Electronic Supplementary Information

Rapid Microwave-assisted Synthesis of Mn_3O_4 – Graphene Nanocomposite and its Lithium Storage Properties

Li Li,[a] Zaiping Guo,*[a,b] Aijun Du,*[c] and Huakun Liu,[a]

[a] *Institute for Superconducting and Electronics Materials,University of Wollongong, Wollonong,2500,Australia. Fax:+61 2 42215225; E-mail: zguo@uow.edu.au*

[b] *School of Mechanical, Materials, and Mechatronic Engineering, University of Wollongong, Wollongong,2500, Australia.*

[c] *Center for Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology and School of Chemical Engineering, University of Queensland, Queensland, 4072, Australia; Email:a.du@uq.edu.qu*

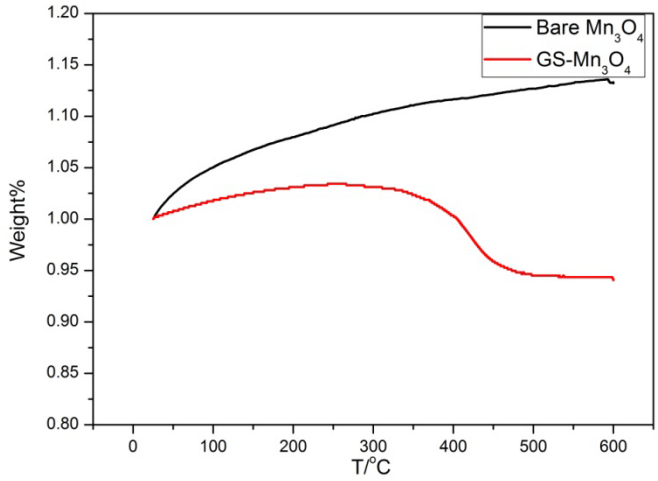

Figure S1. TGA curves of the bare Mn_3O_4 particles and the GS-Mn_3O_4 nanocomposite

Figure S1 shows the TGA curves of the GS-Mn_3O_4 nanocomposite and the bare Mn_3O_4 particles. For the base Mn_3O_4 sample, the weight keeps increasing due to the oxidation of Mn_3O_4 to MnO_2. While the weight of GS-Mn_3O_4 nanocomposite increase below 300 °C , but shows rapid mass loss between 350 and 450 °C, due to the combination of the carbon burnoff and the oxidation of Mn_3O_4 to MnO_2 in this temperature range. The amount of graphene in the composite can be calculated based on the weight change of the two curves, and it is estimated to be about 18.8 wt%.

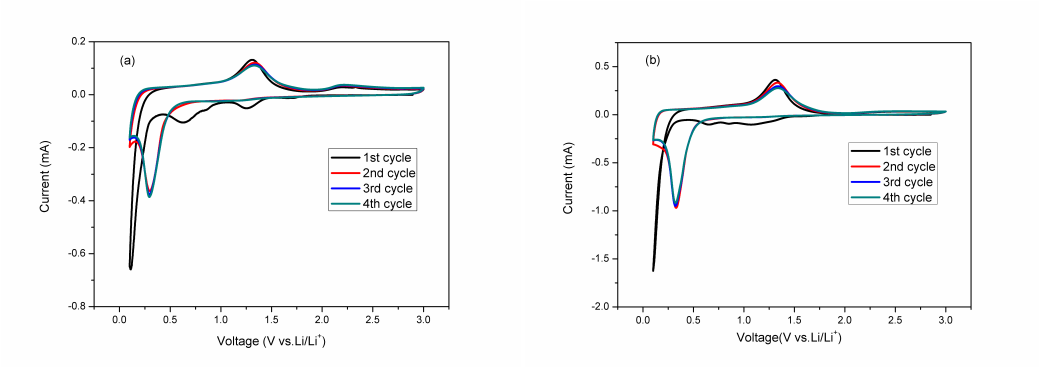

Figure S2 CV curves for the first 4 cycles of (a) GS-Mn_3O_4 nanocomposite and (b) bare Mn_3O_4 nanoparticles with 0.1 mV s^{-1} scan rate in the potential window from 3.0 V to 0.1V.

