



# Electrochemical Growth of Polyaniline Nanowire Arrays on Graphene Sheets in Partially Exfoliated Graphite Foil for High-Performance Supercapacitive Materials



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## ARTICLE INFO

### Article history:

Received 19 January 2017

Received in revised form 10 March 2017

Accepted 5 April 2017

Available online 12 April 2017

### Keyword:

Polyaniline  
nanowire array  
graphene sheets  
supercapacitor  
high mass loading

## ABSTRACT

Direct electrochemical growth of polyaniline nanowire arrays (PANI NWAs) on surfaces of graphene sheets in partially exfoliated graphite foil (Ex-GF) was achieved through electropolymerization of aniline to fabricate hierarchical nanostructured pseudocapacitive electrodes. The PANI NWAs were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Due to the combined merits of PANI NWA and graphene sheets, the hierarchical nanostructured electrodes demonstrated high pseudocapacitive performances. More importantly, fast capacitance fading of pseudocapacitive materials upon mass loading increase can be suppressed by the novel structure, making it a good candidate for supercapacitor electrode with high areal capacitance. The PANI NWA with a high mass loading of  $5.89 \text{ mg cm}^{-2}$  showed an exceptionally high areal capacitance of  $3.57 \text{ F cm}^{-2}$  and a quite high specific capacitance  $607 \text{ F g}^{-1}$ . 72.4% of the capacitance can be retained when the discharge current increase 10 times, demonstrating its high rate capability.

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## 1. Introduction

Graphene and reduced graphene oxide (rGO) have been widely studied in supercapacitors due to their good electric conductivity and large surface area. However, carbon-based materials generally provide limited capacitance as they mainly store charge through electric double-layer. In addition, graphene sheets also suffers from restacking caused by the strong inter-planar van der Waals forces, which greatly decreases the specific surface area and hinders the ion transportation for electrochemical energy storage [1,2]. Incorporating pseudocapacitive materials with graphene and rGO is a promising way to fabricate high performance supercapacitor electrode materials [3]. Binder-free composite electrodes of graphene and pseudocapacitive materials can be constructed through deposition of conducting polymers and their hydrides on graphene electrodes, to avoid the disadvantage of powder samples [4–9]. In 2009, Cheng and co-authors reported a high performance flexible supercapacitor electrode through electrochemical deposition thin polyaniline (PANI) film on freestanding graphene paper. The obtained composite paper displayed a high specific capacitance of  $233 \text{ F g}^{-1}$ , which is much higher than the graphene paper

due to the combined charge storage mechanisms of electric double layer charging/discharging and pseudocapacitive redox reactions [10]. The charge storage properties were further improved through combing the advantages of freestanding graphene paper and PANI nanorod arrays [11]. It was demonstrated that the polymerization of aniline can be controlled to deposit PANI particles on surfaces of rGO nanosheets in 3D porous rGO template, leading to a high PANI (with a mass loading of  $\sim 1.3 \text{ mg cm}^{-2}$ ) based specific capacitance of  $746.7 \text{ F g}^{-1}$  at  $\sim 1.9 \text{ A g}^{-1}$ . It can retain 76.5% of its capacitance after 2000 charge/discharge cycles. The low aniline concentration was ascribed to be the key parameter to control the growth of PANI partical on rGO sheet surface of the rGO template, instead of only around the periphery of the film. In high aniline concentration, large amount of PANI rapidly generated only at the surface of rGO template due to fast polymerization at the beginning of the reaction, blocking the pores of rGO structure. So ammonia persulfate molecules had no time to diffuse into the template to initiate aniline polymerization inside rGO [2]. A high performance 3D RGO/PANI electrode was fabricated through growth of PANI nanowire array (NWA) on surfaces of graphene sheets in 3D RGO by a dilute chemical polymerization procedure in the presence of 0.01 M aniline to guarantee a well-controlled nucleation-growth condition for the PANI nanowires. Due to the formation of PANI nanowire arrays on graphene sheets, the composite electrode displayed an improved rate performance [1]. It was reported that

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heterogeneous deposition of PANI is to be suppressed by low aniline concentration for the chemical growth of polymer NWA on the skeleton of graphene sheets in 3D porous RGO foam [12].

