

Morphology and electrical conductivity of self-doping polyanilines synthesized via self-assembly process

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ABSTRACT

Copolymerization of self doping monomer aniline and oxalic acid (OA)/ acetic acid (AA) in different molar ratio via the self-assembly process were conducted to prepare self-doping polyanilines (SD-PANIs). In this polymerization process, AA or OA plays the roles of surfactant and dopant for the self-doping PANIs. The morphology, UV-Vis absorption behaviour, crystalline density and electrical conductivity of self-doped PANIs are investigated. Depending on molar ratio of aniline to OA/AA, nanotubes structure of polyaniline (PANI) can be formed. Higher concentration of OA leads to increase in the diameter of the tubes in which micelles act as the template in the self-assembly of PANI to form nanotube structures, whereas increase in concentration of AA leads to change the structure of polyaniline from microspheres to nanotubes. The nanotubular structure aggregates to form a bundle structure as the concentration of AA increases. More uniform structure is observed in case of OA than that of AA, which may be due to the bulky structure of OA than AA. Higher absorption intensity in UV-Vis spectra of self-doping PANIs was observed for lower concentration of OA/AA. The crystal structure for the synthesized self-doped PANIs is orthorhombic and the C-N-C angle is larger. High electrical conductivity of the self-doped PANIs was observed as a function of degree of doping. Copyright © 2011 VBRI press.

Keywords: Nanotube structure; conducting polymer; self-doped polyaniline; self-assembly.



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unzipping CNTs, continuous polymer and carbon nanofibers by electrospinning.

Introduction

Conducting polymers have in recent years received a considerable attention because of their interesting electronic and physical properties, chemical stability and their potential technological applications [1-4]. Polyaniline (PANI) is one of the most promising conducting polymers because of its unique properties like ease of preparation in aqueous medium, good stability in air, simplicity in doping, improved electronic properties, controllable by oxidation and protonation state, excellent environmental stability, moderately high conductivity in the doped state and potential applications in electronic devices [5, 6]. Conducting polymers synthesized in the form of nanomaterials are of particular interest since their properties significantly differ from the properties of corresponding macroscopic materials. Recently, nanostructurization of conducting polymers and their composites emerged as a new field of research and

development, directed to creation of new smart materials for use in modern and future technologies [7]. The nanostructured form of the conducting polymers particularly provides advent to this field with high electrical conductivity and high surface area. Researchers have extensively studied nanostructure conducting polymer polyaniline (PANI) [8-11]. Low-dimensional nanostructured PANI, such as nanoparticles, nanofibers and nanotubes, nanosheets and nanobelts, have received considerable attention owing to their huge potential applications, especially in polymeric conducting molecular wires, light-emitting and electronic devices, chemical sensors, and biosensors [12]. In the past few years, several novel methodologies have been developed for the preparation of nanostructured PANI in the form of dispersions, nanowires, nanofibers, and nanotubules [13, 14]. Several studies have synthesized PANIs with various nanostructures, such as microporous structures, hollow microspheres, and nanotubes [15]. In comparison with the external acid doped PANI method, a self-doping monomer does not need to be removed after PANI polymerization because the dopant also plays the roles of surfactant and co-monomer of PANI [16-17]. The nanostructure and morphology of conducting polymers play important roles in determining material properties and their potential applications in technology. PANIs with nanostructures varying from hollow spheres to nanotubes could be produced by simply changing the dopant to monomer molar ratio. Highly crystalline PANI nanotubes could be produced by dicarboxylic acid doping. Self-doping sulfonated PANIs were produced by the electrochemical synthesis method and discussed the nanofiber structure formation mechanism of self-doped PANI [18-22].

This paper studies the preparation of self-doping PANIs with different nanostructures by changing the molar ratio of aniline to OA/AA from 0.1M to 0.4M. The morphology, UV-Vis absorption behaviour, crystalline density and electrical conductivity of self-doped PANIs are investigated.

Experimental

Materials and methods

Aniline (99.5%), oxalic acid (99.5%), acetic acid (99.5%) and ammonium persulphate (99.5%) were procured from E. Merck. Aniline monomer was distilled under reduced pressure. Ammonium persulfate (APS), oxalic acid and acetic acid were used as received. All supplementary chemicals were of analytical grade and solutions were prepared with double distilled water.

The UV-Vis spectra of the polymer solution in Dimethyl Formamide (DMF) were recorded by using UV-1800 Shimadzu automatic recording double beam spectrophotometer in the range of 200-1100nm. XRD patterns were recorded on a Philips PW-700 automatic X-ray diffractometer using Cu-K α radiation of wavelength $\lambda=0.1540$ and 0.1544 and a continuous scan of $2^\circ/\text{min}$ at 35kV and 20mA. SEM images were taken on JEOL JSM-6360 analytical scanning electron microscopes. Room

temperature electrical dc conductivity of the samples was measured by four probe method.

Synthesis of self-doped polyanilines

50 ml of 0.2M aniline and 50 ml of specific molar concentrations (0.1 to 0.4M) of oxalic acid /acetic acid were mixed with stirring at room temperature for 30 min. Then 50ml aqueous solution of 0.2M APS was added drop wise and the reaction was left for 12 hrs. The resulting self-doped PANI precipitate was washed with deionized water and methanol several times. Finally the product was dried in vacuum oven at 80°C for 24 hrs.

