Supporting Information

Long cycling life of Li_2MnSiO_4 lithium battery cathode under the double protection from carbon coating and graphene network

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Experimental Section

Synthesis of RGO@SiO_2 composite. The graphene oxide (GO) was produced via a modified Hummer's method.[1] First, the obtained GO (175 mg) was dispersed into 100 ml de-ionized water containing cetyltrimethylammonium bromide (CTAB, 1g) and NaOH (40 mg) and sonicated to form a homogeneous solution. The obtained solution was stirred for 2h at 40 ℃, followed by slow addition of 0.5 ml tetraethyl orthosilicate (TEOS) and kept for 12 h. The final GO@SiO_2 composite was collected by centrifugation and washed with water and ethanol for several times. The GO was converted into RGO by calcinating at 800 ℃ for 3 h in Ar to obtain the RGO@SiO_2 composite.

Synthesis of RGO@Li_2MnSiO_4@C composite. The RGO@Li_2MnSiO_4@C composite was obtained via a solid-state reaction by using RGO@SiO_2 as a template. In a typical experiment, 0.6 mmol lithium acetate dehydrate, manganese acetate tetrahydrate, RGO@SiO_2 as well as 0.33 mmol citric acid monohydrate were mixed in 10 ml water and sonicated for 3 hours. The above solution was stirred at 70 ℃ to evaporate the water. The obtained mixture was fine ground and calcinated at 400 ℃ for 3 hour in Ar atmosphere. Then, this intermediate product was again ground, pressed into plates, and subsequently reacted at 800 ℃ for 10 hours under Ar atmosphere to get the RGO@Li_2MnSiO_4@C composite. The RGO@Li_2MnSiO_4 was prepared under the same procedure without the addition of citric acid. The pure Li_2MnSiO_4 was synthesized under the same procedure by using SiO_2 particles (~180 nm) as the silicon source with no addition of RGO and citric acid.

Sample characterization: The structure, morphology and element component of the RGO, RGO@SiO_2, and RGO@Li_2MnSiO_4@C samples were carried out by X-ray diffraction (XRD, RIGAKU SCXmini), transmission electron microscope (TEM, JEM-2010), energy dispersive X-ray spectroscopy (EDS, JSM-6700F), X-ray photoelectron spectroscopy (XPS, ESCALAB 250) and Raman spectroscopy (Renishaw 2000, excited at 785 nm). Thermogravimetry analyses (TGA, NETZSCH

STA449C) were measured from 30 to 1000 ℃ at a heating rate of 10 K min^{-1} in air to determine the carbon content in these samples.

Electrochemical measurements:

The electrochemical behaviors were performed via a CR2025 coin-type test cell assembled in an Ar-filled golve box with the concentration of moisture and oxygen below 1 ppm. The working electrode was fabricated by mixing 70 wt% active material (RGO@Li_2MnSiO_4@C or pure Li_2MnSiO_4), 20 wt% conductivity agent (ketjen black, KB), and 10 wt% polymer binder (polyvinyldifluoride, PVDF) with 1-methyl-2-pyrrolidinone (NMP). The resultant slurry was then pasted on stainless steel collector and dried at 80 ℃ for 12 h under vacuum. The electrolyte was 1 M $LiPF_6$ in EC: EMC: DMC (1: 1: 1 v/v). A lithium foil was used as both the counter and the reference electrode. Cells were charged and discharged on a LAND 2001A system over a range of 1.5 V to 4.7 V at room temperature. The loading weight of active material on the stainless steel is about 1.2 ± 0.3 mg cm^{-2}. The specific charge/discharge capacities mentioned in this communication were calculated based on the mass of Li_2MnSiO_4.

