Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

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$MnCO_3/Mn_3O_4$/Reduced Graphene Oxide Ternary Anode Materials for Lithium-Ion Batteries: Facile Green Synthesis and Enhanced Electrochemical Performance

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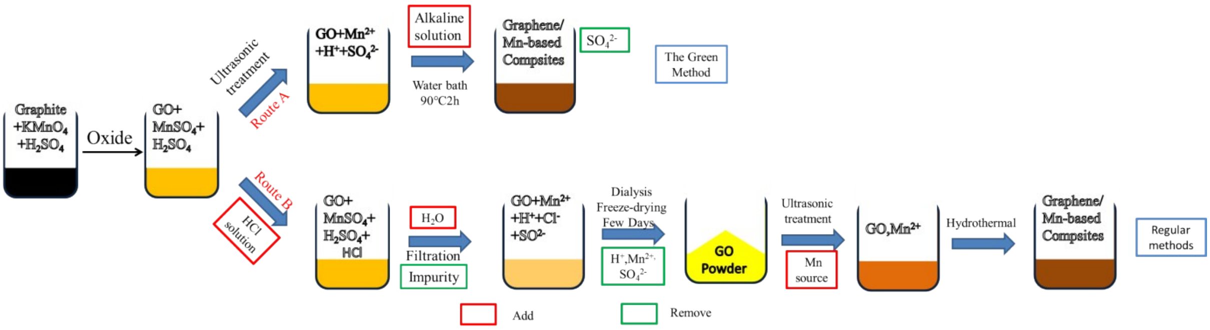

Fig. S1 Schematic illustration of the experimental processes of the Mn-based compound /graphene composites in this work and the regular method in other works. Generally, the fabrication of the RGO composites in the regular methods is started from the oxidation of graphite using Hummers method, followed by adding HCl solution to dissolve impurities and a large amount of water to dilute the solution, along with spending a few days to dialysis the solution to neutral and freeze-dry to get GO powder. Subsequently, the as-obtained GO powder and metal precursor were well dispersed in water or organic solution, then the solution was transferred to a Teflon-lined autoclave and maintained at 120~220 ^{o}C for hours. After washed and dried again, the composites can be obtained, through a time-consuming, raw material wasting process with large amount of acidic effluent discharged.

