Synthesis of three-dimensional porous reduced graphene oxide hydrogel/carbon dots for high-performance supercapacitor

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ABSTRACT

A composite composed of reduced graphene oxide hydrogel/carbon dots (rGH/CDs) is prepared hydrothermally. The composite has a three-dimensional (3D) interconnected network structure and exhibits good electrical conductivity and mechanical robustness, making it ideal electrode materials in supercapacitors. The carbon dots (CDs) in the reduced graphene oxide hydrogel promotes electron transport and reduces the internal resistance and charge transfer resistance in addition to providing a large surface area. The flexible solid-state supercapacitor comprising the 130 μm thick rGH/CDs electrode delivers excellent performance including high gravimetric specific capacitance of 264 F g^{-1} (up to 301 F g^{-1} for a 40 μm thick electrode), areal specific capacitance of 394 mF cm^{-2} (up to 432 F cm^{-2} for a 200 μm thick electrode), excellent cycling stability (9.1% deterioration after 5000 cycles), larger energy density (35.3 Wh kg^{-1}), as well as high power density (516 W kg^{-1}). This study demonstrates the tremendous potential of rGH/CDs in high-performance flexible energy storage devices.

1. Introduction

Flexible solid-state supercapacitors, to satisfy the increasing energy storage demand by portable and flexible electronic products, have attracted a lot of attention [1–6]. Owing to attractive features such as light weight, good flexibility, a large power density and long cycle life, supercapacitors can be used synergistically with conventional batteries [7–16]. Graphene, a unique 2D material suitable for supercapacitors [17], has attracted intense attention due to its excellent mechanical flexibility, electrical conductivity, chemical stability and large specific surface area. In addition, ultrathin graphene films have a small internal resistance and better ion diffusion properties resulting in higher apparent capacitance and rate capability. However, these advantages may not be realized in devices with thick films and large mass loading [8]. For instance, the specific capacitance of supercapacitors composed of ultrathin grapheme films theoretically can reach 550 F g^{-1} [17], but in most flexible solid-state supercapacitors, the specific capacitance is 80–118 F g^{-1} at a current density of 1 A g^{-1} [14–17]. In this respect, macroscopic semiconductor materials with a three-dimensional (3D) porous network structure are attractive electrode materials on account of the good electrical conductivity and mechanical robustness [18,19]. The typical 3D graphene macrostructure such as graphene hydrogels can be prepared by one-step reduction of the graphene dispersion [20–23]. 3D graphene macrostructures possess a large specific surface area (up to 1000 $m^2 g^{-1}$ based on methylene blue molecular absorption) so that electrolyte ions can diffuse rapidly through the porous and interconnected network in the unique graphene gel [24,25]. More recently, 3D graphene materials have been applied to all-solid-state supercapacitor and the supercapacitor has excellent specific capacitance (160–240 F g^{-1}), high rate performance, and cycling stability [20–25].

CDs have been shown to have good potential in chemical and biomedical applications because of the low toxicity and biocompatibility [26–35]. They also have good optical properties and are good electron acceptors and electron donors [36,37]. Recently, the conducting capability of CDs has been characterized by Bhattacharjee et al. [38] and a graphene quantum dots (GQDs)//GQDs symmetrical micro-supercapacitor with a high areal specific capacitance (468.1 μF cm^{-2}) has been fabricated [30]. Nandi et al. have found that fluorescence from the GQDs in the GQDs-PANI hybrid is quenched drastically and the *dc* conductivity increases by three orders of magnitude compared to GQD,
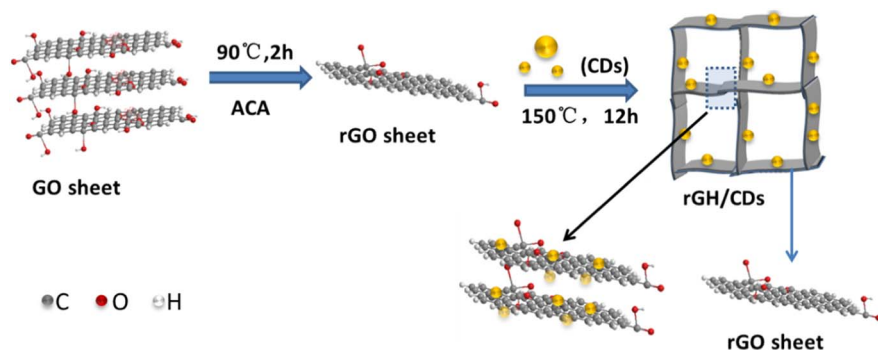
Fig. 1. Schematic illustration of the synthesis of the rGH/CDs composite.

indicating charge transfer between GQDs and PANI chains [38,39]. Fluorescence quenching in the CDs-GO system has been observed and attributed to ultrafast electron transfer from CDs to GO with a time constant of 400 fs [40]. Therefore, it is possible that a supercapacitor based on CDs as well as CDs composites has good electrochemical properties.