1. Y. X. Xu, K. X. Sheng, C. Li and G. Q. Shi, *J. Mater. Chem.*, 2011, **21**, 7376-7380.

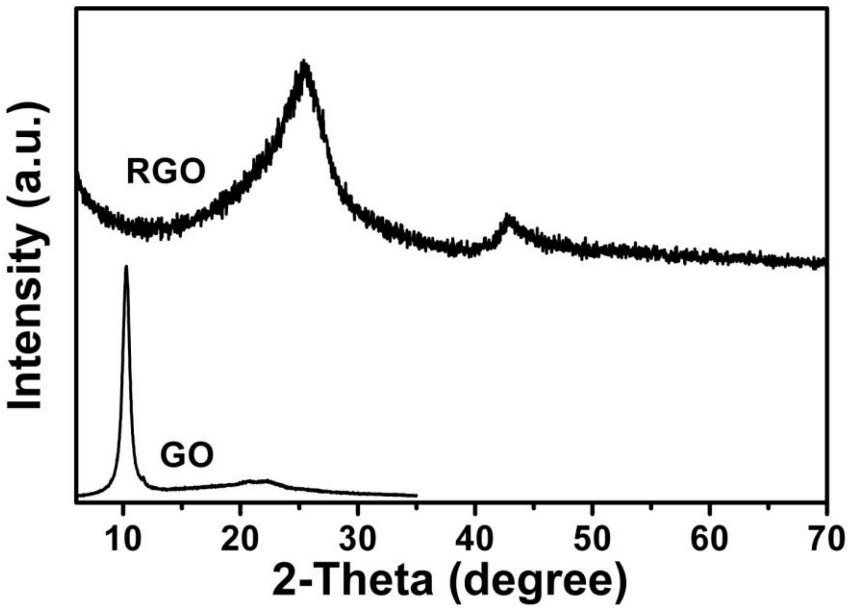

Fig. S1 X-ray diffraction (XRD) patterns of GO and RGO.

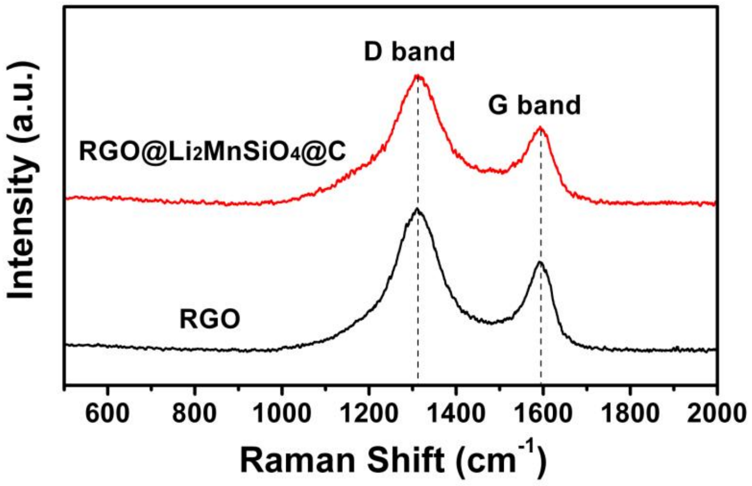

Fig. S2 Raman spectra of the RGO and RGO@Li_2MnSiO_4@C composite.

