Synthetic Metals 160 (2010) 134–138

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Surfactant assisted processable organic nanocomposite dispersions of polyaniline–single wall carbon nanotubes

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ARTICLE INFO

Article history:
Received 14 May 2009
Received in revised form 8 September 2009
Accepted 15 October 2009
Available online 18 November 2009

Keywords:
Polyaniline
SWNT
Surfactant
Organic dispersion
Conductivity

ABSTRACT

In this paper, we report a surfactant assisted processable organic dispersions of conducting form of polyaniline (PANI) with and without single wall carbon nanotubes (SWNTs). We used and compared the role of two anionic surfactants namely, sodium dodecylbenzene sulfonate (NaDBS) and sodium dodecyl sulfate (SDS). Based on our results, we believe that hydrophobic interactions between surfactant tails with SWNTs and the strong interactions between PANI–surfactant headgroups are very much likely to be responsible for stabilizing this three phase system in the organic solvent. In PANI–SWNT nanocomposites prepared using SDS, electronic like band of PANI is significantly affected as well as localization of the charge carriers is observed using UV–vis spectroscopy compared to nanocomposites prepared using NaDBS. These interactions are reflected in lower conductivity of the PAN–SWNT nanocomposites prepared using SDS indicating NaDBS has better doping effectiveness in PANI–SWNT nanocomposites. This facile route offers the processing of PANI–SWNT from single organic medium and in addition, eliminates the steps of de-doping, dissolution in suitable solvent and re-doping to regain the conductivity of the nanocomposite.

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1. Introduction

In general the conducting form of polyaniline is regarded as intractable in nature [1]. In a significant development counter ion induced processability in a range of organic solvents is demonstrated by Cao et al. [2]. After that various authors reported the use of surfactant micellar solutions as a polymerization medium to produce polyaniline nanoparticles [3]. On the other hand to exploit the potential of SWNT, effective exfoliation is a prerequisite. Various methods are reported in literature, which aimed at efficient exfoliation of CNTs either in polymer or solvent [4]. Among the demonstrated approaches, dispersion of CNT with the aid of surfactant involves no chemical reaction and is a one step method to disperse CNT in aqueous media [5]. In addition, it is also reported that surfactant molecules can also act as an 'interfacial link' between nanotubes and polymer through strong hydrophobic interactions [6].

The combinations of polyaniline–single wall carbon nanotubes (SWNTs) are pursued with an interest to find niche applications in the variety of electronic devices [7]. For e.g. Ramamurthy et al. reported nanocomposite using solution processing [8]. CNTs in various wt.% were added to emeraldine base solution of polyaniline. This solution is then poured on ITO coated glass slide and the device was made by vapor doping of polyaniline. Leftrant et al. demonstrated polyaniline–SWNTs nanocomposite by direct dispersion of SWNTs in either a polymer solvent or by chemical polymerization of aniline in the presence of SWNTs [9]. Long et al. demonstrated the use of cationic surfactant with MWNTs and the corresponding effects on conductivity and magneto resistance, etc. [10]. Karim et al. dispersed the SWNTs in 0.1 M HCl by sonication without surfactant and did not observe any chemical interaction between PANI–SWNTs [11]. On the other hand, Zengin et al. also dispersed 10 wt.% MWNTs in 1 M HCl with 3 days of sonication, followed by *in situ* polymerization of aniline [12].

Although there are advances separately on individual processing of conducting form of PANI and carbon nanotubes (CNT), to the best of our knowledge, till date there is no simple route to combine PANI–SWNT nanocomposite in common medium that will facilitate its use in variety of electronic devices or polymer nanocomposites. In this paper, we report the use of anionic surfactant as a common stabilizer for the conducting form of polyaniline as well as for SWNTs that facilitates the combined processing of PANI–SWNT from common organic medium.

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doi:10.1016/j.synthmet.2009.10.020

2. Materials

Highly purified HiPCO® single wall carbon nanotubes were purchased from CNI Inc. (USA). Xylene (mixture of xylenes) is purchased from VWR, UK and used as obtained. Aniline is purchased from Riedel de Haen, Germany. All other chemicals are purchased from Sigma–Aldrich.

3. Experimental

3.1. Scheme-1: polyaniline synthesis

At room temperature, emeraldine salt forms of polyaniline nanofibers (PANI) are synthesized using interfacial polymerization between 1 M HCl in water (25 ml) containing ammonium persulphate and xylene (25 ml) containing aniline. The molar ratio of aniline to ammonium persulphate is kept at 4:1. Details of the polymerization can be found in Ref. [13]. Upon polymerization (12 h) xylene containing unreacted aniline is removed from the top and replaced with equal volume of xylene.

3.2. Scheme-2: organic suspensions of polyaniline without carbon nanotubes

Sodium dodecyl sulfate and sodium dodecylbenzene sulfonate in different weight/volume ratios (0.125, 0.25 and 0.5 g/25 ml) were added separately to the above-mentioned system and rigorously stirred for 3 h. The system is then left idle, during which phase inversion occurs. After phase inversion, organic phase is taken from the top and washed with excess amount of xylene. The filtered material is then dried under dynamic vacuum at 60 °C for 24 h. The surfactant concentration mentioned in this paper is relative to the aqueous phase. The estimation of the amount of the surfactant to be used in preparation of PANI–SWNT nanocomposite is based on maxima in the conductivity obtained at 1 wt.% surfactant (not shown in this paper).

