation was obtained from a 300 W Xe lamp (Newport 6255) without a UV-cutoff filter. Electrochemical impedance spectroscopy (EIS) was performed in a 0.5 M Na₂SO₄ solution with a frequency range from 0.1 Hz to 100 kHz at 0.5 V. The amplitude of the applied sine wave potential in each case was 5 mV, which was carried out using a ZENNIUM electrochemical workstation (Zahner Instruments, Germany), and all electrochemical signals were recorded by a CHI660 B electrochemical analyzer (Chen Hua Instruments, Shanghai, China). All electrodes were the same as those used in IPCE.

2. Electron Spin Resonance Spectroscopy

The formation of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ were detected by electron spin resonance (ESR) measurements which carried on a Bruker A300 ESR spectrometer at room temperature, and the ESR signals of spin-trapped paramagnetic species was verified with 5,5-dimethyl-1-pyrroline N-oxide (DMPO). The involvement of $\bullet\text{O}_2^-$ was detected in methanol due to the instability of $\bullet\text{O}_2^-$ in water and the involvement of $\bullet\text{OH}$ was examined in ultrapure water¹. Fifty microliter aliquots of sample solutions were put into the quartz capillary tubes with internal diameters of 0.9 mm. After The quartz capillary tubes were inserted into the ESR cavity after sealed. The spectra were recorded during a 450 W xenon lamp solar simulator irradiation at selected times.

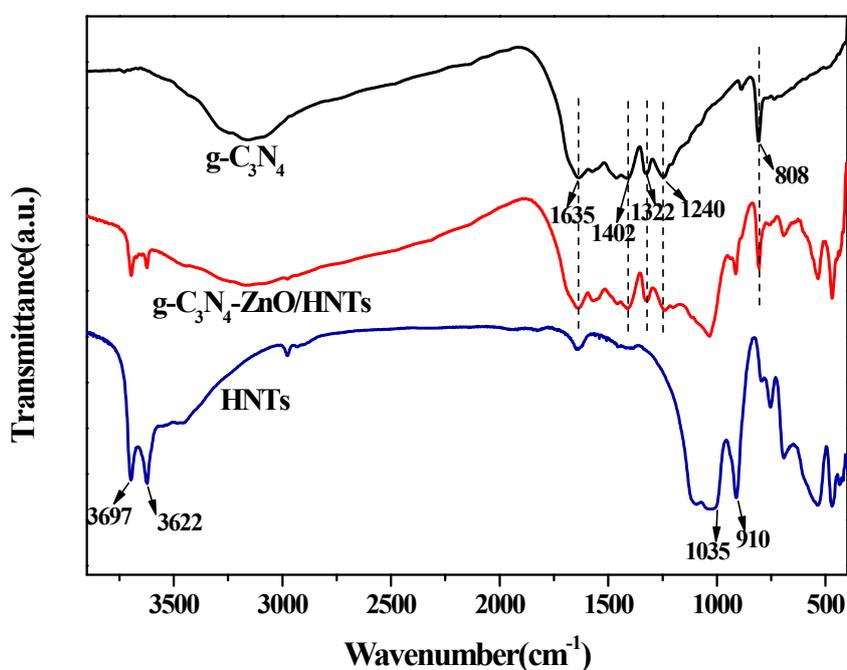


Fig. S1. FT-IR spectra of HNTs, g-C₃N₄ and g-C₃N₄-ZnO/HNTs photocatalysts.