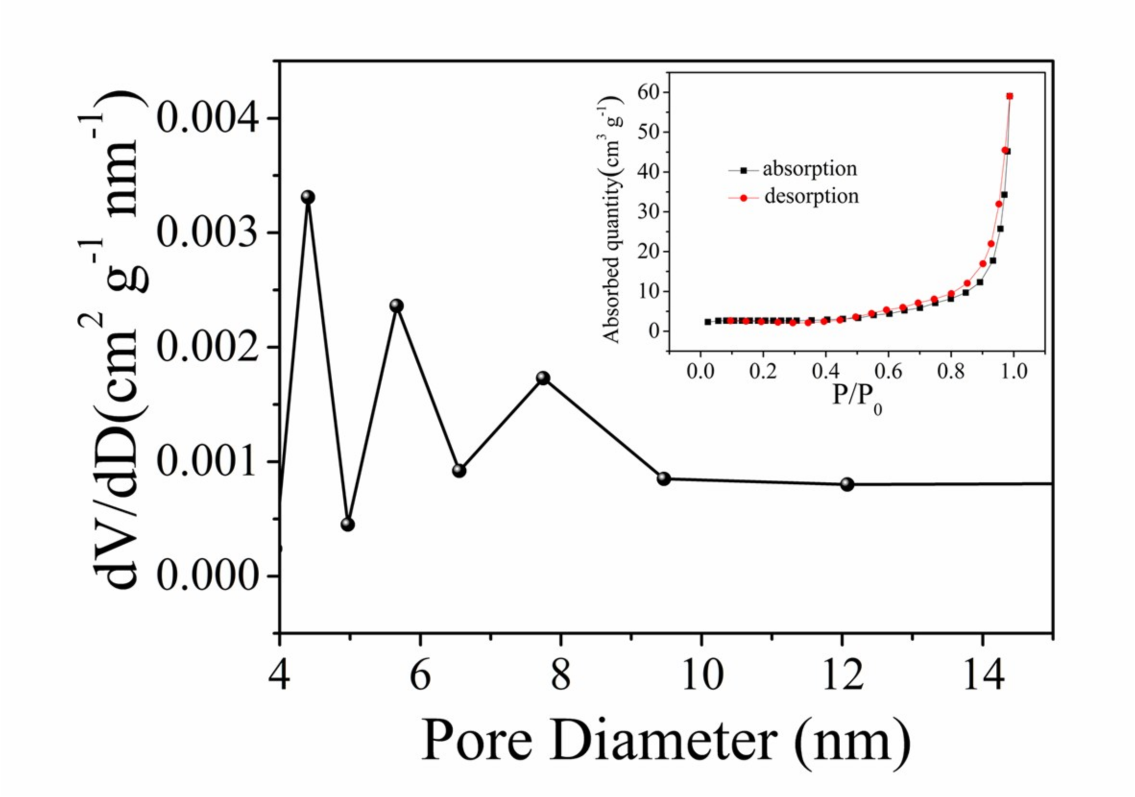

Fig. S2 N_2 adsorption and desorption isotherms and the pore size distribution of the $MnCO_3/Mn_3O_4$/RGO composites

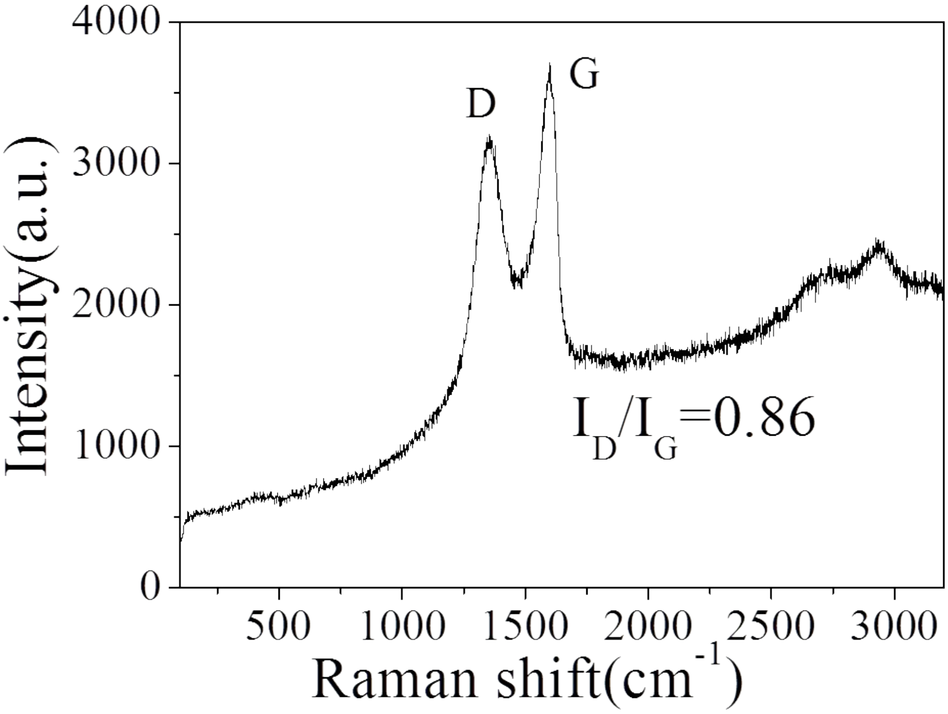

Fig. S3. Raman spectra of GO with the I_D/I_G of 0.86.

