

Electronic Supplementary Information for

Highly active MnO₂ nanosheets synthesis from graphene oxide templates and their application in efficient oxidative degradation of methylene blue

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Preparation of graphene oxide and layered MnO₂ nanosheets

Graphene oxide was prepared using modified Hummers method from flake graphite (average particle diameter of 20 μm, 99.95% purity, Qingdao Tianhe Graphite Co. Ltd., China). Briefly, 2.0 g of graphite and 1.5 g of NaNO₃ (A.R.) were placed in a flask. Then, 150 mL of H₂SO₄ (A.R.) was added with stirring in an ice-water bath, and 9.0 g of KMnO₄ (A.R.) was slowly added over about 1 h. The stirring was continued for 2 h in ice-water bath and continually stirred for 5 d at room temperature. Then 280 mL of 5 wt % H₂SO₄ was added over about 1 h with stirring, and the temperature was kept at 98 °C. The resultant mixture was further stirred for 2 h at 98 °C. After the temperature was reduced to 60 °C, 6 mL of H₂O₂ (30 wt %) was added, and the mixture was stirred for 2 h at room temperature. After centrifugation at 8000 rpm, the solid was redispersed using vigorous stirring and bath ultrasonication for 30 min at the power of 140 W. The centrifugation and ultrasonication were recycled for several times, and then the sample was rinsed with deionized water until the solution was neutral. Thus the graphene oxides were prepared. Then 5 mL of KMnO₄ solution (16 g/L) was added into 100 mL above graphene oxide suspension (about 0.1 g/L), and the mixture suspension was kept in thermostat water bath at 60 °C for 15 h. The resulted materials were rinsed with deionized water and the layered MnO₂ nanosheets were obtained.

