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Effect of dopant on the nanostructured morphology of phenylenediamine synthesized by template free method

ABSTRACT

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The study reports some preliminary investigations on the template free synthesis of a scantily investigated polyaniline (PANI) derivative-Phenylenediamine (PDA) by template free method in the presence of Oxalic acid (OA) (dopant), using Ammonium Persulfate as oxidant. Polymerization of Phenylenediamine (PDA) was confirmed by the FT-IR as well as UV-visible studies. The morphology of Phenylenediamine doped with oxalic acid shows nanofibres was confirmed by Scanning electron microscopy (SEM) studies. It is also observed that the change in morphology changes the electrical conductivity. The oxalic acid as dopant has beneficial effect on the electrical conductivity.

Keywords: *Phenylenediamine; Dopant; Morphology; Nanofibre; SEM.*

INTRODUCTION

Scientific and technological interest in studying nanomaterials has spurred to develop conducting polymeric nanostructures, using reliable and scalable synthetic methods to provide better performance of these materials in the established areas of corrosion, sensors, batteries, and EMI shielding [1–3]. In recent years, electrically conducting and intrinsically colored polymers are widely used in diverse applications. [4]. Polyaniline is one of the most studied conducting polymers due to its chemical stability and relative high conductivity [5]. Chemical oxidative polymerization of aniline is the traditional method for preparing polyaniline in bulk. In the aniline polymerization reaction, an acidic solution is needed to enhance the head-to-tail coupling between aniline monomers. It has been reported that the diameter of nanofibres formed was strongly influenced by the dopant used in the polymerization [6, 7]. Substituted polyaniline continues to be an emerging research area of great interest since these polymers hold the potential to improve upon the properties of polyaniline.

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The polymer of aniline and its derivatives is one of the most widely researched electrically conductive polymers because of their easy preparation, high stability, good electrical conductivity, and high gas-separation ability. Among them, poly (Phenylenediamine) homopolymer is reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoraline repeating unit and exhibiting high thermostability [8,9].

Here we report a facile chemical route for the synthesis of Phenylenediamine (PDA) nanofibres. The nanofibres have nearly uniform diameters. The synthesis is based on the chemical oxidative polymerization of PDA with ammonium peroxydisulfate as the oxidant. Different concentration of Oxalic acid is used for the preparation of Phenylenediamine.

EXPERIMENTAL

Phenylenediamine (PDA), Ammonium peroxydisulfate (APS), oxalic acid (OA) were used as received. All chemicals were of analytical grade. 0.2M PDA and specific molar concentrations (0.1M to 0.4M) of oxalic acid were mixed with stirring at room temperature for 30 min. The stirring was then stopped, 50ml aqueous solution of 0.2M APS was added and the reaction was left for 12 hrs. The resulting PDA precipitate was washed with deionized water, methanol and ether several times. Finally the product was dried in vacuum at 80°C temperature for 24 hrs.

The UV-Vis spectra of the polymer solution in *N,N'*-Dimethyl Formamide (DMF) were recorded by using UV-1800 Shimadzu automatic recording double beam spectrophotometer in the range of 200-1100 nm. Room temperature conductivity of the samples was measured by four probe method. SEM images were analyzed by JEOL 6380-A instrument. The samples were precoated with Pt before scanning. The FTIR spectra of the polymer were taken on a Perkin Elmer Spectrum RXI spectrophotometer in the range 450 to 4600 cm^{-1} .

