A facile one-pot synthesis of polyaniline/magnetite nanocomposites by micelles-assisted method

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Abstract Magnetic nanocomposites based on polyaniline (PANI) and magnetite nanoparticles (Fe$_3$O$_4$ NPs) have been prepared by an in situ self-assembly method in presence of dodecylbenzene sulfonic acid (DBSA) as dopant as well as surfactant. Influence of the aniline to DBSA molar ratio on morphology, magnetic properties, and thermal stability of PANI/Fe$_3$O$_4$ NPs composites has been investigated. Spectroscopic results indicated the interaction between PANI nanorods and Fe$_3$O$_4$ NPs. Scanning electron microscopy and transmission electron microscopy images indicated that PANI rods were decorated with Fe$_3$O$_4$ NPs. Morphologies of nanocomposites were found to be critically dependent on molar ratios of organic acid to monomer. PANI nanorod/Fe$_3$O$_4$ NPs composites showed superparamagnetism and higher thermal stability with small mass fraction of Fe$_3$O$_4$ NPs.

Keywords Intrinsic conducting polymer · Polyaniline · Magnetite nanoparticle · Superparamagnetism

Introduction

Since their discovery, intrinsic conducting polymers (ICPs) have received great attention because of their unique properties coupled with potential technological applications. Compared to other ICPs, polyaniline (PANI) has been the most extensively studied system due to its electrical and electrochemical properties, good environmental stability, high conductivity in doped form, low monomer cost, ease of polymerization and useful for potential applications in energy storage devices, electron field emitters, chemical and biological sensors, actuators, etc. (Wu and Bein 1994; Wang et al. 2001; Zhang et al. 2004; Hatchett and Josowicz 2008; Li et al. 2009). More recently multifunctional nanocomposites based on PANI nanostructures, such as nanotubes, nanofibers, nanowires, and nanorods combined with magnetic nanoparticles have also been investigated for applications such as EMI shielding, catalysis, anti-biofouling, immunity assay, separation and purification of biomolecules, carriers for targeted drug delivery, biosensors and electromagnetic device applications have been reported (Ugelstad et al. 1992; McMichael et al. 1992; Marchessault et al. 1992; Bhatnagar and Rosensweig 1995). Among the various magnetic dispersions, magnetite nanoparticles (Fe$_3$O$_4$ NPs) are useful because of their low toxicity, high saturation magnetization (Raj et al. 1995; Batlle and Labarta 2002; Wilson et al. 2004). All these applications require the Fe$_3$O$_4$ NPs to be chemically stable with uniform particle size, and well dispersed in aqueous medium. Nevertheless, preparation of stable Fe$_3$O$_4$ NPs is a challenge as the nanoparticles possess high surface area to volume ratio and tend to aggregate to reduce their surface energy. In addition, the strong magnetic dipole–dipole interaction and Vander Waal’s attractive forces among the nanoparticles also cause the particles to aggregate (Gupta and Gupta 2005). Consequently, these materials show poor magnetic properties and low dispersibility. One of the important strategies to overcome the above limitations is to shield the Fe$_3$O$_4$ NPs by coating them with macrocyclic surfactants, polymers, inorganic metals, or oxides (Jeong et al. 2007). The surrounding layer around each particle not only avoids further aggregation but also provides a useful platform for more functionalization.

Various synthetic methods have been reported for obtaining magnetic Fe$_3$O$_4$/PANI composites, which include
direct precipitation of iron salt in a solution of polymer, oxidative chemical polymerization, the in situ synthesis of polymer via an oxidative or electrochemical procedure in presence of well-dispersed magnetic nanoparticles (Bai and Shi 2007; Zhang and Wen 2003). Fabrication of thin films of PANI/γ-Fe2O3 using anionic surfactants has also been reported (Mallikarjuna et al. 2005). Raksha et al. (2005) reported Fe3O4/PANI nanocomposites prepared by mixing aqueous solutions of iron (II) sulfate and 1-methyl-2-pyrrolidinone (NMP) solutions of PANI at different pH values. The precipitate obtained from acidic conditions (e.g., at pH = 1) was found to contain a low concentration of Fe3O4 (Wan and Li 1997). Fe3O4/PANI nanocomposites were also prepared by other means such as modification-redoping method, high-energy ball milling method, precipitation–oxidation technique, and chemical oxidative copolymerization of aniline and 5-amino-2-naphthalenesulfonic acid in presence of Fe3O4 NPs (Deng et al. 2002; Yang et al. 2003; Bao and Jiang 2005; Reddy et al. 2007). The obtained nanocomposites showed ferromagnetic behavior with saturation magnetization 9.7 emu g⁻¹. Nanocomposite particles that are prepared by these methods typically showed a significant particle size distribution, containing non-uniform magnetite fraction in composite with aggregates of iron oxide leading to an uncontrolled structure and irreproducible material properties.