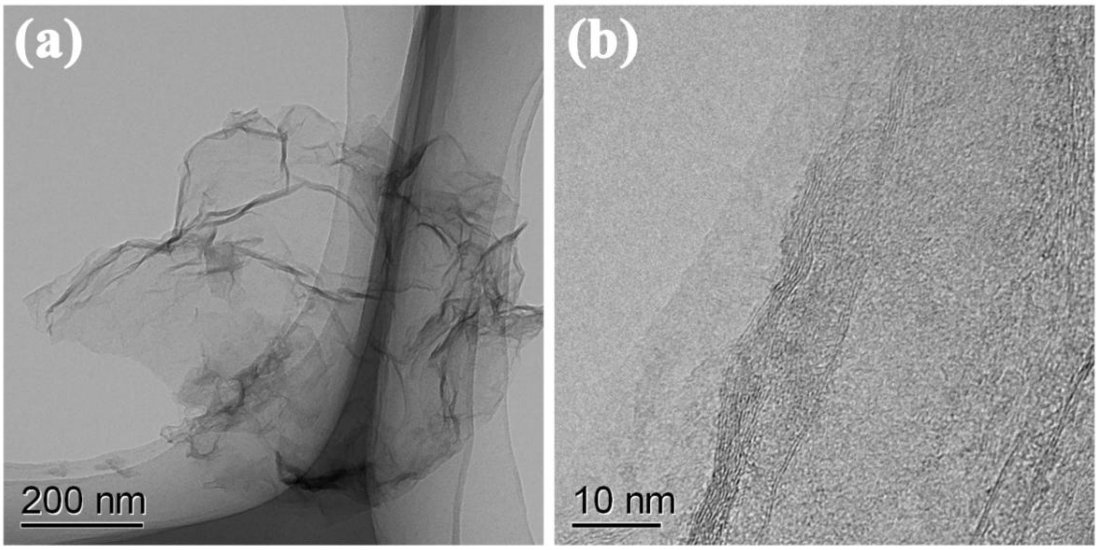

Fig. S3 (a) TEM and (b) HRTEM images of RGO.

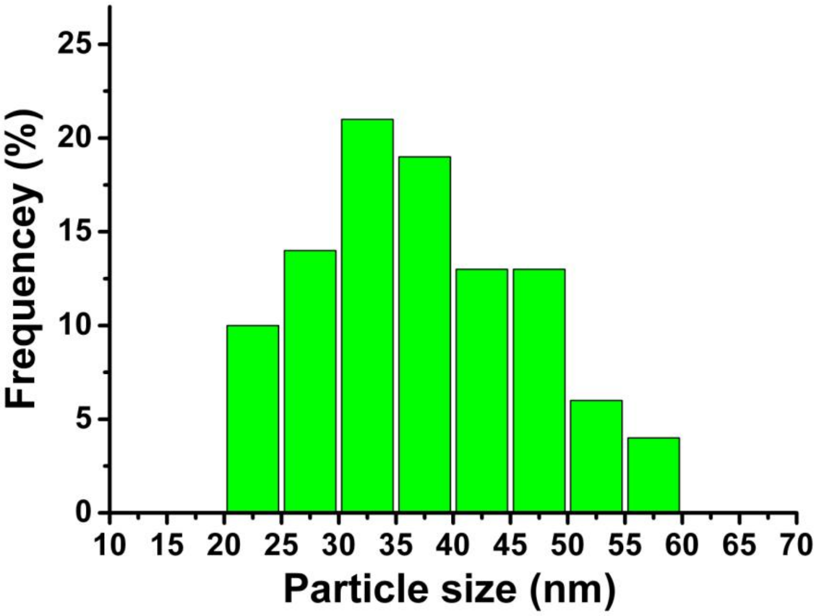

Fig. S4 Particle size distribution of Li_2MnSiO_4 nanoparticles in RGO@Li_2MnSiO_4@C composite.

