



Synthesis and Characterization of Dodecylbenzene Sulfonic Acid doped Tetraaniline via Emulsion Polymerization

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Abstract: In this work, we report preparation and characterization of dodecylbenzene sulfonic acid (DBSA) doped tetraaniline via micelles assisted method using ammonium per sulphate (APS) as an oxidant. Here, DBSA act as dopant as well as template for tetraaniline nanostructures. The synthesized DBSA doped tetraaniline have been well characterized by, Fourier transform infrared spectroscopy, UV-Visible spectroscopy, Scanning electron microscopy and thermogravimetry. The morphologies of tetraaniline were found to be dependent on molar ratios of N-phenyl-1, 4-phenylenediamine to DBSA. The spectroscopic data indicated that DBSA doped tetraaniline. Thermogravimetry studies revealed that the DBSA doping improved the thermal stability of tetraaniline.

Keywords: Conducting polymers, Micelles, Tetraaniline, Thermal stability.

Introduction

Among various conducting polymers, polyaniline (PANI) has a unique position due to its easy synthesis, environmental stability, and reversible acid-base chemistry in aqueous solution. In recent years, PANI has been the focus of intense investigation due to its good electrical conductivity, stability in ambient conditions, and control of the electronic and optical properties by the degree of oxidation and protonation. It has been used in applications such as organic lightweight batteries, microelectronics, electrorheological fluids, and chemical sensors.¹⁻¹⁰ However, like many other conducting polymers, unsubstituted PANI is intractable and suffers from poor processability, mainly because of its rigid, highly conjugated backbone. In order to overcome these limitations, many methods have been developed such as template-synthesis, electron-spinning, interfacial polymerization, electrochemical polymerization, and template-free methods¹¹⁻¹⁶. Among these methods, the emulsion polymerization method has attracted much attention due to its simplicity and processability. In this technique, long chain organic acid is used as dopant as well as soft-template for PANI dispersions.

Among PANI family, tetraaniline have emerged as potential candidates because soluble in common solvents, exhibit similar electroactivity as PANI, and have well-defined structure, designed end group, and monodispersed molecular weight¹⁷. The most interesting form of PANI is emeraldine, which has ca. 50% amine and ca. 50% imine nitrogen, that is one of 4 rings is quinoid, the remaining three being benzoid. Hence, tetraaniline is perfect model compound for PANI since its chemical structure resemble to the EBPANI.

In this paper, we report a facile one-pot synthesis of DBSA doped tetraaniline through DBSA micelle assisted synthesis by in situ self-assembly method. The presence of a high concentration of DBSA can effectively prevent the formation of larger particles, thereby producing nanometersized particles only. The resulting DBSA doped tetraaniline have high thermal stability.

Experimental

Ammonium persulphate [APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$], Sodium hydroxide (NaOH) were obtained from Merck Chemicals, India and used as received. *N*-phenyl-1, 4-phenylenediamine, dodecylbenzene sulfonic acid (DBSA) was purchased from Aldrich, India. Double distilled water was used throughout all the synthetic processes. All other reagents were analytical grade and used without further purification.

Synthesis of DBSA-doped tetraaniline

The DBSA doped PANI with was synthesized via micelle-assisted method using DBSA as dopant as well as surfactant. In typical synthesis involves dissolution of 0.093 g of *N*-phenyl-1, 4-phenylenediamine and 5 ml of DBSA in 50 mL of distilled water in round bottom flask at room temperature under constant magnetic stirring. The reaction mixture was quickly cooled to 0-5 °C using ice-water bath with constant stirring for 2 hours to disperse the *N*-phenyl-1, 4-phenylenediamine homogenously, resulting a milky dispersion of particles of *N*-phenyl-1, 4-phenylenediamine -DBSA complex. Then a pre-cooled, equimolar solution (1mol/L) 1 mL aqueous ammonium persulphate (APS) was added drop wise to the above solution under vigorous stirring. The colour of the reaction mixture slowly turns from a colourless, to light blue and eventually to a dark green. After addition is over, the reaction is allowed to proceed for 5 h at 0-5 °C, before warming it slowly to room temperature. Finally, DBSA doped tetraaniline was obtained. The resulting mixture was centrifugated and washed with distilled water and finally with methanol. The product was then dried under vacuum at room temperature for 12 h. The same procedure has been adopted for preparation of all DBSA doped tetraaniline samples, while varying the molar ratio of *N*-phenyl-1, 4-phenylenediamine to DBSA from 1:1 to 1:5.

