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Rapid preparation of the hybrid of MnO₂ dispersed on graphene nanosheets with enhanced supercapacitive performance

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ABSTRACT

 $MnO_2/graphene$ nanosheets (GNS) hybrid has been readily prepared by a rapid approach of one-pot electrochemical codeposition. Under a negative reduction potential, graphene oxide nanosheets lose oxygen-containing functional group to become GNS, simultaneously MnO_2 derived from $KMnO_4$ is also electrochemically deposited on the electrode. The characterizations of scanning electron microscope and transmission electron microscopy show that MnO_2 nanoflakes are homogenously dispersed on the surfaces of GNS, such microstructure can effectively enlarge the contact area of MnO_2 with electrolyte. The electrochemical measurements indicate that the introduction of GNS significantly enhances the supercapacitive performance of MnO_2 electrode. Notably, the resulting MnO_2/GNS hybrid exhibits a high specific capacitance of 413.1 Fg^{-1} at 1 Ag^{-1} , which is higher than the recently reported MnO_2/GNS hybrids prepared by different methods including electrochemical deposition. Furthermore, the hybrid retains 91.2% of initial capacitance after 2500 cycle, while the MnO_2 only maintains 63.5%. These obviously boosted performances for MnO_2/GNS hybrid are essential for high-efficiency electrochemical energy storage.

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1. Introduction

Electrochemical capacitors, also called supercapacitors, have attracted extensive research interests due to their intrinsic characteristics for electrochemical energy storage, such as higher power density relative to secondary batteries and higher energy density than conventional electrostatic capacitors [1–3]. Generally, supercapacitors can be divided into two main types according to their charge storage mechanism, one is electrochemical double layer capacitors (EDLCs), the other is pseudocapacitors. Thereinto, EDLCs usually use carbonaceous materials as the electrode materials, which are based on the accumulation of pure electrostatic charges in the electric double layers between electrode and surrounding electrolyte. Pseudocapacitors commonly employ transition metal oxides as well as conducting polymers, in which charge is stored by rapid and reversible Faradaic redox reactions across the electrode/electrolyte interface, strictly speaking, the pseudocapacitive electrode materials must display an

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http://dx.doi.org/10.1016/j.electacta.2016.08.109 0013-4686/© 2016 Elsevier Ltd. All rights reserved. electrochemical behavior typical of that observed for a capacitive carbon electrode in mild aqueous electrolyte [4–7].

Among various transition metal oxides, manganese dioxide (MnO_2) has been widely investigated as pseudocapacitive electrode materials owing to its high theoretical specific capacitance, abundant source, and environmental friendliness. However, the intrinsically poor conductivity of MnO_2 ($10^{-6}-10^{-5}$ S cm⁻¹) and low cyclic life limit its electrochemical performance [8]. Besides, the self-aggregation of MnO_2 often occurs due to its high surface energy, consequently reducing its effective contact areas with electrolyte [9].

Graphene, a kind of two-dimension carbon material, has become one of the most promising electrode materials for supercapacitor due to its high conductivity, large specific surface area, and remarkable chemical stability [10,11]. In particular, it can be used as ideal platform to build graphene-based composites with transition metal oxides and conducting polymer for supercapacitor applications [12,13]. Therefore, it is an effective way to enhance electrochemical performances of MnO₂ by forming the hybrids consisted of MnO₂ and highly conductive graphene nanosheets (GNS). Currently, some methods have been proposed to prepare MnO₂/GNS hybrids, such as hydrothermal method [9], microwaveassisted irradiation [13], polymer-assisted chemical reduction [14],







electrodeposition [15], electrophoretic deposition [16], redox procedures [17], soft chemical route [18], and electrostatic coprecipitation [19,20]. However, these approaches show some limitations, for instance, complicated and time-consuming preparation process or employing hazardous chemicals, including high temperature treatment for reducing graphene oxide, low specific capacitance of obtained hybrid, or high cost. So it is still a challenge to prepare the MnO₂/GNS hybrid with superior performances by a simple, green and low-cost method.

