



## Preparation and Characterization of P-TSA Doped Tetraaniline Nanorods *via* Micellar-Assisted Method

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

**Keywords:** Polymer nanostructures, Self-assembly, Micelles, tetraaniline.

### Introduction

Polyaniline (PANI) systems have been emerged as potential candidates for both fundamental research and technological applications because of its unique reversible proton dopability, excellent redox chemistry, environmental stability, variable electrical conductivity, which can be 'tuned', low cost and easy synthesis. Recently, PANI can be used as an electrode material, an electronic material, recordable optical disks, sensors, and in microelectronics. The commercial applications of PANI, however, are limited owing to its poor processability and intractable nature<sup>1-9</sup>. In order to overcome these limitations, many approaches have been developed including self-assembly techniques, incorporations of side chain on PANI chain, solid state approach, hard template, interfacial polymerization and soft template. However, PANI developed from all these methods has lower conductivity. It is therefore desirable to develop a single step method for solution processability of PANI with high conductivity.

A very few reports have appeared during the past century describing the synthesis of oligomers of aniline. It is surprising that the very little attention has paid to these extremely important species on which chemical and physical properties of PANI are based. Studies of

the topological and geometrical isomers formed after oxidation of anile allow one to understand the complexity of the molecular interactions in PANI. Among, PANI oligomers, tetraaniline is most attracted attention because soluble in common solvents, exhibit similar electroactivity as PANI and have well-defined structure, designed end group, and monodispersed molecular weight<sup>10</sup>. 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 present the preparation of para-toluene sulfonic acid (P-TSA) doped tetraaniline nanorods via self-assembly method. Here, P-TSA acts as do pant as well as soft template for tetraaniline nanostructures. The effect of molar ratios of N-phenyl-1, 4-phenylenediamine to P-TSA was investigated.

## Experimental

P-toluene sulphonic acid, 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 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.

### *Preparation of tetraaniline nanorods*

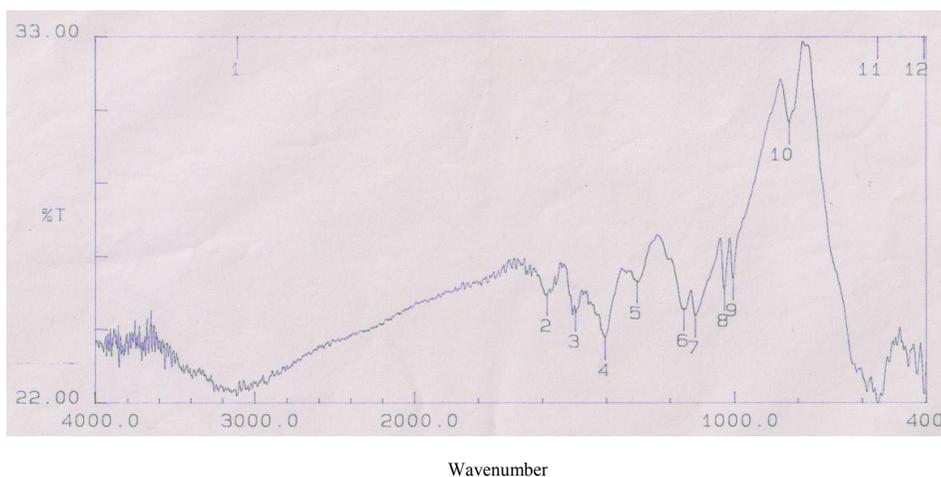
P-toluene sulphonic acid (PTSA) doped tetraaniline was synthesized via micellar assisted method, in which PTSA and aqueous ammonium persulphate were used as surfactant and oxidant, respectively. In a typical procedure, 0.1839 g N-phenyl-1, 4-phenylenediamine and 1.9105 g of PTSA were dissolved in 50 mL of distilled water in round bottom flask with constant stirring for 2h at 0-5 °C. A pre-cooled, equimolar solution (1mol/L) 1 mL ammonium persulphate was added to the reaction mixture to initiate the polymerization of N-phenyl-1, 4-phenylenediamine with constant stirring at 0-5 °C. After addition of oxidant, reaction mixture was allowed to proceed for another 5 h at 0-5 °C. The colour of the reaction mixture was slowly changes from a colourless, to light blue and then to a dark green, which is indicative of formation of PTSA doped tetraaniline. The resulting precipitate was filtered and washed with distilled water and methanol. Finally, the product was dried under vacuum at room temperature for 12 h. The same procedure has been adopted for preparation of all PTSA doped tetraaniline while varying the molar ratio of N-phenyl-1, 4-phenylenediamine to PTSA from 1:1 to 1:5.

