



# Vanadium oxide assisted synthesis of polyaniline nanoarrays on graphene oxide sheets and its application in supercapacitors



Amin Goljanian Tabrizi<sup>a</sup>, Nasser Arsalani<sup>a,\*</sup>, Hassan Namazi<sup>b</sup>, Iraj Ahadzadeh<sup>c</sup>

<sup>a</sup> Research Laboratory of Polymer, Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran.

<sup>b</sup> Carbohydrate Laboratory, Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran.

<sup>c</sup> Research Laboratory of Electrochemical Instrumentation and Energy Systems, Faculty of Chemistry, University of Tabriz, Tabriz, Iran.

## ARTICLE INFO

### Keywords:

Graphene oxide  
Polyaniline  
Nanoarrays  
Supercapacitors  
Nanocomposite

## ABSTRACT

In this work, a novel approach was developed for creation of polyaniline (PANI) nanoarrays on graphene oxide (GO) sheets. *In-situ* polymerizations of aniline monomer, in the presence of two oxidants, were used. For this means, firstly, nanocoons of PANI were created on GO sheets by using  $V_2O_5$  as oxidant, followed by further growth of these structures by using ammonium persulfate (APS) as oxidant to achieve unique nanoarrays of PANI on GO sheets (PANI/GO-V-APS nanocomposite). For comparison, other nanocomposites were also prepared by separately application of APS and  $V_2O_5$  as oxidants. Some characterization techniques including XRD, FT-IR, Raman, FE-SEM, and TGA were used to elucidate the structure of nanocomposites. The results revealed well-formed nanoarrays of PANI on GO for nanocomposites, which synthesized by sequential application of oxidants. Furthermore, PANI/GO nanocomposite prepared by sequential approach showed the highest current density among all the nanocomposites. In addition, the charge-discharge experiments demonstrated that the specific capacitance of the PANI/GO-V-APS composite was  $712 \text{ F g}^{-1}$  at the current density of  $0.5 \text{ A g}^{-1}$  in  $1 \text{ M H}_2\text{SO}_4$  solution, which was significantly higher than that of two other nanocomposites. Moreover, the composite displayed good cycle stability retaining 83% of its original specific capacitance after 6000 charge-discharge cycles. Beside these achievements, the EIS results proved that the capacitance of PANI/GO-V-APS nanocomposite was higher than other nanocomposites.

## 1. Introduction

Supercapacitors are recently introduced technologies with many potential applications in electronic devices due to their unique characteristics including fast and reversible charge-discharge capability, long cycle life, and little impact on the environment [1–3]. Among the candidate materials for supercapacitors, graphene oxide (GO) is a promising candidate owing to its high specific surface area, high power density, long cycle life, and excellent mechanical property [4]. However, because of less conductivity of GO, some electroactive polymers such as polyaniline were utilized to remedy this deficiency and enhance the theoretical specific capacitance [5–8]. In this context, many efforts have been devoted to create polyaniline nano structures on the surfaces of graphene oxide sheets, which can be classified as chemical and physical approaches [9–11]. In the first approach, the functionalization of GO with amino groups is the basic stage to create active heterogeneous sites, followed by the growth of polyaniline nano structures on these sites [12–14]. In the latter approach, the electrostatic interactions between anilinium monomers in acidic solution and oxygen-containing

functional groups on GO sheets is the main feature for heterogeneous growth of polyaniline nano structures [15]. The latter approach is the more promising thanks to its simplicity and needless to functionalization of GO.

Physically, creation of polyaniline nano structures with various morphologies on GO sheets was reported in many documents with considerable pseudocapacitance behavior. Xu et al. [15] prepared hierarchical nanocomposites of polyaniline nanowire arrays on GO sheets *via* dilute polymerization of aniline monomer in the presence of GO. The specific capacitance of the nanocomposite reached as high as  $555 \text{ F g}^{-1}$  at a discharge current density of  $0.2 \text{ A g}^{-1}$ , which was much higher than  $298 \text{ F g}^{-1}$  of random connected PANI nanowires obtained in the same conditions. In addition, the cycle life of this composite is also much better than that of random connected PANI nanowires. Meng et al. [16] developed 3D-RPANI/GO composite by dilute polymerization, which exhibited higher capacitance than 3D-RGO as a result of the pseudocapacitance of PANI. Yu et al. [17] fabricated porous reduced graphene oxide foam/PANI composite by *in-situ* polymerization. The evaluation of its performance in a symmetric device exhibited high

\* Corresponding author.

