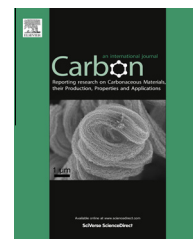


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Graphene with three-dimensional architecture for high performance supercapacitor

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ABSTRACT

Mesoporous graphene with three dimensional structure (3dGR) is prepared by a modified Hummers method and a simple solvent treatment. The solvent-treated graphene nano-sheets show wrinkled structure and agglomerate to form the mesoporous structure. The pore size distribution of 3dGR based on density functional theory (DFT) shows the pore size ranging from 2.3–40 nm. 3dGR shows excellent electrochemical behaviors in both aqueous and organic electrolytes, even though it has fairly small surface area of only 81.7 m²/g. For 3dGR, a capacitance of 341 F/g and energy density of 16.2 Wh/kg are acquired in alkali electrolyte, while those values are 166 F/g and 52.5 Wh/kg respectively in organic electrolyte. In addition, because of the high packing density of 3dGR, higher volumetric power densities of 20.7 and 67.2 Wh/L in alkali and organic electrolytes are obtained. After 1000 cycles of galvanostatic charge/discharge tests, over 96% and 86% of the original capacitance can be retained in alkaline and organic electrolytes.

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1. Introduction

Supercapacitors, also called electrochemical capacitors or ultracapacitors, are capable of providing huge amount of energy in a very short period of time, making them essential to applications in surge power delivery [1,2], portable electronic devices [3,4] and more. Depending on the charge-storage mechanism, supercapacitors can be classified into two categories: electric double-layer capacitors (EDLCs) in which various carbon materials are used as electrode materials [5] and pseudocapacitors in which certain metal oxides or conducting polymers are often used as electrode materials [6,7].

Carbon materials are commonly used in EDLCs devices. Among various carbon materials, activated carbon is the most widely used due to its high specific surface area and affordable cost. Nevertheless, it is known that in order to acquire high capacitance, good electronic conductivity of the electrode material is also important [8]. Comparing to amorphous

carbon, graphitic carbon shows higher electronic conductivity due to its well-developed crystalline structure but often sacrificing the surface area. As a new member of carbon material family, graphene is an atomically thick, two-dimensional (2-D) sheet which composes of sp² carbon atoms arranging in a honeycomb structure [9]. Graphene shows excellent electrical and thermal conductivity while still capable of maintaining extra large specific surface area [10]. Thus, Graphene has been predicted as a potential candidate for EDLC electrode material and graphene-based supercapacitors have already shown some promising results. Ruoff and co-workers are among the pioneers to apply graphene as electrode material in EDLCs to achieve a specific capacitance of 99 F/g in organic electrolyte [11]. More recently, Piner and co-workers prepared graphene by microwave assisted exfoliation and reduction of graphene oxide platelets which were suspended in propylene carbonate. The specific capacitances of supercapacitors based on this graphene material are

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190 F/g in aqueous and 120 F/g in organic electrolytes respectively [12]. Further treating graphene with KOH, the specific capacitance can reach 200 F/g at a current density of 0.7 A/g in ionic electrolyte (EMIM TFSI) [13].

Currently, the reported specific capacitances of graphene-based supercapacitors in aqueous solution are mostly around 200 F/g [4,12,14,15]. These values are very promising, but they are still below expectation. In principle, if the entire surface area of graphene could be used, its capacitance could achieve as high as 550 F/g [16]. Much higher specific capacitances can be achieved when pseudocapacitance is introduced into graphene-based electrode material by addition of metal oxide nanoparticles [17] or conducting polymers [18], such as RuO₂ [19], MnO₂ [20], Fe₂O₃ [21], Ni²⁺/Al³⁺ layered double-hydroxide [22] or polyaniline [23–25], etc. However, the charge/discharge rates will become slower due to the pseudocapacitance contributed from oxide nanoparticles or conducting polymers [26].

One of the major cause for the below-expectation performance of graphene as electrode material for supercapacitors is most likely the agglomeration and restacking of graphene nanosheets, which are the results from van der Waals attractions between the neighboring sheets [10]. It is believed that the aggregation and restacking of the nanosheets reduce the effective surface area of the material on which charges are accumulated to form double-layer capacity, leading to significant loss of capacitance [19].