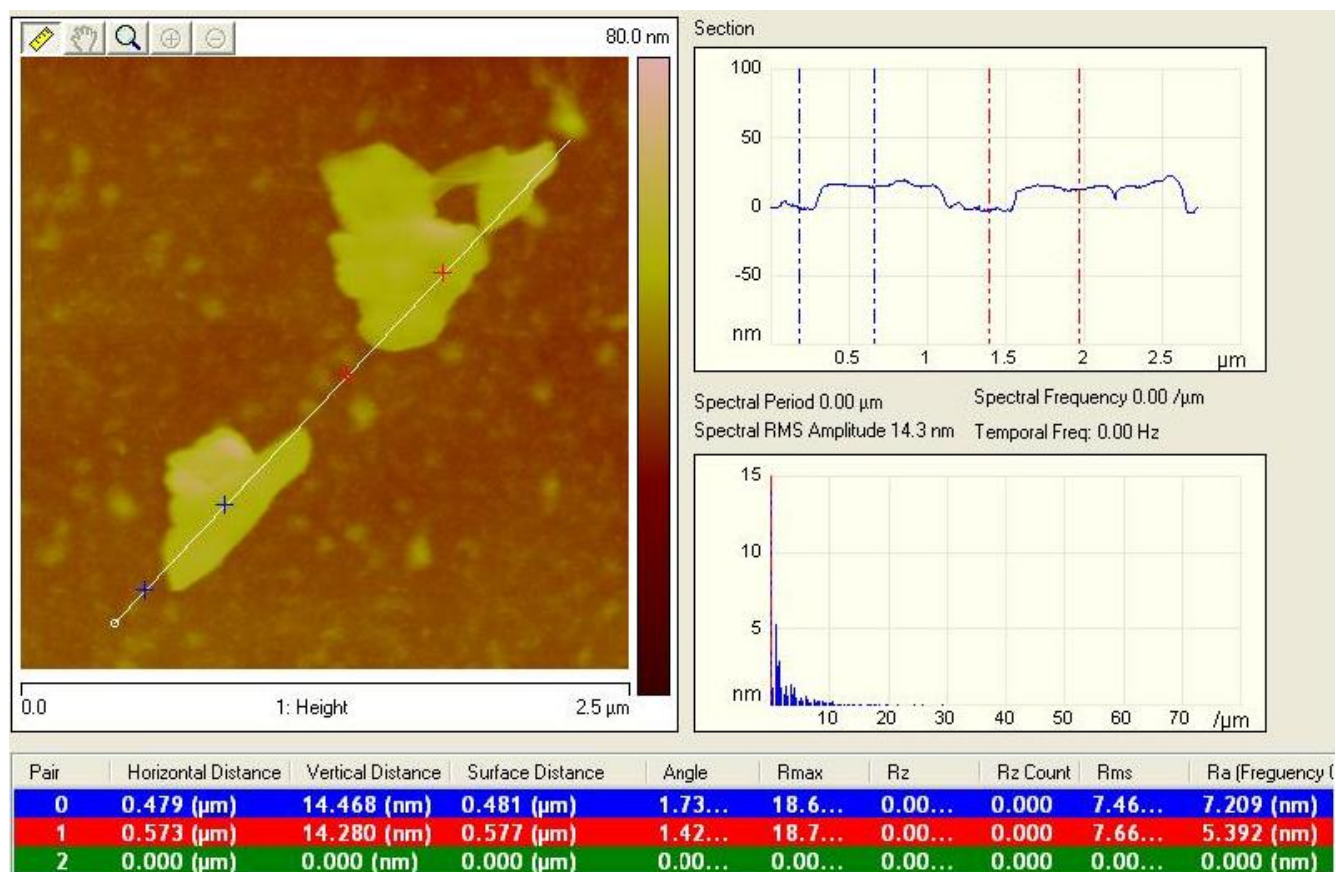


Figure S1. AFM image of the as-prepared MnO₂ sheets.