Characterization

FTIR spectra were recorded over the range of 400-4000 cm^{-1} using a Perkin Elmer SPECTRUM 1000 FTIR spectrometer. The powder samples were mixed thoroughly with KBr and pressed into thin pellets. For UV-Visible phase identification was done by X-ray diffraction using a Siemens AXS D5005 X-ray diffractometer at 1degree per minute with $\text{Cu-K}\alpha$ radiation. For UV- Visible absorption spectra the samples were dissolved in dimethylsulphoxide(DMSO) and spectra were recorded on a Perkin-Elmer double beam LS-50 spectrophotometer. Morphologies of the samples were studied by scanning electron microscopy (SEM). The samples for SEM were mounted on aluminium studs using adhesive graphite tape and sputter-coated with platinum before analysis. Thermal stability of nanocomposite samples was determined from thermogravimetric analysis (TGA, Cahn TG131) with a heating rate of 20 degree per minute under N_2 atmosphere.

Results and Discussion

Figure 1 shows SEM images of the DBSA doped tetraaniline prepared at different molar ratios of N-phenyl-1, 4-phenylenediamine to DBSA. The morphologies of DBSA doped tetraaniline is critically depended on molar ratio of N-phenyl-1, 4-phenylenediamine to DBSA. The tubular morphology is obtained for 1:5 molar ratio of N-phenyl-1, 4-phenylenediamine to DBSA. The particular morphologies were obtained when molar ratios of N-phenyl-1, 4-phenylenediamine to DBSA lower than 1: 5. Here, DBSA is expected to play dual role in the formation of composites as a dopant for tetraaniline as well as a surfactant to form micelles during the polymerization due to the presence of hydrophobic and hydrophilic parts ($-\text{SO}_3\text{H}$ groups of DBSA). Here, N-phenyl-1, 4-phenylenediamine is hydrophobic. In an aqueous solution containing mixture of N-phenyl-1, 4-phenylenediamine and DBSA, a complex formation is expected due to acid–base type interactions between the $-\text{SO}_3\text{H}$ group in DBSA and $-\text{NH}_2$ group in. Further, the N-phenyl-1, 4-phenylenediamine – DBSA complex and serve as nucleation site for growth nanorods. The size of the initial micelles also increases with an increase in the content of the surfactant and also the number and diameter of the micelles should be affected by the concentration of the DBSA surfactant, and consequently the diameter of the nanotubes will change as well.

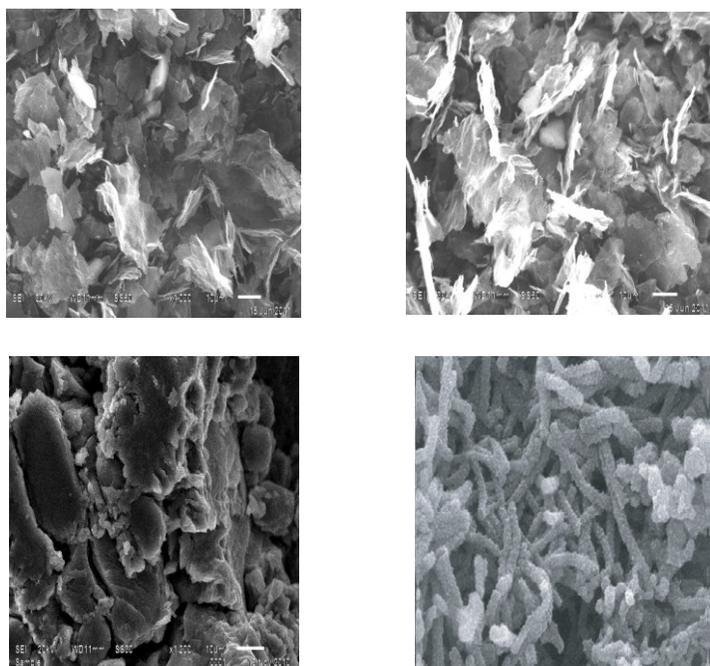


Figure 1. SEM image of DSBA doped tetraaniline prepared at different molar ratios of N-phenyl-1, 4-phenylenediamine to DBSA (a) 1:2, (b) 1:3, (c) 1:4, and (d) 1:5.

The UV-Vis absorption spectrum of tetraaniline in the doped and undoped form is shown in Figure 2 (a). Un-doped tetraaniline exhibits two electronic absorption bands at with λ_{max} at 330 nm and 630 nm approximately with λ_{max} at 330 nm and 630 nm approximately. The broad absorption at 630 nm for tetraaniline has been assigned to quinoid formation in the backbone of the polymer¹⁸. The band around 285-350 nm is assigned to the $\pi - \pi^*$ electronic transition of the benzene rings in the polymer backbone. Characteristic

absorbance maxima in the doped polymer are observed at 425 nm and 822 nm in the spectra of tetraaniline¹⁹. They are due to the polaron band transitions in the doped tetraaniline.

