Hydrothermally reduced nano porous graphene–polyaniline nanofiber composites for supercapacitor

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ARTICLE INFO

ABSTRACT

Hydrothermally reduced porous graphene (PGs) and polyaniline (PANI) nanofiber composites (PGs–PANI) were prepared by interfacial polymerization of aniline in the presence of reduced porous graphene (PGs) under acidic conditions. Hydrothermal reduction of graphene oxide (GO) produced graphene quantum dots (GQDs) along with porous reduced graphene (PGs). The removal of nano sized GQDs generate several round shaped edges in the graphene, which facilitated improved charge storage. In addition to preparation of porous graphene, we developed an approach to process the PGs. We envisioned preparing conjugated polymer as processing material. The capacitive behavior of PGs was characterized using cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) techniques. The specific capacitance of hydrothermally reduced GO (PGs) and PGs–PANI composites was 185 F/g and 357 F/g at 0.1 A/g in 1 M H_2SO_4 electrolyte. The energy density of PGs–PANI composite was obtained 49.58 W h/kg at a power density of 71.8 W/kg.

1. Introduction

Energy conversion is as important as energy storage. Supercapacitors are one of the attractive storage devices because they bridge the gap between batteries and conventional capacitors. They possess higher energy densities than dielectric capacitors and exceptional long cyclability and higher power densities than conventional batteries [1,2]. Graphene [3–8] and conjugated polymer [9–14] based capacitors are widely explored due to the possibility of fabricating flexible and light weight supercapacitors. Variety of approaches had been developed to fabricate graphene based supercapacitors. Polyaniline grafted reduced graphene oxide, various graphene/polyaniline nanofiber composites [15–19] etc. have been employed as a supercapacitor material. The partially reduced graphene oxide nanosheet/polyaniline nanowafer (GNS/PANI) composites reported to exhibit a specific capacitance value of 329.5 F/g at 5 mV/s [20] and chemically modified graphene and polyaniline (PANI) nanofiber composites showed a specific capacitance of as high as 480 F/g at a current density of 0.1 A/g [21].

Recent reports indicate that more charges are stored at the edges of graphene [22–24]. This has not been explored as an approach to prepare materials for supercapacitors. We hypothesized that the edges in graphene can be expanded using porous graphene (PGs). The porous graphene can be prepared by removing graphene quantum dots (GQDs). The removal of nanosized GQDs generate several round shaped edges in the graphene, which is likely to facilitate improved charge storage. In addition to preparation of porous graphene, it is essential to develop an approach to process the PGs. We envisioned preparing conjugated polymer as processing material. Polyaniline nanofibers (PANI Nano) can be easily synthesized by interfacial polymerization [25–27]. We propose to incorporate the PGs during the synthesis of PANI Nano. This material was used as electroactive component in supercapacitors, which showed capacitance of 357 F/g. This capacitance is more than double of PGs' capacitance (185 F/g). Thus, use of combination of PANI Nano and PGs has synergistic effect in improving the performance of supercapacitors [28,29].

2. Experimental

2.1. Materials and methods

Porous graphene (PGs) have been synthesized by hydrothermal treatment of GO in autoclave at 180 °C for 12 h. This simple process resulted in producing both GQDs and porous reduced grapheme (PGs) [30,31]. The reduction is carried out using a simple hydrothermal method without any reducing agent. To prepare PGs and polyaniline nanofiber composites (PGs–PANI) by in situ

interfacial polymerization method, distilled aniline (0.3 g, 3.2 mmol) was dissolved in 10 mL of 1 M HCl solution in 20 mL chloroform ($CHCl_3$) solvent and suspension of porous reduced graphene oxide (10 mg/20 mL) in aqueous solution was prepared. Then finally ammonium peroxydisulfate (APS) (0.18 g, 0.8 mmol) in 10 mL of 1 M HCl aqueous solution was added dropwise into the aqueous layer (top layer). Polymerization was clearly observed in about 2 min with the characteristic green color of polyaniline emeraldine salt at the interface of the two layers. The bilayer solution was then allowed to keep at room temperature overnight. Then, 100 mL of D.I. water was added to the mixture followed by filtration and washing with water, ethanol and hexane successively and finally the composite was dried under vacuum at 60 °C.

Here we demonstrate the preparation of PGs–PANI nanofiber composites using an in situ polymerization method to achieve a reasonably homogeneous dispersion of graphene sheets within the PANI matrix [21].

The morphology of the GO, PGs and PGs–PANI was examined by transmission electron microscopy (TEM). X-ray diffraction (XRD) measurements were carried out for structural understanding of the graphene materials. Attenuated total reflectance (ATR)-infrared spectroscopic (ATR-IR) analyses were carried out to find out changes in different functionalities after hydrothermal modification. All the electrochemical measurements were performed using a multi channel autolab MAC 80038 instrument in a conventional three-electrode cell that consists of a PGs and PGs–PANI containing electrode material coated working electrode, a large platinum foil as a counter electrode, and Ag/AgCl as a reference electrode respectively. The electrolyte solution, 1.0 M H_2SO_4 solution, was purged with N_2 prior to the each measurement.