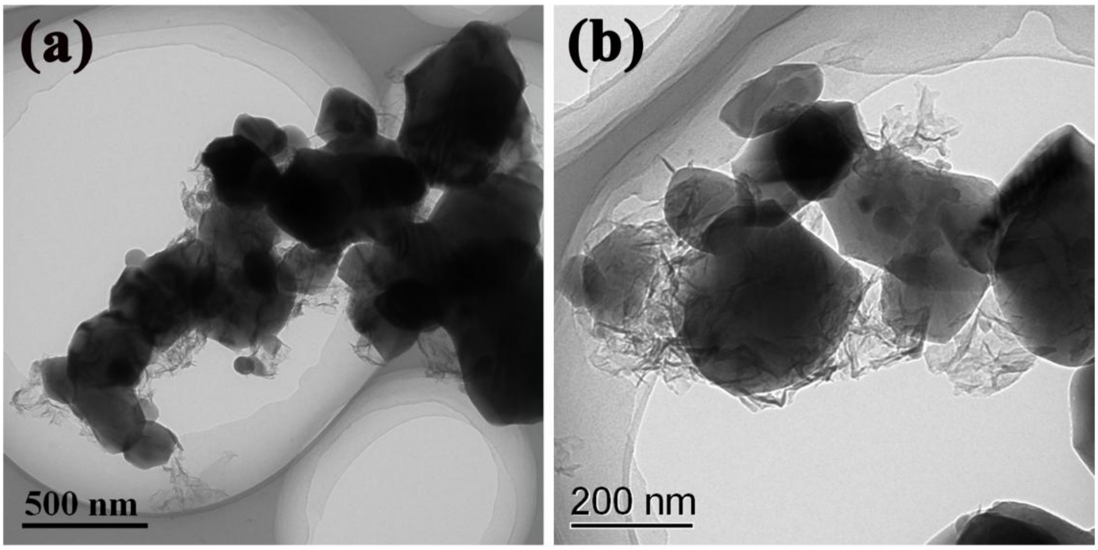

Fig. S5 TEM images of the RGO@Li_2MnSiO_4 composite.

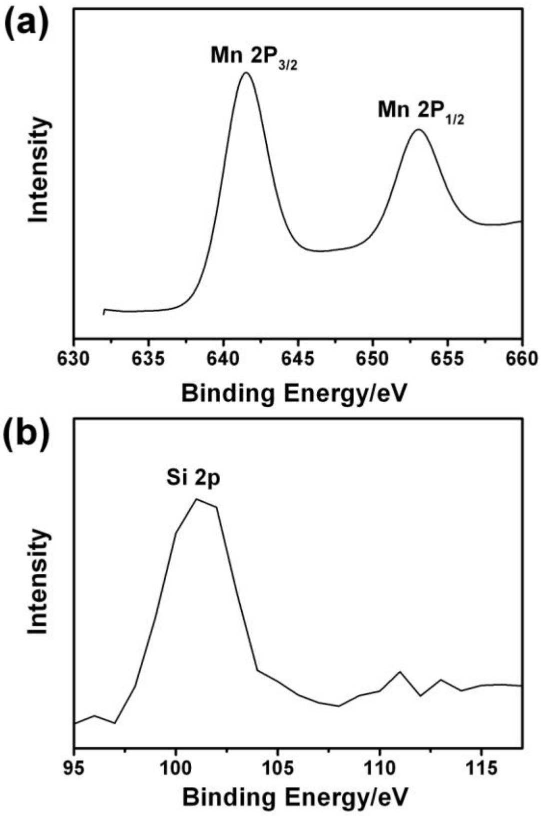

Fig. S6 High resolution XPS spectra of the (a) Mn 2p and (b) Si 2p in the RGO@Li_2MnSiO_4@C composite.

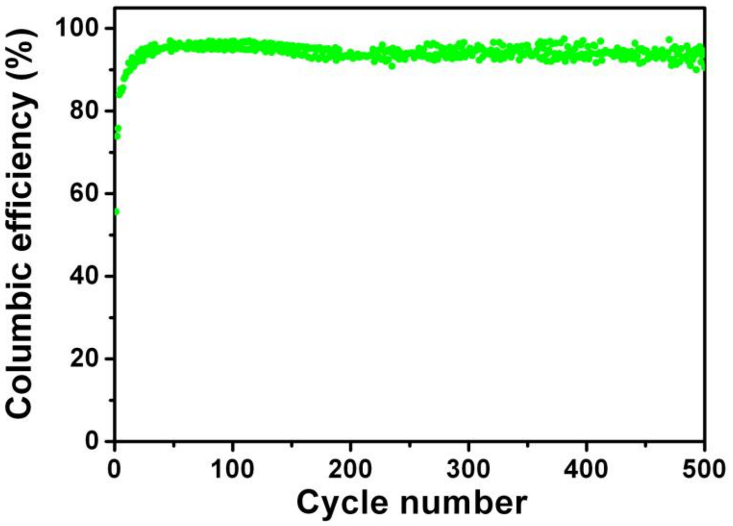

Fig. S7 Columbic efficiency of the RGO@Li_2MnSiO_4@C composite at 1C between 1.5 V and 4.7 V.

