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A unique solar radiation exfoliated reduced graphene oxide/polyaniline nanofibers composite electrode material for supercapacitors

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ABSTRACT

Solar radiation exfoliated reduced graphene oxide (SRGO) and polyaniline nanofibers (PANi NFs) containing composite is synthesized using the typical chemical oxidative polymerization. The composite exhibits an excellent specific mass capacitance of ~655 F/g owing to an optimal chemical interaction between SRGO and PANi NFs in the composite. Specific mass capacitance of the composite remains almost constant at different current densities making it expedient as a working electrode material in supercapacitors.

1. Introduction

Any hybrid supercapacitor's performance depends mainly on its working electrode material [1,2]. In this context, various composite materials constituted by graphene (in modified forms namely graphene oxide (GO), reduced GO, functionalized GO and few-layered graphene) and polyaniline (PANi) (in different morphologies) have been recently developed [3–5]. It is observed that the processing of these composites is greatly influenced by the synthesis procedures of graphene (in modified forms) [3]. Owing the innate nature of these procedures, it is more than often noticed that the graphene does not properly blend with PANi. In this work, processing and characteristics of a unique composite (constituted by solar radiation exfoliated reduced graphene oxide (SRGO) and polyaniline nanofibers (PANi NFs)) material exhibiting an excellent specific mass capacitance of ~655 F/g are discussed.

2. Synthesis procedure

As-synthesized GO was spread over a petri dish and sunlight was focussed on to GO using a converging lens leading to photo-thermal reduction and simultaneous exfoliation of GO (owing to rapid local heating of GO) to obtain SRGO. Synthesis procedures of GO and SRGO and other experimental details are included in Supplementary data (SD). Polymerization of aniline in the presence of SRGO (Fig. S1, SD) was carried out by first taking 250 ml of aqueous HCl (1 M) in a 1 L round-bottom flask and adding 20 ml of vacuum distilled aniline to it; to this reaction mixture, 1 wt% of as-synthesized SRGO (relative to the amount of aniline) was added and the resultant mixture was ultrasonicated for 1 h to disperse SRGO uniformly. The resultant mixture was then cooled to 0 °C using an ice bath. The polymerization was then initiated by rapidly adding (1:4 M ratio w.r.t. aniline) ammonium perdisulfate (APS) to the reaction mixture. During APS addition, temperature of the reaction mixture was maintained in 0–5 °C range. After APS addition, the reaction mixture was stirred for 4 h. Then the suspension was filtered to obtain a wet cake which was washed with water, then with methanol, and finally with diethyl ether. The washed dark green coloured cake was finally dried at 90 °C under vacuum for 48 h to obtain SRGO/PANi NFs composite (Fig. 1).

3. Results and discussion

It is evident from secondary electron micrographs (Fig. 1(a) and (b)) that PANi NFs (diameter=20–50 nm) have nucleated and grown all over the SRGO surfaces. Such fibrous morphology was previously found advantageous [6]. Raman spectra of GO, SRGO and SRGO/PANi NFs composite are shown in Fig. 2. Well-documented D and G bands (Fig. 2(a)) at 1334 and 1596 cm^{-1}, respectively, are identified in both GO and SRGO cases. The intensity ratio (I_D/I_G) in the case of SRGO is greater in comparison to that of GO. This indicates a decrease in the size of the in-plane sp^2 domains and the removal of the oxygen functional groups from

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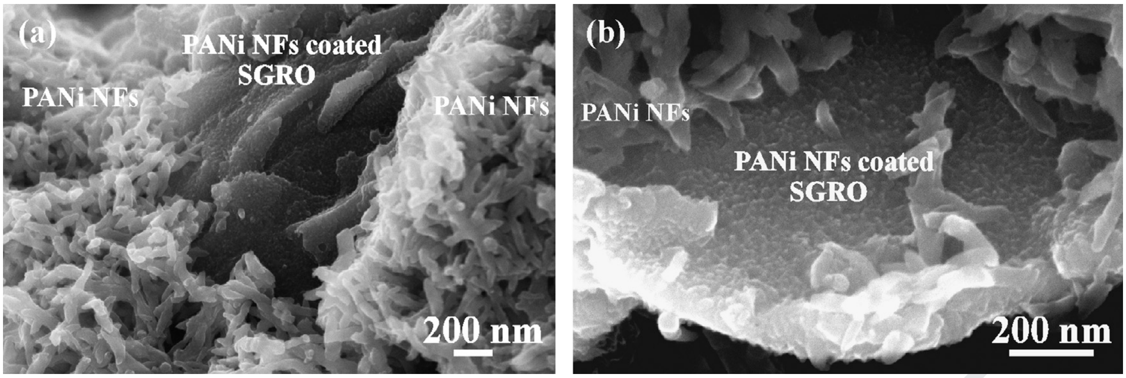

Fig. 1. Secondary electron micrographs ((a) and (b)) of SGRO/PANi NFs composite.

