Facile Synthesis of MnO₂ Nanoparticles Well-dispersed on Graphene for the Enhanced Electrochemical Performance

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Graphene/MnO₂ (GN/MnO₂) composites have been facile synthesized via a liquid phase route. The results of the morphology reveal that MnO₂ nanoparticles about 20 nm are well-dispersed on the surface of the graphene nanosheets. The stable structure, through promoting the interfacial electron and lithium ion transport, improve the electrochemical performance of GN/MnO₂ with increasing 80% of the special capacity. The graphene in the composite accommodate volume change and increase electrical conductivity. Meanwhile the MnO₂ nanoparticles prevent the stacking of the graphene sheets, maintaining the stability of the GN/MnO₂ composites. So the stable characteristic structure by facile liquid phase route can be employed for other metal oxide composites of electrode or photocatalysis materials.

Keywords: graphene, MnO₂, lithium ion batteries

1. INTRODUCTION

The efficient energy storage and conversion technologies are necessary for extensive use of renewable energy. Some application such as portable electric vehicles and hybrid electric vehicle can meet the need of our information rich, mobile society. So the lithium ion batteries (LIBs), the noted electrochemical systems for energy storage and conversion, are pursued by many peoples [1-2]. But the commercially used graphite, based on the formation of LiC₆, owns the theoretical capacity of 372 mA h g⁻¹ [3]. It is too low to hamper its wide usage for LIBs in the surging consumer electronic devices, which can not satisfied for the market of renewable power applications. So it is imperative to explore new electrode materials and novel designs for higher energy density, lower cost, flexibility, non-toxicity, and better stability [4].
One approach of increasing lithium storage capacity is to use high theoretical capacities anode materials. Some oxidates, SnO$_2$, FeO, Co$_3$O$_4$ and NiO have been widely researched due to their higher theoretical capacities (>600 mA h g$^{-1}$) compared with the commercial graphite anode material (372 mA h g$^{-1}$). In particular, MnO$_2$ are stable, nontoxic and environmentally benign, and have a high specific capacity (>1230 mA h g$^{-1}$). Much effort is thus devoted to synthesize and control the structure of MnO$_2$-based materials [5-7]. However, the performance of MnO$_2$-based anodes remains inferior due to two main issues: (i) the pristine MnO$_2$ has a low electrical conductivity ($10^{-5}$–$10^{-6}$ S/cm) which limits the electron transport; (ii) a large volume change of MnO$_2$ occurs during the lithiation and delithiation processes, which leads to severe electrode crush, serious safety concerns and rapid loss of discharge capacity during the cycling [7,8].

The orthohexagonal structure of graphene, made of sp$^2$ bonded carbon atoms, have attracted a lot of researchers. Graphene has been extensively used in physics, chemistry and materials science because of its good conductivity, well flexibility and special machanical property [9]. Yoo et al. investigated the graphene nanosheets (GNS) as the electrode materials for LIBs and the enhanced lithium storage capacity in 2008 [10]. The charge capacity of GNS was 540 mAh g$^{-1}$ at beginning, and the capacity increased up to 730 mA h g$^{-1}$ and 784 mA h g$^{-1}$. The author explained the results attributing to graphene’s unique structural of high surface area, better electric, chemical stability and thermal conductivity. Because of this, graphene has been used as perfect frameworks for graphenen-based composites as potential electrode materials [11]. Furthermore, Cui and co-workers has reported the study for Fe$_3$O$_4$ nano-particles attached onto the reduced graphene oxide sheets via a two-step hydrothermal method. The composite of Fe$_3$O$_4$/reduced graphene oxide has a improved rate capability compared with the bare Fe$_3$O$_4$ nanoparticles as the anode materials for LIBs [12].

In this work, the hybrid nanostructure graphene/MnO$_2$ (GN/MnO$_2$) is fabricated using a simple and environmentally-benign liquid method. The structure and morphology of prepared MnO$_2$ and GN/MnO$_2$ composite are observed, and their electrochemistry phenomenon are analyzed. We demonstrate that stable GN/MnO$_2$ composite exhibit enhanced electrochemical capability, comparing with the pure MnO$_2$. The GN/MnO$_2$ composite can be used a promising alternative anode material for lithium ion batteries.

### 2. EXPERIMENTAL & METHODS

#### 2.1 Sample preparation

All chemicals were of analytical grade and were used without further purification unless otherwise specified. The synthesis process showed in Fig.1. First, GN were got by chemical reduction of the graphene oxide (GO) by hydrazine hydrate. GO nanosheets were prepared from nature graphite powders by using a modified Hummers method reported previously [13]. Then, graphene/MnO$_2$ composites were prepared with in situ MnO$_2$ deposition on the surface of graphene via a simple one-step liquid method. 50 mg GN and 0.22 g Mn(Ac)$_2$ were dissolved in 100 ml distilled water under the condition of constantly stirring. The 26 mg KMnO$_4$ (dissolved in 10 ml distilled water) was slowly
added into the above solution, then continuously stirred for 2 h. The precipitate was obtained and washed for 5 times, last dried at 60 °C under vacuum for 6 h. In this way, the MnO2/graphene composites powders were synthesized. The MnO2 without GN were prepared with above method for comparison.

