Supplementary Information

Superior high rate capability of MgMn$_2$O$_4$/rGO nanocomposites used as a cathode material for aqueous rechargeable magnesium ion battery

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Synthesis of MgMn$_2$O$_4$ nanomaterials

MgMn$_2$O$_4$ nanomaterials were prepared by sol-gel method. First, the masses of magnesium nitrate hexahydrate, manganese nitrate tetrahydrate, citric acid and ethylene glycol were weighed according to the molar ratio of 0.5 : 1 : 3 : 9, then the weighed products were completely dissolved in 30 mL of deionized water. The mixture became viscous gel after being stirred for 12 h at a constant temperature of 80°C. After being dried in a vacuum oven at 200°C for 12 h, the sample was fully ground using a mortar. Finally, the MgMn$_2$O$_4$ nanomaterials were obtained by calcining for 10 h at 550°C. The specific preparation process is shown in Fig. S1.
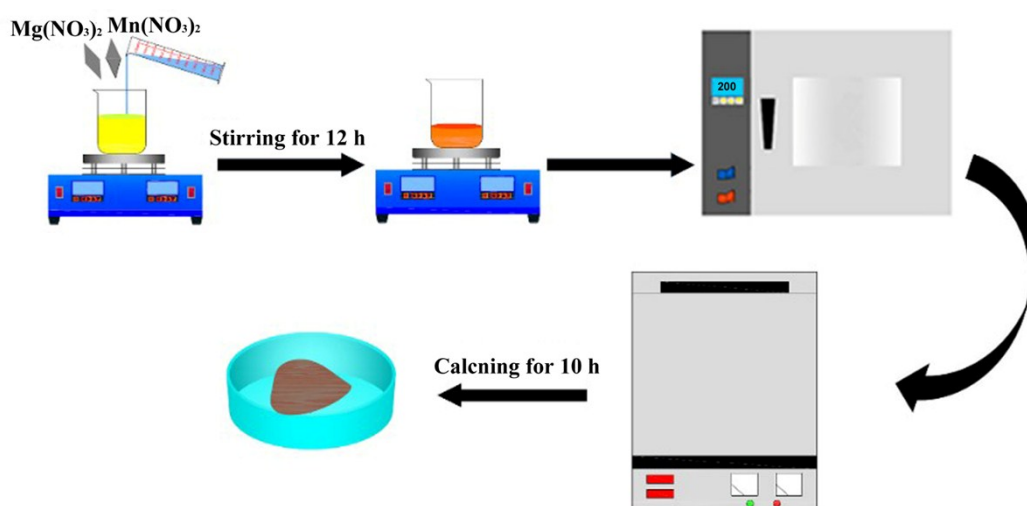
Fig. S1 Preparation flow chart of the MgMn$_2$O$_4$ nanomaterials.

Synthesis of MgMn$_2$O$_4$/GO nanomaterials

Graphene oxide (GO) was prepared according to the modified Hummers method.[1] The MgMn$_2$O$_4$/rGO nanomaterials were prepared by the mechanical stirring method. Typically, a certain amount of MgMn$_2$O$_4$ and GO were respectively weighed and uniformly dispersed in 30 mL of deionized water with ultrasound for 1 h. Then the mixture was kept stirring at 70°C for 12 h using a magnetic stirrer. The sample was washed with deionized water and dried in a vacuum oven at 80°C. Finally, the MgMn$_2$O$_4$/rGO nanomaterials were obtained by calcining in a muffle furnace at 350°C for 2 h. The specific preparation process is shown in Fig. S2.
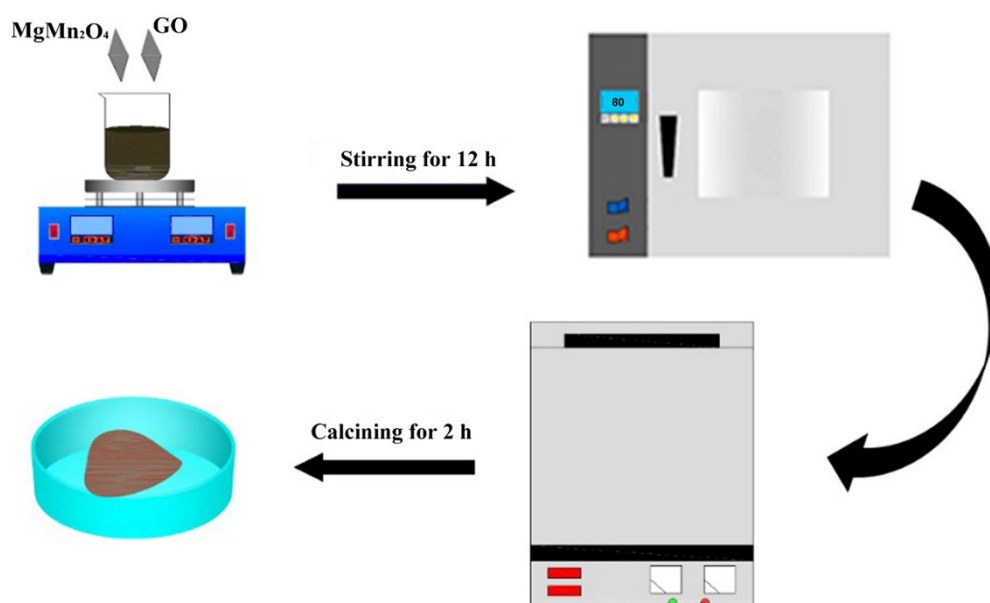
**Fig. S2** Preparation flow chart of the MgMn$_2$O$_4$/rGO composite materials.