In this contribution, an easy and rapid one-pot cathodically electrochemical codeposition method is put forward to prepare the MnO₂/GNS hybrid. Carbon nanotube films (CNFs), one kind of favorable substrate for flexible electric devices owing to its superior flexibility, excellent electrical conductivity, and mechanical strength [21], are used as the electrode substrate to obtain a highly flexible, ultrathin, and lightweight electrode architecture. Under the negative reduction potential, the graphene oxide (GO) nanosheets lose oxygen-containing functional group to form GNS. Simultaneously, MnO₂, KMnO₄ is used as the source of Mn, is also electrochemically deposited on the electrode by the following reduction reaction [22]: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$. For comparison, MnO₂ electrode has also been prepared under the same electrochemical procedure just without GO in the deposition bath. The composition and morphology of the hybrid were studied using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM), and transmission electron microscopy (TEM). The electrochemical behaviors of MnO₂/GNS hybrid and MnO₂ electrodes were characterized and compared with cyclic voltammetry (CV), galvanostatic charge/ discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS). The MnO₂/GNS hybrid prepared by this rapid and feasible electrochemical method is expected to significantly promote the dispersion of MnO₂, consequently effectively improving the electrochemical performances of MnO₂ for supercapacitor applications.

2. Materials and methods

2.1. Materials

KMnO₄, LiClO₄, Na₂SO₄ were analytical grade and all of them were supplied by Sinopharm. Natural graphite powder (325 mesh) was purchased from Tianjin Guangfu Research Institute. GO was synthesized from the natural graphite powder with the modified Hummers method [23]. Highly conductive flexible carbon nanotube films (thickness of 20 μ m) were obtained from Suzhou Hengqiu Tech. Inc.

2.2. Electrode preparation

The aqueous deposition bath containing 0.01 M KMnO₄, 0.5 mg mL^{-1} GO, and 0.1 M LiClO₄ was dispersed adequately under ultrasonication prior to use. Electrodeposition was carried out with a three-electrode cell, in which CNFs $(1 \text{ cm} \times 1 \text{ cm} \text{ of conductive})$ areas) acted as the working electrode, a large area Pt foil served as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. As shown in Fig. 1, the GNS/MnO₂ hybrid was deposited rapidly on the CNFs substrate with applying a constant reduction potential of -1.2 V vs. SCE for 5 min. During this cathodically electrochemical codeposition, the GO nanosheets lost oxygen-containing functional group to become GNS, MnO₄⁻ was simultaneously reduced to MnO₂. For comparison, MnO₂ deposited CNFs electrodes were prepared with the same procedure above just without GO in the deposition bath. The loading mass of GNS/ MnO_2 hybrid and MnO_2 was 0.10 and 0.15 mg cm⁻², respectively, which was determined from the weight difference of substrate



Fig. 1. Schematic representation for the rapid electrochemical preparation of MnO_2/GNS hybrid electrode.

before and after deposition, using a MS105DU Mettler-Toledo microbalance with an accuracy of 10 $\mu g_{\text{-}}$

2.3. Characterization of composition and morphology

XRD patterns were recorded by a Rigaku Ultima IV X-ray diffractometer. The FT-IR spectra were obtained with a Bruker Tensor 27 FT-IR Spectrometer, the test samples were prepared by potassium bromide tableting. The morphology of electrode materials was observed with a field emission scan electron microscope (SEM, JSM-6701F, JEOL) and a high resolution transmission electron microscopy (TEM, JEM-2100, JEOL). For the FT-IR, XRD, and TEM characterizations, the samples were scraped from deposits coated Pt sheet for tests.

2.4. Electrochemical measurements

The electrochemical measurements of GNS/MnO_2 and MnO_2 electrodes including CV, GCD, and EIS were carried out using a CHI 660E electrochemical workstation (Chenhua, China) in 1.0 M Na₂SO₄ aqueous solution with three-electrode system, in which a saturated calomel electrode (SCE) served as reference electrode and a large area Pt foil as the counter electrode. The CV and GCD curves were tested between potentials of 0 to 0.8 V vs. SCE. EIS was recorded in the frequency range from 10⁵ to 0.1 Hz with 5 mV amplitude with respect to the open circuit potential.

3. Results and discussion

3.1. Composition and morphology

Fig. 2a shows the XRD patterns of GO and MnO_2/GNS hybrid. In the case of GO pattern, a sharp peak situating at 10.9° (002 plane of GO sheets) is observed, which is related with the enlarged interlayer spacing of GO nanosheets due to the introduced oxygencontaining groups [24]. The broad peak at 21.4° reveals that the GO sheets have some aggregations [25,26]. Nevertheless, for the pattern of MnO_2/GNS hybrid, the peak at 10.9° of GO disappears, while a broad diffraction peak appears at around 25° (002 plane of GNS), which can be ascribed to the decreased interlayer spacing owing to the reduction of GO sheets to GNS [8]. Furthermore, the hybrid displays the same diffraction peaks of MnO_2 presented in the pure MnO_2 pattern. The four diffraction peaks at 12.3°, 21.5°, 36.5°, and 66.0° can be indexed to the crystal planes of (001), (101), (111), and (020) in birnessite-type MnO_2 (JCPDS card No. 42-1317, δ -MnO₂) [27,28], respectively, These peaks are broad and weak,



Fig. 2. (a) XRD patterns of GO, MnO_2 , and MnO_2/GNS hybrid; (b) FT-IR spectra of GO and MnO_2/GNS hybrid.

suggesting that the crystallinity of electrodeposited MnO_2 in the hybrid is relatively poor.

