Research Article

Low Temperature Synthesis of MnO_2 /Graphene Nanocomposites for Supercapacitors

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MnO_2 /graphene nanocomposites were synthesized through a simple route in a water-reflux condenser system. The as-prepared composites were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Raman microscope, and Brunauer-Emmett-Teller surface area analysis. Capacitive properties of the synthesized composite electrodes were investigated via cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectrometry in a 0.5 M Na_2SO_4 electrolyte. Results show that this method can control the morphology and structure of MnO_2 loaded onto the graphene sheets. Because excessive MnO_2 enwrapping graphene would affect the overall conductivity, the composite prepared by lower temperature has better characteristics of supercapacitor. 60- MnO_2 /graphene composite (48 wt% MnO_2) displays the specific capacitance as high as 350 F/g at 1000 mA/g, which is higher than that of 100- MnO_2 /graphene (302 F/g), and it is almost two times higher than that of MnO_2 (163 F/g). Furthermore, the composite exhibits excellent long cycle life along with ~93% specific capacitance retained after 5000 cycle tests.

1. Introduction

Supercapacitors are excellent electrical energy storage devices, exhibiting high power density, excellent reversibility, and cycle ability [1]. Amongst all the materials, carbon and metal oxide materials have been conceived as promising electrode materials for electrochemical supercapacitors (ESCs), in which energy is stored due to the formation of an electrical double layer at the interface of the electrode or due to electron transfer between the electrolyte and the electrode through fast faradic redox reaction [2].

Graphene, which was synthesized by Novoselov and Geim in 2004, is conceived as electrochemical capacitors because of its excellent electrochemical performance [3]. As a new carbonaceous material, graphene possesses evident advantages for the applications in ESCs because of its large theoretic specific surface area and efficient electron transfer channels. As a rising star in carbon family,

graphene has attracted a great deal of attention in recent years. Peng et al. [4] had synthesized a high-performance in-plane supercapacitor based on hybrid nanostructures of quasi-2D ultrathin MnO_2 /graphene nanosheets, exhibiting high specific capacitances of 267 F/g at current density of 0.2 A/g and 208 F/g at 10 A/g and excellent rate capability and cycling stability with capacitance retention of 92% after 7000 charge/discharge cycles. Chen et al. [5] had prepared graphene and nanoacicular MnO_2 composite material by chemical coprecipitation method with adding KMnO_4 to MnCl_2 solution dispersed with graphene, in which the mass fraction of MnO_2 was about 90% ($\text{MnO}_2 : \text{G} = 9.8 : 1$), and the sample capacitance in 1 M Na_2SO_4 solution for 198 F/g. Li et al. [6] had loaded MnO_2 onto graphite oxide (GO) surface by citrate reduction potassium permanganate; then the paper G/MnO_2 complexes were formed under high temperature reduction in argon atmosphere. And its capacitance value was 256 F/g in 0.1 M Na_2SO_4 solution. Cheng et al. [7]

FIGURE 1: Synthesis schematic of amorphous MnO_2 /graphene nanocomposites.

had prepared MnO_2 /graphene composite by electrostatic self-assembly process. The negatively charged colloidal graphene nanosheets and positively charged MnO_2 were uniformly mixed; then MnO_2 was assembled on the graphene nanosheets via electrostatic attraction. Graphene materials with different oxide being supported were researched by Rakhi et al. [8], where MnO_2 /graphene capacity was 245 F/g. Wang et al. [9] had prepared the composites of integrated 1D MnO_2 nanowires and 2D graphene sheets at nanoscale under the mild condition of 100°C . Wu et al. [10] had prepared MnO_2 /graphene composites and graphene asymmetric capacitor.

In the process of preparing electrodes, the methods of depositing activated materials on collectors are the most crucial element to affect the performance of supercapacitors [11]. Electrophoretic deposition (EPD) is the most economical and versatile method for depositing and coatings, which enables the formation of high purity deposits of uniform thickness on substrates with complex shape [12].