Material characterizations

X-ray diffraction (XRD, EMPYREAN) was carried out to investigate the crystalline phases of the synthesized materials using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. The morphologies of the materials were observed by using a scanning electron microscope (SEM, HITACHI S-3400N). For measurement of electronic conductivity, the samples were prepared into thin film electrodes on a copper substrate with the thickness about 30 μm. Then, the electrical conductivities of the materials were measured by the two-electrode method using the Precision Premier II Ferroelectric Tester (Radiant, Inc.).

Electrochemical measurements

The electrochemical experiments were performed by using a conventional three-electrode electrochemical cell, which is consisting of a working electrode (active material), a counter electrode (graphite rod) and a reference electrode (saturated calomel electrode, SCE). The working electrode was made by a slurry containing 80% active material, 10% super-P, and 10% PVDF binder dissolved in NMP, and carbon cloth was used as the current collector. The specific preparation process of the working electrode is as follows: firstly, we weighed a certain amount of active material and super-P according to the mass ratio of 8 : 1, and grind them in a mortar until well mixed. Then, the desired mixed slurry was obtained by mixing with the corresponding mass of PVDF solution. The mixed slurry was uniformly spread on a carbon cloth and kept it at 80°C for 24 h in a vacuum oven to be sufficiently dried, and then naturally cooled to room temperature to obtain the working electrode. The working electrode was 1×1 cm^2 in size with the active substance mass loading of $\sim$5.5 mg cm^{-2}. The electrolyte used was 0.5 mol L^{-1} MgCl$_2$ dissolved in deionized water. Galvanostatic charge-discharge cycling performance was performed on a LANHE automatic battery tester (CT2001A, China). Cyclic voltammetry (CV) was carried out with a multi-channel potentiostat (VMP3/Z, Bio-Logic).

The XRD patterns of the electrode materials are shown in Fig. S3. It can be seen that there is no significant difference between the diffraction peaks of the two electrode materials. The positions of the main diffraction peaks are 2θ = 18.18°, 32.87°, 36.84°, 44.72° and 60.64°, consistenting with the powder diffraction standards (JCPDS) card No. 72-1336. It indicates that the samples are the pure spinel $MgMn_2O_4$, and there is no other impurity. However, we can find that there are no characteristic diffraction peaks of rGO in the XRD patterns of $MgMn_2O_4$/rGO composite material, due to the low content of rGO in the materials.
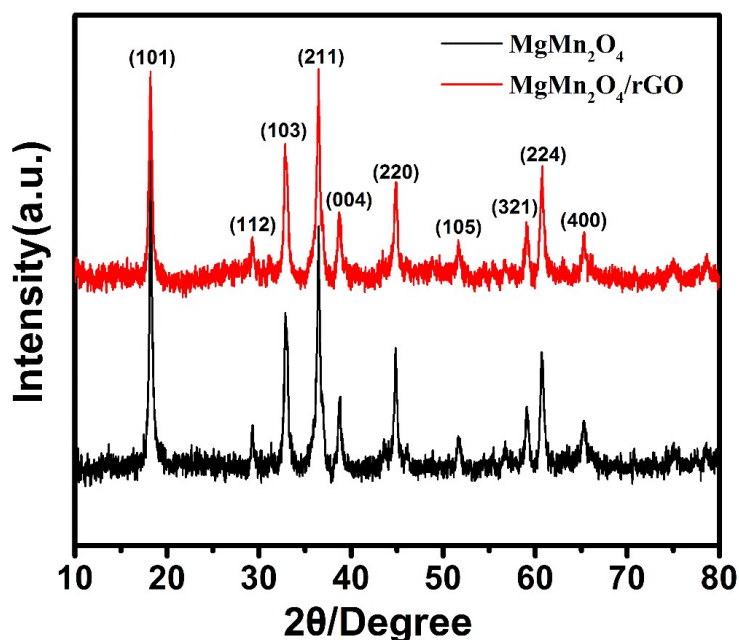
Fig. S3 XRD patterns of the $MgMn_2O_4$ and $MgMn_2O_4$/rGO composite materials.

