

Effect of Polymer Concentration on the Formation & Morphologies of Polyaniline Nanoparticles

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Abstract— A series of polyaniline (PANI) nanoparticles with different polymer concentrations were synthesized with ammonium peroxydisulfate as initiator and sodium dodecylsulfate (SDS) as emulsifier. We examined the effect of high PANI concentrations on the formation and morphologies of PANI nanoparticles by Fourier transform infrared (FTIR) spectroscopy, Ultra-Violet-Visible (UV-Vis) spectroscopy, dynamic light scattering (DLS) and scanning electron microscopy (SEM) techniques. FTIR studies are used to check the formation of PANI. DLS and SEM experiments are respectively used to determine the size and morphologies of PANI nanoparticles.

Key words: Polyaniline; nanoparticles; FTIR; SEM; light scattering

I. INTRODUCTION

Polyaniline (PANI) nanoparticles have attracted considerable interest due to their applications in anti-corrosive polymer coatings and sensors [1-8]. Further PANI is very cheap, non-corrosive, and easily available. The synthesis of PANI in form of nanoparticles is very important to rectify the poor processability of PANI because PANI is not soluble in common organic solvents.

Tian and co-workers [1] reported PANI nanostructure-based polymer coatings improved the anticorrosion properties by increasing coating adhesion, producing a high potential of the metal and the self-healing of the engraved area. Chen et. al. [3] reported that the waterborne PANI/P-PVA containing coatings (PANI/P-PVA content, 2.5 wt %) exhibited high protection due to the higher impedance values after 30 days of salt spray tests. Murat [5] reviewed on various conducting polymer coatings including PANI used for corrosion protection of metals. Lindfors et. al. [6] reported the effect of pH on the PANI dispersions and the PANI nanoparticle dispersions can be used as a pH indicator solution. Kunzo and colleagues [7] have demonstrated that the gas-sensing characteristics of PANI film or PANI-based nanocomposite films.

Dispenza et. al. [9] investigated the usage of the polymeric surfactant as a soft template and found the morphology and the properties of the PANI dispersions can be controlled by polymeric surfactant. Zeng et. al. [10] elaborated the effect of the oxidants on the morphology, micro structure and electro chemical properties of nanostructured PANI. It was found that using FeCl₃ and K₂Cr₂O₇ as oxidants results in faster formation and higher yield of PANI than with ammonium peroxydisulfate (APS) as a single oxidant. Moulton et. al. [11] examined the electrochemical and spectroscopic properties of the PANI /DBSA nano dispersion. Cyclic voltammetry studies showed that the nano dispersion showed three oxidation states. Kim et. al. [12] found that initial shape of surfactant aggregates

(micelles) and the molar ratio of surfactant to aniline monomer decide the PANI particle morphology.

Earlier studies indicated that physical properties of the PANI nanoparticles depend on concentrations of monomers and also doping by different acids. Size of these nanoparticles depends on the stabilizers, chemical oxidants used and temperature. In the present work, we reported for the first time the role of high concentrations of PANI (0.125 and 0.15 M) on the formation and morphologies of PANI nanoparticle dispersions.

II. EXPERIMENTAL

A. Preparation of PANI nanoparticles dispersion

PANI nanoparticles dispersion with different concentrations (0.03 M, 0.07 M, 0.1 M, 0.125 M and 0.15 M) were prepared as per the previous reports []. Table 1 lists the polymerization conditions used for the synthesis of PANI nanoparticles dispersion. Initially, sodium dodecylsulfate (SDS) was dissolved in the deionized water to obtain the 0.2 M micellar solution. This micellar solution was used as template for the synthesis of PANI nanoparticles dispersion. Different concentrations of aniline were mixed separately in the micellar solution. The initiator solution was prepared by adding ammonium peroxydisulfate (APS) in the deionized water. The micellar solution having aniline and initiator solution were degassed separately by nitrogen gas for 10 and 5 min respectively to remove the oxygen. Then the polymerization was carried out by pouring the initiator solution drop-by-drop into the solution having the mixture of SDS and aniline under continuous stirring for 18 hours by magnetic stirrer. Initially light green colour was noticed. With increase in time dark green colour solution was observed. This suggested the formation of PANI. Figure 1 indicates the photographs of different concentrations of PANI nanoparticle dispersions. All reactions were conducted at room temperature.

