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Synthesis of MnO_2-graphene composites with enhanced supercapacitive performance via pulse electrodeposition under supergravity field

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ABSTRACT

A method of pulse electrodeposition under supergravity field was proposed to synthesize MnO_2-graphene composites. Supergravity is very efficient for promoting mass transfer and decreasing concentration polarization during the electrodeposition process. The synthesis was conducted on our homemade supergravity equipment. The strength of supergravity field depended on the rotating speed of the ring electrode. 3D flower like MnO_2 spheres composed of nanoflakes were acquired when the rotating speed was 3000 rpm. Graphene nanosheets play as a role of conductive substrates for MnO_2 growing. The composites are evaluated as electrode materials for supercapacitors. Electrochemical results show that the maximum specific capacitance of the MnO_2-graphene composite is 595.7 F g^{-1} at a current density of 0.5 A g^{-1}. In addition, the composite exhibits excellent cycle stability with no capacitance attenuation after 1000 cycles. The approach provides new ideas for developing supercapacitor electrode materials with high performance.

1. Introduction

Since it was prepared by Geim and Novoselov in 2004 [1], graphene has attracted extensive attention due to its excellent properties, such as high electronic conductivity, good thermal stability and prominent mechanical strength [2]. Additionally, owing to its unique one-atom-thick two-dimensional (2D) structure, graphene possesses high specific surface area with the theoretical value of 2600 m^2 g^{-1} [3,4]. So graphene shows great potential in the field of energy storage. There have been many researches on graphene-based materials for supercapacitors. However, the relatively lower specific capacitance is a major deficiency of carbon materials, which are commonly studied as electrodes for electrochemical double layer capacitors (EDLCs) [5,6]. Therefore, the combination of graphene and metal oxides has become one of research focuses. It could achieve the synergistic effect of the two types of capacitance and good performance could be obtained. Graphene is usually as the substrate, which provides a conductive network to connect the anchored metal oxide nanoparticles [7,8]. It is beneficial for metal oxides to give full play to their large capacitance.

Among numerous metal oxides, MnO_2 is one kind of the most promising pseudo-capacitor electrode materials due to its high theoretical specific capacitance, environmental compatibility and low cost [9–11]. Up till now, graphene/MnO_2 composites have been widely studied as active electrode materials for supercapacitors. The high electronic conduction and its large area surface of graphene combined with MnO_2 with pseudocapacitance, greatly improved the specific capacitance and cycle performance, which are promising in the development of supercapacitors. How to achieve the best combination and synergistic effect is a research focus. Many methods were applied and the results were excellent [12–14]. Hydrothermal method is the most common one. Yang et al. prepared nitrogen-doped graphene-ultrathin MnO_2 sheet composites by a hydrothermal method, with a capacitance of 257.1 F g^{-1} at 0.2 A g^{-1} and a retention of over 94.2% of the original capacitance after 2000 cycles [15]. Chen's group produced MnO_2 nanolamellas by in situ substitution of the framework of graphene, using $KMnO_4$ solution and graphene dispersion as reagents in the redox reaction at ambient temperature. The electrochemical properties as supercapacitor electrodes of the as-prepared product are more competitive than MnO_2 [16]. Besides that, electrodeposition is a very promising method for the synthesis of nano-composites, owing to its low cost, facile process and high-quality product, especially, morphology-controlled growth by adjusting the deposition parameters [17]. It has been applied broadly. He et al. reported a fabrication of three-dimensional (3D) graphene network by AP-CVD growth graphene on Ni foam. After

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dissolving the Ni foam, a 3D graphene with a foam-like network was obtained, and then loaded MnO_2 by electrodeposition [18]. Zhao and coworkers demonstrated an approach including electrophoretic deposition of graphene on nickel foam and then electrodeposition of MnO_2 on the graphene coated nickel foam [19]. Our group previously reported a method of electrodepositing MnO_2 under supergravity field, which exhibited larger specific surface area and a higher capacitance than that under normal gravity [20].

Herein, we report a facile fabrication of MnO_2-graphene composites by pulse electrodeposition under supergravity field. Pulse electrodeposition has positive effects on grain refinement for deposits. The effect of supergravity on electrodeposition is mainly decreasing concentration polarization and promoting mass transfer during the electrodeposition process, so MnO_2-graphene composites could be acquired at a lower electrolyte concentration. However, it cannot be achieved under normal gravity field. Additionally, noxious chemicals and harsh conditions are avoided during the preparation of graphene, so the strategy is green. The microstructure and electrochemical performance of the composite were investigated, which showed tremendous application potential in supercapacitors.