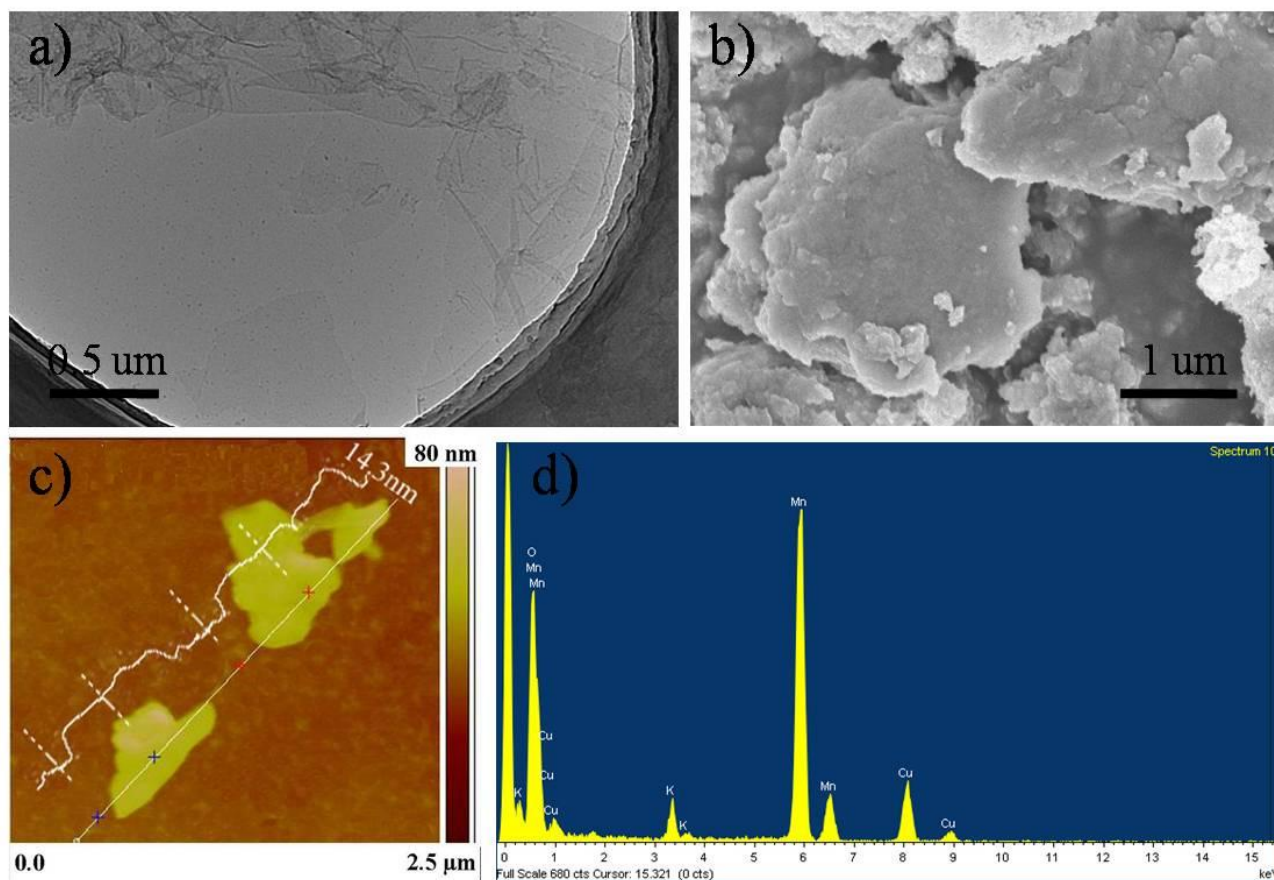


Figure S2. a) TEM image of graphene oxide template; b) SEM image of layered MnO₂ nanosheets; c) AFM of layered MnO₂ nanosheets; d) EDS of layered MnO₂ nanosheets on copper grid and the contents of the corresponding elements. [Figure S1c is reproduced from Ref. 1]

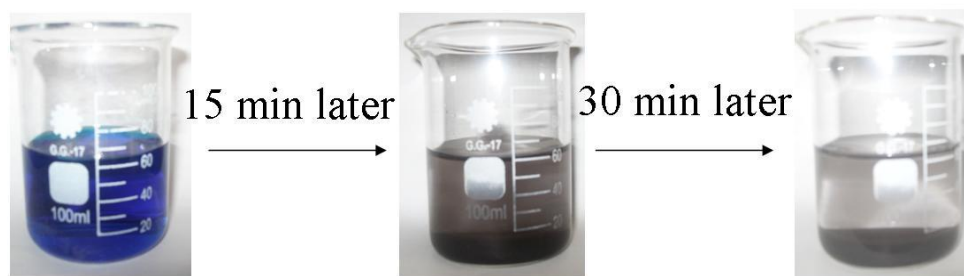
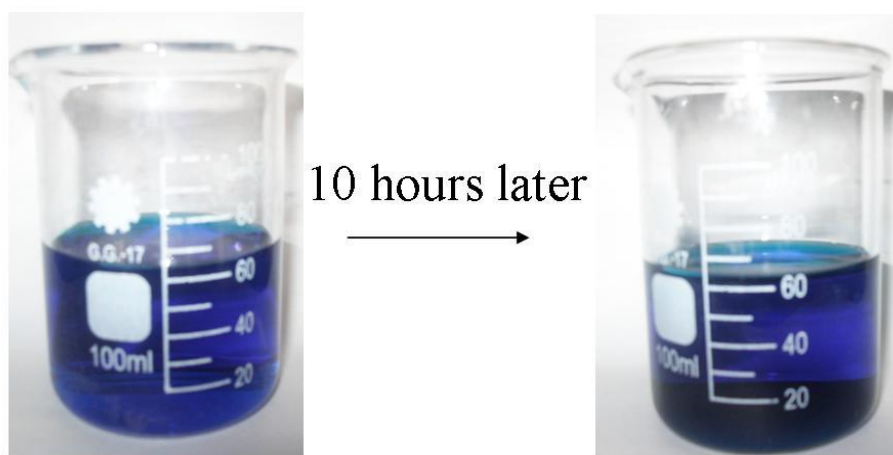


Figure S3. The pictures of the MB dye (40 mg/L) suspension taken at different time intervals of the degradation using layered MnO_2 nanosheets (0.75 g/L) at $\text{pH}=3.1$.