In this paper, we reported a facile method to prepare MnO_2 /graphene composites as novel electrode materials by a water-reflux condenser system under different temperatures and fabricating electrodes by using electrophoretic deposition. The preparation schematic illustration of hybrid material was shown in Figure 1. For this composite, graphene served mainly as a highly conductive support, which could also provide a large surface for the deposition of nanoscale MnO_2 . The capacitive behaviors of the MnO_2 /graphene nanocomposites under different temperatures were investigated and compared with that of the MnO_2 electrode in $0.5\text{ M Na}_2\text{SO}_4$ electrolyte solution. The electrochemical tests showed that 60- MnO_2 /graphene composite performed a better capacitive behavior as compared with pure MnO_2 and 100- MnO_2 /graphene electrodes.

2. Experiments

2.1. Synthesis of MnO_2 /Graphene Composites. In this paper, thin layer graphene materials were synthesized from graphite flake ($20 \times 50 \times 1\text{ mm}$) as an electrode and source of graphene using a modified electrochemical exfoliation [13]. More details of the synthesis on graphene had been reported elsewhere [14]. MnO_2 was prepared by redox reaction between acetylene black and KMnO_4 under a traditional chemical precipitation method. With graphene as carrier, the MnO_2 particles showed nucleation and growth. In the first step, 100 mL of graphene water suspension (2.5 mg/mL) was subjected to ultrasonic vibration for 1 h. Then KMnO_4 powder (0.5 g) and acetylene black (0.03 g) were added into above graphene suspension. Subsequently, the aqueous suspension was reflux-condensed in a thermostatic water bath by constant magnetic stirring at the temperature of 60°C and 100°C for 8 h, respectively. Finally, the black deposit was filtered, washed several times with distilled water and alcohol, and dried at 70°C for 12 h in a vacuum oven. The sample collected after drying is designated as X- MnO_2 /graphene, where X denoted the synthesis temperature. For comparison, the pure MnO_2 was prepared at 60°C under the same condition.

2.2. Characterization Methods. The resulting mass percentages of MnO_2 in the composites were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500). Furthermore, in order to examine the mass percentage of MnO_2 in the MnO_2 /graphene composites, thermogravimetry- (TG-) differential scanning calorimetry (DSC) experiments (STA 449C, NETZSCH, SELB, Germany) were carried out. The crystallographic structures of the materials were determined by X-ray diffraction (XRD, D/max-2500/pc) with $\text{Cu K}\alpha$ radiation $\lambda = 1.5405\text{ \AA}$. Raman spectra were recorded on a microscopic confocal Raman spectrometer (Labram HR 800) with an excitation of 514 nm laser light. The Brunauer-Emmett-Teller (BET) specific surface areas were evaluated based on nitrogen adsorption isotherms at -196°C on a NOVE 4000e analyzer. The microstructure of the samples was investigated by a field-emission scanning electron microscopy (FESEM, S-4800) and a transition electron microscopy (TEM, JEOL JEM2010).

2.3. Preparation of Electrodes and Electrochemical Measurement. The fabrication of working electrodes is shown in Figure 2.

The aqueous suspension of composites with a concentration of 1.0 g/L was used for the electrophoretic deposition [15]. The nickel foam substrates ($1 \times 1\text{ cm}$) were cleaned by ultrasonic treatment in ethanol for 30 min and drying under vacuum at room temperature. Two parallel nickel foams were used as electrodes at a distance of 1 cm. EPD was conducted at a constant voltage of 10 V for a deposition time of 10 min. After deposition, the samples were dried under vacuum at room temperature. The loading mass of each electrode was about 2 mg.

The electrochemical measurements were performed in a three-electrode system with a platinum foil electrode and

FIGURE 2: The fabrication procedure of MnO_2 /graphene electrode.

a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. The Ni foam was coated with composites (1×1 cm) as the working electrode. The measurements were carried out in a 0.5 M Na_2SO_4 aqueous electrolyte at room temperature. Galvanostatic charge/discharge curves were measured in the potential range of $-0.2 \sim 1.0$ V at current density of 1000 mA/g. Cyclic voltammograms tests were carried out at potentials between -0.2 and 1.0 V at scan rates of 50 mV/s. Electrochemical impedance spectroscopy was carried out without DC bias sinusoidal signal of 5 mV over the frequency range from 10 kHz to 0.1 Hz.

