Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Ultrasound-Assisted Approach to Synthesize Mn_3O_4/RGO Hybrids with High Capability for Lithium Ion Batteries

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Experimental Section：

Synthesis of GO:

GO was synthesized from natural graphite powder according to a modified Hummers method.[25] Briefly, 0.9 g of graphite powder was added into a mixture of 7.2 mL of 98% H_2SO_4, 1.5 g of $K_2S_2O_8$, and 1.5 g of P_2O_5. The solution was kept at 80 ^oC for 4.5 h, followed by thorough washing with water. Thereafter, the as-treated graphite was put into a 250 mL beaker, to which 0.5 g of $NaNO_3$ and 23 mL of H_2SO_4 (98%) were then added while keeping the beaker in the ice bath. Subsequently, 3 g of $KMnO_4$ was added slowly. After 5 min, the ice bath was removed and the solution was heated up to and kept at 35 ^oC under vigorous stirring for 2 h, followed by the slow addition of 46 mL of water. Finally, 40 mL of water and 5mL of H_2O_2 was added, followed by water washing and filtration. The exfoliation of graphene oxide was then dispersed in ethylene glycol (5mg mL^{-1}) under ultrasonication for 2 h to yield a homogeneous suspension.

Synthesis of Mn_3O_4/RGO hybrids:

1 mmol $Mn(OAc)_2$ was dissolved in 10 ml water. Then 3 ml GO solution was dropped in followed by added 200 ul *Tert*-butylamine. After ultrasound treatment for 5 minutes, the products were purified by centrifugation and washed with water for three times.

Synthesis of H-Mn_3O_4/RGO hybrids:

The as-obtained Mn_3O_4/RGO was further hydrothermal treated in water at 180 ^oC for 12 h.

Characterization:

The X-ray diffraction patterns of the products were collected on a Rigaku-*D*/max 2500 V X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. XPS measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K_α X-ray radiation as the X-ray source for excitation.

Electrochemical measurements:

The test cell consisted of a working electrode and a lithium foil which were separated by a Celgard 2400 membrane. The electrolyte solution was prepared by dissolving 1 M LiPF6 in EC-DMC (1 : 1 w/w). The working electrodes were prepared by casting slurry containing 80 % active material, 10 % acetylene black and 10 % polyvinylidene fluoride (PVDF) onto a copper foil. After vacuum drying at 80 ^oC for about 24 h, the electrode disks were punched and weighed. Each electrode has approximately 1–3 mg of active material. Galvanostatic charge–discharge cycling tests were performed using a LAND CT2001A multi-channel battery testing system in the voltage range between 0.01 and 3 V at room temperature.

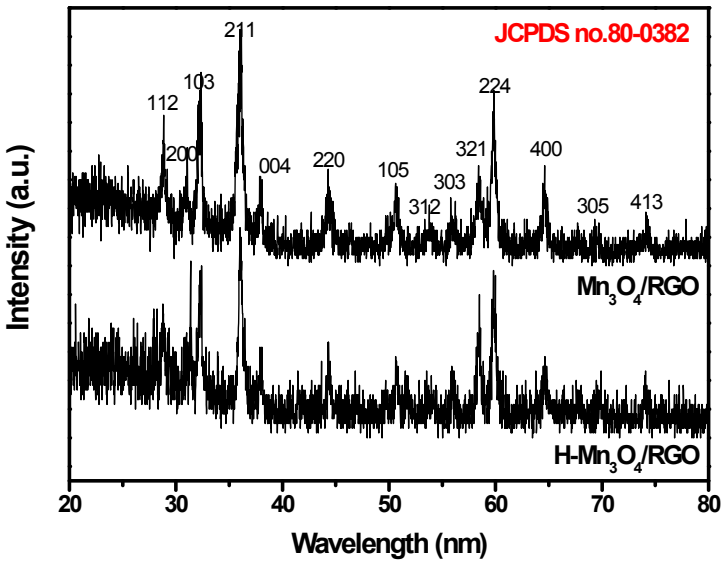

Fig. S1. XRD patterns of the Mn_3O_4/RGO and H-Mn_3O_4/RGO hybrids. All the peaks correspond well with those of Mn_3O_4 with a tetragonal spinel structure (space group I41/amd, JCPDS no.80-0382).

