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Fabrication of three-dimensional porous graphene–manganese dioxide composites as electrode materials for supercapacitors

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HIGHLIGHTS

- Three-dimensional porous graphene–MnO_2 composites were fabricated.
- MnO_2 particles were formed and uniformly distributed on the graphene sheets.
- The composites exhibited interpenetrating porous structure.
- The composites gave a high specific capacitance of $800\,F\,g^{-1}$.

GRAPHICAL ABSTRACT
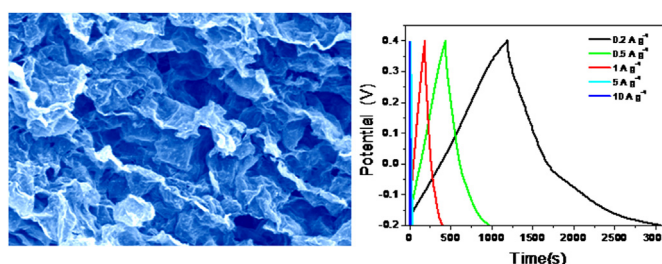
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ABSTRACT

Three dimensional (3D) porous graphene–MnO_2 (PGR–MnO_2) composites as electrode materials for supercapacitors were fabricated via deposition of MnO_2 particles on 3D PGR produced from freeze–drying method. Field emission scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy were used to characterize morphologies and composition of the produced PGR–MnO_2 composites. By immersing PGR into $0.1\,M$ $KMnO_4/K_2SO_4$ for different time, it was found that MnO_2 particles with the size of about $200\,nm$ were formed and uniformly distributed on the GR sheets. The obtained PGR–MnO_2 composites still remained 3D interpenetrating porous structures. Electrochemical methods including cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge were carried out to investigate electrochemical properties and capacitive performance. The results showed that the PGR–MnO_2-2 h composite (immersing the PGR into $0.1\,M$ $KMnO_4/K_2SO_4$ for 2 h) gave the best capacitive performance among these produced composites. The PGR–MnO_2-2 h composite gave the maximum specific capacitance of $800\,F\,g^{-1}$ with the maximum energy density of $40\,W\,h\,kg^{-1}$ at the current density of $0.1\,A\,g^{-1}$. The good capacitive performance was attributed to the unique 3D porous structure of the PGR–MnO_2 composites and the synergistic effect of GR with high conductivity and MnO_2 particles with good pseudocapacitive properties.

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1. Introduction

Supercapacitors have received extensive attention and much interest due to their excellent charge and discharge characteristics, high power density and good stability [1–4]. According to the type of electrode materials used, supercapacitors can be divided into the electric double-layer supercapacitors and pseudocapacitors. Many carbon materials including graphite, porous carbon, carbon nanotubes and graphene (GR) have many advantages of chemical inertness, wide potential window and rich source. Carbon materials are usually used as electrode materials for fabrication of electric double-layer supercapacitors [5–12]. However, carbon materials

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used in supercapacitors have the weakness of low specific capacitance. Some metal oxides (RuO_2, MnO_2, NiO, etc.) and conducting polymers (polyaniline, polyrrole, etc.) mainly are used to fabricate pseudocapacitors. The capacitive performance is realized from the oxidation–reduction process at electrode surfaces. Compared with the electric double-layer capacitors, they give higher specific capacitance. Among these electrode materials, RuO_2 has high specific capacitance and stability, but excessive production costs limit its wide application in supercapacitors [13]. MnO_2 with low-cost, low-toxicity, simple synthesis process is an ideal capacitor material and its theoretical specific capacitance can reach $1370 \, F \, g^{-1}$. However, the specific capacitance of supercapacitors based on pure MnO_2 is low resulting from poor electric conductivity of MnO_2 [14]. Therefore, improving the conductivity of MnO_2 is an effective way to produce supercapacitors with high specific capacitance. Combining excellent pseudocapacitance property of MnO_2 and high conductivity of carbon materials can improve the capacitive performance [15–25]. Composites of MnO_2–carbon nanotube or MnO_2–GR have been fabricated, and they gave good capacitive performances. These composites were usually produced by electrostatic assembly or hydrothermal method, and exhibited two-dimensional (2D) structures. For example, MnO_2–polyrrole–GR composites with sandwich structures were produced by co-assembly of MnO_2, polyrrole and graphene oxide and then reduction, and the maximum specific capacitance of $404 \, F \, g^{-1}$ was obtained [21]. MnO_2 petal nanosheets and nanorods were deposited onto the GR sheets by one-step hydrothermal method and the remarkable specific capacitance of $516.8 \, F \, g^{-1}$ at the scan rate of $1 \, mV \, s^{-1}$ was obtained [22]. However, MnO_2-GR composites with 2D structures easily agglomerated due to the strong π–π interactions between GR sheets, and this resulted in the decrease of active area and capacitive performance of electrode materials [26,27].