3. Results and Discussion

3.1. Microstructure Characterizations. The self-limiting deposition of nanoscale MnO_2 on the surface of graphene is used here by redox reaction between acetylene black and KMnO_4 under a water-reflux condenser system. The reaction is featured by electron transfer from the acetylene black to the oxidant upon direct contact, and the redox reaction between acetylene black and KMnO_4 in a pH neutral solution is shown in Figure 2. As carbon materials, graphene is the crystalline state, and acetylene black is amorphous. Therefore, graphene needs to overcome the higher barrier and requires more energy than acetylene black during the oxidation reaction. Because of the low temperature experiment, in this reaction, the acetylene black serves as a sacrificial reductant and converts aqueous permanganate (MnO_4^-) to insoluble MnO_2 , which deposits on the surfaces of graphene.

A relatively easier method was adopted to estimate the mass percentage of MnO_2 in the MnO_2 /graphene. Figure 3 shows TG and DSC curves of graphene and 60- MnO_2 /graphene. At about 584°C , the graphene sample burned up with a residual mass of 5%, which were some residue impurities. The DSC curve of MnO_2 /graphene showed a reduction in sample weight below 332°C , and the corresponding dehydration of the composite was 20%; then the following weight loss was due to the oxidation of graphene. It can be seen from the TG curve of 60- MnO_2 /graphene that, at the temperature up to 700°C , the residual mass was about 53%. Therefore, the mass percentage of MnO_2 in the MnO_2 /graphene was

estimated to be 48%. The mass percentage of MnO_2 in the 60- MnO_2 /graphene was also determined by using ICP-AES and it correlates well to the TG/DSC experiments.

XRD patterns confirm MnO_2 /graphene with mixed crystalline and amorphous parts (Figure 4). Three broad peaks at 2θ around 37.2° , 56.1° , and 66.3° can be indexed to γ -type MnO_2 (JCPDS 18-0802) [16]. Broad peaks were related to a poorly crystallized compound originating from the small grain size and approximately amorphous state of the powder. The peak at 2θ around 56.1° corresponding to the (301) crystal plane of MnO_2 cannot be observed after graphene was introduced, indicating that the stacking of the graphene sheets was disorderly. Compared with the MnO_2 and graphene, the diffraction peaks of MnO_2 /graphene had been changed. It is no longer pure MnO_2 phases; the contours of the peaks are substantially the same. At the corresponding diffraction angles, there are the peaks of both graphene and MnO_2 . Therefore, it can be concluded that the presence of graphene cannot change the crystal structure of MnO_2 . The above analysis shows that the MnO_2 /graphene nanocomposites are composite materials with two-phase structure and MnO_2 as the main crystalline phase. With graphene as a carrier, the MnO_2 particles showed nucleation and growth.

Raman spectra are performed to indicate the structures of carbon materials by the resulting characteristic G and D bands sensitive to disorder and defects [17]. Figure 5 displays the Raman spectra of graphite, graphene, and 60- MnO_2 /graphene. The existence of G band at 1582 cm^{-1} and D band at 1351 cm^{-1} in the spectrum of graphite indicates the ordered sp^2 structure. It is observed that I_D/I_G increases in the Raman spectroscopy of graphene and 60- MnO_2 /graphene, indicating that more disordered carbon or defects are introduced from the reaction of carbon with MnO_4^- [18]. It can be seen that the typical Raman spectrum of MnO_2 sample appears in the vicinity of 601 cm^{-1} and the peak is caused by the symmetric stretching vibration of Mn-O bond.

The typical FESEM image of graphene is shown in Figure 6(a). It can be seen that the graphene sheets have wrinkles and folds with a thin layer. After the redox reaction

FIGURE 3: TG (a) and DSC (b) curves of graphene and 60-MnO₂/graphene.

FIGURE 4: XRD patterns of graphene, MnO₂, and 60-MnO₂/graphene.

between acetylene black and KMnO₄ through a water-reflux condenser system (Figure 1), as can be seen from Figures 6(b)~6(d), the graphene sheets were decorated homogeneously with microcrystalline shape MnO₂. Because the microcrystalline MnO₂ can self-assemble into mesh structure, the surface atoms are disordered and are with more atomic space, which make the proton diffusion coefficient larger. This prepared porous network such as MnO₂ is an effective means to improve the utilization of active material.