Table S1 Electrical conductivity of the MgMn$_2$O$_4$ and MgMn$_2$O$_4$/rGO samples

	MgMn$_2$O$_4$	MgMn$_2$O$_4$/rGO
Electronic conductivity [S cm^{-1}]	1.07×10^{-10}	2.13×10^{-6}

The relationship between electrical conductivity and magnesium ion diffusion coefficient.

The chemical diffusion coefficient is a transport parameter reflecting both the ionic and electronic transports that occur within an active material. It can be expressed as a product of a self-diffusion coefficient $D_{Mg(self)}$ and a Wagner factor Φ.[2-3]

$$D_{Mg} = D_{Mg(self)} \times \Phi \tag{1}$$

$D_{Mg(self)}$, which is majorly determined by the structural properties of the material, is related to the ionic mobility or viscosity of an active material. The Wagner factor Φ, which generally reflects the influence of electrons motion on the diffusion of the ions in the internal electric field, fundamentally depends on the mobilities and concentrations of the ions and electrons in the active material. Incorporation of reduced graphene oxides (rGO) optimizes the interfacial properties of MgMn$_2$O$_4$ and improves the electrical conductivity of the electrode materials. Therefore, the diffusion of Mg^{2+} ions is facilitated under a stronger internal electric field.
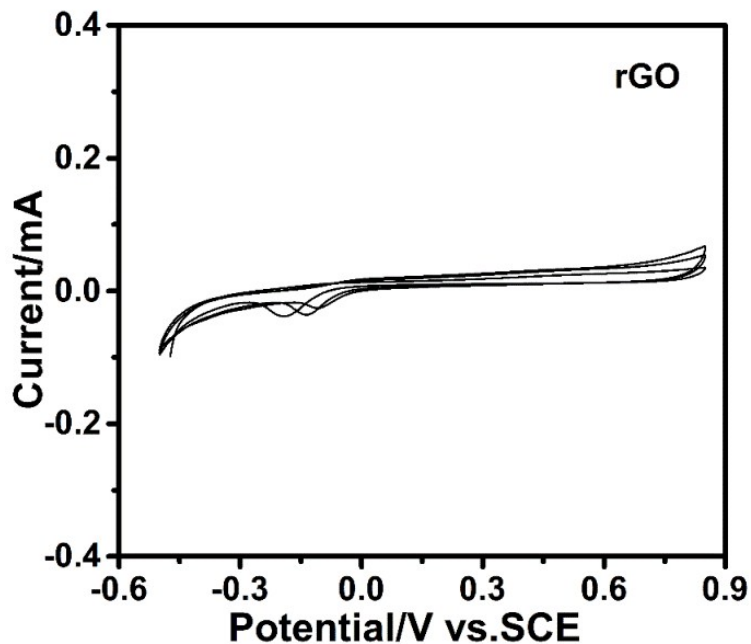
Fig. S4 The initial three CVs of the rGO at a scan rate of 0.1 mV s^{-1}.
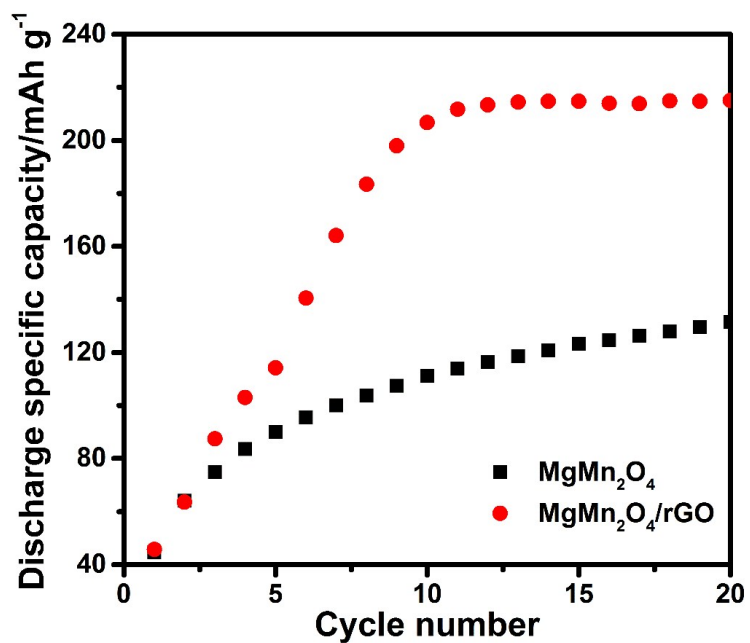
Fig. S5 Cycling performance of the $MgMn_2O_4$ and $MgMn_2O_4$/rGO

