Synthesis of reduced graphene oxide/thorn-like titanium dioxide nanofiber aerogels with enhanced electrochemical performance for supercapacitor
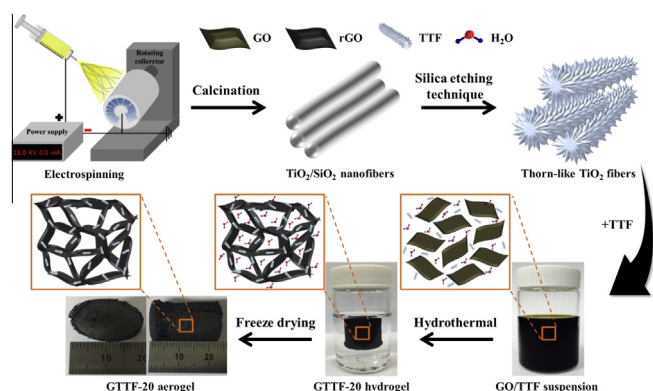
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GRAPHICAL ABSTRACT

Schematic of the fabrication of the GTTF-20 aerogel.

ARTICLE INFO

ABSTRACT

Reduced graphene oxide (rGO)/thorn-like TiO_2 nanofiber (TTF) aerogels, or GTTF aerogels, with different TTF weight ratios were successfully prepared by electrospinning, silica etching and hydrothermal combination method. During the hydrothermal reaction, the rGO nanosheets and TTF self-assembled into three-dimensional (3D) interconnected networks, in which the TTF is loaded onto the rGO nanosheets. The electrochemical performance of the GTTF aerogels was assessed using cyclic voltammetry and galvanostatic charge–discharge measurements in a 1 M aqueous Na_2SO_4 electrolyte. The TTF-to-rGO ratio of the aerogel material significantly affected the electrochemical performance of the aerogel electrodes, and the GTTF aerogels prepared with 20 wt% TTF (denoted GTTF-20) exhibited excellent electrochemical performance. The maximum specific capacitance of this aerogel electrode was 178 F/g at a current density of 1 A/g. The GTTF-20 aerogel also exhibited good electrochemical stability with a capacitance degradation of less than 10% after 3000 cycles. We can deduce that the electrochemical performance of the as-prepared aerogels may be enhanced by increasing the chemical interactions between rGO and TiO_2. The results indicate that the GTTF aerogels show enormous potential for application in energy storage devices.

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1. Introduction

Supercapacitors (SCs) are widely applied in portable electronics and smart-grid electrochemical energy storage because they have higher energy densities than electrostatic capacitors and higher power densities than batteries [1,2]. There are two typical types of SCs depending on the charge storage mechanism: electric double-layer capacitors (EDLCs), where the charge is absorbed on the surface of an electrode, and pseudocapacitors (PCs), which undergo reversible faradaic redox reactions near and on the surface [3,4].

Researchers have recently turned their attention toward inexpensive high-energy-density electrode materials owing to their high power density retention and cycling stability. Better performance can be obtained from SCs by combining EDLC materials with PCs. Graphene, a two-dimensional carbon nanostructure that comprises a single layer of sp^2-bonded carbon atoms, has attracted considerable attention from both experimental and theoretical researchers in recent years owing to its exceptional electrical, mechanical, chemical and thermal properties. Consequently, graphene is regarded as one of the more promising electrode materials for SCs [5–8]. However, despite their theoretical usefulness, graphene nanosheets suffer from problems associated with agglomeration or restacking caused by van der Waals interaction, which reduce their specific surface area and capacitance. To prevent agglomeration, a metal/metal oxide or a conducting polymer can be inserted between the layers of graphene nanosheets [9,10]. The inserted material provides a sufficient gap between the layers, maintaining the high surface area of the nanosheets and ensuring reactant accessibility.

Transition-metal oxides such as MnO_2, SnO_2, Co_3O_4, NiO and RuO_2 contribute pseudocapacitance to a material, but they have disadvantages that hinder their efficient application, such as their scarcity, high cost, poor rate capability, low electrical conductivity and reversibility during the charge-discharge process. Consequently, researchers have conducted theoretical studies and experiments to find low-cost alternatives. Several materials have been considered, including TiO_2, Fe_2O_3 and ZnO. Among them, TiO_2 is widely used in solar cells, photocatalysts, sensors and Li-ion batteries owing to its chemical stability, low cost, environmental benignity and abundance [11–14]. Thus, combining graphene with TiO_2 as alternative current-collector materials in SCs has attracted much research attention [15–17]. Pristine TiO_2 has a low electrochemical capacitance due to its high electrical resistance and low specific surface area. However, modification of the TiO_2 nanostructure can improve its specific surface area and specific capacitance. For example, Salari et al. produced TiO_2 nanotubes (TiO_2 NTs) and compared their electrochemical behavior with that of nanocrystalline TiO_2 powders. Their results demonstrated that TiO_2 NTs exhibited distinct advantages over TiO_2 powders in terms of SC performance [18]. Additionally, Xiang et al. used the hydrothermal method to produce reduced graphene oxide (rGO)–TiO_2 nanoparticles and nanobelts for SC electrodes, and reported that the capacitance of the TiO_2 nanobelts was higher than that of the TiO_2 nanoparticles [19].