Compared with Figure 6(b), it can be seen from Figure 6(c) that the reaction temperature of 100°C makes the network structure become compact. Therefore the corresponding specific surface area decreases. The subsequent

FIGURE 5: Raman spectra of graphite, graphene, and 60-MnO₂/graphene.

electrochemical experiment shows that the composite prepared by 60°C has better supercapacitor. The highly porous structure can shorten the diffusion path for charge-carrier ions, while the large liquid-solid interface facilitates ion exchange between the electrode and electrolyte. Furthermore, excessive MnO₂ on graphene wrapped will affect its overall conductivity. Figure 6(e) shows the HRTEM images of 60-MnO₂/graphene. The MnO₂ exhibits the same interlayer spacing, 0.72 nm, corresponding to (002) crystal planes,

FIGURE 6: SEM images of graphene (a), 60-MnO₂/graphene (b), and 100-MnO₂/graphene (c); TEM (d) and HRTEM (e) images of 60-MnO₂/graphene.

indicating there was no change in the lattice structure of MnO₂ after graphene was introduced.

Figure 7 displays the nitrogen adsorption-desorption isotherms and pore size distribution curves calculated by BJH method. In the low relative pressure ($P/P_0 < 0.4$), the adsorption and desorption curves coincide because there are monolayer adsorption and reversible process. At the higher relative pressure region (P/P_0 0.4~0.75) and high relative pressure (P/P_0 0.8~1.0), all isotherms have significant hysteresis, indicating their mesoporous characteristics [19]. It can be seen from Figure 7(a) that 60-MnO₂/graphene has relatively cliffy hysteresis loop at high P/P_0 , suggesting the presence of certain micropores in the 60-MnO₂/graphene sample. The specific surface area for each sample was obtained by BET method and the values for MnO₂, 60-MnO₂/graphene, and 100-MnO₂/graphene were 223.1, 327.8, and 296.9 m²/g, respectively. BJH analysis for mesopore distribution is shown in Figure 7(b); the pore volumes for 60-MnO₂/graphene and 100-MnO₂/graphene are, respectively, 0.45 and 0.31 mL/g. It can be seen from Figure 7(b) that the pore size distribution of 60-MnO₂/graphene is wider than 100-MnO₂/graphene. The pore size of the 100-MnO₂/graphene sample is mainly centered around 5 nm and the 60-MnO₂/graphene is in range of the 3~6 nm. It is well known that the pore sizes in the range of 3~6 nm contribute to improving the capacitance [20]. The pore structure of network such as MnO₂ is the main channel of electrolyte penetration; the existence of rich mesoporous are good for the full contact between materials surface and electrolyte surface and improve the utilization rate of materials.

3.2. Electrochemical Behavior. The CV curves of MnO₂, 60-MnO₂/graphene, and 100-MnO₂/graphene composites at a 50 mV/s scan rate in 0.5 M Na₂SO₄ aqueous solution are shown in Figure 8(a). It is clear that all of the CV curves are almost ideally rectangular, exhibiting the typical electrochemical double-layer capacitive behavior with a very rapid current response on voltage reversal at each end potential and high reversibility [18]. Obviously, 60-MnO₂/graphene and 100-MnO₂/graphene show higher integrated area than MnO₂ electrode, which indicates the excellent electrochemical performance. The specific capacitance enhancement for the mesoporous MnO₂/graphene composite electrodes may be attributed to two reasons: MnO₂ particles coating on the surfaces of graphene can greatly reduce the diffusion length of Na⁺ and improve the diffusion rate of Na⁺ during the charge/discharge process, improving the electrochemical utilization of MnO₂. In addition, graphene in the composites not only acts as the support for the deposition of MnO₂ particles but also provides the high electrical conductivity of the overall electrode due to the excellent conductivity of graphene. The lack of symmetry in MnO₂/graphene is probably due to combined double-layer and pseudocapacitive contribution to the total capacitance.