In this paper, we report the synthesis of magnetic and conducting polymer composites based on Fe3O4 NPs on DBSA-doped PANI matrix using ammonium persulfate (APS) as an oxidant in presence of FeCl3 NPs (Deng et al. 2002; Yang et al. 2003; Bao and Jiang 2005; Reddy et al. 2007). The obtained nanocomposites showed ferromagnetic behavior with saturation magnetization 9.7 emu g⁻¹. Nanocomposite particles that are prepared by these methods typically showed a significant particle size distribution, containing non-uniform magnetite fraction in composite with aggregates of iron oxide leading to an uncontrolled structure and irreproducible material properties.

Experimental details

Materials and methods

Aniline and DBSA were purchased from Aldrich. Aniline was double distilled under reduced pressure and stored at 0–5 °C. Other reagents viz ammonium persulfate [APS, (NH4)2S2O8], ferric chloride hexahydrate (FeCl3·6H2O), iron (II) sulfate heptahydrate (FeSO4·7H2O), ammonia (NH3·H2O), sodium hydroxide and methanol were of AR grade from Merck, India and all these chemicals were used as received without any further purification. Milli-Q water with resistance greater than 18 MΩ was used for the preparation of all solutions.

Surface morphology was examined by scanning electron microscopy (SEM) using JEOL-JSM6610 LV equipped with an electron probe-micro analyzer. Transmission electron microscopy images were obtained (TEM model FEI TECNAI G2 S-Twin) at an accelerating voltages of 120 and 200 kV. X-ray diffraction patterns (XRD) were collected using a Siemens AXS D5005 X-ray diffractometer at 1 degree per minute with Cu-Kα radiation. Fourier transform infrared (FTIR) spectra were recorded over the range of 400–4,000 cm⁻¹ using a Perkin Elmer SPEC-TRUM 1000 FTIR Spectrometer. Powder samples were mixed thoroughly with KBr and pressed into thin pellets. For UV–Visible absorption spectra, the samples were dissolved in dimethylsulfoxide (DMSO) and spectra were recorded on a Perkin-Elmer double beam LS-50 spectrophotometer. Room temperature magnetization measurements versus applied magnetic field were carried out using VSM, Lakeshore 665, USA. Thermogravimetric analysis (TGA) was done using, Cahn TG131 system with a heating rate of 20 °C min⁻¹ under N2 atmosphere.

Preparation of DBSA-doped PANI/Fe3O4 nanocomposites

The DBSA-doped PANI/Fe3O4 nanocomposite was synthesized as follows. In a typical experiment, 0.093 g of aniline was added drop wise to 1 ml of DBSA contained in 50 ml of Milli Q water under vigorous stirring. The reaction mixture was quickly cooled to 0–5 °C using ice-water bath with constant stirring for 2 h to obtain a milky dispersion of particles of anilinium–DBSA complex. Then, a pre-cooled solution of 1 ml aqueous ammonium persulfate (1 mol/L) was added dropwise to the above under vigorous stirring. The color of the reaction mixture slowly turns from colorless to light blue and eventually to dark green. After the addition is complete, reaction mixture is maintained at 0–5 °C for 5 h, before allowing it to attain room temperature to yield DBSA-doped PANI. Then, 10 ml of 1 mol L⁻¹ FeCl3·6H2O and 10 ml of 0.5 mol L⁻¹ FeSO4·7H2O aqueous solutions were rapidly injected into the above reaction mixture and slowly heated up to 65 °C under stirring, followed by the addition of 5 ml of 25 % NH4OH. Color of the reaction mixture turns black indicating the formation of magnetite. The reaction mixture was suggested to vigorous stirring for 5 h until a very viscous PANI/Fe3O4 NPs nanocomposite was obtained. The obtained product was centrifuged washed with distilled water followed by methanol and dried under vacuum at room temperature for 12 h. The same procedure has been adopted for preparation of all DBSA-doped PANI/Fe3O4 NPs composites, except for varying the molar ratio of DBSA to aniline from 1:1 to 1:5.