B. Characterization of PANI nanoparticles dispersion

FTIR spectra were recorded on the Perkin-Elmer Spectrum 2 model spectrometer. UV-Visible spectra were monitored by a Systronics Double Beam UV-VIS Spectrophotometer, 2202. Hydrodynamic diameter of PANI nanoparticles were measured by Particle analyser-Nano plus. Surface morphologies of various PANI nanoparticles were observed by Scanning electron microscope (Carl-Zeiss, EVO-18).

S. No.	Concentration M (g)		
	Aniline	SDS	APS
1	0.03 (0.2779)	0.2 (5.7657)	0.015 (0.3443)
2	0.07 (0.6518)	0.2 (5.7669)	0.035 (0.7980)
3	0.1 (0.9352)	0.2 (5.7652)	0.05 (1.1445)
4	0.125 (1.1651)	0.2 (5.7670)	0.0625(1.4270)
5	0.15 (1.3898)	0.2 (5.7615)	0.075 (1.7139)

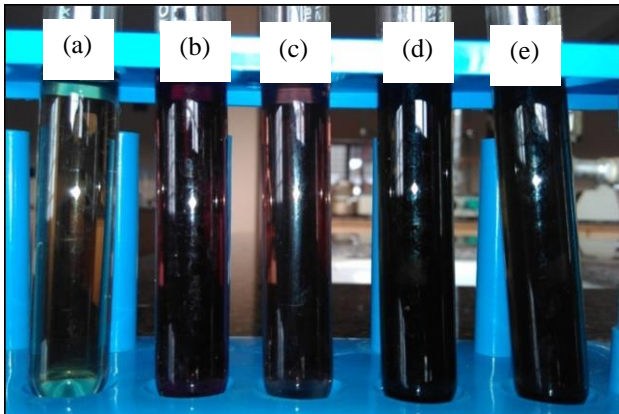


Fig. 1: Photographs of PANI nanoparticle dispersions with different concentrations of PANI. (a) 0.03M, (b) 0.07M, (c) 0.1M, (d) 0.125 M and (e) 0.15 M.

III. RESULTS & DISCUSSION

A. FTIR studies

To confirm the formation of PANI, FTIR measurements were carried out. FTIR spectra for various concentrations of PANI nanoparticles are shown in Figure 2. The peaks at 1590 and 1500 cm^{-1} are assigned to the presence of usual quinoid and benzoid deformations of the emeraldine form of PANI. These FTIR spectra confirm the formation of PANI.

B. UV-Vis spectroscopic studies

Figure 3 shows the UV-VIS absorption spectra of PANI nanoparticle dispersions with different concentrations of PANI. Three absorption bands were observed at 400–450 nm, 550 nm and 730–800 nm wavelength. The absorption bands 400–450 nm and 730–800 nm are attributed to level of doping and polaron formation, respectively. The amplitude of the peak around 400 nm was found to increase with increase of monomer concentration. This observation is consistent with previous report [12].

