

**Control of Manganese Dioxide Crystallographic Structure in the Redox Reaction
between Graphene and Permanganate Ions and Their Electrochemical
Performance**

*Chenchen Ji¹, Haoqi Ren³, Shengchun Yang^{*1,2},*

1 School of Science, Key Laboratory of Shanxi for Advanced Materials and Mesoscopic Physics, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, 710049, People's Republic of China.

2 Collaborative Innovation Center of Suzhou Nano Science and Technology, Suzhou Academy of Xi'an jiaotong University, 215000, Suzhou, People's Republic of China.

3 Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China.

***Corresponding author**

Tel: +86-29-82663034. Fax: +86-29-82665995. E-mail: ysch1209@mail.xjtu.edu.cn

(S.C. Yang)

According to the previous study, the graphene sacrificial template shows many advantages toward the fabrication of MnO₂ pseudocapacitance materials, such as the templating process described in these study is much simpler than the conventional template methods. And the obtained samples show controllable structure with a high specific surface area.^{1,2} What is more, the layered structure and a high surface area make the graphene was reactive, and leading to the simultaneous complete replacement of the template by the corresponding materials.^{1,2}

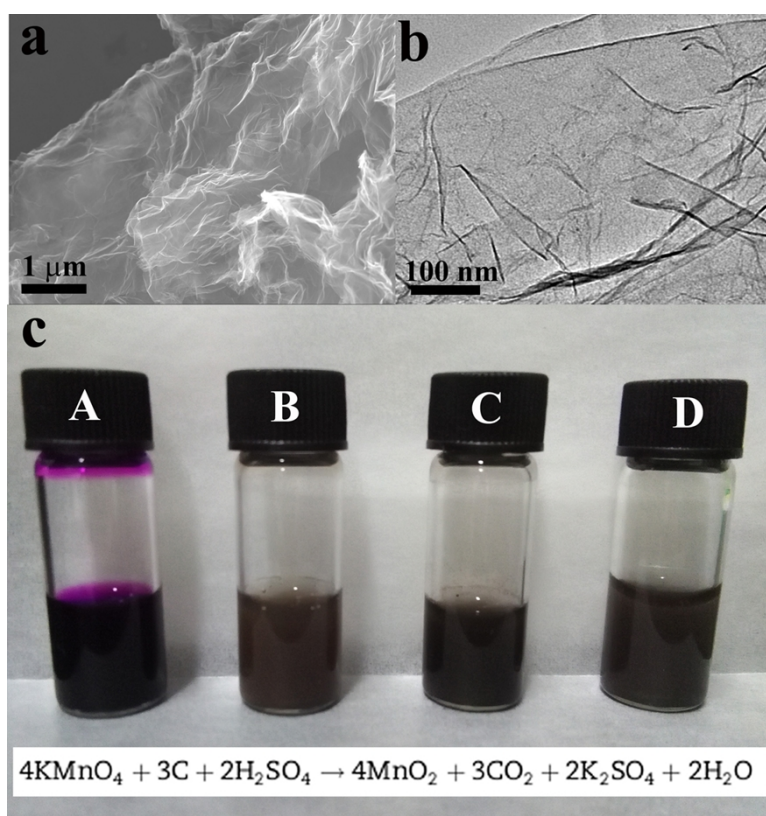


Fig. S1 (a and b) SEM and TEM images of the pristine graphene. (c) Photographs demonstrating the reaction between graphene and KMnO₄ solution. (A) Purple color of the solution after the reaction without adding any amount of graphene. Color change of the solution from Purple color to black-brown suspension after the reaction for the (B) $\alpha+\gamma$ -MnO₂, (C) δ -MnO₂ and (D) α -MnO₂ reaction systems.

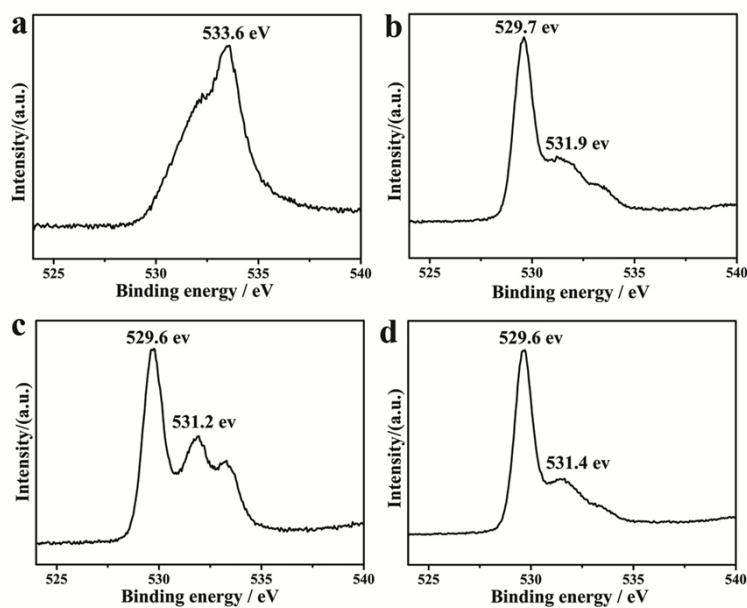


Fig. S2 XPS spectra of the O 1s region for the (a) graphene, (b) $\alpha+\gamma$ -MnO₂, (c) δ -MnO₂ and (d) α -MnO₂ samples.