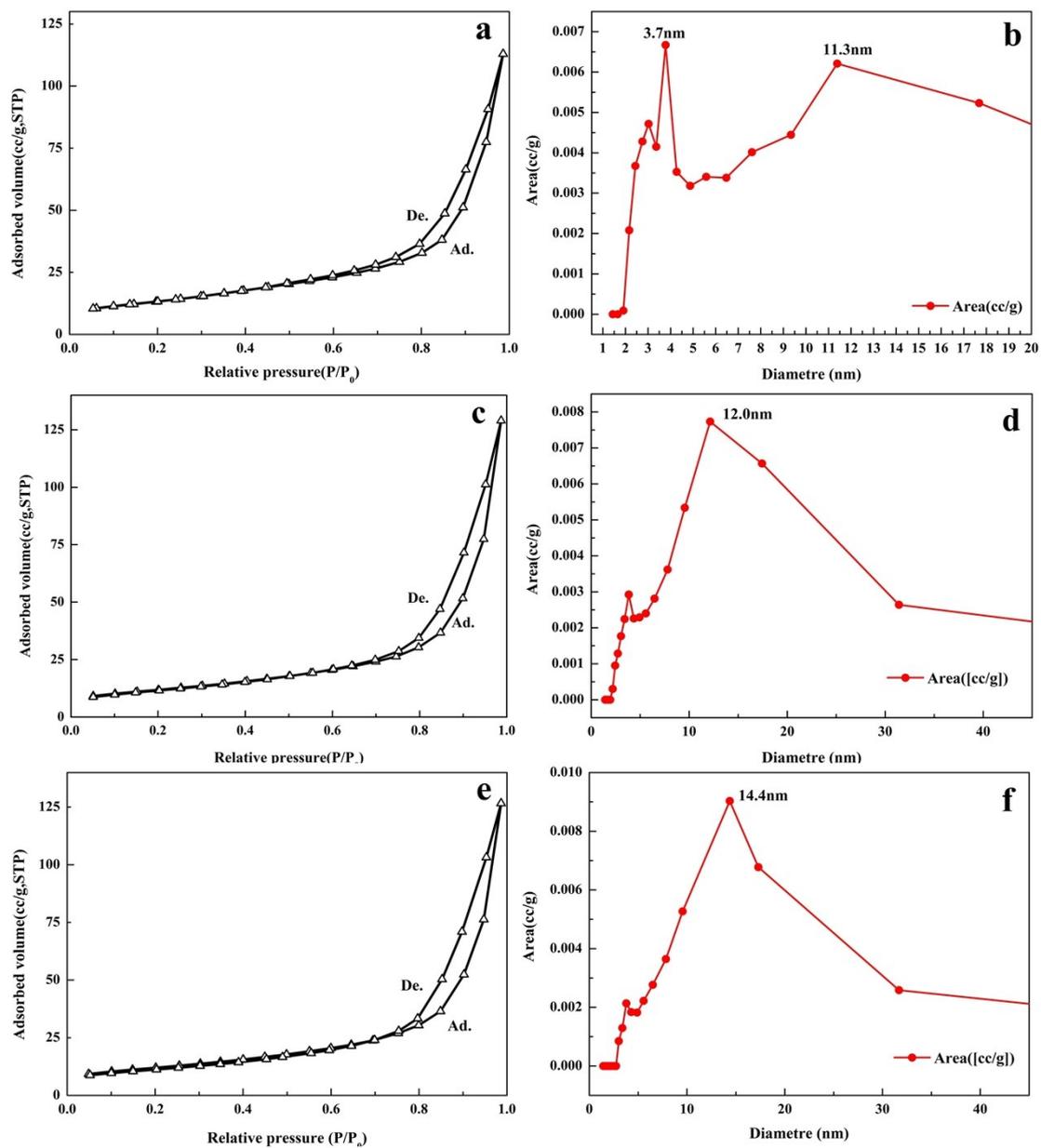


Fig. S2. N_2 adsorption-desorption isotherm and corresponding pore-size distribution curves of (a)

(b)HNTs, (c) (d)ZnO/HNTs, and (e) (f)g-C₃N₄-ZnO/HNTs.

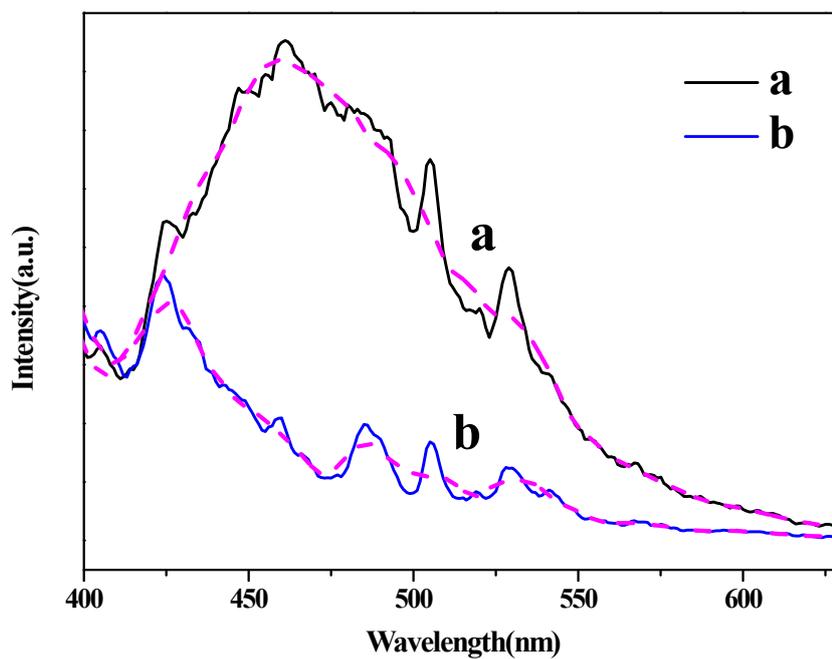


Fig. S3. PL spectra of (a) $g\text{-C}_3\text{N}_4$ and (b) $g\text{-C}_3\text{N}_4\text{-ZnO/HNTs}$.