In this study, rGO/thorn-like TiO_2 nanofiber (TTF) aerogels, or GTTF aerogels, with different TTF weight ratios were successfully synthesized via a two-step method, and used as electrodes for SCs. The TTF was prepared through a electrospinning and silica etching combination method. GTTF aerogels with three-dimensional (3D) hierarchical porous structures were then fabricated from rGO nanosheets and TTF via hydrothermal synthesis and then followed by freeze-drying of the resultant GTTF hydrogels. The unique interconnected porous structure and the synergistic effect of the rGO and TTF afford greatly improved SC performance.

2. Experimental

2.1. Materials

Graphite flakes (Sigma-Aldrich Co.), potassium permanganate ($KMnO_4$, ⩾99.3%, OCI Co.), phosphoric acid (H_3PO_4, ⩾85%, Samchun Co.), sulfuric acid (H_2SO_4, 98%, Daejung Co.), hydrochloric acid (HCl, 35%, Samchun Co.) and hydrogen peroxide (H_2O_2, ⩾30%, OCI Co.) were used to synthesize improved graphene oxide. The reagents used in the synthesis of bare TTF were tetrabutyl titanate (TBT, 97%, Sigma-Aldrich Co.), tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich Co.), polyvinylpyrrolidone (PVP, M_w = 1,300,000 g/mol, Sigma-Aldrich Co.), methanol (MeOH, ⩾99.8%, Sigma-Aldrich Co.) and acetic acid (HAc, ⩾97%, Sigma-Aldrich Co.).

2.2. Synthesis of graphene oxide and reduced graphene oxide aerogel

Improved graphene oxide (GO) was manufactured from natural graphite flakes using a previously reported improved method [20]. In a typical synthesis, 3.0 g of graphite flakes and 18 g of $KMnO_4$ were added to a mixture comprising 360 mL of H_2SO_4 and 40 mL of H_3PO_4. This mixture was vigorously stirred at 50 °C for 12 h and then cooled to room temperature, poured onto ice along with 3 mL of H_2O_2, and filtered through a glass fiber paper. The remaining solid material was then washed with water, HCl and EtOH several times to remove the residual $KMnO_4$. The GO obtained on the filter was dried *in vacuo* overnight at room temperature. To manufacture the rGO, 200 mg of the as-prepared GO was ultrasonicated in 50 mL of deionized (DI) water for 1 h. The suspension was then transferred to a 100 mL Teflon-lined stainless-steel autoclave and hydrothermally reduced at 180 °C for 6 h. The resultant hydrogel was then cooled naturally to room temperature and freeze dried (−80 °C) for 3 days *in vacuo* to obtain the rGO aerogel.

2.3. Synthesis of thorn-like TiO_2 nanofibers

A scalable electrospinning technique was adopted to synthesize the TTF [21]. First, a mixture of 2.1 mL of TBT, 0.5 mL of TEOS, 34 mL of MeOH and 1.5 mL of HAc was magnetically stirred for 1 h to achieve homogeneity. Subsequently, 1.5 g of PVP was added to the mixture, which was further stirred for another 6 h at room temperature. Then, the mixture was transferred to a 12 mL syringe fitted with a 23G needle. The procedure was performed using a controlled electrospinning setup (Nano NC). The distance between the needle and the aluminum foil static collector was maintained at 12 cm under an applied AC voltage of 18 kV and a flow rate of 1 mL/h, which was achieved using a syringe pump (KDS 200). The temperature and relative humidity were sustained at 25 ± 2 °C and 50 ± 5% during the spinning process. The material was dried at 80 °C for 12 h and followed by calcining at 500 °C for 2 h to obtain TiO_2/SiO_2 nanofibers. Then, a silica etching technique was employed by using the following alkali treatment process: The obtained TiO_2/SiO_2 nanofibers were transferred to a polytetrafluoroethylene beaker containing 75 mL of a 5 M NaOH solution, and the solution was heated at 60 °C under vigorous stirring for 6 h in a water bath. Next, the etched nanofibers were transferred to a beaker containing a 0.1 M HCl and left undisturbed for 12 h to remove the residual sodium salt. Then, the acid-treated nanofibers were filtered and washed with DI water until the filtrate was neutral. Finally, the obtained TTF was dried *in vacuo* at 80 °C for 24 h.