5 Figure S4. The pictures of the MB (40 mg/L) suspension before and after 10 hour-interaction with the purchased MnO_2 at $\text{pH}=3.1$ (0.75 g/L).

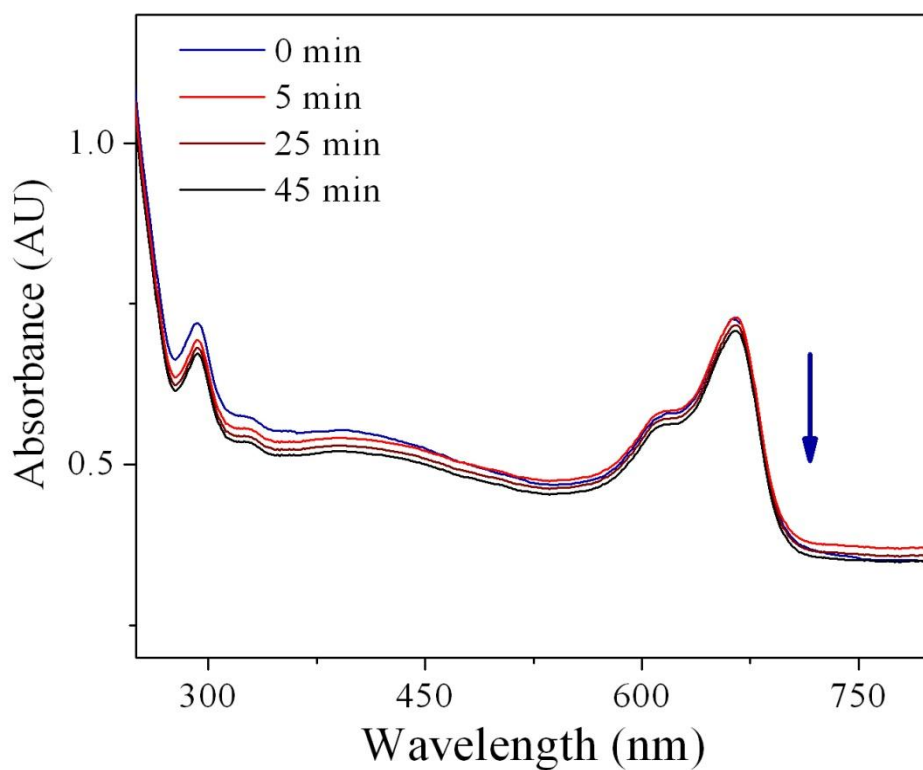


Figure S5. The UV-Vis spectra of MB solution, obtained by removing MnO_2 using sufficient oxalate acid solution after different interaction time with MnO_2 nanosheets at $\text{pH}=9.0$. The initial MB dye concentration is 10 mg/L, and the concentration of MnO_2 nanosheets is 0.75 g/L.