2. Experimental

2.1. Synthesis of the MnO_2-graphene composite

All reagents used in the work were of analytical grade. Graphene oxide (GO) was prepared from graphite powder by the modified Hummers method [21]. An appropriate amount of GO was treated upon microwave irradiation to obtain graphene. The microwave oven (Galanz-WD900B) was first operated at the power of 720 W, and for a reaction time of 60 s, then another 60 s at the power of 540 W. During the process, microwave assisted exfoliation and reduction of GO, which avoided the use of toxic hydrazine hydrate. The synthesis of MnO_2-graphene composite was using pulse electrodeposition under supergravity field in the presence of graphene.

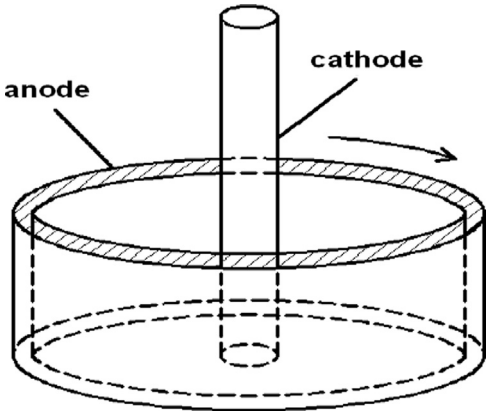

Fig. 1. Sketch of electrodes in the supergravity equipment.

First, 30 mg graphene was dispersed in 600 mL of $MnSO_4$ aqueous solution (0.004 mol L^{-1}) and sonicated for 20 min. Then, pulse electrodeposition was performed in the supergravity equipment, where the titanium ring was used as the anode and the stainless steel pipe as the cathode (Fig. 1). The titanium ring was fastened to the base and rotated at a high speed driven by a motor. The intensity of the supergravity was controlled by the rotating speed. In this experiment, the speed was chosen 0 rpm, 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm and 5000 rpm. The as-prepared MnO_2-graphene composites were denoted as MG-0, MG-1000, MG-2000, MG-3000, MG-4000 and MG-5000, respectively. A current density of 0.8 mA cm^{-2}, a duty ratio of 60% and a pulse frequency of 1000 Hz were applied to the formation of MnO_2-graphene composites with a deposition time of 60 min. And the reaction was always kept at the room temperature. After the electrodeposition, the product was scraped from the titanium ring and washed with distilled water and then dried in a vacuum oven at 60 °C. The schematic representation of the preparation procedure of the MnO_2-graphene composite was illustrated in Fig. 2. For comparison, free MnO_2 was prepared under supergravity field with the rotating speed of 3000 rpm, but graphene was in absence.

2.2. Materials characterization

X-ray diffraction (XRD) patterns were conducted on a D-max-2500/PC X-ray diffractometer (Rigaku, Japan) with Cu $K\alpha$ radiation (λ=0.15406 nm) under a voltage of 40 kV and a current of 100 mA. X-ray photoelectron spectroscopy (XPS) was obtained using Kratos XSAM-800 with Al $K\alpha$ radiation source. Morphologies of the samples were studied with a scanning electron microscopy (SEM) S-4800 (Hitachi, Japan) and a transmission electron microscopy (TEM) HT7700 (Hitachi, Japan). Thermo gravimetric analysis (TGA) was performed with a DTG-60A thermal analysis system (Shimadzu, Japan) under air atmosphere, at a heating rate of 10 °C min^{-1} from room temperature to 800 °C.

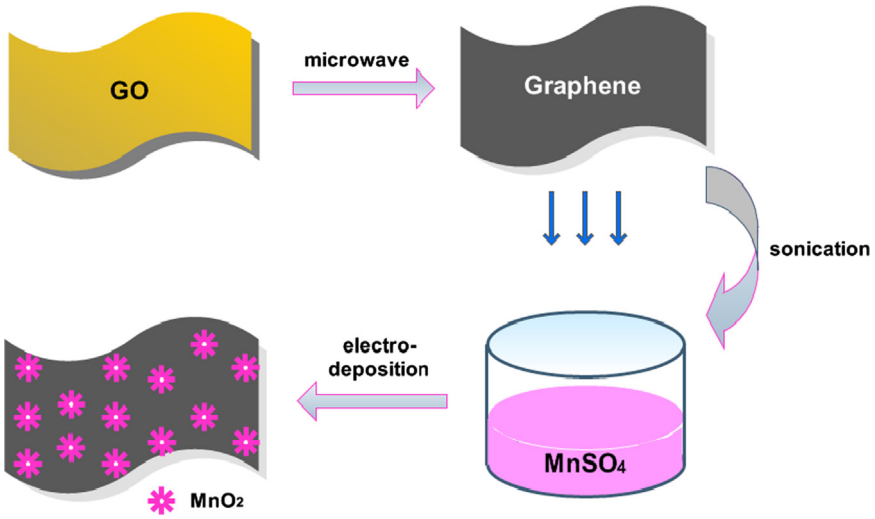

Fig. 2. Synthetic strategy illustration of MnO_2-graphene composites.