3. Results and discussion

Graphene oxide dispersion (4 mg/mL) was prepared in DMF by sonicating for 30 min. Then the dispersion was placed in Autoclave and heated at 180 °C for 12 h.

After the treatment in Autoclave, the reaction mixture was allowed to cool to room temperature. Then, the reaction mixture was dialyzed in a dialysis bag (3.5 kDa) for 3–4 days to separate out GQDs. The GQD free PGs in the dialysis bag were further washed with deionized (DI) water and ethanol and dried under vacuum. In order to identify the generation of GQDs from the graphene and formation of PGs, we collected the dialysis solution that was used for floating the dialysis bag. If GQDs were generated and released via the pores of the dialysis bag, then the solution outside of dialysis bag should be fluorescent. The fluorescence will be a function of the GQDs. We were gratified to note blue fluorescence, which indicates that the GQDs are ∼2–4 nm. We also dropped the solution on TEM grid. The TEM images showed the formation of GQDs with a diameter of ∼2–4 nm (Fig. 1). This is an indirect evidence for the formation of PGs from GOs by removal of GQDs. The ATR-IR spectra of GOs were recorded using powder sample (Fig. 2a). A broad peak corresponding to hydrogen bonding was observed around 3200 cm^{-1}. On the other hand, this peak almost disappeared in case of PGs. This indicates that the PGs preparation involves removal of GQDs and probable reduction of GO to graphene. Furthermore, evolution of a peak at 1555 cm^{-1}, indicates the restoration of sp^2 carbon in PGs upon removal of GQDs from GOs. PXRD was used to understand the formation of PGs (Fig. 2b). Please note that this experiment does not provide information about porosity, however, we must get information on conversion from GOs to graphene. The PXRD of GOs was found to exhibit peak at 2θ of 10.1°. After GQDs preparation, the resultant PGs showed no peak at 2θ of 10.1°. Furthermore, the PGs showed a new broad peak with peak maxima at a 2θ of 25.6°. The appearance of the peak at 25.6° is an indication of formation of graphene. The BET surface area for PGs was found to be 294 m^2/g.

Graphene oxide has been reported to show a specific surface area of 68–161 m^2 g^{-1} [32–34]. TEM experiments showed ∼2–4 nm diameter GQDs, which was collected from the dialysis solution (Fig. 1). The TEM of PGs did not show the pores due to very small pores formed during the PGs preparation. All these experiments indicate the formation of PGs, which is the envisioned and
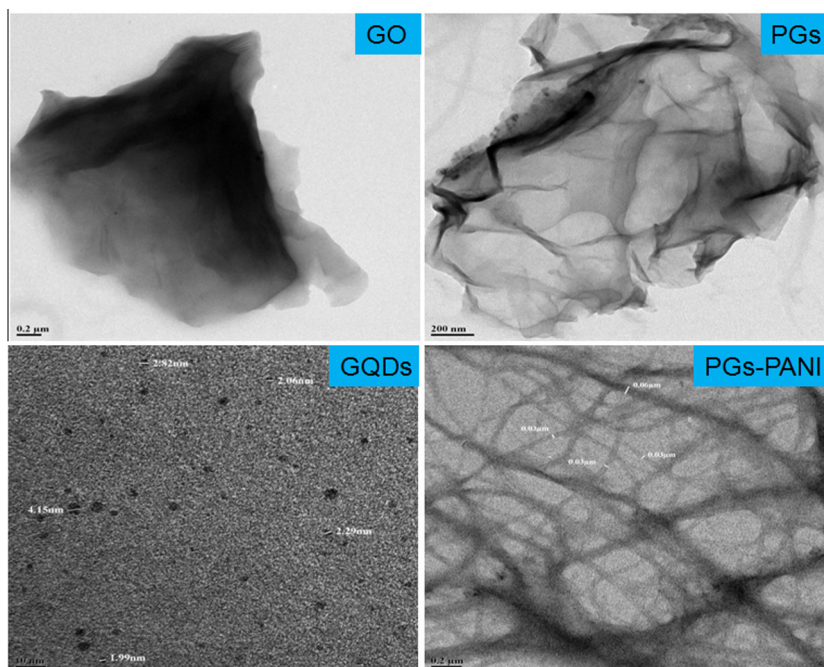
Fig. 1. TEM images of graphene oxide (GO), reduced porous graphene oxide (PGs) (scale bar 200 nm for both) and graphene quantum dots (GQDs) (scale bar 10 nm) and PGs–PANI composites (scale bar 200 nm), respectively.