Computational details:

Following the conventional definition of the zigzag/armchair nanoribbon, a (8 × 10) single graphene layer containing 80 carbon atoms is used to match a (3 × 2) eight atomic layer thick stoichiometric Mn_3O_4 (001) surface slab containing 72 Mn and 96 O atoms, with three bottom layers fixed at bulk positions in a supercell (12.03 × 17.42 × 26 $Å^3$). The whole system contains 248 atoms in all with around 1400 valence electrons. All the calculations are performed by using the plane-wave basis Vienna Ab-initio Simulation Package (VASP) code [1-2] implementing the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. [3] A damped van der Waals correction is also incorporated based on Grimme's scheme [4] to better describe the non-bonding interaction between graphene and the Mn_3O_4(001) surface. For an all-electron description, the projector augmented wave method is used to describe the electron-ion interaction.[5-6] The cut-off energy for plane waves is chosen to be 500 eV, and the vacuum space is at least 18 Å, which is large enough to avoid interaction between periodical images. A Monkhorst-Pack mesh of K-points (2 × 1 × 1) and (4 × 2 × 1) is used respectively to sample the two-dimensional Brillouin zone for geometry optimization and for calculating the charge density. The convergence of the tolerance force on each atom during structure relaxation was set to 0.005eV/Å, and spin-polarization is included through all the calculations.

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3 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

4 S. Grimme, *J. Comput. Chem.* 2006, **27**, 1787.

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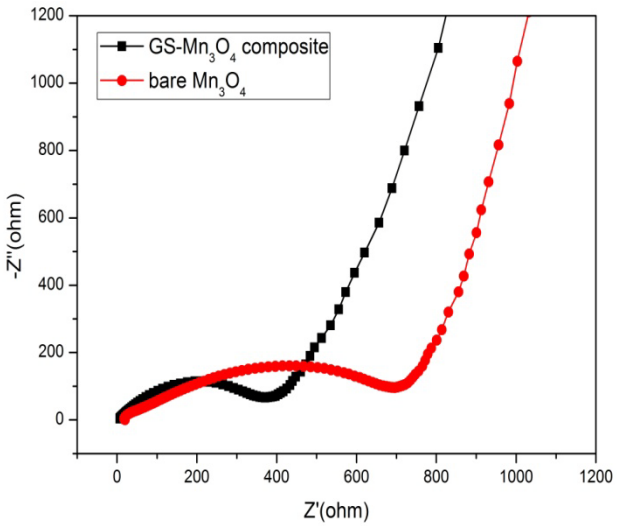

Figure S3. Nyquist plots for bare Mn_3O_4 and GS- Mn_3O_4 composite electrodes at the open circuit potential of fresh cells in the frequency range of 100 kHz to 10 mHz

To verify that the graphene nanosheets are responsible for the good performance of the cells, electrochemical impedance measurements were conducted on the as prepared bare Mn_3O_4 and GS-Mn_3O_4 at the open circuit potential of fresh cells in the frequency range of 100 kHz to 10 mHz, as shown in Figure S3. At high frequencies, the impedance response exhibits one semicircular loop, and there is a sloping straight line in the low-frequency regime. The intercept on the Z axis in the high -frequency region corresponds to the resistance of the electrolyte (R_s). The semicircle in the middle frequency range indicates the charge-transfer resistance (R_{ct}) through the electrode/electrolyte interface. The inclined line in the low-frequency region represents the Warburg impedance (Z_w), which is related to solid-state diffusion of Li ions in the electrode materials. From Figure S3, it can be observed that the diameter of the semicircle of GS-Mn_3O_4 nanocomposite is smaller than that of the bare Mn_3O_4, indicating that the GS-Mn_3O_4 nanocomposite has the lower charge transfer resistance, so it can be assumed that the nanocomposite containing graphene has higher electronic conductivity than the bare Mn_3O_4 particles, further proving the significant role of graphene in this nanocomposite, which is also consistent with the results of the theoretical computation .