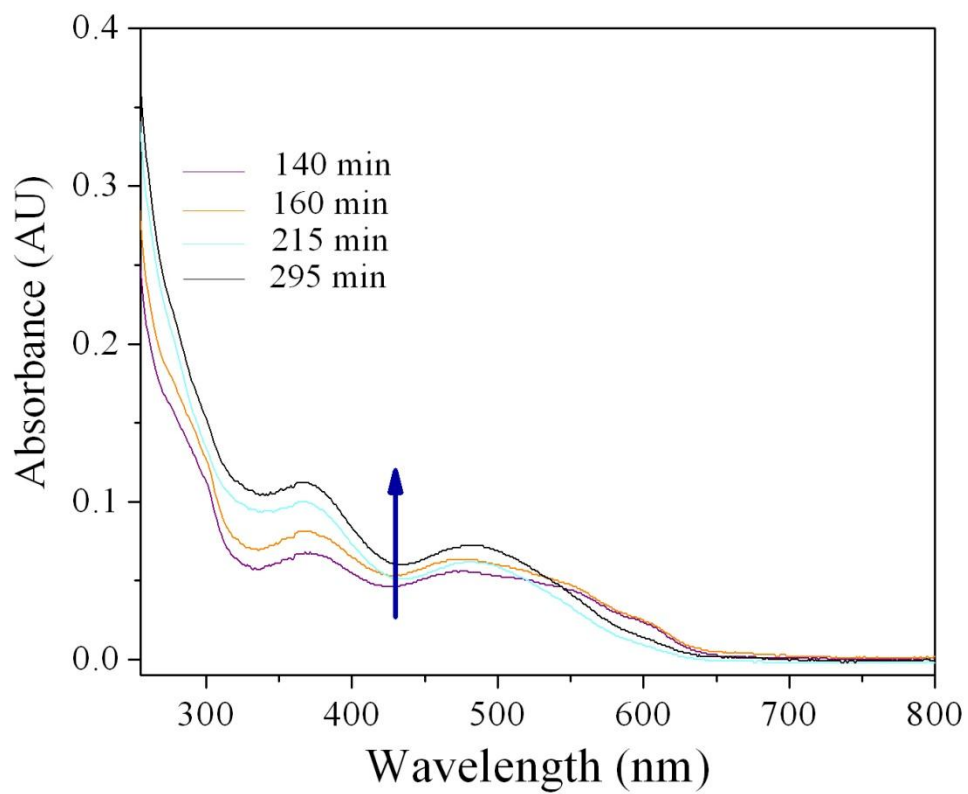


Figure S6. The UV-Vis absorbance spectra of MB dye solution taken at the later period of the oxidation process at pH=3.1. The initial MB dye concentration is 10 mg/L, and the concentration of MnO₂ nanosheets is 0.75 g/L.