The cycling stability of MnO₂, 60-MnO₂/graphene, and 100-MnO₂/graphene electrodes was also evaluated by CV test at a 50 mV/s scan rate for 5000 cycles. As shown in Figure 8(b), the 60-MnO₂/graphene electrode retained about 93.1% of initial capacitance after 5000 cycles, while that of the MnO₂ retained only about 80%, demonstrating excellent electrochemical stability of such electrode material. The different electrochemical stability between MnO₂/graphene and MnO₂ may be due to the discrepant double-layer and

FIGURE 7: N₂ adsorption-desorption isotherms (a). Pore size distributions calculated by BJH (b).

pseudo capacitance contributions. As is well known, the double-layer process only involves a charge rearrangement, while pseudocapacitive is related to a chemical reaction, and the double-layer capacitors have a better electrochemical stability. Accordingly, as-synthesized MnO₂/graphene makes more double-layer contribution compared to that of MnO₂ owing to the presence of graphene.

To get more information about the potential of as-synthesized MnO₂/graphene nanocomposites as electrode materials for supercapacitors, galvanostatic charge/discharge measurements were carried out. As illustrated in Figure 8(c), during the charging and discharging steps, the charge curves are almost symmetric to their corresponding discharge counterpart with a slight curvature, indicating the pseudocapacitive contribution along with the double-layer contribution. The specific capacitances (C_s) are calculated according to $C_s = I \times \Delta t / (m \times \Delta V)$ from the discharge curves, where I is the constant discharge current, Δt is the discharge time, and ΔV is the potential drop during discharge, and m (g) is the mass of active electrode material. The C_s values of MnO₂, 60-MnO₂/graphene, and 100-MnO₂/graphene electrodes are 163, 350, and 302 F/g, respectively.

EIS measurements were generally applied to evaluate the electrochemical properties of the as-prepared electrode samples. Typical Nyquist plots of EIS for these electrodes are displayed in Figure 8(d). All the impedance plots are composed of a semicircle in the high frequency range and a straight line in the low frequency range. The measured impedance spectra were analyzed on the basis of the equivalent circuit, which is

given in the inset of Figure 8(d). At very high frequencies, the intercept at real part (Z') is a combinational resistance of ionic resistance of electrolyte, intrinsic resistance of substrate, and contact resistance at the active material/current collector interface. It can be seen from Figure 8(d) that a major difference is the semicircle, which corresponds to the charge transfer resistance (R_{ct}) caused by the Faradaic reactions and the double-layer capacitance on the grain surface. Comparing the impedance plots of these electrodes, it is apparent that the values of R_{ct} gradually decrease with introducing graphene and lower synthesis temperature. The slope of the curve is called the Warburg resistance, which is a result of the frequency dependence of ion diffusion or transport in the electrolyte to the electrode surface. So, the increased slope for MnO₂/graphene electrodes is attributed to the increased diffusion and migration pathways of electrolyte ions during the charge/discharge processes.

Compared with 100-MnO₂/graphene, the electrochemical performances of 60-MnO₂/graphene nanocomposite are greatly improved because of the following reasons. The graphene in composite also can provide additional sites for (C^+) storage, which leads to an enhanced reversible capacity for the electrode. When the synthetic temperature is higher, the graphene surface was covered by excessive MnO₂, which reduced the charge conduction properties of the graphene, no longer shaped a continuous conducting network, and increased the diffusion resistance of electrolyte ions in the composite electrode. Therefore the 60-MnO₂/graphene has better supercapacitor than that of 100-MnO₂/graphene.

FIGURE 8: (a) CV curves at 50 mV/s. (b) Cycle number at 1 A/g. (c) Galvanostatic charge/discharge curves at 1 A/g. (d) Nyquist plots of electrodes; inset is the electrical equivalent circuit used for fitting impedance spectra.

4. Conclusions

MnO₂/graphene nanocomposites had been fabricated through a simple soft chemical route in a water-reflux condenser system and investigated with regard to their electrochemical properties as supercapacitor. The morphology and structure of MnO₂ on graphene substrate could be controlled

by adjusting the synthesis temperature, which is important for generating high electrochemical performances. The specific capacitance values of 60-MnO₂/graphene composite (48 wt% MnO₂) electrode reached 350 F/g at 1000 mA/g, which is two times higher than that of pure MnO₂ (163 F/g). It exhibited an excellent cycling stability with about 93% capacitance retention after 5000 times of charge/discharge

cycle in 0.5 M Na₂SO₄ electrolyte, indicating a good application potential in supercapacitors as well as other power source systems.

Conflict of Interests

The authors declare that they have no direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of them.

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