The excellent capacitive performance of the supercapacitor with a 3D graphene macrostructure can be prepared with a liquid electrolyte, but it requires a relatively complex packaging process to prevent leakage of the liquid electrolyte and is usually incompatible with flexible applications. In this work, a novel flexible solid-state supercapacitor based on rGH/CDs films is fabricated using H_2SO_4-polyvinyl alcohol (PVA) gel as the electrolyte. The device has excellent characteristics (for example, 70% retention at 20 A g^{-1}), high gravimetric specific capacitance (264 F g^{-1} at 1 A g^{-1}), areal specific capacitance of 394 mF cm^{-2}, and stability (specific capacitance retention of 90.9% after 5000 charging/discharging cycles at 5 A g^{-1}).

2. Experimental

2.1. Chemicals and materials

Polyethylene glycol 200 (PEG-200) (CP), glucose (GC) (AR), NaOH (99.7 wt%), H_2SO_4 (98 wt%), $KMnO_4$ (99.5 wt%), H_2O_2 (30 wt%), HCl (37 wt%), sodium nitrate (99.95 wt%), PVA (AR), graphite powder (GP), and ascorbic acid (ACA) were used in the experiments and the aqueous solutions were prepared with deionized water.

2.2. Synthesis of graphene oxide (GO)

The GO was prepared by the modified Hummer method [41]. Briefly, 2 g of natural graphite flake were mixed with 46 mL of H_2SO_4 (98 wt%) and 2 g of sodium nitrate in a conical flask and stirred for 0.5 h in an ice-water bath. Then, 6 g of $KMnO_4$ (99.5 wt%) were added slowly to the mixture while the temperature was kept at less than 20 °C for 1.5 h, followed by stirring for 1.5 h at 35 °C. The solution was diluted with 80 mL of deionized water and stirred for 30 min at 95 °C. 20 mL of H_2O_2 (30 wt%) were added slowly and the mixture was filtered and washed 10 times with 0.5 mol L^{-1} HCl, followed by removal of the residual sulfate ions with deionized water. Finally, the GO was freeze-dried at − 60 °C under vacuum conditions.

2.3. Synthesis of rGH

The rGH samples were prepared by a hydrothermal reduction method. Briefly, 242 mg of ascorbic acid (ACA) powder were added to 15 mL of 4 mg/mL aqueous GO dispersion and sonicated for 2 h. The suspension was maintained at 90 °C for 2 h. Then the rGO suspension was sealed in a Teflon-lined autoclave and maintained at 120 °C for 12 h. Finally, the rGH was freeze-dried at − 60 °C under vacuum conditions.

2.4. Synthesis of carbon dots (CDs)

The CDs were prepared by a simple one-step hydrothermal method [42]. One g of glucose, 3 mL of PEG-200, and 15 mg of NaOH were introduced to 35 mL of deionized water and stirred for 0.5 h. The mixture was sealed in a Teflon-lined autoclave and heated to 150 °C for 6 h. After cooling to room temperature, the brown solution was filtered through a 0.22 μm membrane several times. The solution was dialyzed for 48 h to remove residual reactants in deionized water and the CDs were freeze-dried at − 60 °C under vacuum conditions to yield a brown powder.

2.5. Synthesis of rGH/CDs

As shown in Fig. 1, the rGH/CDs composite was fabricated hydrothermally. 40 mg of CDs were added to 10 mL of 4 mg/mL aqueous rGO dispersion and sonicated for 2 h. The suspension was sealed in a Teflon-lined autoclave and heated to 150 °C for 12 h. After cooling to room temperature, the sample was taken out with a tweezer for subsequent experiments.

2.6. Materials characterization

The surface morphology of the samples was examined by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-5600LV) and the Raman scattering spectra were acquired on a dispersive Raman spectrometer (Jobin Yvon XploRA) between 0 and 2000 cm^{-1}. The optical absorbance was determined by ultraviolet-visible spectrophotometry (UV–vis; PerkinElmer Lambda 35) and photoluminescence (PL) measurements were performed on the Edinburgh FLS 920. In the time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA Fluoro Maxe-4). All the measurements were carried out at room temperature.

2.7. Electrochemical measurements

The electrochemical measurements were performed on the CHI660E electrochemical workstation and the specific capacitance was calculated from cyclic voltammetry (CV) and galvanostatic charging/discharging curves and respectively expressed as C_1 and C_2 (F g^{-1}) as follows: [43–45]

$$C_1 = \frac{2}{mv(V_f - V_i)} \int_{V_i}^{V_f} i \, dV \tag{1}$$

$$C_2 = \frac{2i\Delta t}{m\Delta U} \tag{2}$$

where m is rGH/CDs mass of one electrode (g), V(V) is working potential with initial potential V_i and final potential V_f, and v is the potential scan rate, i is the discharge current (A), Δt is the discharge time