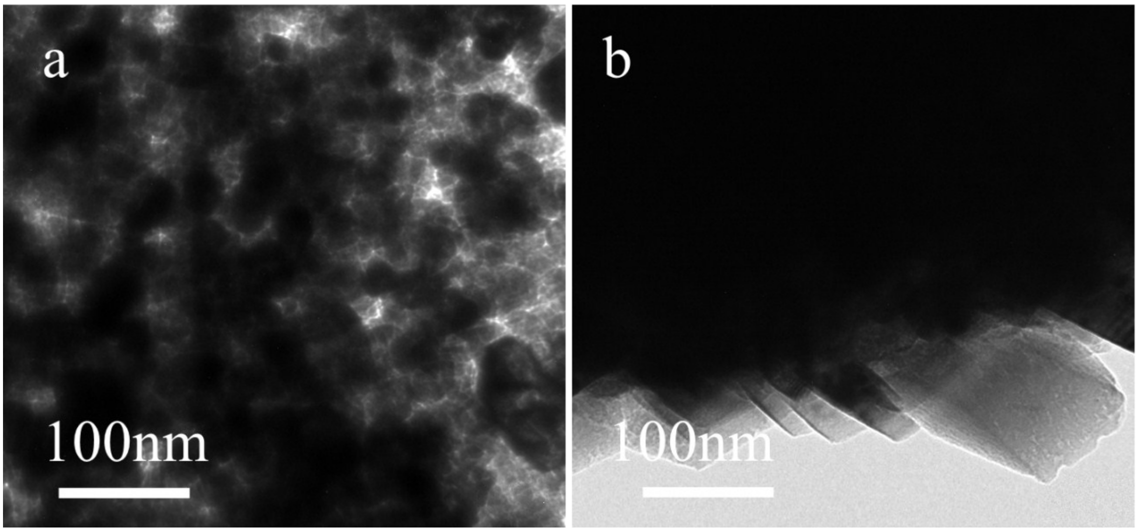

Fig. S4 TEM image of (a) $MnCO_3/Mn_3O_4$/RGO ternary composite and (b) $MnCO_3$/RGO composite.

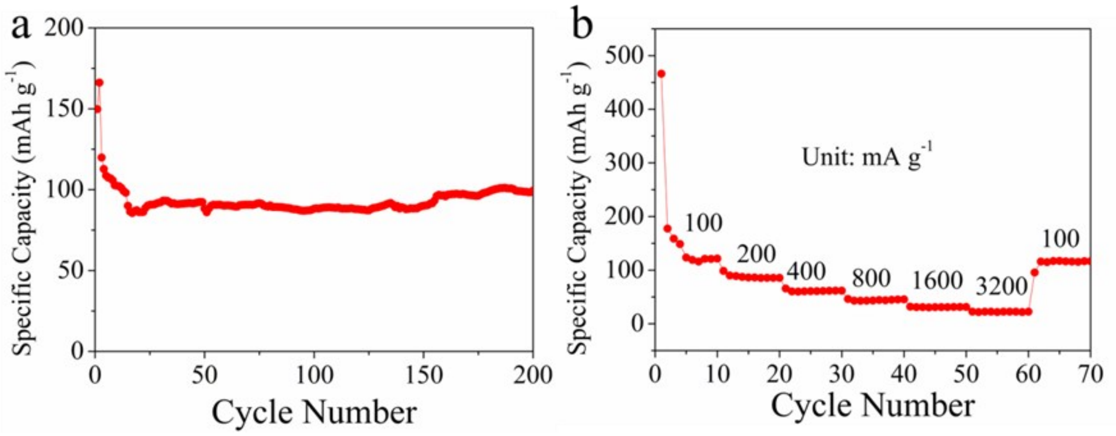

Fig. S5 (a) Cycling performance at 200 mA g^{-1}; (b) Rate capabilities of RGO

The reversible capacity of RGO after 200 cycles is 102 mAh g^{-1} at 200 mA g^{-1}. In addition, the RGO exhibits reversible capacities of 150, 107, 60.1, 43.7, 31.1, and 22.3 mAh g^{-1} at the current density of 100, 200,400, 800, 1600, and 3200 mA g^{-1}, which are far lower than the $MnCO_3/Mn_3O_4$/RGO composites. These results fully indicate that the RGO in the composite mainly acts as conductive and protective matrix to promote the diffusion of ion and buffer the volume expansion of $MnCO_3$ and Mn_3O_4, and almost have no contribution to the specific capacity.