E-mail address: [arsalani@tabrizu.ac.ir](mailto:arsalani@tabrizu.ac.ir) (N. Arsalani).

specific capacitance ( $790 \text{ F g}^{-1}$ ). Hao et al. reported the preparation of cross linked-polyaniline (CPA) nano-pillar arrays adsorbed on the surface of reduced graphene oxide (RGO) followed by two-step reduction using cyclic voltammetry. The composite showed very high specific capacitance of  $1532 \text{ F g}^{-1}$  at a scan rate of  $10 \text{ mV s}^{-1}$ . Based on this brief literature review, *in-situ* polymerization of dilute solution of aniline in the presence of substrate is the dominant method for the preparation of PANI nano structures on GO sheets. In another study, Li et al. synthesized 1D polyaniline nanofibers with micrometer length and nanometer diameters containing nano rod-like structures of polyaniline on micro fibers surfaces using vanadic acid as oxidant. It was our motivation to investigate the possibility of creating nano arrays of polyaniline on GO sheets via  $\text{V}_2\text{O}_5$  as oxidant. To the best of our knowledge, there is not any report in literature in this context.

In this work, our goal is to investigate the preparation of polyaniline nano arrays on GO sheets by sequential application of  $\text{V}_2\text{O}_5$  and ammonium peroxide sulfate as oxidants.  $\text{V}_2\text{O}_5$ , as a weak oxidant, was used to create PANI nanocones as heterogeneous active sites on GO sheets, which followed by further growth of these sites with ammonium persulfate to achieve nanowires with well-defined morphology and porosity. At the end, the electrochemical behavior of synthesized PANI/GO nanocomposite was evaluated in a supercapacitor device.

## 2. Experimental

### 2.1. Materials

Pristine graphite, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and ammonium persulfate (APS), Vanadium oxide ( $\text{V}_2\text{O}_5$ ) were all purchased from Merck and were used as received. Aniline was purchased from Aldrich and distilled before use.

### 2.2. Preparation of graphene oxide (GO)

An improved Hummers method [18] was used to synthesis GO from natural flake graphite. In brief, graphite powder (1.0 g) was dispersed in a mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  (120 and 13.5 mL, respectively) and stirred during 24 h. Then,  $\text{KMnO}_4$  (6.0 g) was gradually added into above solution under continuous stirring at a temperature below  $30^\circ\text{C}$  followed by stirring at room temperature for 3 days. After cooling down to room temperature, the reaction mixture poured into 400 mL frozen water and subsequently, 5 mL of  $\text{H}_2\text{O}_2$  was added. The resulting suspension was washed by centrifugation with 10% HCl; then, by water to remove residuals. The obtained graphite oxide was sonicated to achieve a stable GO dispersion in water. Finally, the resultant dispersion was subjected to centrifugation at 5000 rpm to remove the un-exfoliated graphite oxide. The purified GO was diluted by water to achieve  $1 \text{ mg mL}^{-1}$  GO dispersion for further use.

### 2.3. Synthesis of PANI/GO nanocomposite by different oxidants

(A) *Synthesis of PANI/GO nanocomposite by sequential addition of  $\text{V}_2\text{O}_5$  and APS (PANI/GO-V-APS)*: PANI/GO nanocomposite was synthesized by *in-situ* polymerization in the presence of GO and aniline monomer [15]. For 100 mL of GO dispersion ( $1 \text{ mg mL}^{-1}$ ), 500 mg of  $\text{V}_2\text{O}_5$  and 10.25 mL  $\text{HClO}_4$  (1 M) were added, then, sonicated for 30 min. After cooling down to  $0\text{--}4^\circ\text{C}$ , aniline was added (0.05 M), followed by stirring the resultant mixture for 60 min. After that, the APS solution was added to the mixture (the molar ratio of APS:Aniline was 3:2) and stirred in ice bath during 24 h. Finally, the product was repeatedly washed with water and methanol to remove the residual oxidant. The final precipitate was freeze-dried.

(B) *Synthesis of PANI/GO nanocomposite by  $\text{V}_2\text{O}_5$  (PANI/GO-V)*: The procedure was similar to procedure (A) but here, the APS was not added.

(C) *Synthesis of PANI/GO nanocomposite by APS (PANI/GO-APS)*: The procedure was similar to procedure (A) without the addition of  $\text{V}_2\text{O}_5$ .