### *Characterization*

The UV-Visible absorption spectra of the samples were recorded on a Perkin-Elmer double beam LS-50 spectrophotometer. The samples were dissolved in dry dimethylsulphoxide (DMSO) and centrifuged to remove any undissolved polymer. The clear solutions were taken in quartz cuvettes. The infrared spectra were recorded over the range 4000 - 400  $\text{cm}^{-1}$  in a Perkin-Elmer Model SPECTRUM 1000 FTIR spectrometer. The powdered samples were mixed thoroughly with KBr and pressed into thin pellets. Morphology of PTSA doped tetraaniline was studied by scanning electron microscopy (SEM). Thermal stability of nanocomposite samples was determined from thermogravimetric analysis (TGA, Cahn TG131) with a heating rate of 20 degree per minute under  $\text{N}_2$  atmosphere.

## Results and Discussion

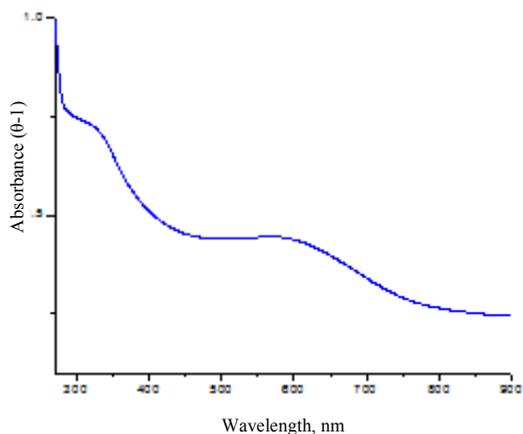
Molecular structure of P-TSA doped tetraaniline was characterized by UV-Visible spectroscopy, Fourier-transform infrared (FTIR) spectroscopy and X-ray diffraction pattern (XRD). The FT-IR spectra (Figure 1) of the synthesized tetraaniline samples were in good agreement with the earlier reports on tetraaniline.<sup>11-15</sup> The peaks at 3163, 1589 and 1496  $\text{cm}^{-1}$  attributed to N-H stretching vibration, C=C stretching of quinoid phenyl and benzenoid phenyl rings, respectively. The peak at 1404 is due to stretching frequency of B-N=Q moiety (B refers to benzenoid and Q refers to quinoid ring). The presence of this peak confirms that the formation of phenazine units. These phenazine units acts as initiation sites for the growth of tetraaniline tubes indicating self-assembly of phenazine units as previously reported by Trchova *et al.* is partially doped with PTSA, while completely absent in fully doped tetraaniline.



**Figure 1.** FTIR spectra of PTSA doped tetraaniline prepared at 1:5 molar ratio of N-phenyl-1, 4-phenylenediamine to PTSA.