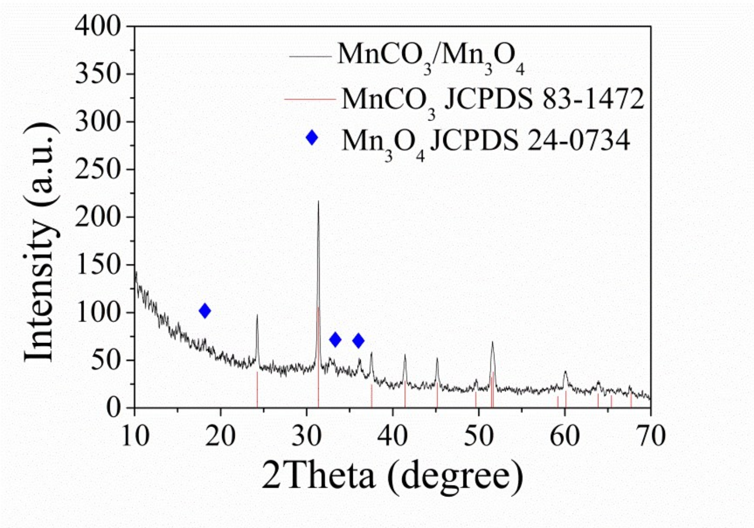

Fig. S6 The XRD pattern of $MnCO_3/Mn_3O_4$ composite

From the XRD data, the Bragg reflection peaks are consistent with the $MnCO_3$ structure (indicated by red line) and the peaks indicated by blue square at 18º, 32º and 36ºcorrespond to the (101), (103) and (211) reflections of Mn_3O_4 crystals (PDF card No. 24-0734). The XRD data indicate that the composites are composites of $MnCO_3$ and Mn_3O_4 without impurity phase.

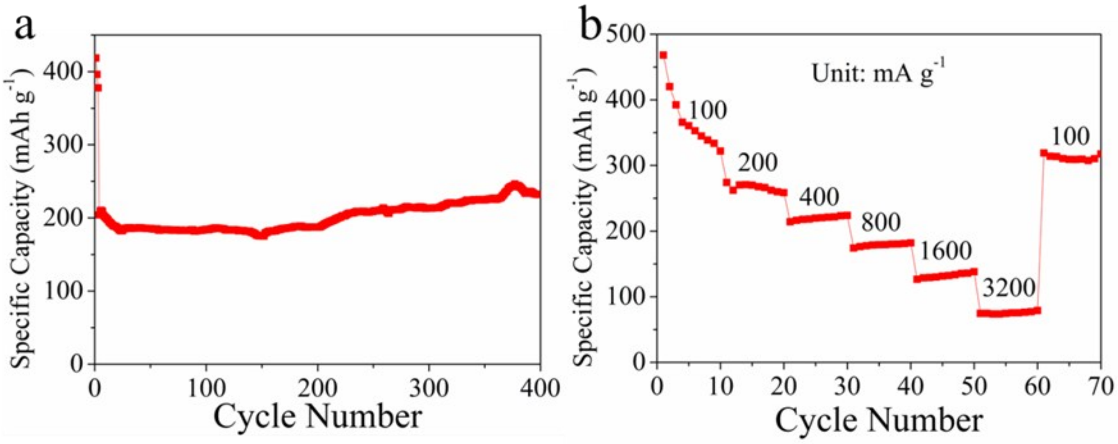

Fig. S7 (a) Cycling performance at 1000 mA g^{-1} (b) rate capability of $MnCO_3/Mn_3O_4$ composite

After 400 cycles at 1000 mA g^{-1}, the retained capacity of the $MnCO_3/Mn_3O_4$ electrode was about 235 mAh g^{-1}. Mn-based composite without RGO exhibited average discharge capacities of about 370, 266, 220, 179, 132, 76 and 312 mAh g^{-1} at corresponding current densities of 100, 200, 400, 800, 1600, 3200 and 100 mA g^{-1}, respectively. The results indicate that, without the RGO, the Mn-based composite has a relatively low capacity and poor rate performance.