![Figure 1. Schematic of the Formation of GN/MnO2 Composites.](image)

2.2 Material characterization

X-ray diffraction (XRD) patterns were obtained by a Bruker D-8 advanced X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm) in the range of 10° ≤ 2θ ≤ 70°. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images were received, through a SEM (Quanta 200F) with an acceleration voltage of 3 kV and a TEM (JEM-2010FEF) with an acceleration voltage of 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) tests were carried out on a PHI 5700 XPS/ESCA system with a monochromatic Al Kα (1486.6 eV).

2.3 Preparation of lithium-ion batteries

Electrochemical performances of graphene, MnO2 nanoparticles and GN/MnO2 composites were investigated with coin-type cells (CR2025). The working electrodes were prepared by a slurry (80 wt% active material, 10 wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP), and 10 wt% carbon black) coating procedure. Test cells were assembled in an argon-filled glove box with the metallic lithium foil as the reference and counter electrodes. The electrolyte was 1.0 mol dm⁻³ LiPF6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The galvanostatically charged and discharged were measured in the range of 0.01–3.0V (vs. Li/Li⁺) at room temperature using a NEWWARE battery test system. AC impedance measurement was carried out using a CHI604C (Shanghai Huachen Electronics Ltd.) electrochemical working station in the 100 KHz to 10mHz frequency range.

3. RESULTS AND DISCUSSION

XRD patterns of graphene and graphene/MnO2 are shown in Fig.2. In the pattern, all the peaks of GN/MnO2 hybrid and MnO2 are distinguishable. The diffraction angles at 12.84°, 18.28°, 28.84°, 37.66°, 41.88°, 49.78°, 56.18°, 60.34°, 65.72° and 69.34°, can be assigned to (110), (200), (310), (211),
The images of Fig. 3(a) further illustrates the present of MnO$_2$ on the graphene surfaces. X-ray photoelectron spectroscopy (XPS) spectra of C1s, O1s and Mn2p orbitals of the GN/MnO$_2$ hybrid are shown in Fig. 3. The Mn2p spectrum of GN/MnO$_2$ composite is presented in Fig. 3(b), where the peaks of Mn2p$_{3/2}$ (642.1 eV) and Mn2p$_{1/2}$ (653.7 eV) are observed. They have a spin energy separation of 11.6 eV in good accordance with the reported datum on MnO$_2$[16], which ensures the presence of MnO$_2$ in the composite. Fig. 3(c) shows the pure spectra of C1s, which can be suited as two peaks at binding energies of 284.6 and 288.4 eV, meaning two different chemical valencies of carbon existing in the sample. The peaks at 284.6 eV can be assigned to contributions of C-C (sp$^2$) bonds [17]. While the peak at 288.4 eV comes from the existence of C-OOH bonds [18]. It can be attribute that GN is the reduction product of graphene oxide. Fig. 3(d) shows the high resolution spectra of O1s. In the case of GN/MnO$_2$ hybrid, the curve fitting of O1s peak basically indicates two components centered at 529.6 and 531.3 eV. The O1s peak at 529.6 eV is assigned to the oxygen bonded with manganese (Mn-O) in MnO$_2$ crystal lattice [19]. The another peak is obviously ascribed to the surface hydroxide radical of carbon phase [20].
Figure 3. XPS spectra measured at the surface of GN/MnO$_2$ composites.

The morphology images of MnO$_2$, GN/MnO$_2$ composites and GN are shown in Fig. 4. Pure MnO$_2$ was prepared by liquid phase method at room temperature. From Fig. 4(a), the diameters of the MnO$_2$ nanoparticles range about 100 nm, and the morphologies of MnO$_2$ are in good agreement with reported data [21]. The particle of MnO$_2$ has the reunited phenomenon, while the particle on the surface of graphene (Fig. 4(b)) is homogeneous. Fig. 4(c) is the image of the graphene after chemical reduction, and the graphene exhibit the morphology similar to thin silk. It has a large flat surface which could avail for anchoring the MnO$_2$. And it can work as the buffer limiting the volume change when the electrochemistry reactions occur.

Figure 4. SEM images of MnO$_2$ (a), GN/MnO$_2$ composite (b) and TEM images of GN (c).

The TEM and HRTEM images of the GN/MnO$_2$ composites are shown in Fig. 5. It is clear that many MnO$_2$ nanoparticles about 20 nm anchored on the surface of graphene and the MnO$_2$ particles disperse homogeneously (Fig. 5(a)). The structure of well-dispersed nanoparticles on the graphene will provide large surface area.
Meanwhile, the stable three-dimensional structure is constructed by particle MnO2 and graphene sheets which would restrict the stacking and accumulating of graphene and keep the strong structure. So the well-distributed particles can provide clear and coherent path of Li\textsuperscript{+} transportation and more exposed surface which would promote the Li\textsuperscript{+} diffusion. The HRTEM image of Fig. 5(b) reveals the crystal feature of MnO2 nanoparticle and clear lattice fringes of well-crystallized MnO2. The distances between the two fringes are 0.31 nm, 0.49nm, 0.16nm, 0.24nm respectively, corresponding to the (310), (200), (600), (211) lattice planes [22]. All these images could present the uniformity structure of the composite which is reasonable for the enhanced capacity.