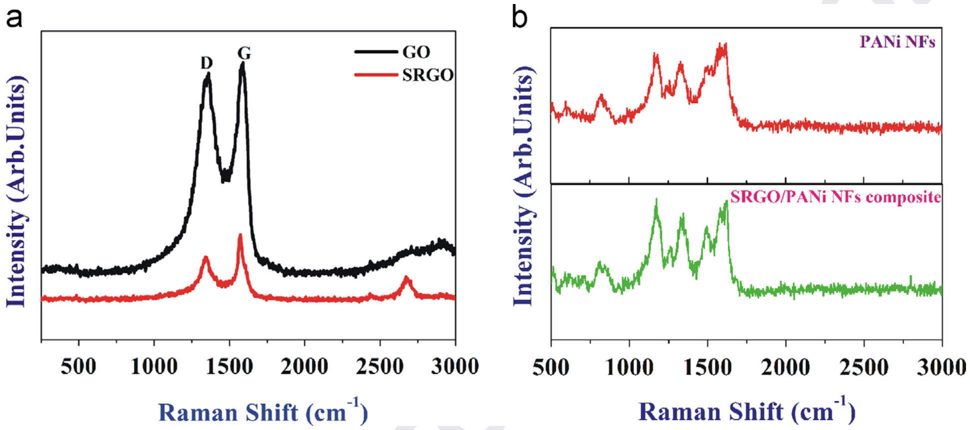

Fig. 2. Raman spectra of (a) GO and SRGO and (b) PANi NFs and SRGO/PANi NFs composite.

GO. The intensity of D band in the case of SRGO is higher in comparison to that of GO indicating that SRGO has defects and partially disordered structure. Raman spectrum of PANi NFs [6] (Fig. 2(b)) resembles that of PANi in emeraldine salt form (SD). Raman spectrum of SGRO/PANi NFs composite shows clear differences in comparison to that of PANi NFs (Fig. 2(b)). The spectrum reveals shift in wave numbers and change in intensity of typical Raman bands of PANi. C–H bending (at ~1169 cm^{-1}) in the quinoid rings of PANi is prominent in the case of composite. This implies that the presence of SRGO stabilizes the polaronic structure of PANi. In other words, PANi is more polaronic in the presence of SRGO. Similarly C=N stretching (at ~1339 cm^{-1}) associated with the quinoid rings (bipolarons) of PANi is also prominent in the case of composite.

Other Raman bands at ~608 (and ~824 cm^{-1}), ~1245 cm^{-1}, ~1497 cm^{-1}, ~1566 cm^{-1} and ~1618 cm^{-1} corresponding to out-of-plane C–H vibrations in the aromatic rings, C–N of the benzene diamine units, C–C plus C–N stretching, C=C of the quinoid rings, and C–C of the benzenoid rings, respectively in PANi are also identified in the case of composite. The presence of the benzene rings in the polaronic structure could amplify π–π interaction with the graphitic walls (between the delocalized electrons of the SRGO and the aromatic rings of the PANi). During the synthesis as the monomer polymerizes over the SRGO walls it stabilizes the above mentioned π–π interactions. The so attained polaronic character allows the further formation of planar polymer chains (favouring the stacking of the chains over SRGO), and the predominance of benzenoid rings favours the π–π interaction with the SRGO. X-ray diffraction (XRD) analysis (please see SD) of the composite (Fig. S2, SD) clearly indicates the formation of SRGO/PANi NFs composite in which PANi NFs are in semi-crystalline state [6,7]. All in all, Raman scattering and XRD analyses indicate the formation of the composite and a definite chemical interaction between the components constituting the composite. The analyses also clearly indicate that the interaction between the components is enhanced in comparison to a similar composite with thermally exfoliated reduced GO [7].

Brunauer–Emmett–Teller (BET) specific surface areas of GO, SRGO and SRGO/PANi NFs composite are 51.3, 107.5 and 197.5 m^2/g, respectively. Interestingly, the specific surface area of the SRGO/PANi NFs is higher than that of pure SRGO indicating that SRGO is well-dispersed in the composite and it has inhibited the restacking of the graphene sheets. The composite is found to exhibit mesoporosity (with pore sizes in the range 10–50 nm) (Fig. S3, SD) which can play a major role in enhancing the performance of supercapacitor devices as it allows the fast diffusion of electrolytes and thereby improving electrolyte access to high interfacial area. Moreover, the low hysteresis in N_2 adsorption/desorption isotherm (Fig. S3, SD) of composite indicates its capacity to store more charges when used as an electrode.

Cyclic Voltammetry (CV) curves of SRGO/PANi NFs composite are shown in Fig. 3(a). The characteristics (superposition of SRGO and PANi NFs [6,7] characteristics) observed in the case of SRGO/PANi NFs composite is similar to other composites [3,6]. Appearance of the pair of redox peaks and reversible charge–discharge behaviour [6,7] are evident (Fig. 3(a)). The peak current in the case of composite was higher than that of PANi NFs [6] and SRGO, indicating that SRGO has effectively increased the composite's capacitance [7]. The area under composite's CV curve (at same scan rate) is larger than that of GO, SRGO (Fig. S4, SD) and PANi NFs [6] implying a higher specific mass capacitance for the composite.

Specific capacitance C_S values of GO, SRGO and SRGO/PANi NFs composite at a scan rate of 5 mV/s are 36.2, 112.5 and 654.8 F/g, respectively. C_S values at different scan rates (Fig. 3(b)) clearly show

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