FT-IR spectra are tested to further confirm the composition of the hybrid, which is shown in Fig. 2b. For the spectrum of GO, the peak at 1703 cm⁻¹ can be attributed to the C=O stretching of carbonyl, the peak located at 1235 cm⁻¹ is ascribed to the C-OH stretching vibration, and the adsorption peak at 1055 cm⁻¹ is the characteristic peak of C=O=C [24,29,30]. Another absorption peak located at 1628 cm⁻¹ originates from the stretching vibration of the adsorbed aromatic C=C [31]. In the case of the spectrum of MnO₂/GNS hybrid, since the GO is reduced to graphene, the peaks at 1703, 1235, and 1055 cm⁻¹ corresponding to oxygen-containing groups of GO almost disappear. Moreover, the peak at 1631 cm⁻¹ derived from C=C stretching vibration in GNS can be observed. The peak located at 530 cm⁻¹ originates from the Mn-O bond of MnO₂ [8,9]. The FT-IR spectra further reveal that MnO₂/GNS hybrid has been successfully synthesized.

The surface morphology is an important feature of electrode materials used for electrochemical devices, which directly influences their electrochemical performance. As shown in Fig. 3a, the morphologies of as-prepared MnO₂ and MnO₂/GNS



Fig. 3. (a) SEM images of MnO_2 and MnO_2/GNS hybrid; (b) TEM image of MnO_2/GNS hybrid.

hybrid are observed with SEM. We can see from the image of MnO_2 that the self-aggregation of MnO_2 nanoflakes occurs, consequently forming nanospheres with dimensions in the range of 0.4-1.0 μ m. Furthermore, the SEM image of MnO_2/GNS hybrid clearly displays that a large number of GNS are introduced into the hybrid. In particular, the self-aggregation of MnO_2 nanoflakes does not occur, and they are homogenously dispersed on the surfaces of GNS, which results in that the relatively smooth GNS surfaces become much rougher. Compared with the MnO_2 nanospheres caused by the self-aggregation, the dispersion of MnO_2 nanoflakes on the GNS with a large surface area is extremely beneficial to increase the contact area of MnO_2 with electrolyte. In addition, we can also see

that the introduction of GNS makes the hybrid less compact, and it displays a 3D porous nanostructure, which allows electrolyte easily penetrating to the inner of hybrid, consequently accelerating the interfacial reaction. The morphology of MnO₂/GNS hybrid is further characterized by TEM (Fig. 3b). Likewise, it can be observed that the dispersed MnO₂ is anchored on the surface of GNS, even if the hybrid suffered from long time ultrasonication during the sample preparation for TEM tests. This strong interaction enables fast electron transfer between GNS and MnO₂.

3.2. Electrochemical behaviors

The electrochemical performance of MnO₂ and MnO₂/GNS hybrid is initially evaluated by CV measurements with a threeelectrode configuration in 1.0 M Na₂SO₄ aqueous solution. As shown in Fig. 4a, a pair of symmetric Faradaic redox peaks at around 0.45 V vs. SCE, originating from the redox transitions of Mn between different oxidation states of Mn⁴⁺ and Mn³⁺: MnO₂ + H⁺ + $e^- \leftrightarrow MnOOH$ [16], are observed in both MnO_2 and MnO_2/GNS hybrid, indicative of their reversible pseudocapative behavior. Furthermore, besides 10 mV s⁻¹, it can be also seen from Fig. 4b that MnO₂/GNS hybrid electrode shows CV curves with larger area than those of MnO_2 electrode ranging from 50 to 200 mV s⁻¹. This indicates that the introduction of GNS significantly enhances the supercapacitive behavior of MnO₂. Moreover, compared to MnO₂ electrode, all of the characteristic CV shapes of MnO₂/GNS hybrid electrode almost do not change with the increase of scan rate, even the redox peaks can be observed up to the high scan rate of 200 mV s⁻¹, indicating its superior rate capability due to the fast redox reaction.