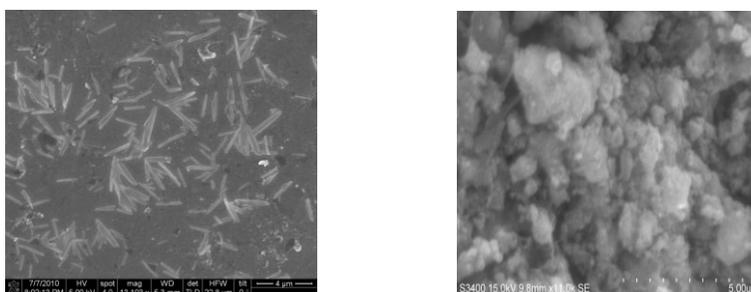
The peak at 1307  $\text{cm}^{-1}$  is assigned to C-N stretching vibrations of the 1, 4-disubstituted benzene ring of tetraaniline. The peaks at 1167 and 1132  $\text{cm}^{-1}$  attributed to N=Q=N modes of tetraaniline and PTSA respectively. The peaks at 1035, 617 and 1008  $\text{cm}^{-1}$  are due to symmetric and asymmetrical vibrations of O=S=O, S-O, S-C and C-H of PTSA respectively, indicating the presence of the sulfonate group. Sulfonate group of PTSA interact with protonated imine nitrogen in neighbouring chain and stabilize tetraaniline in the form of nanotubes by ionic bonding. In addition to the characteristic tetraaniline peaks, FTIR spectra of tetraaniline nanotubes showed additional peak at 831  $\text{cm}^{-1}$ , which can be ascribed to C-H out of plane bending of 1,4-disubstituted benzene rings of tetramer.

Figure 2. Shows the UV-Visible spectra of P-TSA doped tetraaniline which is in complete agreement with literature reports.<sup>16-17</sup> The UV-Visible absorption spectrum in dimethyl sulfoxide (DMSO) showed three distinct bands at 272, 321 and 591 nm. Absorption bands at 3621 and 591 nm have been assigned to  $\pi \rightarrow \pi^*$  transition of benzenoid rings in the tetraaniline chain and the transition caused by inter chain charge transfer from two adjacent benzenoid ring to the quinoid ring of tetraaniline chain respectively. The additional absorption band at 272 is ascribed as the  $\pi \rightarrow \pi^*$  transition in benzenoid ring in P-TSA. Both absorbance bands of tetraaniline were blue shifted from those of pure tetraaniline, indicating that there is some interaction between P-TSA and tetraaniline backbone.



**Figure 2.** UV-Visible spectrum of PTSA doped tetraaniline prepared at a molar ratio of *N*-phenyl-1, 4-phenylenediamine to PTSA for 1:5.

Figure 3 shows that the scanning electron microscopy (SEM) image of PTSA doped tetraaniline nanorods. We can see that most the resulting PTSA doped tetraaniline are in the form of rod for molar ratio 1:5. The morphologies of tetraaniline were critically depended upon molar ratio of *N*-phenyl-1, 4-phenylenediamine to PTSA. Tetraaniline nanorods formed only when the molar ratio of *N*-phenyl-1, 4-phenylenediamine to PTSA is 1:5.

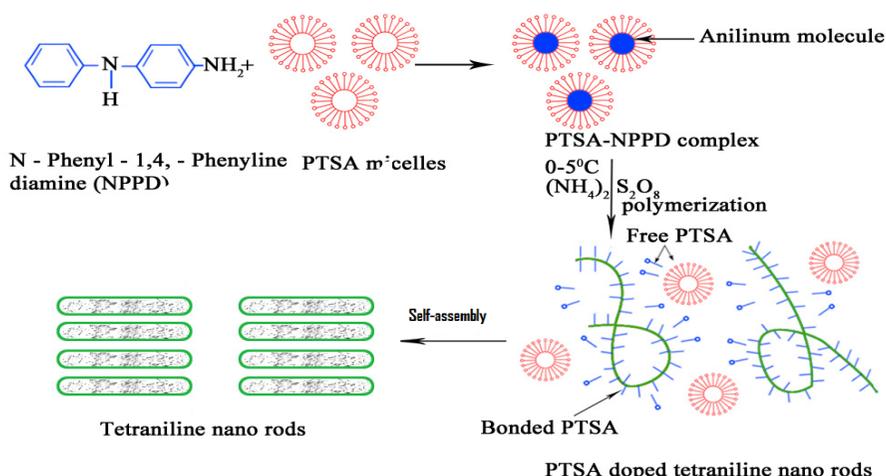


**Figure 3.** SEM images of PTSA doped tetraaniline prepared at different molar ratios of *N*-phenyl-1, 4-phenylenediamine to PTSA (a) 1:5, (b) 1:1.