Results and discussions

Synthesis of PANI nanorods/Fe3O4 NPs composite is based on the oxidative chemical polymerization of aniline in an
acidic environment using ammoniumpersulfate (APS) as the oxidant in presence of a surfactant. In the present study, DBSA is used as a surfactant. In aqueous solution, DBSA forms micelles due to its hydrophilic group (–SO$_3$H) and hydrophobic alkyl group. DBSA also forms dopant-aniline salts with aniline, which act as “soft template” for growth of PANI rods. With progressive polymerization growth of nanorods is controlled by elongation process and of excess DBSA present prevents the formation of larger particles via steric hindrance and limit PANI rods to nanometer size. Fe$_3$O$_4$ NPs formed inside DBSA micelle reactor during sedimentation process get inserted on to the PANI rods. –SO$_3$ groups of DBSA limits the size of Fe$_3$O$_4$ NPs by forming of a protection layer around the particle through the hydrophilic –SO$_3$ group. Aggregation of such particles is arrested by the repulsive forces due to the hydrophilic alkyl groups surroundings each particle.

TEM micrographs of as prepared crude PANI/Fe$_3$O$_4$ and final dried powder after in dispersed in dimethyl sulfoxide (DMSO), are presented in Fig. 1. TEM micrographs depicted in Fig. 1 clearly show the rod like morphology of PANI with average diameter ranging from 18 to 45 nm and length a few hundred nanometres. TEM image of composite samples (Fig. 1b) shows that the Fe$_3$O$_4$ NPs are of 5–8 nm in size. Electron diffraction (ED) pattern obtained from the particles given in Fig 1c is in good agreement with the characteristic electron diffraction pattern of Fe$_3$O$_4$ NPs of spinel structure. Figure 1d shows the particle size distribution of Fe$_3$O$_4$ NPs in the composite.

TEM micrographs of of morphologies of DBSA-doped PANI/Fe$_3$O$_4$ NPs composites for different molar ratios of DBSA to aniline is shown in Fig. 2. From the SEM images (Fig. 2a, b) it can be seen that the rod-like morphology of PANI is obtained for 1:5 molar ratio of DBSA to aniline. Composite samples prepared with 1:4, 1:3, and 1:1 molar ratios of DBSA to aniline, shown in
Fig. 2c–e, did not show formation of rod like structure. Concentration of DBSA to aniline apparently seems to have an influence on the morphology of nanocomposites.

Molecular structure of nanocomposite was studied by XRD, UV–Visible and FTIR spectroscopy. XRD patterns of PANI/Fe$_3$O$_4$ composites presented in Fig. 3, consists of...
two broad peaks at $\theta = 21^\circ$ and $25^\circ$ that can be ascribed to the periodicity parallel and perpendicular to the polymer chain of PANI (Zang et al. 2006). The diffraction patterns centered at $\theta = 30.47^\circ$, $35.63^\circ$, $43.35^\circ$, $57.22^\circ$, $63.06^\circ$, could be indexed as (220), (311), (400), (511), and (440) planes of magnetite (JCPD file No. 19-0629).

Figure 4 shows UV–Vis spectra of PANI/Fe$_3$O$_4$ samples for different molar ratios of DBSA to aniline. It can be seen from the Fig. 4 that there are two characteristic peaks are one at 310 and other at 610 nm. The former arises due to $\pi \rightarrow \pi^*$ transitions, while the latter is due to transition of inter chain charge transfer from two adjacent benzenoid rings to the quinoid ring of PANI chain. Blue shift of both absorption bands as compared to those of pure PANI indicates some type of interaction between Ferric ions with nitrogen atom of PANI. Besides these two peaks, there is a small shoulder peak at 270 nm due to the $\pi \rightarrow \pi^*$ transition in the benzenoid rings of DBSA, confirming the presence of DBSA in the nanocomposites.

