# Three-dimensional reduced graphene oxide-grafted polyaniline aerogel as an active material for high performance supercapacitors

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ABSTRACT

Three-dimensional polyaniline grafted reduced graphene oxide (3D RGO-*g*-PANI) composite was prepared by an efficient two-step method. Firstly, graphene oxide sheets were grafted with PANI chains, forming graphene oxide grafted PANI composites. Secondly, RGO-*g*-PANI aerogels were obtained from GO-*g*-PANI composites by hydrothermal and drying processes. The 3D RGO-*g*-PANI aerogel composite was used as active materials to coat the glassy carbon electrodes for checking the electrochemical properties for supercapacitor application. The obtained specific capacitance was $1600\,F\,g^{-1}$ at a very high current density of $12\,A\,g^{-1}$ and an excellent cycle stability (91.3% capacitance retention after 3000 cycles), suggesting its potential application for a high performance supercapacitors.

## 1. Introduction

Supercapacitors have attracted increasing attention for energy storage applications because they can provide higher power density than batteries and higher energy density than conventional capacitors [1–3]. Many composites have been developed as active electrode materials for supercapacitors, such as carbon materials, conductive polymers and transition metal oxides/hydroxides [4–9]. Generally, carbon based materials are used in the electrical double layer capacitors (EDLCs) with the pure electrostatic charges accumulated at the electrode–electrolyte interface, whereas metal oxides and conducting polymers are used in the pseudocapacitors with fast and reversible redox or Faradaic reactions of the electroactive sites on the surface of the electrodes. Generally, in both EDLCs and pseudocapacitors, the electrochemical performance greatly depends on the surface area of electrode materials. Normally, a larger surface area is desired to achieve higher capacitance. However, proper pore size with control over the specific surface area of electrode materials is very important because the high microporosity will lead to a significant drop of capacitance at high current density [10].

Graphene, a two-dimensional (2D) sp²-hybridized carbon material, might be one of the best choices as a potential candidate for supercapacitor materials because of its excellent mechanical, electrical, thermal properties, large surface area, and high chemical stability [11]. As an electrode material for supercapacitors, graphene can provide a fully accessible high surface specific area and high conductivity [12]. However, a key issue is how to avoid the restacking of graphene sheets or 2D graphene-based composite materials during electrode preparation. Although 3D hierarchical graphene materials with high surface areas and rich pore structures are extensively tested for EDLCs [10,13]. Unfortunately, the specific capacitance is relative low at a high current density due to their large pores and low conductivity. Therefore, it is necessary to construct novel 3D structures by combining with high capacitance electrode materials, such as transition metal oxides/hydroxides and conductive polymers.

In this paper, 3D graphene-*g*-PANI (RGO-*g*-PANI) aerogels were synthesized via polymerization and hydrothermal methods. The chemical and physical properties of the prepared aerogel composite was measured on X-ray diffractometers (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, transmitted electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The RGO-*g*-PANI aerogel composites were used as modified materials of supercapacitor electrodes.

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## 2. Experimental

### 2.1. Materials

Aniline (99%, Aldrich) was distilled under reduced pressure and stored in 5 °C before use. Graphite powder (99.995%, Alfa Aesar) and the other reagents were used as received. GO was prepared by an improved Hummers method [9].

### 2.2. Synthesis of GO-g-PANI composite

GO-NH$_2$ and GO-g-PANI were prepared as described in previous work [14]. Typically, 0.5 g GO was dispersed in 100 mL anhydrous dimethylformamide. Subsequently, N-Hydroxysuccinimide (1.71 g) and N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride (2.88 g) were added to the above suspension and stirred for 2 h at 0 °C under a N$_2$ atmosphere. After that, 1.9 mL 1,3-diaminopropane was added and stirred for another 12 h at room temperature. The product was collected and washed several times with water and ethanol, and dried in a vacuum oven for 12 h at room temperature.

In a typical preparation of GO-g-PANI, 10 mg GO-NH$_2$ was first added into 10 mL HCl (1 M) solution and sonicated for 30 min. This suspension was cooled in an ice bath to 0 °C. Aniline (0.5 mL) was then added to above suspension with continuous stirring, after which, a freshly prepared solution of 1.35 g K$_2$S$_2$O$_8$ in 10 mL water was added slowly while stirring under cool conditions. The reaction was continued for a further 5 h in an ice bath. The product was filtered and washed with a diluted HCl solution to remove any unreacted monomer and oxidant. The product was then washed several times with deionized water and hexane followed by drying under vacuum for 12 h at 45 °C.

### 2.3. Synthesis of RGO-g-PANI aerogels

The GO-g-PANI composites were prepared as described in our previous report [14]. In a typical preparation of RGO-g-PANI aerogels, 30 mg GO-g-PANI composite was first dispersed in 10 mL DI water and bath-sonicated for 30 min (3 mg/mL). This mixture was transferred to a 15 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 6 h to form a hydrogel. This hydrogel was purified in a large amount of DI water for 1 week to wash out the unreacted components in the system. The water was then replaced by ethanol for three days to make an alcogel. The alcogel was dried by freeze-dried method to obtain RGO-g-PANI aerogels. For comparison, the RGO aerogel was synthesized using the same above procedure but with adding GO (3 mg/mL) suspension in the autoclave.