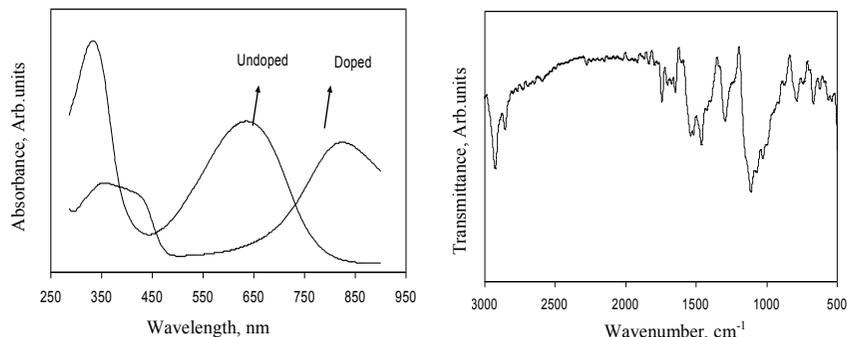


Figure 2. (a) UV-visible spectra (b) FTIR spectra of DSBA doped tetraaniline prepared.

Figure 2 (b) shows the FT-IR spectrum of tetraaniline doped with DBSA. In the spectrum, the peaks at 1467 , 1548 cm^{-1} indicate that the aromatic ring is retained in the polymer. The band at 1467 cm^{-1} corresponds to the stretching of benzene rings and the peak at 1548 cm^{-1} corresponds to the stretching frequency of quinone ring. The presence of these two bands clearly shows that the polymer is composed of the amine and imine units²⁰⁻²¹. It also exhibits distinct peak at 2924 cm^{-1} , which is assigned to the aromatic C-H stretching. The peak at 1294 cm^{-1} corresponds to the C-H in-plane deformation²². Also the peak at 1116 cm^{-1} corresponds to the sulfonic acid group. The presence of vibration band of the dopant ion and other characteristic bands confirm that the polymer is in the conducting emeraldine salt form. The bands at about 561 cm^{-1} are assigned to the out-of-plane C-H bending motions of the aromatic rings. The peak at 790 cm^{-1} is characteristic of para-substituted aromatic rings, which indicates the formation of polymer²³.

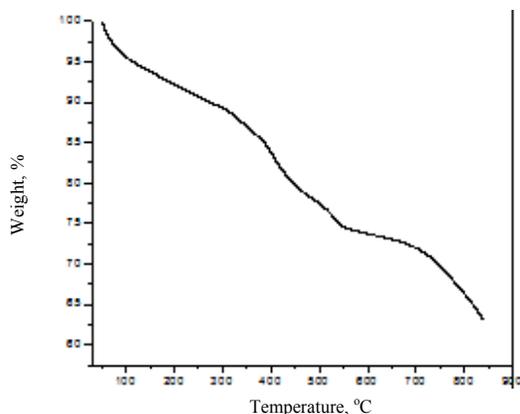


Figure 3. TGA curves of DSBA doped tetraaniline under N_2 flow at a heating rate of 20°C per minute.

Figure 3 shows a TG curve of DBSA doped tetraaniline prepared for N-phenyl-1, 4-phenylenediamine to DBSA ratio of 1:5 under N_2 flow at a heating rate of 20°C per minute from 50 - 850°C . Three main inflection regions can be observed. The first region at lower temperatures ($<200^\circ\text{C}$) is due to removal water, excess of unbound DBSA and other volatiles in DBSA doped tetra aniline. The weight loss in temperature range of 200 - 450°C

can be ascribed to the degradation of bound DBSA and decomposition of tetraaniline chain. The third weight loss region of 450-840⁰C is due to decomposition of tetraaniline chain. Thermal studies indicated that thermal decomposition of tetraaniline chain occurs at higher temperature for DBSA doped tetraaniline as compared to pure tetraaniline.

Conclusion

In summary, DBSA doped tetraaniline can be successfully prepared by using ammonium persulphate as oxidant in presence of soft template, DBSA via *in-situ* self-assembly method. It is found that morphologies of DBSA doped tetraaniline were depended on molar ratios of N-phenyl-1, 4-phenylenediamine to DBSA. The spectroscopic data indicated that formation of DBSA doped tetraaniline. The thermal studies revealed that the DBSA doped tetraaniline is higher thermal stable than pure tetraaniline.

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