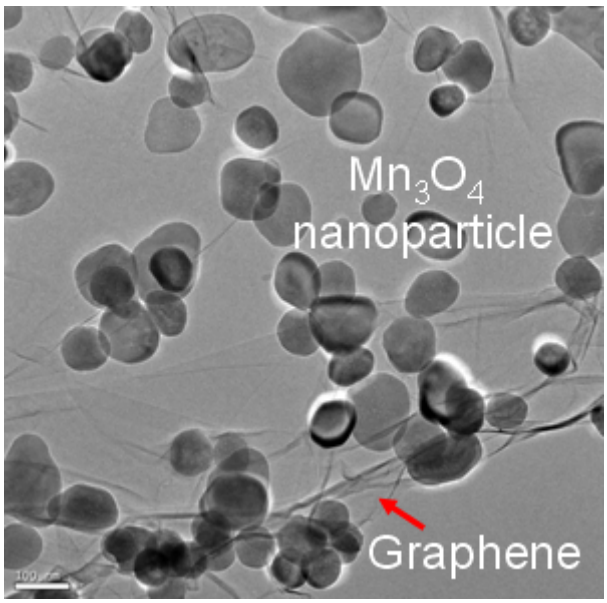

Fig. S2. TEM image of H-Mn_3O_4/RGO

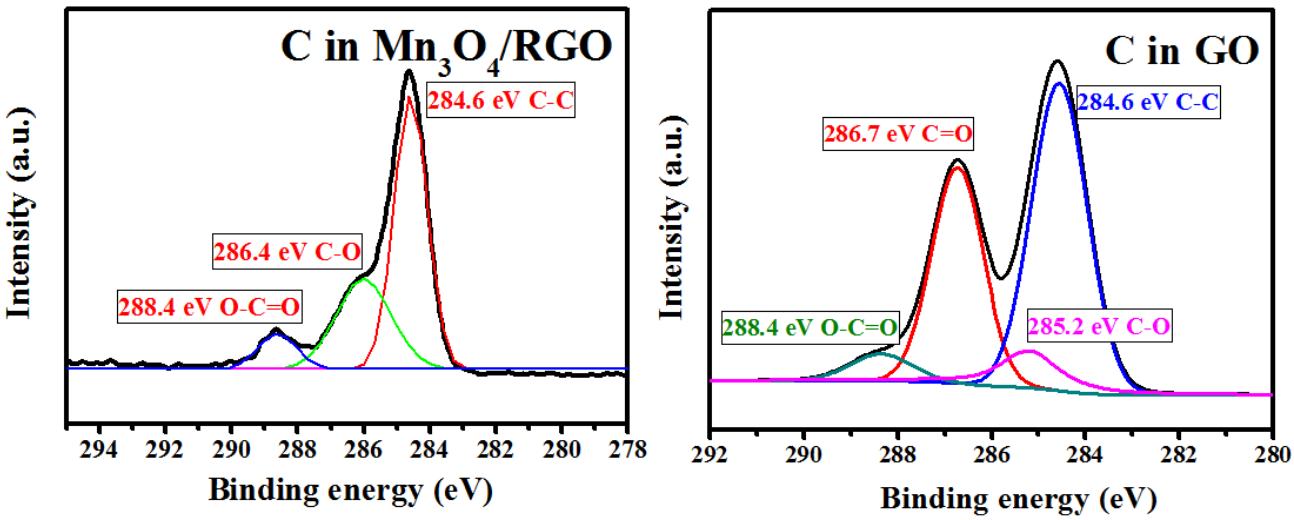

Fig. S3. The XPS spectra of C in Mn_3O_4/RGO and GO nanosheets.

Table S1. Typical Mn_3O_4 based anode materials for LIB applications

	Special particle shapes	Content of Mn_3O_4 (wt %)	Specific capacity at low current density	Specific capacity at high current density	Reference
Bare Mn_3O_4	sponge like powder	100	800 mA h g^{-1} after 40 cycles at 0.25 C		16
Mn_3O_4/graphene	nanoparticles	90	810 mA h g^{-1} after 40 cycles at 40 mA g^{-1}	351 mA h g^{-1} after 10 cycles at 1600 mA g^{-1}	9
Mn_3O_4/graphene	nanoparticles	81.2	900 mA h g^{-1} after 40 cycles at 50 mA g^{-1}	200 mA h g^{-1} after 10 cycles at 2000 mA g^{-1}	15
Mn_3O_4/graphene	needles	62.3	675 mA h g^{-1} after 100 cycles at 75 mA g^{-1}		17
Mn_3O_4@carbon	nanorods	98.8	473 mA h g^{-1} after 50 cycles at 40 mA g^{-1}		18
Mn_3O_4/ordered mesoporous carbons	nanoparticles	20	802 mA h g^{-1} after 50 cycles at 100 mA g^{-1}		19
Mn_3O_4/CNT	nanoparticles	42	592 mA h g^{-1} after 50 cycles at 100 mA g^{-1}	387 mA h g^{-1} after 10 cycles at 1000 mA g^{-1}	20

Table S2. Element analysis of GO and Mn_3O_4/RGO according to XPS results

	C-C (%)	C-O (%)	C=O (%)	O-C=O (%)	C/O
GO	48.6	8	35.8	7.6	1/0.58
Mn_3O_4/RGO	84.7	9.2	0	6.1	1/0.21