FTIR spectra of the PANI/Fe$_3$O$_4$ nanocomposites shown in Fig. 5 are in good agreement with earlier reports (Hasik et al. 2006). The characteristic peaks at 3,450 and 3,150 cm$^{-1}$ are assigned to N–H stretching vibrations of amino groups, which are indicative of $–NH_2$ groups in the structural units of the PANI rods. The strong bands at about 1,589 and 1,496 cm$^{-1}$ arise because of quinoid rings and benzenoid ring units. The presence of these bands clearly indicates that the PANI is composed of both amine and the imine units. The observed band at 1,408 is ascribed to stretching frequency of B–N = Q moiety (where B refers to benzenoid phenyl rings and Q refers to quinoid phenyl ring) and confirms the presence of phenazine units. These phenazine units act as initiation centres for growth of PANI nanostructures (Kim et al. 2000). The band at 1,307 cm$^{-1}$ corresponds to C–N stretching vibration mode of the 1, 4-disubstituted benzene ring of PANI. The peaks at 1,176 and 1,132 cm$^{-1}$ can be attributed to N=Q=N modes of PANI and DBSA respectively. The bands at 1,035, 617, and 1,008 cm$^{-1}$ are due to symmetric and asymmetrical vibrations of O=S=O, S–O and C–H of DBSA which confirms
the doping of DBSA in PANI nanocomposites. The band at 831 cm\(^{-1}\) can be attributed to the characteristic C–H out of plane bending of 1, 4-disubstituted benzene rings of PANI. Since Fe\(_3\)O\(_4\) belongs to inverse spinel structure, Fe\(^{3+}\) ions are situated in two different lattice sites. The bands at 565 and 426 cm\(^{-1}\) could therefore be attributed to the intrinsic Fe–O vibrations of tetrahedral and octahedral Fe\(^{3+}\), respectively. The above spectroscopic data clearly confirms that ferric ion is coordinated with the nitrogen atom of quinine rings of PANI (Waldron 1955; Wan 1989).

Figure 6 shows variation of magnetization as a function of field for PANI/Fe\(_3\)O\(_4\) nanocomposites at room temperature. The magnetization curves are indicative of superparamagnetism as there are no hysteresis loops with remanence and coercivity. Saturation magnetization (Ms) values equal to 57, 36, 13 and 7 emu/g were obtained for the samples with 1:1, 1:3, 1:4, and 1:5 molar ratios of DBSA to aniline. These Ms values obtained were much lower than that of bulk Fe\(_3\)O\(_4\) (Ms = 92 emu/g) (Gee et al. 2003). In general, the decrease in Ms is thought arise from the finite size effect and surface effect. But in the present case, the decrease in Ms may be attributed to substantial increase in the volume fraction of non-magnetic DBSA concentration (1:1 to 1:5).

Figure 7 depicts the thermogravimetric curves for pure PANI and PANI/Fe\(_3\)O\(_4\) nanocomposites under nitrogen atmosphere studied at a heating rate 20 °C/min in the temperature range of 40–840 °C. Three weight loss regions were observed for pure PANI and PANI/Fe\(_3\)O\(_4\) nanocomposite samples. The initial weight loss up to 150 °C is due to the removal of water, excess of unbound DBSA and other volatiles in composites. The second weight loss between 150 and 350 °C is ascribed to degradation of the bound DBSA. The third weight loss between 500 and 840 °C corresponds to degradation of PANI. The enhanced thermal stability of composites as compared to pure PANI may be due to the interaction between PANI and Fe\(_3\)O\(_4\) NPs, which restricts the thermal motion of PANI chain in the composite.

Conclusions

We have demonstrated a simple and reproducible one-pot synthesis of PANI nanorods containing Fe\(_3\)O\(_4\) NPs using APS as an oxidant in presence of DBSA as surfactant via in situ self-assembly method. DBSA was found to modify PANI. SEM and TEM techniques indicated that Fe\(_3\)O\(_4\) NPs are coated on surfaces of PANI nanorods. Morphology and magnetic properties of nanocomposites were found to be critically dependent on the molar ratios of DBSA to aniline. Magnetic measurements indicated the formation of single domain particles that exhibited superparamagnetism. Thermo-gravimetric data indicated that the thermal stability of nanocomposite is higher as compared to pure PANI.

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