Fig. 4c exhibits the GCD curves of MnO_2 and MnO_2/GNS hybrid electrodes at the GCD current density of 5 A g⁻¹. The GCD curves of

the two types of electrodes are not straight lines, which are distinct from the curves of EDLCs with nearly linear plots, manifesting their pseudocapacaitive behavior, this agrees well with the results of CV tests. Additionally, it can be obviously seen that the MnO₂/GNS hybrid electrode displays longer discharge time and lower IR drops produced by the internal resistance of electrodes than those of MnO₂ electrode. It should be noted that low internal resistance is very importance for the devices of electrochemical energy storage. because less energy will be wasted to produce heat during the processes of charging/discharging [32]. The specific capacitance of electrodes can be calculated from GCD curves according to the following equation: $C_m = (I \times t)/(m \times \Delta V)$, where C_m is the specific capacitance of the electrode in Fg^{-1} , I the discharge current in A, t the discharge time in s, m the mass of electroactive materials in g, and ΔV the potential window in V. Fig. 4d shows that MnO₂/GNS hybrid delivers significantly higher specific capacitance compared with MnO₂ at various GCD current densities. Moreover, the specific capacitance of MnO₂/GNS hybrid shows smoother decline with the adding of current density, retaining 68.4% of initial capacitance when the current density increases from 1 Ag^{-1} to 20 Ag^{-1} , which is higher than 59.8% of MnO₂, demonstrating the MnO₂/GNS hybrid possesses better rate capability. Notably, the resulting MnO₂/GNS hybrid presents a high specific capacitance of 413.1 F g^{-1} at 1 A g^{-1} , which is larger than that of recently reported MnO₂/graphene hybrids prepared by different methods including electrochemical deposition (Table 1). Compared with the previous reports, better performance exhibited in this work could be due to the reason that the hybrid exists in the form of porous thin films attached directly on the highly conductive substrate of CNFs, and the hybrid shows a favourable microstructure that MnO₂ nanoflakes are homogenously dispersed on the surface of GNS. These features enable electrolyte easily penetrating to the inner of hybrid, consequently



Fig. 4. CV curves at the scan rates of $10 \text{ mV s}^{-1}(a)$, 50 to $200 \text{ mV s}^{-1}(b)$, GCD curves at the current density of $5 \text{ Ag}^{-1}(c)$, and the relationship of specific capacitance with GCD current density (d) of MnO₂ and MnO₂/GNS hybrid electrodes. Data shown in (d) are the mean \pm standard error of the mean (n = 3).

Table 1

Comparison of specific capacitance of the recently reported MnO₂/Graphene hybrids prepared by different methods including electrochemical deposition.

Preparation method	Test condition	$C_m/\mathrm{F}~\mathrm{g}^{-1}$	References
Spraying and heating method	$0.25 \mathrm{A}\mathrm{g}^{-1}$	267	[8]
Hydrothermal method	$5 {\rm mV} {\rm s}^{-1}$	218	[9]
Hydrothermal microwave irradiation and chemical vapor deposition	$1 \mathrm{A} \mathrm{g}^{-1}$	305	[13]
Polymer-assisted chemical reduction	$1 \mathrm{A} \mathrm{g}^{-1}$	325	[14]
Thermal reduction and electrochemical deposition	$10 {\rm mV} {\rm s}^{-1}$	125.93	[15]
Electrophoretic deposition and two-step electrochemical deposition	$1 \mathrm{A} \mathrm{g}^{-1}$	392	[16]
Two-step redox procedures	$10 {\rm mV} {\rm s}^{-1}$	327.5	[17]
Soft chemical route	$0.15 \mathrm{A}\mathrm{g}^{-1}$	216	[18]
Electrostatic co-precipitation	$1 \mathrm{A} \mathrm{g}^{-1}$	367	[19]
Electrostatic self-assembly	$0.2 \mathrm{\AAg^{-1}}$	319	[33]
Hard template method and hydrothermal process	$0.2 \mathrm{A}\mathrm{g}^{-1}$	266.3	[34]
Electrochemical deposition	$10 {\rm mV} {\rm s}^{-1}$	122	[35]
Thermal reduction and electrochemical deposition	$1 {\rm mV} {\rm s}^{-1}$	234.2	[36]
One-pot electrochemical codeposition	$1 \mathrm{A} \mathrm{g}^{-1}$	413.1	This work

the electroactive materials, especially for MnO₂, can be adequately utilized. Additionally, better synergistic effects of MnO₂ and GNS can be caused by this favourable microstructure.