3.3. Scheme-3: exfoliation of single wall carbon nanotubes

For exfoliation of SWNT, literature reported route is followed [5]. Using ultrasonication, exfoliation parameters are optimized at 0.2% SWNTs in aqueous phase. Above this concentration, the viscosity of the sample increased considerably.

3.4. Scheme-4: organic 'nanocomposite' dispersions of PANI–SWNT

'Organic nanocomposite dispersions' of PANI–SWNTs in various SWNT concentrations are prepared by *in situ* synthesis of polyaniline in Scheme-3. *In situ* synthesis is followed with the same experimental parameters as mentioned in Scheme-1. Based on the polyaniline yield, corresponding SWNT wt.% in dry nanocomposites are 0.3, 2 and 3.8% respectively and henceforth mentioned in this paper.

3.5. Characterization

At room temperature, FT-IR spectra are recorded using KBr pellet on Infrared Excalibur instrument. UV–vis spectroscopy on organic dispersions is done on Hewlett-Packard 8453 spectrometer. Co-linear four probe conductivity measurements were performed on the compressed pellets (200 bar, 10 min) using nanovoltmeter (Keithley 2182A) and programmable current source (Keithley 6220) at room temperature. To obtain SEM image, sample is first coated with approx. 10–15 nm gold layer using evaporator and images are obtained on Field Emission Gun SEM (LEO 1530 VP) instrument. The continuous wave electron spin resonance spectra (X-band at 9.44 GHz) were recorded in a rectangular cavity of a Bruker ESP300E at room temperature. The powder samples were inserted in open tubes. The modulation frequency of the experiments was 100 kHz. The modulation amplitude was 5 G and microwave power 1.26 μW (attenuation 52 dB).

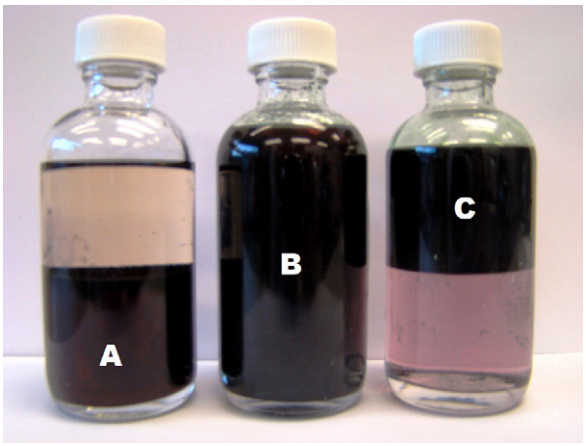

Fig. 1. Phase inversion phenomenon in steps from (A) PANI as prepared, (B) intermediate state and (C) organic dispersion.

4. Results and discussion

The phase inversion phenomenon is depicted in Fig. 1.

It is important to note that phase inversion phenomenon is observed with anionic surfactants only. If organic phase is removed and an anionic surfactant is added to the aqueous phase containing PANI, viscous gel-like system results. The phase inversion phenomenon can then be explained by a mechanism shown in Fig. 2. When anionic surfactant is added in aqueous media, it dissociates into free cations (Na^+ ions in this case) and alkyl chain bearing anions (SO_3^-/SO_4^- ions in case of NaDBS and SDS respectively). The Na^+ ions then react with the chlorine ion(s) on PANI backbone to form NaCl. The alkyl chains bearing bulkier SO_3^-/SO_4^- group then dope polyaniline and the hydrophobic nature causes the phase inversion. We have not performed any experiments with non-ionic surfactants.

The phase inversion phenomenon is also applicable to organic nanocomposite dispersions of PANI–SWNT as well. It is important to note that if xylene is added to Scheme-3, SWNTs alone does not make the transition to the organic phase. But when PANI is synthesized *in situ* in the nanocomposite makes transition from aqueous to organic phase. This observation indicates that strong complex interactions between PANI–surfactant–SWNT are a prerequisite to obtain the organic nanocomposite dispersions and correspondingly explained in hypothetical model under Fig. 8.

The morphology analysis is performed using FEGSEM and is shown in Fig. 3. The nanofiberous morphology is in agreement with the literature reported method [12]. The SEM of PANI–SWNT–SDS is not shown because it is observed that during sample preparation, SDS crystals were phase separated that hindered morphological analysis.

FT-IR spectra of pristine PANI and corresponding nanocomposites are depicted in Fig. 4. The major peaks in PANI are in agreement with the literature reported values of emeraldine salt of polyaniline [14,15]. The spectra are normalized with respect to intensity at 1300 cm^{-1} in neat PANI. Irrespective of the type of surfactant, the intensities of the quinoid and benzenoid rings are decreased

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