The oriented open nanostructure of PANI NWA directly grown on graphene sheets is very helpful to achieve the high capacitance and high rate advantages of supercapacitors. It is helpful to address the “dead volume” problem to effectively utilize active materials for charge storage. Moreover, facile electron transportation channels can be constructed through graphene sheets and the NWA, while the voids among the polymer nanowire would provide ion diffusion path for fast Faradaic reactions. So the growth of ordered nanostructures of PANI on surfaces of graphene sheets has been widely studied, mostly through wet chemical process [13–17]. Compared with chemical polymerization of aniline on graphene sheets to get powder samples of the composite, which binder materials are needed for the following electrode fabrication, electrochemical polymerization enables active materials to be deposited on electrodes directly, resulting in uniformity, good adhesion and compact interface. However, reports on such topic are very limited and mostly on surfaces of solid substrates, instead of on graphene sheets. Liu and coauthors reported a step-wise electrochemical growth of PANI NWA on Pt, Au, Ti and Si plate and investigated their potential application in chemical- and bio-sensing [18,19]. Wang and coauthors successfully fabricated PANI NWA on Au plate through one-step constant current polymerization of aniline at low current. The PANI NWA with low mass loading (although not provided in the paper, it can be deduced from the small amount of charge of  $Q=0.036\text{C}$  passed for aniline polymerization) displayed a high specific capacitance of  $950\text{Fg}^{-1}$  at  $1\text{Ag}^{-1}$ . However, only 500 cycles stability test was shown, which is insufficient for supercapacitor application [20]. PANI nanorod array was electrochemically grown through using a mixed solvent of water and ethanol (with a 1:1 volume ratio) on surfaces of graphene paper that was fabricated through simultaneous assembly and reduction of graphene oxide dispersion [21]. The obtained composite film displayed a high composite based specific capacitance of  $763\text{Fg}^{-1}$  at  $1\text{Ag}^{-1}$ , however, it could only retain 64.2% of its capacitance upon 10 times current increase. PANI nanocone array was reported to be electrochemical deposited on 3D graphene network. It was reported by the authors that the nanocone array growth was attributed to the low polymerization current density. The obtained sample with the mass loading of ca.  $0.5\text{mgcm}^{-2}$  exhibited a high specific capacitance of  $751\text{Fg}^{-1}$  at  $1\text{Ag}^{-1}$ , and 88.4% of its capacitance was retained when the discharge current increased 10 times [22].

Recently, Feng et al. demonstrated the fabrication of GO/PANI nanocomposite electrode through interfacial electrochemical growth of PANI nanorod array on negatively charged GO sheets, which were originally suspended in aqueous phase and adsorbed on stainless steel foil as a sublayer due to the existence of electric field. The growth of PANI nanorod array was ascribed to the stable low aniline concentration at water/chloroform interface for the necessary low polymerization rate. The afforded PANI nanorod array displayed a high specific capacitance of  $1095\text{Fg}^{-1}$  at  $1\text{Ag}^{-1}$ , however the mass loading may be low as deduced from the small amount of charge of  $Q=0.09\text{C}$  for aniline polymerization. The rate capability was also needed to be further improved (with 60% capacitance retention upon 20 times current increase) [23].