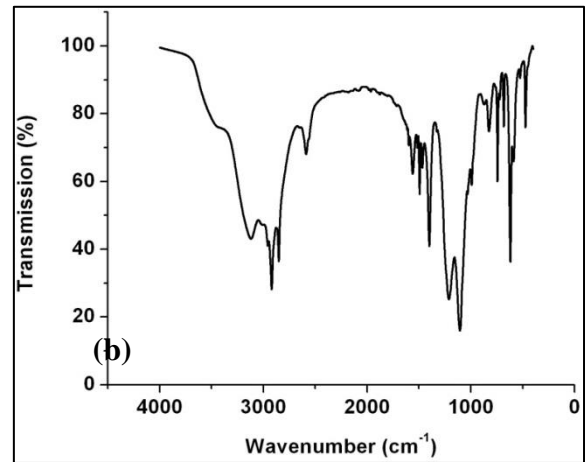
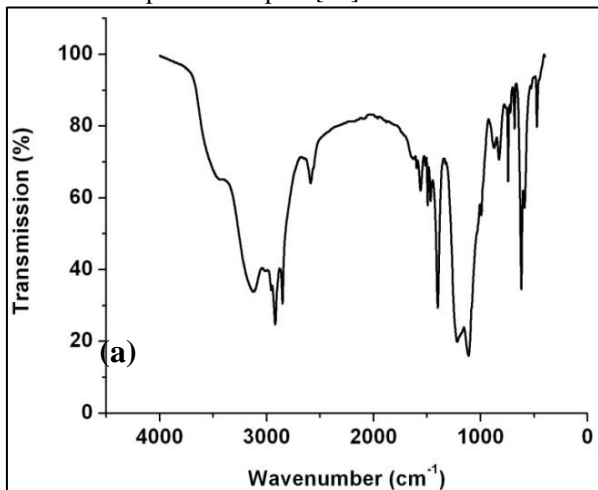


Fig. 2: FTIR spectra of PANI nanoparticles with different concentrations of PANI. (a) 0.1M and (b) 0.15 M.

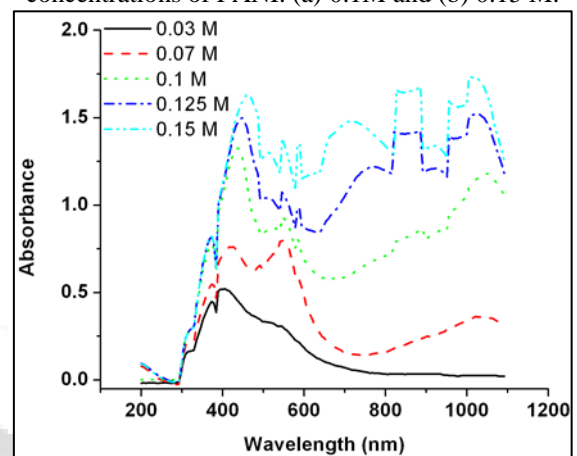
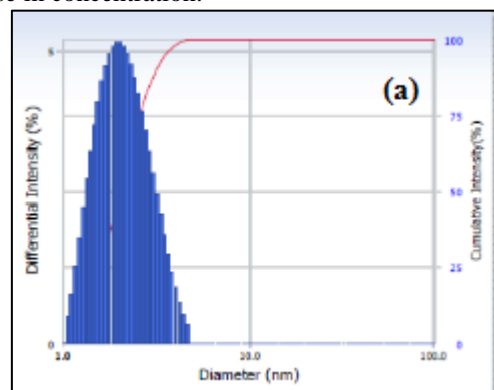


Fig. 3: UV-Vis spectra of PANI nanoparticles with different concentrations of PANI.

C. DLS results

To get insight about size of the PANI nanoparticles, DLS measurements were performed. PANI particle size distributions for different concentrations of PANI are presented as in the Figure 4. It was found from this figure that for the case of 0.03 M PANI, the size of particles is around 5 nm. In the case of 0.1 M PANI, there are two distributions of particles. First distribution is around 5 nm and second is about 400 nm. For highest PANI concentration of 0.15 M, the average particle size is found to be 450 nm. From these observations, it can be concluded that the size of PANI particles was found to increase with increase in concentration.