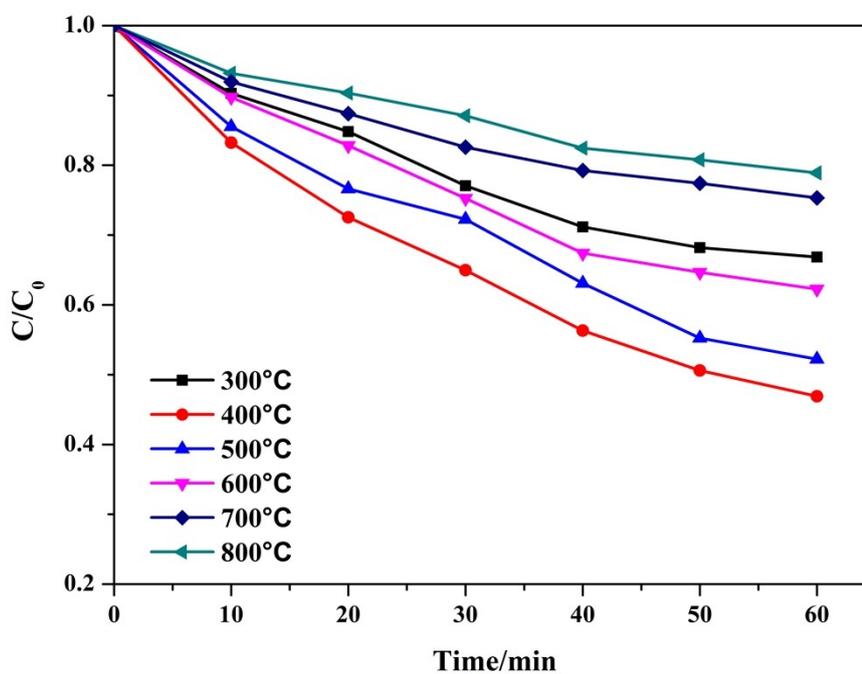


Fig. S4. Photocatalytic degradation of TC with ZnO/HNTs (with different calcination heat) as

photocatalysts under visible-light irradiation.

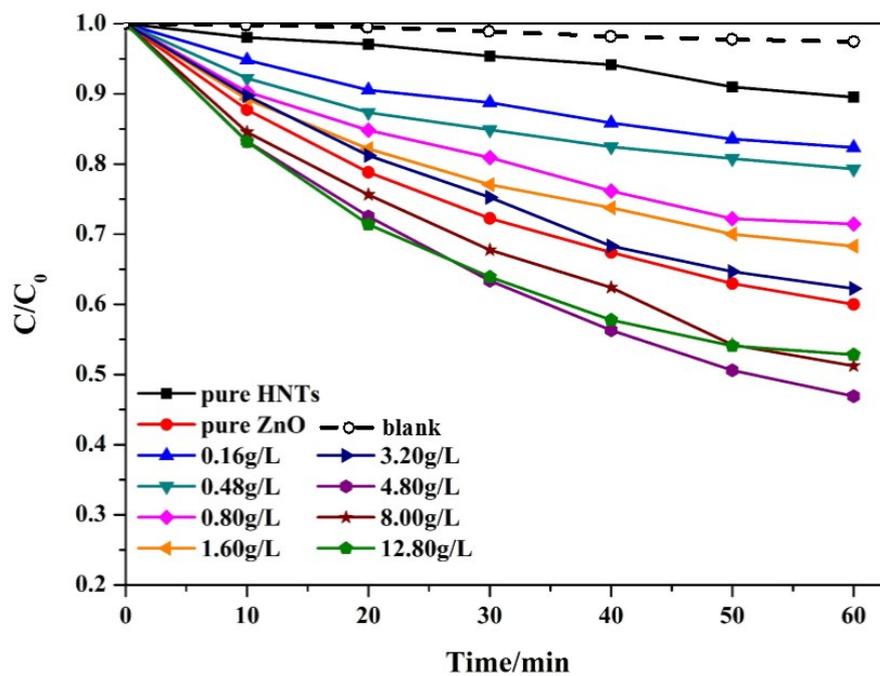


Fig. S5. Photocatalytic degradation of TC with ZnO/HNTs (with different concentration of Zn(NO₃)₂) as photocatalysts under visible light irradiation.

1. W. Wang, T. W. Ng, W. K. Ho, J. Huang, S. Liang, T. An, G. Li, J. C. Yu and P. K. Wong, *Appl. Catal. B: Environ.*, 2013, **129**, 482-490.