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of PDA doped with 0.1M and 0.4M concentration of oxalic acid shown in Figure 1. For 0.1M dopant concentration, a broad peak around 3,455 cm^{-1} for NH-stretching vibration and peaks corresponding to imine stretching mode appear at 1,720 cm^{-1} . Similarly peak at 1,590 cm^{-1} is assigned to the N = Q = N, quinonoid ring, skeletal vibrations. The peak at 1,476 cm^{-1} is appears due to N–C–N, benzenoid ring, skeletal vibrations. For 0.4M concentration, a peak at 3461 cm^{-1} shows NH-stretching vibration and peaks corresponding to imine stretching mode appear at 1718.6 cm^{-1} , while the peak at 1588.9 cm^{-1} is assigned to the N = Q = N, quinonoid ring, skeletal vibrations. The peak at 1475.3 cm^{-1} is appears due to N–C–N, benzenoid ring, skeletal vibrations [10]. This observation confirmed that, polyphenylene diamine is formed at 0.1 M and 0.4 M dopant concentration. Interestingly it is observed that at 0.1M dopant concentration, the band at 567 cm^{-1} assigned as the amine deformation became weak in the flake like morphology, but not in the nanofibres. Moreover at 0.4M dopant concentration, the band at 673.6 cm^{-1} from the benzenoid ring deformation appeared in the spectrum of the flake like morphology, but it is weak in the nanofibres morphology.

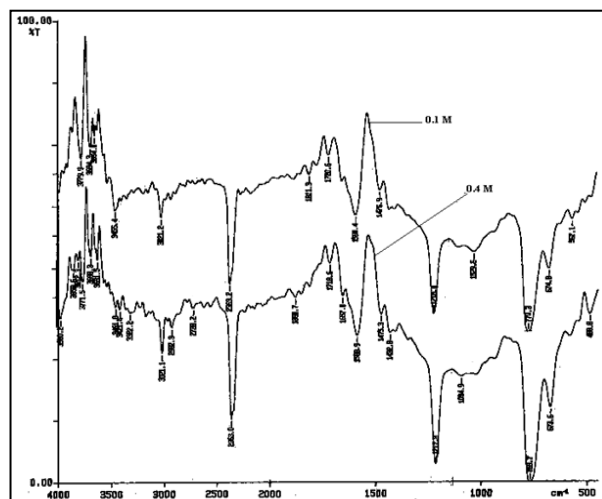


Fig.1. FTIR Spectra of polyphenylenediamine doped with 0.1M and 0.4 M oxalic acid.

SEM analysis

Morphological picture of polyphenylenediamine at 0.1 M and 0.4 molar concentration of dopant are shown in Figure 2. The SEM image of polyphenylenediamine doped with 0.1 M concentration of oxalic acid nanostructures reveals a well-interconnected dense network structure of PDA nanospheres shown in Figure 2a. The spheres appear to be of uniform sizes. The strong intra and intermolecular H-bonding interactions in PDA lead to extensive coiling of the polymer chains resulting in spherical morphology. But as the concentration of oxalic acid increases i.e. at 0.4 M concentration, this intermolecular hydrogen bonding between PDA and oxalic acid may grows PDA in fiber like morphology as shown in Figure 2b.

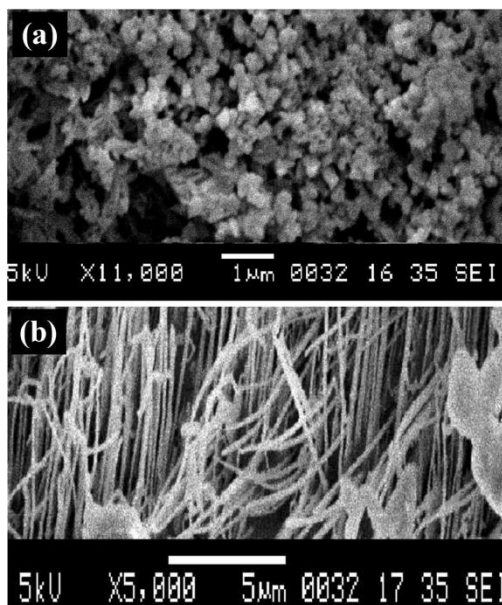


Fig. 2. a) SEM image of polyphenylenediamine doped with 0.1M oxalic acid. b) SEM image of polyphenylenediamine doped with 0.4M oxalic acid.