samples at the current density of 50 mA g^{-1} for the initial 20 cycles.

We performed galvanostatic charge-discharge tests at different current densities for electrode materials in a voltage window of -0.5 V ~ 0.85 V. Fig. S5 shows the charge-discharge curves of the two electrodes at different current densities, ranging from 50 mAh g^{-1} to 1000 mAh g^{-1}. It can be seen that the $MgMn_2O_4$/rGO composite electrode has a more pronounced discharge plateau, which means that the $MgMn_2O_4$/rGO composite material can insert more magnesium ions and achieve higher discharge specific capacity. The discharge specific capacities of the $MgMn_2O_4$ and $MgMn_2O_4$/rGO at the current density of 50 mA g^{-1} are 131.4 mAh g^{-1} and 211.8 mAh g^{-1}, respectively. In particular, the discharge specific capacity of the $MgMn_2O_4$/rGO reached 140.1 mAh g^{-1} at the current density of 1000 mA g^{-1}. This is because the coated rGO significantly improves the electronic conductivity of the material and promotes the rapid transport of magnesium ions. Therefore, the $MgMn_2O_4$/rGO composite electrode is promising to exhibit the excellent electrochemical property.
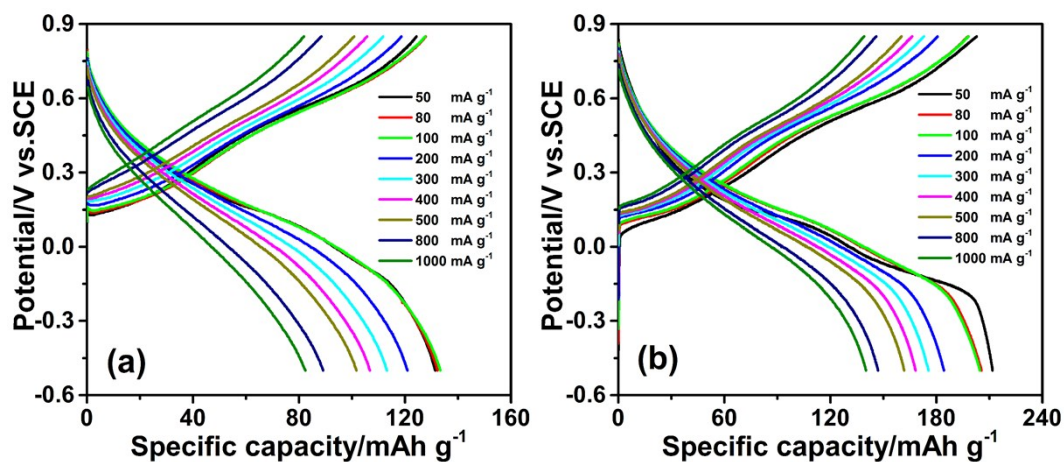
Fig. S6 Charge-discharge curves of the $MgMn_2O_4$ (a) and $MgMn_2O_4$/rGO

(b) at different current densities.

Table S2 Study on the $MgMn_2O_4$ cathode material for magnesium ion batteries

Research Team	Current Density	Discharge Specific Capacity
Our work	50 mA g^{-1}	211.8 mAh g^{-1}
Our work	200 mA g^{-1}	181.4 mAh g^{-1}
Cabello[4]	0.06 mA g^{-1}	160 mAh g^{-1}
Yin[5]	27.2 mA g^{-1}	162 mAh g^{-1}
Nupur[6]	45.5 mA g^{-1}	42 mAh g^{-1}
Shi[7]	200 mA g^{-1}	152.8 mAh g^{-1}

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