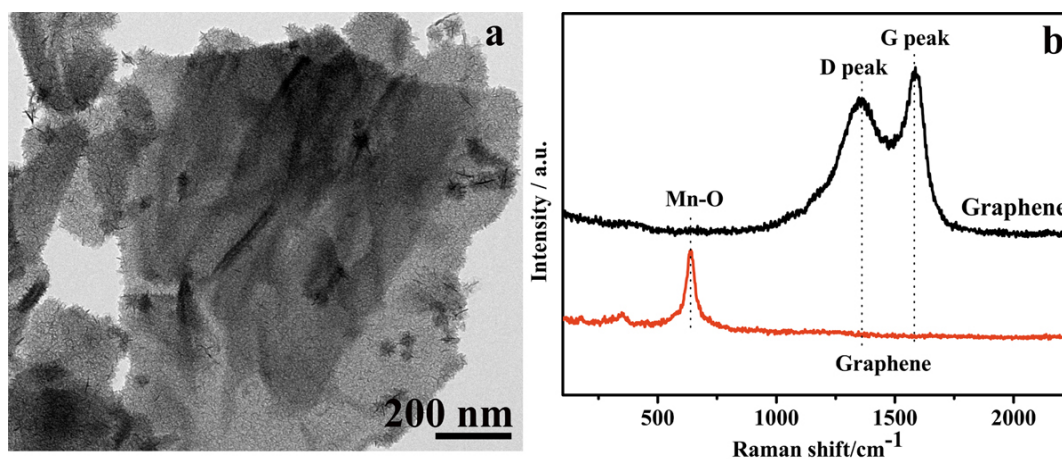


Fig. S3 (a) TEM images of the sample prepared when the amount ratio of graphene : KMnO₄ = 10 mg : 100 mg at 85 °C without adding any H₂SO₄. (b) The corresponding Raman spectra of the graphene and the as-prepared samples.

Fig. S3a shows that the folded and wrinkled characters of graphene transformed to the obtained MnO₂ sample (prepared when the amount ratio of graphene : KMnO₄ = 10 mg : 100 mg at 85 °C without adding any H₂SO₄). The complete disappearance

of the D and G bands of graphene and the appearance of the peaks located at 630 cm^{-1} can be observed in the raman spectra, which indicated the yield of pure MnO_2 with the depletion of graphene (Fig.S3b).

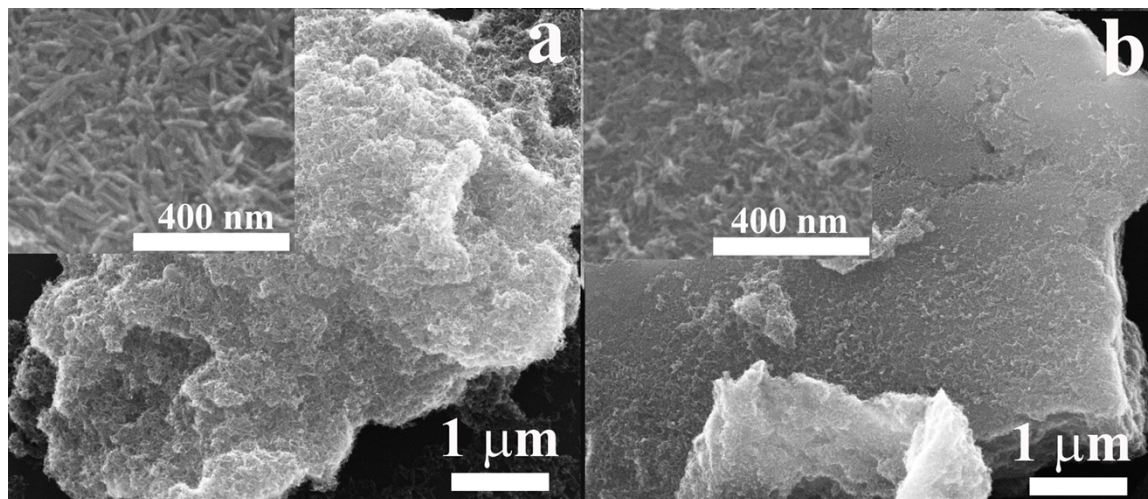


Fig. S4 SEM image of the sample prepared when 10 mg graphene and 100 mg KMnO_4 was used at $85\text{ }^\circ\text{C}$ with (a) $500\text{ }\mu\text{L H}_2\text{SO}_4$, (b) $5\text{ mL H}_2\text{SO}_4$.

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