UV-Visible Studies

Figure 3 shows the UV-Vis absorption spectra of PDA doped with different concentrations of oxalic acid in DMF as a solvent. UV-Visible spectroscopy is a powerful tool for the study of protonation effect (and hence the formation of different oxidation states of the polymer) as well as for the elucidation of the interactions between the solvent, the dopant and the polymer chains. The spectra reveal the presence of two absorption

bands, one in the visible region and the other in the UV region in the polymers. The band in the UV region corresponds to $\Pi-\Pi^*$ transition and the band in the visible region corresponds to the inter-ring charge transfer associated with excitation from benzenoid to quinoid moieties [11]. It has been observed that as the concentration of oxalic acid increases, the spectra shifts towards the higher wavelength i.e. it shows red shift.

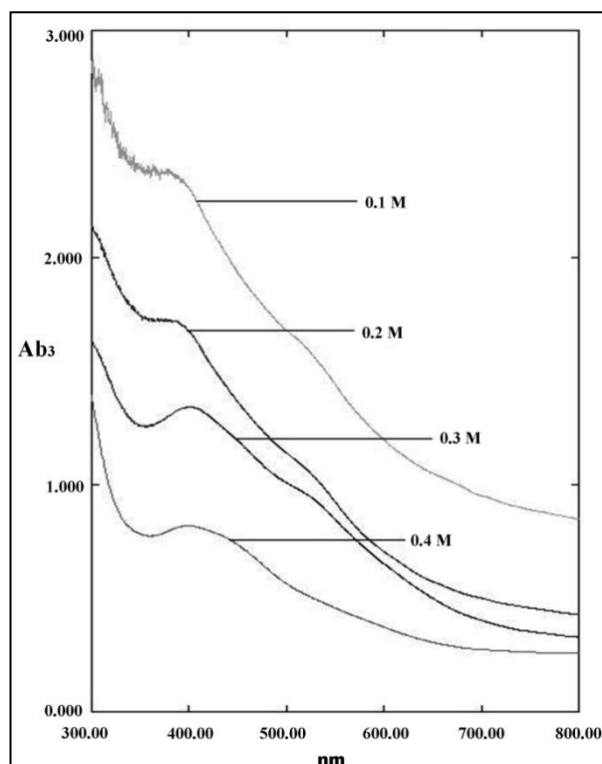


Fig. 3. UV-Vis spectra of polyphenylenediamine doped with 0.1M to 0.4M Oxalic acid.

Conductivity Study

The PDA to OA mole ratio and reaction time effects on the room temperature conductivity of PDA-OA are summarized in Table 1. Conductivity increased significantly from 3.17×10^{-8} to 1.76×10^{-7} S/cm as the concentration of dopant (oxalic acid) increases i.e. 0.1M to 0.4M.

As the concentration of oxalic acid increases, conductivity goes on increasing. This increase in conductivity with increase in temperature is the characteristic of “thermal activated behavior” [12]. The increase in conductivity could be due to increase of efficiency

of charge transfer between the polymer chains and the dopant with increase in temperature [13].

It is also possible that the thermal curing affects the chain alignment of the polymer, which leads to the increase of conjugation length and that, brings about the increase of conductivity. The molecular rearrangement on heating also possible, which makes the molecular conformation favorable for electron delocalization [14].

Table 1. Room temperature and high temperature conductivity of polyphenylenediamine doped with oxalic acid

Oxalic acid Concentration	Conductivity S/Cm	
	25 ^o C	125 ^o C
0.1M	3.17×10^{-8}	5.28×10^{-8}
0.2 M	4.56×10^{-8}	6.32×10^{-8}
0.3 M	1.53×10^{-7}	2.30×10^{-7}
0.4 M	1.76×10^{-7}	3.56×10^{-7}

CONCLUSION

Phenylenediamine doped with different molar concentrations of oxalic acid was synthesized by chemical oxidative polymerization in the presence of ammonium persulfate as the oxidant. It was found that the formation of nanofibres, since oxalic acid act as dopant. The morphology of PDA changed from nanospheres to nanofibres by increasing the concentration of oxalic acid. We discovered a very simple method to enhance the quality of PDA by adding an additive such as oxalic acid in the reaction medium during the polymerization process. Different nanostructures and larger conductivity have been achieved in this work.

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