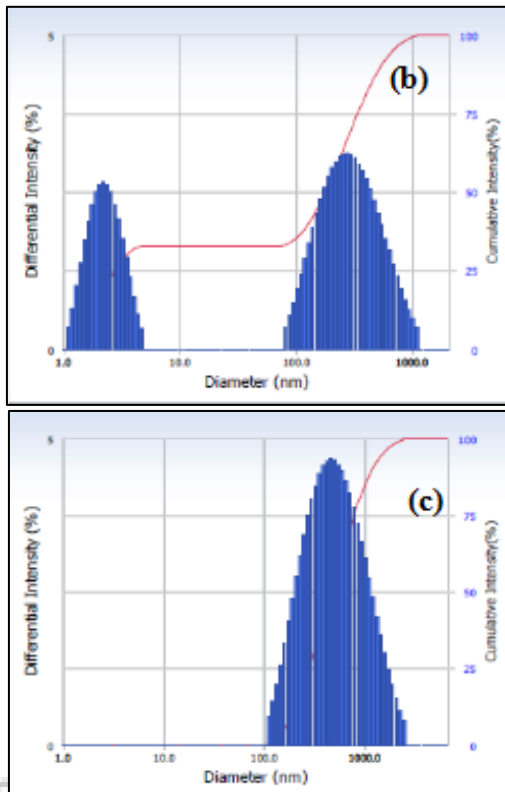


Fig. 4: Influence of concentration of PANI on the size of the PANI nanoparticles. (a) 0.03M, (b) 0.1M and (c) 0.15 M.

D. Surface morphological studies

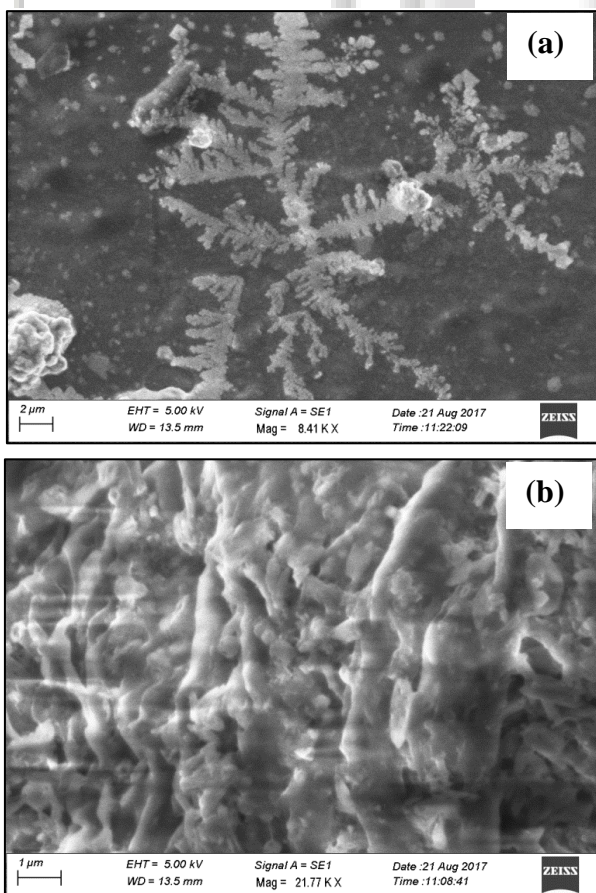


Fig. 5: Concentration dependence of surface morphologies of PANI nanoparticles. (a) 0.03M and (b) 0.15 M.

In order to correlate and support the DLS results, the variation of particle size and surface morphologies of PANI nanoparticles with respect to concentrations of PANI was observed by SEM. It was observed that smaller size particles in the order of nanometer were formed for lowest concentration (0.03 M) of PANI. However, in the case of 0.15 M PANI, very big particles in the range of sub-micron were noticed. These SEM observations are agreed with DLS results.

IV. CONCLUSIONS

PANI nanoparticles having various polymer concentrations have been successfully prepared using surfactant as a template by oxidation polymerization. The role of high PANI concentrations (0.125 M and 0.15 M) was investigated. The formation of PANI was confirmed FTIR experiments. DLS and SEM results indicated that particle size increases with increase in concentration of PANI. The present study proposed that the PANI nanoparticle dispersions may be potential candidate for anti-corrosive coatings.

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