Herein, we studied the electrochemical growth of PANI NWAs on surfaces of graphene sheets which were partially exfoliated from graphite foil (Ex-GF). PANI NWAs were successfully grown from aniline solutions with a wide concentration range of 50 to 500 mM at appropriate polymerization current or charge. Moreover, NWAs with high polymer loading can be fabricated, leading to pseudocapacitive materials with large areal capacitance. A

seamless connection between polymer, graphene sheets and graphite substrate was achieved, ensuring a facile electron and ion transfer in the composite. PANI NWA with a relatively high polymer mass loading of  $1.29\text{mgcm}^{-2}$  ( $Q=2.7\text{C}$  passed for aniline polymerization) displayed a high specific capacitance of  $840\text{Fg}^{-1}$  at  $1\text{Ag}^{-1}$ . An excellent rate capability was also demonstrated, 86.5% of the capacitance was retained at 10 times increase of the discharge current. PANI NWA with a mass loading as high as  $5.89\text{mgcm}^{-2}$  was also successfully fabricated through prolonged polymerization at high current. It showed an exceptionally high areal capacitance of  $3.57\text{Fcm}^{-2}$  and a quite high specific capacitance  $607\text{Fg}^{-1}$ , and 72.4% of the capacitance can be retained when the discharge current increase 10 times. This opens up a new direction for the fabrication of pseudocapacitive materials with large areal capacitance to meet the requirement of supercapacitors with high volumetric capacitance—one of the key factors for its application in portable energy storage system, while also maintaining good rate capability and cyclic stability.

## 2. Experimental

### 2.1. Materials

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received, except for aniline which was distilled under reduced pressure before use. Graphite foil (GF) produced from natural expanded graphite was obtained from SGL group (Germany).

### 2.2. Partial exfoliation of graphite foil

Partial exfoliation of graphite foil was conducted by two electrochemical steps as described in our previous report [24]. In the first step, the graphite foil ( $1\times 1\text{cm}^2$ ) was potential dynamically scanned between 0.5 and 1.8 V at  $20\text{mVs}^{-1}$  in  $0.5\text{MK}_2\text{CO}_3$  aqueous solution for six cycles, using a platinum plate and a SCE as counter and reference electrodes, respectively. Subsequently, the working electrode was treated in  $1\text{M KNO}_3$  by advanced cyclic voltammetry from  $-0.9$  to  $1.9\text{V}$  at  $20\text{mVs}^{-1}$  for ten cycles, with the potential holding at  $1.9\text{V}$  for 5 s at each cycle. The obtained partial exfoliated graphite foil (Ex-GF) electrode was washed with ethanol and de-ionized water to remove residuals.

### 2.3. Electrochemical fabrication of ordered polyaniline nanowire arrays on partial exfoliated graphite foil

Electrochemical fabrication of ordered PANI NWA was conducted on the Ex-GF ( $1\times 1\text{cm}^2$ ) through electrochemical polymerization of aniline in aqueous solutions containing  $1\text{M HClO}_4$  and 50, 100 and 500 mM aniline, respectively, with a platinum plate and a SCE as the counter and reference electrode. The polymerizations were carried out at a constant current density of  $0.5\text{mAcm}^{-2}$  for 1.5 h ( $Q=2.7\text{C}$ ) to afford PANI NWA electrodes labeled as PANI 50 mM–0.5 mA–2.7 C, PANI 100 mM–0.5 mA–2.7 C and PANI 500 mM–0.5 mA–2.7 C.

The electropolymerization at  $0.5\text{mAcm}^{-2}$  in solutions containing 100 mM and 500 mM aniline were also prolonged to 3 h ( $Q=5.4\text{C}$ ) and 6 h ( $Q=10.8\text{C}$ ), respectively to afford PANI 100 mM–0.5 mA–5.4 C and PANI 500 mM–0.5 mA–10.8 C. The electropolymerization in the solution containing 500 mM aniline was also conducted at  $1.0\text{mAcm}^{-2}$  for 3 h ( $Q=10.8\text{C}$ ) to afford PANI 500 mM–1.0 mA–10.8 C.

To investigate the influence of polymerization current on PANI NWA fabrication, electropolymerizations were also conducted in 50 mM aniline at 0.2 and  $1.0\text{mAcm}^{-2}$  for 3.75 h and 45 min,

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