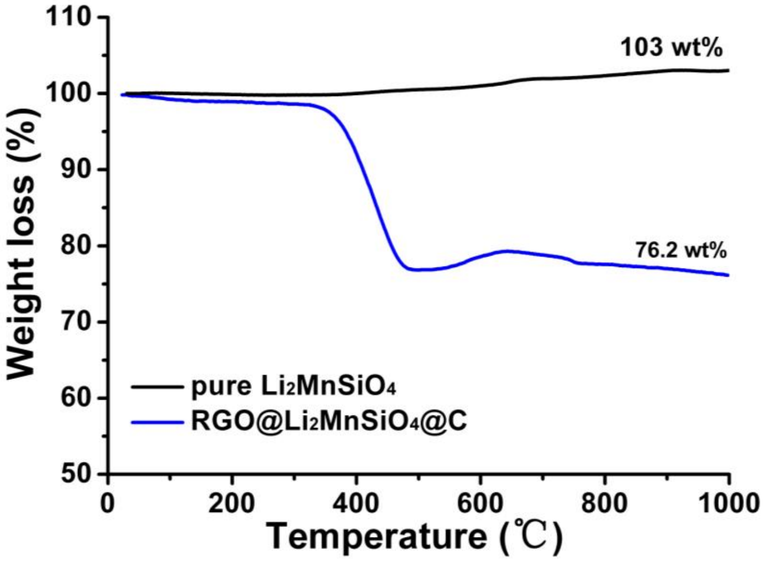

Fig. S8 Thermal gravimetric analysis (TGA) curves of pure Li_2MnSiO_4 and RGO@Li_2MnSiO_4@C composite at a heating rate of 10 ℃ min^{-1} between 30 and 1000 ℃.

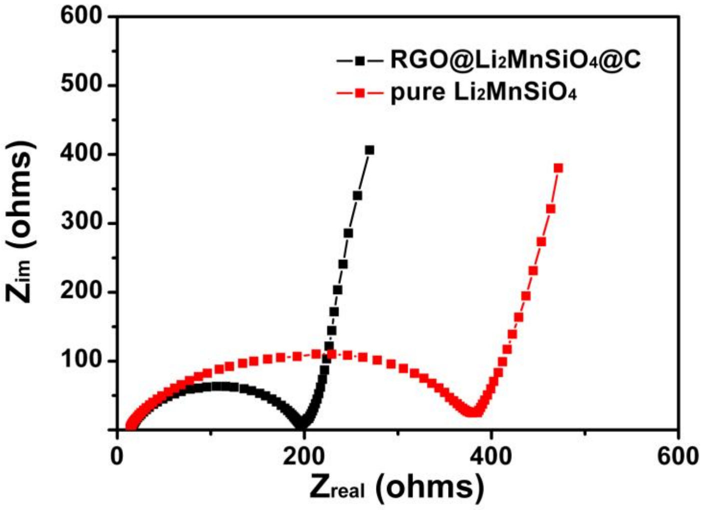

Fig. S9 Electrochemical impedance spectra for pure Li_2MnSiO_4 and $RGO@Li_2MnSiO_4@C$ composite.