Figure 5. TEM and HRTEM images of GN/MnO2.

Figure 6. the first Galvanostatic Discharge/charge Curves for MnO2 (a) and GN/MnO2 composite (b); Capacity vs. cycle number at 100mA/g for MnO2 and GN/MnO2 composite; (c) discharge capacity; (d) charge capacity.
To confirm the improving effect of the GN/MnO$_2$ for the electrochemical performance, the charge and discharge voltage profiles of the MnO$_2$ and GN/MnO$_2$ were got by using half-cell test as anode materials. The rate capability was tested using the same method. Fig. 6(a) and (b) is the charge/discharge curves of MnO$_2$ and GN/MnO$_2$ nanocomposites in the 1st cycles, respectively. The discharge curves of MnO$_2$ and GN/MnO$_2$ have the same plateau at the voltage of 0.7 V. This can be explained that the solid electrolyte interface (SEI) layer is formed and the electrolyte is decomposed on the electrode surface [23]. The platform at 0.5 V can be surveyed in the following discharge processes by GN/MnO$_2$ and MnO$_2$. It shows that the initial discharge/charge capacity of GN/MnO$_2$ at the rate of 100 mA g$^{-1}$ is 462.22 and 282.25 mA h g$^{-1}$, respectively. That of MnO$_2$ is 256.53 and 186.03 mA h g$^{-1}$, respectively. The capacity of GN/MnO$_2$ composite is higher than that of MnO$_2$, enhanced 205.69 mA h g$^{-1}$. Fig. 6(c) and (d) show the cyclability of MnO$_2$ and GN/MnO$_2$ composites. From Fig. 6(c), it can be seen that the discharge capacity after 30 cycles of GN/MnO$_2$ composites maintain 262.29 mA h g$^{-1}$, but the capacity of MnO$_2$ is 156.45 mA h g$^{-1}$. As shown in Fig. 6(d), the charge capacity after 30 cycles of GN/MnO$_2$ is 224.50 mA h g$^{-1}$ which is nearly double times compared with capacity of MnO$_2$. Such a enhanced performance can be ascribed to the following points. One is the uniform size of nanoparticles and MnO$_2$ nanoparticles well-distributed on the graphene, which may reduce the heaped up of graphene sheets and provide the high surface area. This stable structure could come into being stable route for Li$^+$ transmission in charge/discharge process. Another is graphene that has the high electrical conductivity which facilitates electrons transporting from graphene to MnO$_2$ nanostructures. And the excellent flexibility of graphene would limit and remit the volume change of enlarging or shrinking at the process of lithium embedded in and out [24].

Fig.7 depicts the Nyquist plots of MnO$_2$ nanoparticles and GN/MnO$_2$ composites. The semicircle in the middle frequency range indicates the charge and discharge transfer resistance [25]. It can be clearly seen that the charge and discharge transfer resistance of GN/MnO$_2$ electrode is smaller than MnO$_2$. This explains the enhanced performances of composite material at lithium ion diffusion and the electronic transmitting thus enhancing the lithium storage capacity. More importantly, the uniform size and well-distributed MnO$_2$ nanoparticles may relieve the stacking of graphene sheets and keep the high surface area. Consequently, the lithium storage capacity and the cycling performance of GN/MnO$_2$ composite can be enhanced.

Figure 7. Electrochemical impedance results of MnO$_2$ and GN/MnO$_2$ electrodes.
4. CONCLUSION

In summary, the GN/MnO$_2$ composite is prepared as an anode for lithium ion battery via a liquid phase route. The homogenous MnO$_2$ nanoparticles about 20 nm anchored on the surface of graphene. The composite has high specific capacity of 462.22 mA h g$^{-1}$ at 100 mA g$^{-1}$. And after 30 cycles, the capacity of GN/MnO$_2$ is nearly double times compared with the capacity of MnO$_2$. The enhanced electrochemical performance is due to the integration of graphene and MnO$_2$. They formed the stable hybrid structure of homogeneous MnO$_2$ nanopaticles well-dispersed on the graphene surface, the structure not only increases the contact area facilitating electrochemistry reaction between Li$^+$ and the electrode but also reduces the resistance in charge and discharge process. Another, the graphene acts as the conductive link for electron transport, the MnO$_2$ nanostructures support graphene laryer from stacking. The suitable structures of the prepared composite enhance the diffusion of electrons and the transfer of lithium ions. At last, the electrochemical performances of the GN/MnO$_2$ are improved. The prepared method can be extended for other metal oxide, and the stable structure constructed by graphene will be a alternative for the composites.

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