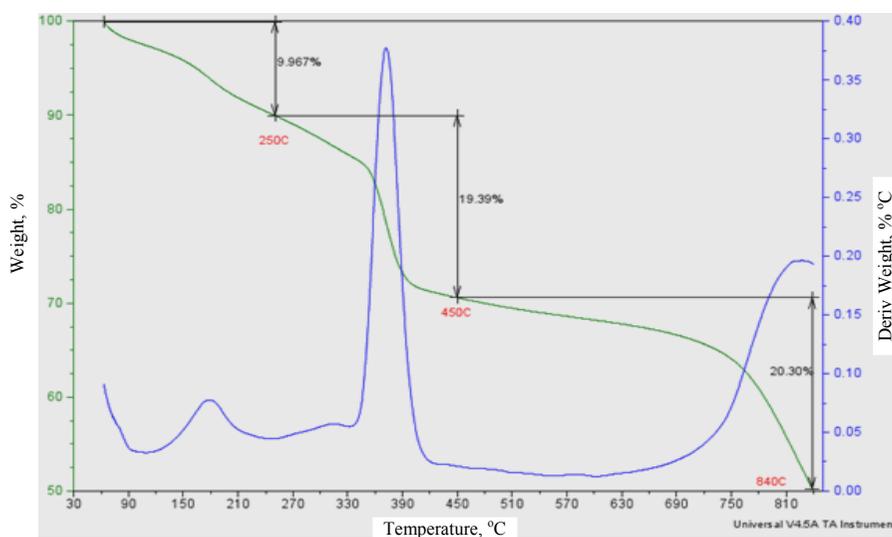
Figure 4 shows the formation mechanism of PTSA doped tetraaniline nanorods. Here, PTSA is expected to play dual role in the formation of composites as a dopant for tetraaniline as well as a surfactant to form micelles during the polymerization due to the presence of hydrophobic and hydrophilic parts ( $-\text{SO}_3\text{H}$  groups of PTSA). Here, *N*-phenyl-1, 4-phenylenediamine is hydrophobic. In an aqueous solution containing mixture of *N*-phenyl-1, 4-phenylenediamine and PTSA, a complex formation is expected due to acid–base type interactions between the  $-\text{SO}_3\text{H}$  group in PTSA and  $-\text{NH}_2$  group in. This anilinum–PTSA complex acts as site for growth of tetraaniline nanostructures. Further, the *N*-phenyl-1, 4-phenylenediamine–PSS complex could self assembled into nanorods.

Figure 5 shows a TG-DTG curve for P-TSA doped tetraaniline nanorod prepared at 1:5 molar ratio of *N*-phenyl-1, 4-phenylenediamine to PTSA. TG-DTG is recorded under  $\text{N}_2$

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 (<250 °C) is due to removal water, unbound P-TSA and other volatiles in tetra aniline nanorod. The weight loss in temperature range of 250-450 °C can be ascribed to the removal of bound PTSA and decomposition of tetraaniline chain. The third weight loss region of 450-840 °C is due to decomposition of tetraaniline chain. Thermal studies indicated that thermal decomposition of tetraaniline chain occurs at higher temperature for PTSA doped tetraaniline nanorod as compared to undoped tetraaniline.



**Figure 4.** Schematic illustration of preparation of PTSA doped tetraaniline nanorods.



**Figure 5.** TG-DTG of PTSA doped tetraaniline nanorods prepared at a molar ratio of N-phenyl-1,4-phenylenediamine to PTSA for 1:5.

## Conclusion

In summary, we have demonstrated a simple, reproducible, and facile method of preparation of tetraaniline nanorod via micellar assisted method using PTSA as dopant as well as soft template. The morphology of tetraaniline was depended on molar ratio of *N*-phenyl-1, 4-phenylenediamine to PTSA. PTTSA- anilium complex act as nucleation site for growth of tetraaniline nanorods. The spectroscopic data established the interaction between PTSA and tetraaniline. TG data indicated that PTSA doping enhanced the thermal stability of tetraaniline nanorods.

## Acknowledgment

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