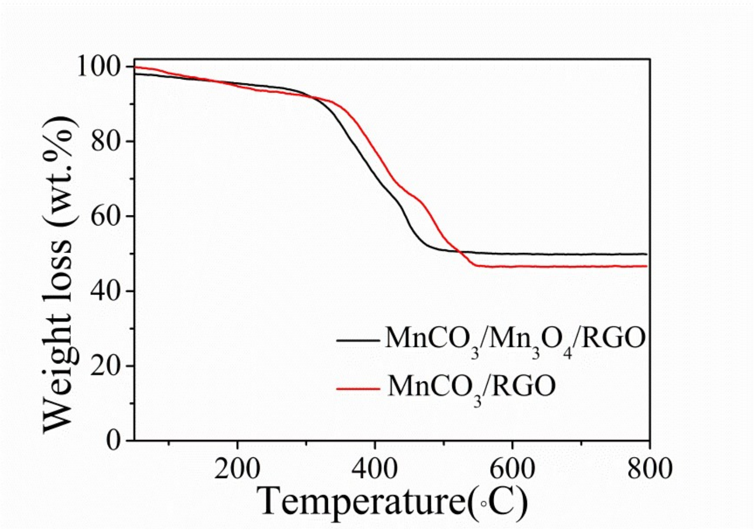

Fig. S8 TGA curve of $MnCO_3/Mn_3O_4$/RGO and $MnCO_3$/RGO composite, which is obtained in air flow at a ramp rate of 10 °C min^{-1}.

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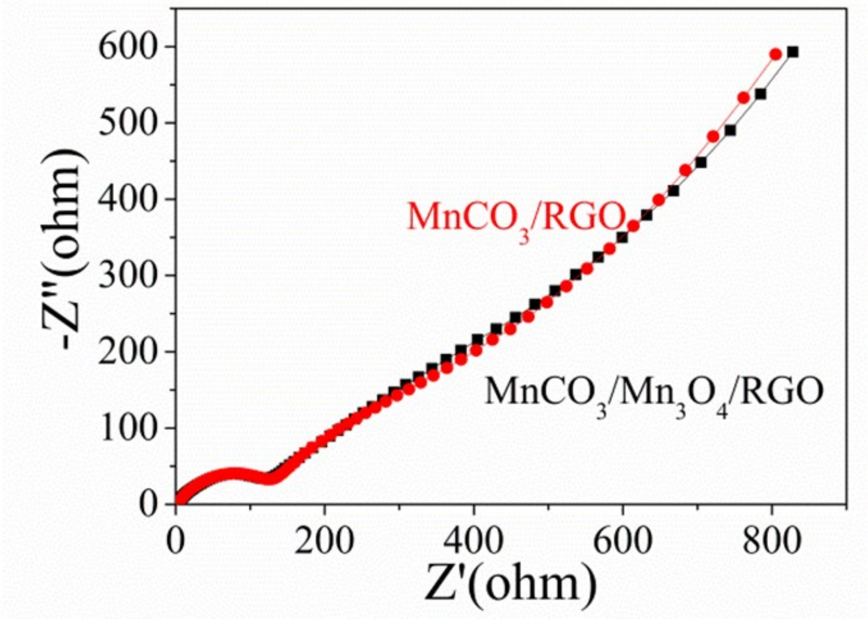

Fig. S9 EIS curve of the MnCO$_3$/Mn$_3$O$_4$/RGO and Mn$_3$O$_4$/RGO composites at the 15th cycle.

Table S1. Comparison of the electrochemical performances of this work with the other $MnCO_3$/RGO composites.

Anode	Residual capacity (mAh g^{-1})/cycles	Current (mAg^{-1}) or C	Ref.
$MnCO_3/Mn_3O_4$/RGO	988mA h g^{-1}/200th cycle 532mA h g^{-1}/800th cycle	100 1000	This work
$MnCO_3$/RGO	755mA h g^{-1}/100th cycle	0.5C	1
$MnCO_3$/RGO	845mA h g^{-1}/100th cycle	0.2C	2
$MnCO_3$/RGO	1098mA h g^{-1}/60th cycle 775mA h g^{-1}/100th cycle	46 233	3
$MnCO_3$/RGO	1474 mA h g^{-1}/400th cycle	100	4
$MnCO_3$	656.8 mA h g^{-1}/100th cycle	100	5
$MnCO_3$	40 mA h g^{-1}/50th cycle	44	6

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