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MnO_2-wrapped hollow graphitized carbon nanosphere electrode for supercapacitor

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ABSTRACT

MnO_2-wrapped hollow graphitized carbon nanospheres (MnO_2/HGC) electrodes are prepared by a cooperative template wrapping method. hollow Graphitized carbon nanospheres (HGC) are firstly obtained by carbonizing phenolic resin followed by etching the SiO_2 template, then the MnO_2 ultrathin nanoplates are coated on the surfaces of the HGC nanospheres through a redox reaction between $KMnO_4$ and HGC nanospheres. The as-prepared MnO_2/HGC hollow nanospheres possess porous structure and large specific surface area ($\sim$230 $m^2 g^{-1}$). The specific capacitances of MnO_2/HGC nanosphere electrodes with different mass ratios of MnO_2 to HGC are about 340–380 $F g^{-1}$ at a scan rate of 5 $mV s^{-1}$ in Na_2SO_4 solution, and shows relative good cycling performance of the initial capacitance after 1000 cycles. The good specific capacitance is ascribed to the novel hollow nanosphere structure, which possesses high surface-to-volume ratio, and makes it easy for the mass diffusion of electrolyte and transmission of ions and electrons and also maintains the mechanical integrality.

1. Introduction

Over the past few years, clean and renewable energy has driven intensive research efforts toward the development of alternative energy storage and delivery systems because of the tremendous energy consumption and the fossil fuel crisis [1–3]. In the field of energy storage applications, one of the greatest challenges is to develop low–cost energy storage devices with high energy density and high power density [4,5]. Electrochemical capacitors, which are also known as supercapacitors, have attracted considerable attentions because they can bridge the function for the power/energy gap between traditional dielectric capacitors having high power output and batteries/fuel cells with high energy storage as well as unique properties, such as high power, long cycle life, fast charge–discharge rate, and low maintenance cost, which makes the rapid storage and release of energy possible [6–8].

Supercapacitors can be categorized as electric double layer capacitor and pseudocapacitor on the basis of their charge storage mechanisms [9,10]. It has been demonstrated that pseudocapacitors can yield much higher specific capacitance and energy density than electric double layer capacitor [11]. Up to now, porous carbon, conducting polymers, and transition-metal oxides are promising candidates for the electroactive materials of electrochemical capacitors [12,13], but each kind of these materials has its own advantages and disadvantages. Porous carbon materials show long cycle life and good mechanical properties, but their specific capacitance is low [14], while transition-metal oxides and conducting polymers have high specific capacitance in a suitable potential window of charge storage/delivery [15]. Therefore, it is of great importance to develop new electrode materials with high capacitance and improve performance relative to existing electrode materials.

Manganese oxide (MnO_2) is a typical electrode material for pseudocapacitors due to its low cost, abundance, high theoretical specific capacitance (1370 $F g^{-1}$) and good environmental compatibility [16,17]. In the developing process of manganese oxides as ideal electrode materials, the challenge is how to improve their electron conductivity and the ion diffusion/penetration rate, and how to inhibit the dissolution of the electrode materials [18,19]. Graphene is considered to be the most promising electrical double-layer capacitor material due to its high electrical conductivity, good electrochemical stability, high surface area and superior mechanical property [20,21]. However, the actual capacitive behavior of pure graphene is much lower than the anticipated value due to the fact that it usually suffers from serious agglomeration during preparation [22]. It has been found that the capacitance of graphene can be improved by combining with some

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pseudocapacitive electrode materials, such as conducting polymers or transition-metal oxides [23–28]. Many graphene-manganese oxide nanocomposites with good capacitance have been prepared by the surface redox reaction and electrodeposition methods [29–31]. Although these graphene-manganese oxide nanocomposites show good capacitance performance, the energy density is yet unsatisfactory and it can not be well resolved [32,33]. Therefore, there is a need to develop suitable electrode materials that possess high-energy and high-power densities simultaneously [34].

Hollow structure nanospheres, especially hollow macroporous core-ultrathin mesoporous shell nanospheres may be chosen as promising electrode materials for supercapacitor because these materials possess high surface-to-volume ratio, hollow inner space, and stable structure integrity, and are more favorable for the mass diffusion of electrolyte and transmission of ions and electrons, which can be used to improve the energy and power densities simultaneously [35,36]. Therefore, some carbon−based electrode materials and carbon-metal oxide hybrid electrode materials with novel hollow structure have been prepared, and they show promising super capacitance as electrode materials [37–40]. In the present work, MnO_2-wrapped hollow graphitized carbon nanosphere electrode for supercapacitor was prepared by a cooperative template wrapping method [41]. The schematic representation of the preparation of the MnO_2-wrapped hollow graphitized carbon nanospheres is shown in Fig. 1. Hollow Graphitized carbon nanospheres (HGC) was firstly obtained by the self-assembly, calcination and carbonization of phenolic resin followed by the etching of the SiO_2 template, and then the MnO_2 shells were in situ coated on the surfaces of the HGC nanospheres through a redox reaction between $KMnO_4$ and HGC nanospheres. By means of a hybrid effect between MnO_2 nanosheets with high specific capacitance and HGC nanospheres with good conductivity and long cyclic life, the as-prepared MnO_2-wrapped hollow graphitized carbon nanosphere (MnO_2/HGC) electrode is expected to possess a porous structure for easy electrolyte access, and to enhance its specific capacitance.