### 2.4. Characterization

The prepared material was measured on SEM (Hitachi, S-4200), TEM (JEM 1400, JEOL), and XPS (Kratos AXIS ULTRA). The FT-IR (Tensor 37, Brucker) spectra were conducted over 400–4000 cm$^{-1}$ with 32 scans at a resolution of 16 cm$^{-1}$. The electrochemical measurements were performed on Autolab PGSTAT100N (Metrohm, Netherlands) in a three-electrode system at room temperature. Platinum foil and AgCl/Ag electrode were used as the counter and reference electrodes, respectively. The working electrode was prepared by mixing the prepared sample (2 mg, 80 wt.%) with 15 wt.% carbon black and 5 wt.% polytetrafluorene ethylene (PTFE), and coated onto carbon paper collector (1.0 cm × 1.0 cm). The electrolyte is a 1 M H$_2$SO$_4$ solution.

The specific capacitance ($C_s$) was calculated using the equation: $C_s = It/m\Delta V$, where $C_S$, $I$, $t$, $m$, and $\Delta V$ are the capacitance (F g$^{-1}$), discharge current (A), discharge time (s), mass of active materials

(g), and discharge potential range (V), respectively. The power density and energy density are calculated from the following equations, respectively: $E = 0.5C_s\Delta V^2$; $0.5C_s\Delta V^2$; $P = E/t$, where $E$, $P$, $C_s$, $\Delta V$ and $t$ are the energy density (W h kg$^{-1}$), the power density P (kW kg$^{-1}$), the specific capacitance (F g$^{-1}$), discharging potential range (V), and the discharge time (s).

## 3. Results and discussion

### 3.1. Synthesis of the RGO-g-PANI aerogels

Fig. 1 shows photographs of the suspension of GO-g-PANI before and after hydrothermal treatment. The color of the GO-g-PANI suspension changed from grayish to black. The morphology of the prepared products was confirmed by SEM and TEM images. Fig. 2 presents SEM images of RGO aerogel, PANI and RGO-g-PANI samples at different magnifications. RGO showed an interconnected and porous 3D graphene structure, in which thin graphene sheets with distinct edges, wrinkled surfaces and foldings were clearly observed (Fig. 2a). Pure PANI revealed dendritic nanofibers with diameters of approximately 100 nm and lengths of micron size (Fig. 2b). The composite morphology showed the presence of both PANI and graphene with a 3D network at different magnifications (Fig. 2c and d). Although there is the presence of polymer chains in the composite structure, it still has a high porosity. This porous structure can facilitate electrolyte ion trapping and access to the surface of the electrode, which will enhance the electrolyte ion transportation during the charge/discharge process. The morphology of all above samples is better presence in the TEM images (Fig. 3). The G-g-PANI aerogel showed a much different morphology from PANI and bare RGO aerogel due to the polymer nanofibers connecting the graphene sheets. The content of PANI in the RGO-g-PANI composite is 84.5 wt.% that is
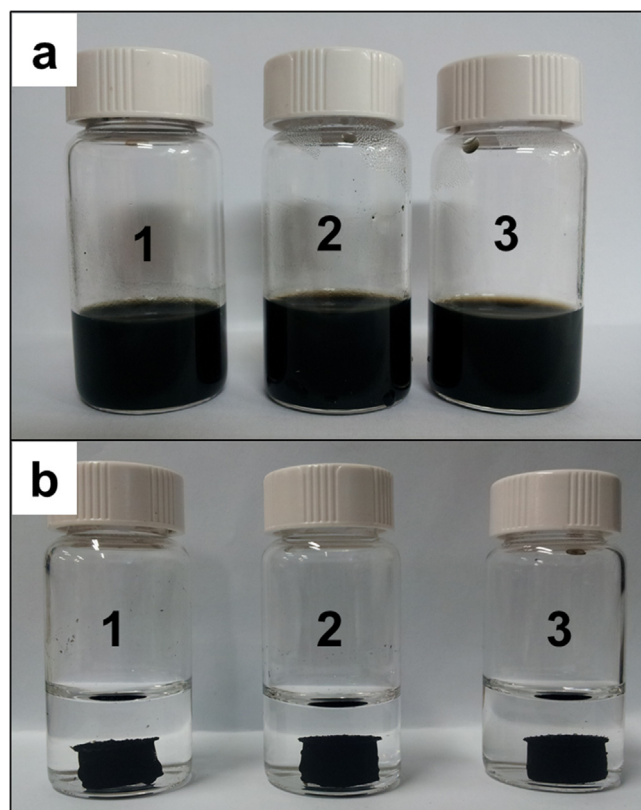


**Fig. 1.** Photographs of GO-g-PANI suspensions before and after hydrothermal treatment to form hydrogels.