In recent years, three dimensional (3D) porous graphene (PGR) has been a research focus because of its interconnected porous structure, effective active surface, high mass transfer speed [28–33]. Based on these advantages, 3D PGR are expected to have potential applications in many fields such as electrode materials, catalysis, adsorption, separation and so on. Fabrication of 3D PGR–MnO_2 composites will be useful and effective for improvement of capacitive performance. However, to our knowledge only less related research has been reported. 3D carbon nanotubes-GR foams have been fabricated with Ni foams as the templates by chemical vapor deposition [23]. MnO_2 particles were formed on these porous foams to prepare 3D carbon nanotubes-GR-MnO_2 hybrid foams and they showed good capacitive properties. Wang et al. [24] prepared PGR at $180\,^\circ C$ for $12\,h$ by hydrothermal method, and then deposited MnO_2 on the PGR to prepare PGR–MnO_2 composites. The specific capacitance from the porous composite could reach $211.5 \, F \, g^{-1}$ at a scan rate of $2 \, mV \, s^{-1}$. However, development of facile and low-cost methods to prepare 3D PGR–MnO_2 materials still remains a considerable challenge. We recently have developed a novel method to produce 3D PGR monolith via freeze–drying method. The obtained monolith had interpenetrating porous structure of GR sheets. This method is facile, low-cost and no template is required. Considering the unique microstructure of the 3D PGR, in this paper the 3D PGR was used as the support for deposition of MnO_2 to fabricate electrode materials of supercapacitors with high capacitive performance. MnO_2 particles were deposited onto the PGR by immersing it into a $KMnO_4/K_2SO_4$ solution. Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize morphologies and composition of the produced PGR–MnO_2 composites. Electrochemical methods including cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge were carried out to examine electrochemical and capacitive properties.

2. Experimental

2.1. Chemicals and reagents

Graphene oxide (GO) was purchased from Nanjing JCNano. Tech. Co., LTD. Nafion (5% in a mixture of lower aliphatic alcohols and water) was from Sigma-Aldrich. $KMnO_4$, K_2SO_4 and KOH were purchased from Sinopharm Chemical Reagent Co., LTD. Polyvinyl alcohol (PVA, *Mw* 9000–10,000) was from Sigma-Aldrich. Sodium dodecyl sulfate (SDS) was purchased from Shanghai Zhanyun Chemical Co., Ltd. All reagents and chemicals were analytical grade, and all solutions were prepared using distilled water.

2.2. Apparatus

Morphologies of the samples were observed with a SU-70 Field emission scanning electron microscopy with an energy dispersive spectrometer (EDS) at an accelerating voltage of $15\,kV$. The samples were coated with platinum before observation. XRD patterns were obtained from D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation operated at $40\,kV$ and $40\,mA$. XPS measurements were operated with an ESLAB 250 spectrometer (ThermoFisher SCIENTIFIC). Electrochemical experiments were carried out on an electrochemical workstation (CHI 660D, Shanghai ChenHua Instruments Co. LTD.) in $0.1\,M$ KOH solutions at room temperature. The three-electrode system was used with the modified glassy carbon electrode (GCE, $3\,mm$ diameter) as working electrode, a platinum wire as counter electrode and an Ag/AgCl (saturated KCl) electrode as reference electrode.

2.3. Procedures

3D PGR monolith was prepared according to our developed method. $30\,mg$ GO was dispersed into $2.0\,wt\,\%$ PVA solution containing $0.04\,g\,ml^{-1}$ SDS. Then the suspension was freeze dried and the porous GO composite was obtained. The GO composite was calcined at $700\,^\circ C$ in nitrogen for $3\,h$ to produce the PGR monolith. The PGR monolith was cut into small pieces, and then the small GR piece was immersed into a $0.1\,M$ $KMnO_4/K_2SO_4$ solution in a bath at $80\,^\circ C$ for 1, 2 and $3\,h$. After that, the resulted PGR composite was taken out and washed with large amounts of water until no red color appeared in the water. Finally the porous composite was put in an oven at $80\,^\circ C$ overnight and the PGR–MnO_2 composites were obtained. The corresponding products were labeled as PGR–MnO_2-$1\,h$, PGR–MnO_2-$2\,h$ and PGR–MnO_2-$3\,h$ according to the dipping time.

The produced PGR–MnO_2 composites were dispersed into 1% Nafion solutions with ultrasonication to prepare $4\,mg\,ml^{-1}$ PGR–MnO_2 suspensions. The GCE was polished with $0.3\,\mu m$ alumina powder, and then it was washed with ethanol and distilled water, respectively, and dried in nitrogen to clean the electrode surface. $5\,\mu l$ of the PGR–MnO_2 suspension was dropped onto the GCE and dried at room temperature to prepare the modified electrodes. The mass of PGR–MnO_2 composite on the electrode was $20\,\mu g$. The electrochemical properties were studied with cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge in $0.1\,M$ KOH solutions. EIS was examined within the frequency range from 0.1 to $10^5\,Hz$ with the direct current potential limited at the open circuit potential and an AC voltage amplitude of $50\,mV$.

The specific capacitance was calculated from the CV curves according to the equation:

$$c = \frac{\int I \, dV}{mVv}$$