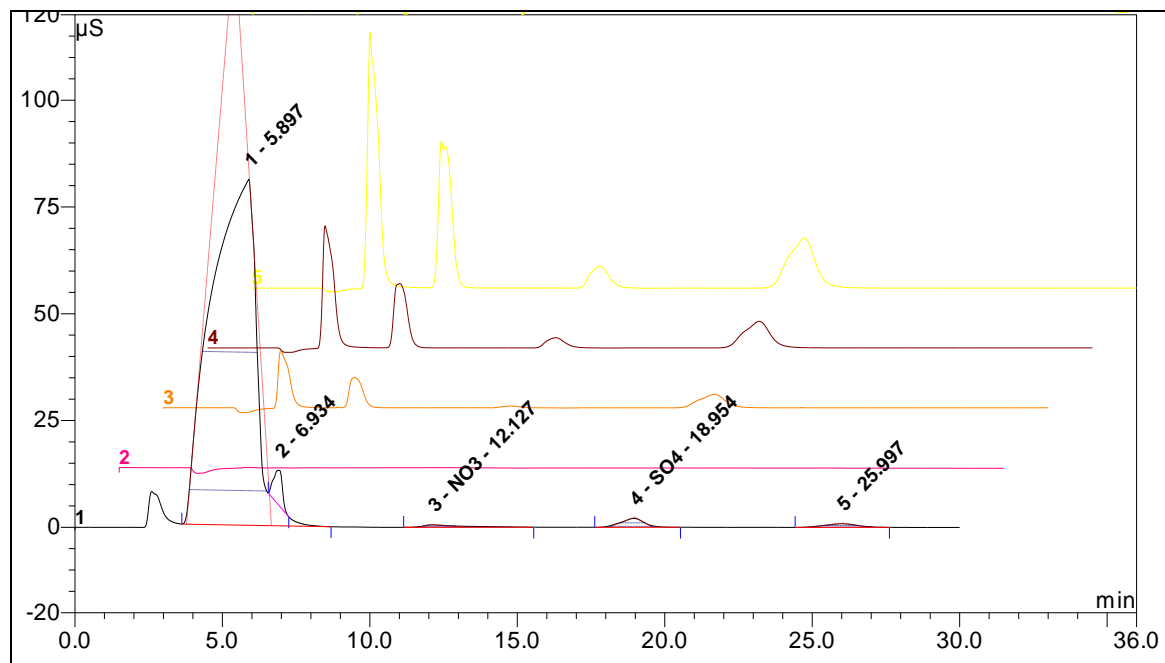


Figure S7. The ion chromatogram of SO_4^{2-} and NO_3^- in the final degradation system at $\text{pH}=3.1$ (line 1) and the standard solution with different concentrations of F^- , Cl^- , SO_4^{2-} and NO_3^- (lines 2, 3, 4). The retention time of SO_4^{2-} and NO_3^- is 18.85 min and 12.13 min, respectively.

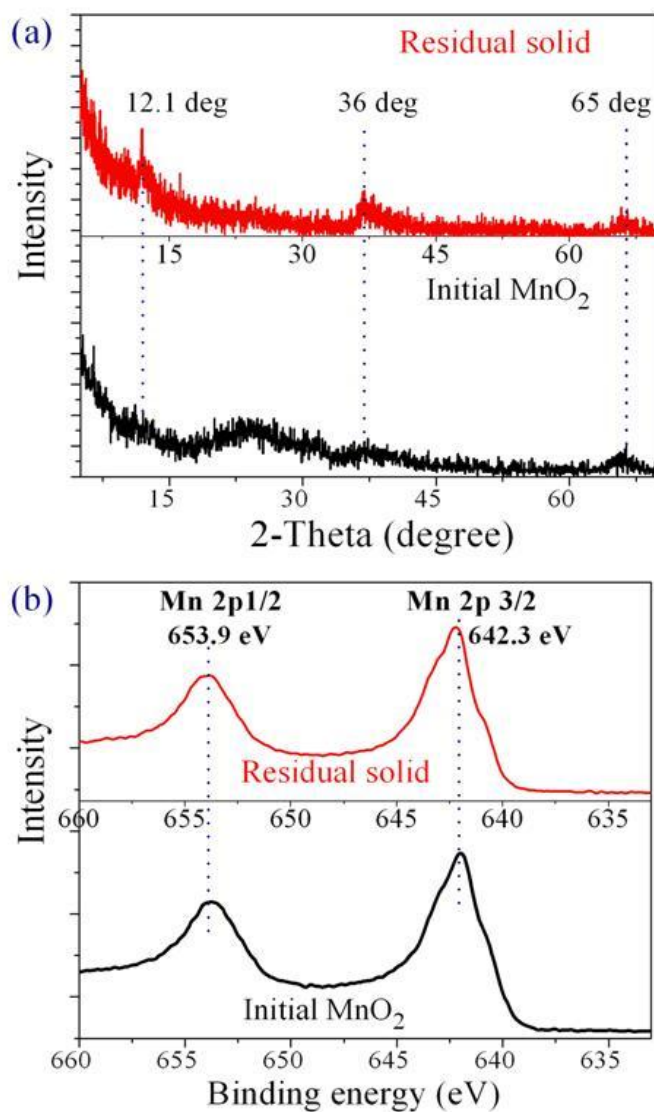


Figure S8. The XRD and XPS analysis of the residual solid (after degradation for 300 min) in the degradation suspension and the initial layered MnO₂ nanosheets.

References

- 5 [1] G. Zhao, J. Li, L. Jiang, H. Dong, X. Wang and W. Hu, *Chem. Sci.* 2012, **3**, 433.