To date, the most widely used and studied synthetic method to make graphene is via graphite oxide (GO) route due to the scalability [27]. How the GO is exfoliated and reduced has strong impacts on the structure and surface characteristics of the graphene obtained. For instance, highly wrinkled structure and atomistic perforations may make the sheets less stiff and more permeable thus may inhibit restacking [18]. Liu et al. reported that mesoporous (2–25 nm) structured graphene could be prepared by a modified Hummers method and reducing the GO suspension in a forced convection oven. The curved structure may hinder the nanosheets from face to face restacking, thus to maintain high capacitance [28].

In this study, mesoporous graphene with three dimensional structure (3dGR) is prepared by a modified Hummers method and a simple solvent treatment. The results of electrochemical measurement indicate that 3dGR exhibits good electrical double-layer capacitance performance. Capacitance values as high as 341 F/g in aqueous and 166 F/g in organic electrolytes have been achieved. The energy densities obtained in aqueous and organic electrolyte are 16.2 Wh/kg and 52.5 Wh/kg respectively.

2. Experimental

2.1. Chemicals

Graphite powder (spectroscopically pure), sulfuric acid (95–98%), sodium nitrate (AR grade), potassium permanganate (AR grade), 30% hydrogen peroxide (AR grade), potassium hydroxide (AR grade) and acetonitrile (AR grade) are from Sinopharm Chemical Reagent Co. Tetraethylammonium

tetrafluoroborate (NEt₄BF₄, 99%) is obtained from Alfa Aesar. All reagents are used as received.

2.2. Preparation of GO

GO was synthesized from natural graphite by a modified Hummers method [23,29]. Typically, graphite (5 g) and NaNO₃ (2.5 g) were mixed with 120 mL of H₂SO₄ (95%) in a 500 mL flask. The mixture was stirred for 30 min in an ice-water bath. While maintaining vigorous stirring, potassium permanganate (15 g) was added to the suspension slowly to keep the reaction temperature below 20 °C. Upon completion of potassium permanganate addition, the ice-water bath was removed, and the mixture was kept stirring at room temperature for overnight. As the reaction proceeded, the mixture gradually became pasty, and the color turned into light brownish. After overnight stirring, 150 mL of H₂O was slowly added to the paste with vigorous agitation and the paste color changed to yellow. The diluted suspension was stirred for another 15 min before 50 mL 30% H₂O₂ was added to the mixture. For purification, the mixture was washed with deionized (DI) water for several times until pH ≈ 7. After filtration and drying under vacuum, GO was obtained as brownish powder.

2.3. Preparation of treated GO with ethanol (GO-T) and 3dGR

GO powder were dispersed in ethanol by 2 h ultra-sonication in a beaker. The GO ethanol dispersion was stirred at ambient conditions to allow the ethanol to evaporate. Black powder was obtained after ethanol totally evaporated in 2 days. The powder was further dried in air at 60 °C, and named as GO-T.

3dGR was prepared according to the reported method [22]. In a typical experiment, 0.1 g of GO-T was dispersed in 50 mL of DI water, and then was ultrasonicated for 1 h before 0.1 mL of hydrazine monohydrate was added. The mixture was heated to 95 °C and held at that temperature for 1 h. The mixture was kept stirring until it was cooled to room temperature. Finally, 3dGR was obtained as a black powder after filtration, several DI water washes and overnight vacuum drying at 60 °C.

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200 diffractometer, using Ni-filtered Cu K α radiation. Nitrogen adsorption-desorption measurements were carried out at 77 K on a Micrometrics ASAP 2020 system. The sample was degassed below 1.33 Pa at 363 K for 1 h and then 623 K for another 6 h before the measurement. High-resolution transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100F TEM at 200 kV on a lacey network support film. Scanning electron microscopy (SEM) was performed on a JEOL JSM-6700F microscope. The element contents and chemical bonding were investigated by X-ray photoelectron spectroscopy (XPS, Microlab 310F with a dual anode X-ray source). Raman spectra of the films were recorded using a Renishaw MicroRaman spectrometer with an excitation length of 633 nm.

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