EIS is conducted to study the characteristics of electrode/ electrolyte interface including the charge transfer and ion diffusion. Fig. 5 illustrates the Nyquist plots of MnO₂ and MnO₂/ GNS hybrid electrodes. Compared with the MnO₂ electrode, the straight line in low frequency region for the MnO₂/GNS electrode leans more towards the imaginary axis, indicating better capacitive behavior. The equivalent series resistance (ESR) can be determined from the intersection of the plot at the x-axis, which mainly derives from the solution resistance, the intrinsic resistance of electroactive materials, and the contact resistance at the interface of electroactive materials/current collector [37]. The inset of Fig. 5 exhibits that the intercept at x-axis for MnO₂/GNS hybrid electrode is smaller than that of MnO₂ electrodes, which suggests a smaller equivalent series resistance. EIS tests further indicate that the introduction of GNS improves electrochemical capacitive performance and reduce internal resistant of the MnO₂ electrode.

3.3. Cycle stability and Ragone plot

Cycle life is a critical performance required for the electrodes of supercapacitor in the practical use. Fig. 6a presents the cycle

stability of MnO_2 and MnO_2/GNS hybrid electrodes tested by 2500 CV cycles at the scan rate of 50 mV s⁻¹. We can see that the cycle test for MnO_2/GNS causes an increase in the capacitance up to 800 cycles. It is probably related to a cycle test induced improvement for the surface wetting of the electrode [38,39], which can be ascribed to more available electroactive surface area with the cycles caused by the introduced GNS with large surface area. Besides, the MnO_2/GNS hybrid electrode retains 91.2% of the initial capacitance after 2500 CV cycles, while the MnO_2 electrode only maintains 63.5%, manifesting the cycle life of MnO_2 electrode is significantly promoted after the introduction of GNS.

Ragone plots, depicting the relationship of specific energy density (E) and power density (P), are further employed to compare the supercapacitive performance of the MnO₂ and MnO₂/GNS hybrid. The E (Wh kg⁻¹) and P (W kg⁻¹) of electrodes can be calculated according to the GCD curves by the following equations, respectively: $E = (C_m \Delta V^2/2) \times 1000/3600$ and $P = 3600 \times E/t$ [40], where C_m is the specific capacitance in F g⁻¹, ΔV the potential window subtracting IR drop in V, and t the discharge time in s, 1000 and 3600 were used for the unit conversion between g and kg, and s and h, respectively. It can be seen clearly from Fig. 6b that the MnO₂/GNS hybrid electrode presents obviously higher energy and power densities than those of the MnO₂ electrode, and about 1.6 times increase of energy density is obtained for the MnO₂/GNS hybrid than that of MnO₂. In addition, the MnO₂/GNS hybrid exhibits higher retention rate of energy density with the increase



Fig. 5. Nyquist plots of MnO_2 and MnO_2/GNS hybrid electrodes, inset is the EIS in high-frequency region.



Fig. 6. Relationship of capacitance retention rate and cycle number (a) and Ragone plots (b) of MnO₂ and MnO₂/GNS hybrid electrodes.

of power density. Herein, the MnO_2/GNS hybrid achieves the maximum energy density of 36.7 Wh kg^{-1} and the highest power density of 7.7 kW kg^{-1} , which are also higher than previously reported MnO_2 /graphene hybrids prepared by other methods [9,16,33]. It should be pointed out that the energy density and power density of the hybrid reported herein are obtained by three-electrode system, they maybe have difference with the actual performance for supercapacitor electrode in practice use. In short, the remarkably enhanced supercapacitive performance for the MnO_2/GNS hybrid can be attributed to the following three aspects: (i) The dispersion of MnO_2 on the GNS with a large surface increases the contact area of MnO_2 with electrolyte; (ii) GNS make up the disadvantage of low conductivity of MnO_2 and make the hybrid less compact; (iii) The better synergistic effects derived from the formed hybrid microstructure of MnO_2 decorated GNS.

4. Conclusions

In summary, we have put forward a rapid preparation method of MnO_2/GNS hybrid by one-pot electrochemical codeposition. The introduction of GNS obviously improves the dispersion of MnO_2 , and significantly boosts the capacitive behaviors and cycle stability of MnO_2 , in particular, the MnO_2/GNS hybrid shows a high specific capacitance of 413.1 F g⁻¹ at 1 A g⁻¹, which is larger than that of the recently reported $MnO_2/graphene$ hybrids prepared by differnt methods including electrochemical deposition. The hybrid we have prepared further extends the application of graphene, and is very promising for use in the low-cost, high-efficiency electrochemical capacitors. Also this facile rapid preparation approach we have developed can be further extended to GNS-based hybrids with other metal oxide.

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