2. Experimental

2.1. Preparation of HGC and MnO_2/HGC nanospheres

Silica nanospheres were prepared according to a modified Stöber method [42]. Typically, 25 mL of deionized water, 25 mL of ethanol and 3 mL of ethyl silicate were mixed for 30 min under vigorous stirring at room temperature. Then 6 mL of ammonia (27%, aqueous solution) was added into the above suspension. After reacting for 3 h under vigorous stirring, the obtained precipitation was collected by centrifugation, washed with ethanol and deionized water repeatedly and dried in air, SiO_2 nanospheres were prepared.

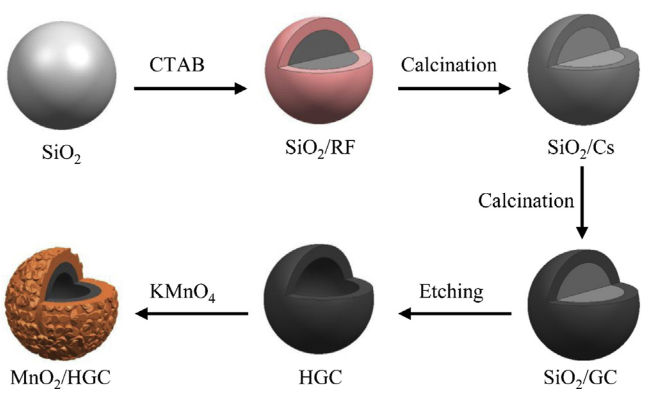

Fig. 1. Schematic representation of the preparation of the MnO_2/HGC hollow nanosphere.

Carbon-encapsulated silica nanospheres (SiO_2@Cs) were prepared by a versatile cooperative template-direct coating method [38]. 0.8 g of the as-obtained SiO_2 nanospheres were homogeneously dispersed in deionized water (70.4 mL) by ultrasonication, followed by adding 2.3 g of hexadecyltrimethyl ammonium bromide, 0.35 g of resorcinol, 28.2 mL of ethanol and 0.1 mL of ammonia, and stirred at 35 °C for 30 min to form a uniform dispersion. Then, 0.5 mL of a formalin solution (14.4 M) was added to the above dispersion and the dispersion was stirred for 6 h. The obtained mixture was aged at room temperature overnight without stirring. The product SiO_2@resorcinol-formaldehyde resin (SiO_2@RF) was collected by centrifugation and then washed with deionized water and ethanol several times. It was heated to 150 °C from room temperature at 5 °C min^{-1} and kept at this temperature for 1 h under argon atmosphere. Then the temperature was raised to 600 °C and kept for 2 h, the pyrolyzed product SiO_2@Cs was obtained. In order to graphitize the carbon, the calcination temperature was raised to 800 °C and kept at this temperature for 90 min under an argon atmosphere, SiO_2/graphitized carbon was obtained. SiO_2/graphitized carbon was then treated with 10% HF solution to etch the silica, the resulted precipitate was washed with deionized water for several times, dried at room temperature, the hollow graphitized carbon nanosphere was obtained, which was abbreviated as HGC.

0.1 g of HGC was dispersed in 100 mL deionized water via ultrasonic processing using a KQ-600 kDE Digital Ultrasonic cleaning device (600 W, 80% amplitude) in a water bath for 1 h at room temperature. Then 2.63 g of $KMnO_4$ was added into HGC homogeneous dispersion under vigorous stirring for 3 h at 60 °C, the obtained products were washed with deionized water for several times and dried at room temperature, MnO_2-wrapped graphitized carbon nanospheres with hollow structure were finally prepared, which was abbreviated as MnO_2/HGC. By changing the mass ratios of $KMnO_4$ to HGC, MnO_2/HGC nanospheres with different mass ratios of MnO_2 to HGC were prepared using the same procedure.

2.2. Materials characterization

X-ray diffraction (XRD) measurements were carried out using a D/Max-3c X-ray diffractometer with Cu Kα ($\lambda = 0.154$ nm), scanning from 5° to 70° and using an operation voltage and current of 40 kV and 30 mA, respectively. Transmission electron microscope (TEM) images were collected by using a JEM-2100 microscope. Specimens for TEM observation were prepared by dispersing the material powder into ethanol by an ultrasonic treatment. X-ray photoelectron spectroscopy (XPS) investigation was performed with a K-Alpha spectrometer using Al Kα radiation (1486.6 eV) at a power of 150 W (accelerating voltage 12 kV, current 6 mA) in a vacuum of 8.0×10^{-8} mPa. The binding energy scale was calibrated with respect to adventitious carbon (C1s). A Beckman coulter-type N_2 adsorption–desorption apparatus (ASAP 2020M) was used to investigate the pore property degassing at 120 °C for 8 h. Mn content in samples were determined by atomic absorption spectrometry (AAS) after the obtained materials were dissolved in a mixed solution of HCl (1.0 mol L^{-1}) and H_2O_2 (28%) (v/v = 5:1).

2.3. Electrochemical measurements

The electrochemical behaviors of the as-prepared materials were measured by an IVIUMSTAT electrochemical workstation (Ivium Technologies BV Co., The Netherlands) which is a three-