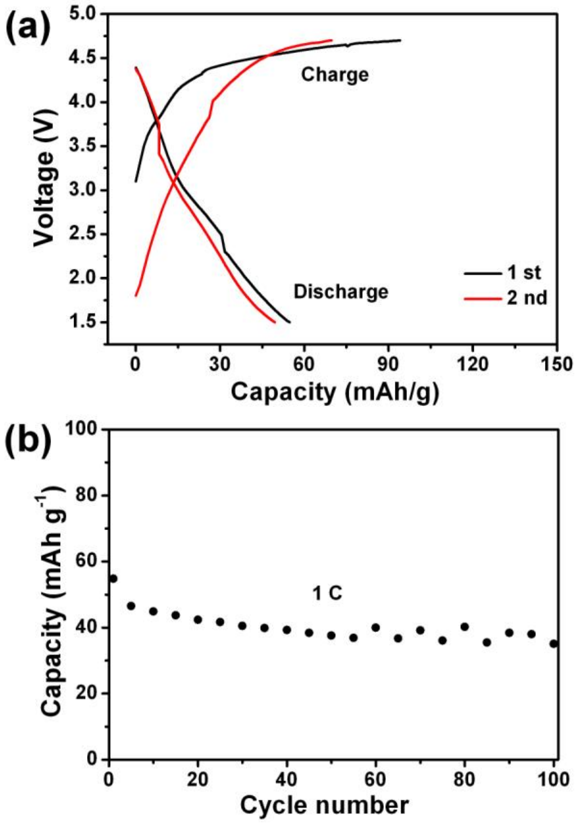

Fig. S10 (a) The first and second charge-discharge curves, and (b) cycling performance of pure Li_2MnSiO_4 cathode at a rate of 1C between 1.5 V and 4.7 V.

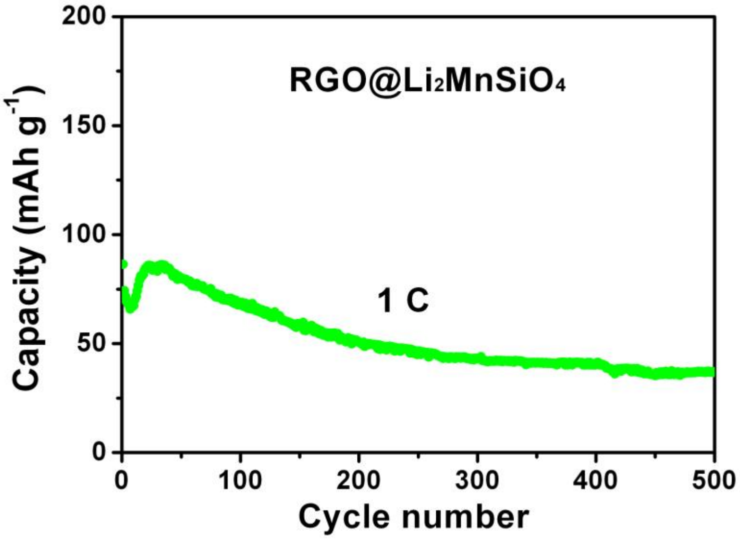

Fig. S11 Discharge capacity versus cycle number of the RGO@Li2MnSiO4 electrode between 1.5 V and 4.7 V at 1C.

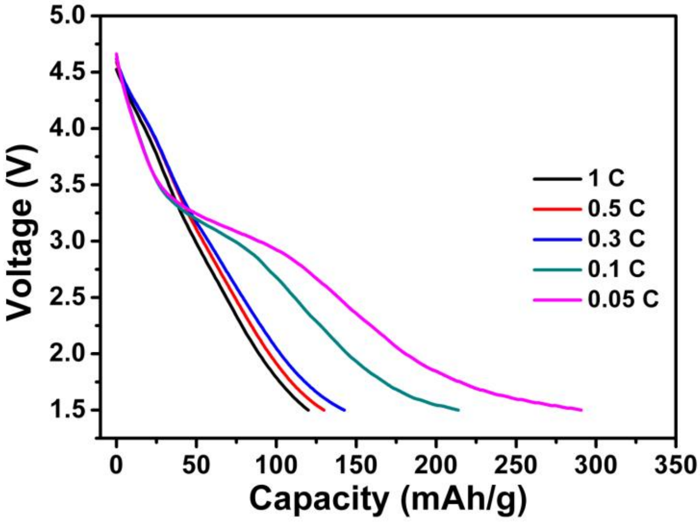

Fig. S12 The typical discharge curves of the RGO@Li_2MnSiO_4@C composite at various current densities.