The preparation of neat PANI nanofibers was also carried out similar to method (C) without the addition of GO in the reaction mixture.

### 2.4. Instruments

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics TENSOR 27 spectrometer using KBr pellets. The morphology and microstructure of the synthesized sample was characterized by a field-emission scanning electron microscopy (FE-SEM MIRA3 FEG-SEM, Tescan, Czech). The Raman spectra of samples were measured by Bruker Raman Instrument (Germany). The XRD patterns of samples were recorded on a Siemens D-500 Diffractometer using  $\text{Cu K}\alpha$  radiation (wavelength,  $\lambda = 1.5406^\circ\text{A}$ ) in the  $2\theta$  range of  $10^\circ\text{--}80^\circ$ . The thermo-gravimetric analysis (TGA) was performed with a thermal analysis system (Linseis L81A1750, German), within a temperature range of  $25\text{--}800^\circ\text{C}$  and a heat rate of  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.

### 2.5. Electrochemical measurements

In order to construct working electrodes, firstly, slurry was prepared from a mixture of 80 wt.% active materials (PANI/GO nanocomposite), 10 wt.% carbon black, and 10 wt.% polyvinylidene fluoride dissolved in *N*-methylpyrrolidone; then, it was kneaded and the resultant pastes were pressed onto carbon paper and dried at  $60^\circ\text{C}$  for 12 h for further evaluation. In a three-electrode system, 1 M  $\text{H}_2\text{SO}_4$  was used as the electrolyte, platinum wire and saturated calomel electrodes were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV), galvanostatic charge-discharge (GSCD) and the electrochemical impedance spectroscopy (EIS) of the prepared electrode materials were performed by an Electrochemical Station (SP-150, Bio-Logic). The frequency range of EIS data was from 100 kHz to 0.01 Hz and the amplitude of the sinusoidal voltage was 5 mV.

## 3. Results and discussion

A schematic of two-step synthesis of nanoarrays of PANI on GO via *in-situ* oxidative polymerization of aniline by sequential application of  $\text{V}_2\text{O}_5$  and APS as oxidants is represented in Scheme 1. As shown in schematic, in the first step, the  $\text{V}_2\text{O}_5$  acts as a nucleation agent for polymerization of anilinium monomer on GO sheets and in the second step, the presence of APS accelerates the nanoarray growth. Whereas in the absence of  $\text{V}_2\text{O}_5$ , the growth of PANI chains on GO surface is disordered, maybe due to the formation of some micelles as a result of homogenous nucleation. On the other hand, the nanoarrays are not only formed on GO sheets, but also in the solution phase.

Fig. 1 shows the FT-IR spectra of GO, neat PANI, and the PANI/GO nanocomposites synthesized by  $\text{V}_2\text{O}_5$ , APS, and sequential application of them as oxidant at  $0\text{--}4^\circ\text{C}$  for 24 h. The FT-IR spectrum of GO illustrates the presence of C=O at  $1734 \text{ cm}^{-1}$ , benzenoid C=C at  $1610 \text{ cm}^{-1}$ , C–O–C at  $1059 \text{ cm}^{-1}$ , C–OH at  $1224 \text{ cm}^{-1}$ , and O–H at  $3427 \text{ cm}^{-1}$  [13,19,20]. For neat PANI, the peaks at  $1555$  and  $1480 \text{ cm}^{-1}$  correspond to the characteristic C–C stretching of the quinoid and benzenoid rings, respectively. The peaks at  $1309$  and  $1243 \text{ cm}^{-1}$  are related to C–N and C=N stretching vibrations. The peak at  $1130 \text{ cm}^{-1}$  is assigned to the in-plane bending of C–H. The peak at  $799 \text{ cm}^{-1}$  is attributed to the out-of-plane bending of C–H bonds. The wide band nearby  $3400 \text{ cm}^{-1}$  are attributed to N–H stretching in the quinoid ring of the emeraldine base and emeraldine salt along with O–H stretching of water [21,22]. The prepared PANI/GO nanocomposites had distinctly some of the characteristic peaks of GO and PANI, indicating the presence of a conductive nanocomposite structure. Furthermore, slightly decrease in the intensities of the peaks

Download English Version:

<https://daneshyari.com/en/article/4907840>

Download Persian Version:

<https://daneshyari.com/article/4907840>

[Daneshyari.com](https://daneshyari.com)