Results and discussion

Fig. 1(a) and 1(b) shows the UV-Vis absorption spectra of self-doped PANI with different concentrations of oxalic acid (OA) and acetic acid (AA) respectively in DMF. The spectra reveal the presence of two absorption bands as those of reported polyaniline, one in the visible region and the other in the UV region. 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 [23, 24].

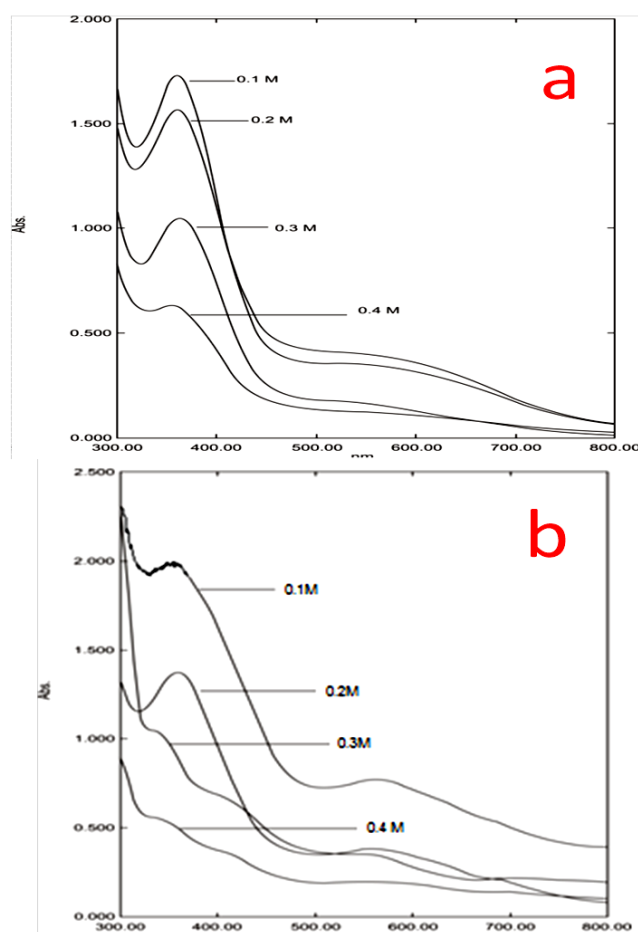


Fig. 1. (a) UV-Vis spectra PANI-AA (0.1M to 0.4M) (b) UV-Vis spectra of PANI-OA (0.1M to 0.4M).

The first absorption band at 360 nm was attributed to the reduced state (leucoemeraldine) of self-doped PANIs. The results indicate that PANI-OA/AA 0.1M concentration exhibits higher absorption intensity than those of higher concentrations, which corresponds to the lowest aniline unit content in the polymer backbone. Low aniline to OA/AA ratio and high degree of doping was favorable to the reduced state formation in the backbone of self-doped PANI [25].

The second absorption band results due to bipolaronic nature. As the concentration increases the bipolaronic band decreases as well as corresponding to the partial oxidation state of self-doped PANIs, was observed. This partial oxidation state was assigned as the intermediate state between the leucoemeraldine form containing benzenoid rings and the emeraldine form containing conjugated quinoid rings in the main chain of the PANI.

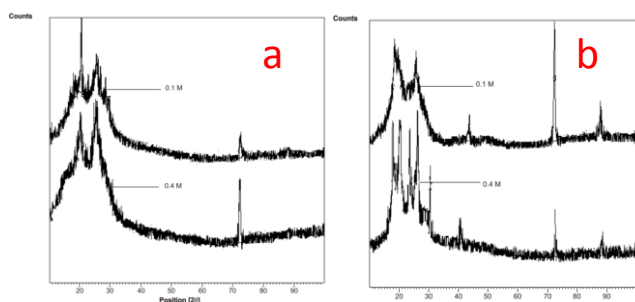


Fig. 2. (a) XRD pattern of PANI-OA (0.1M) and (0.4M) (b) XRD pattern of PANI-AA (0.1M) and (0.4M).

Table 1. Data of XRD spectra of self-doped PANIs.

SD-PANI	2θ	d_{obs} (Å)	d_{cal} (Å)	% rel. int.
0.1M (OA)	21.64	4.332	4.334	100
	26.07	1.307	1.313	33.3
	72.34	1.036	1.032	13.7
0.4M (OA)	20.92	4.414	4.410	60.2
	26.21	2.321	2.332	46.1
	72.16	1.303	1.308	100
0.1M (AA)	20.15	4.832	4.827	30.5
	26.05	3.471	3.465	32.3
	44.23	1.750	1.739	19.4
	72.04	1.308	1.310	100
	86.54	1.103	1.110	21.6
0.4M (AA)	20.14	4.980	4.978	100
	22.34	4.342	4.337	72.4
	25.08	3.781	3.780	56.8
	26.12	3.408	3.410	86.2
	42.66	3.064	3.067	35.1
	72.18	2.940	2.937	47.9
	86.21	1.294	1.291	31.0

The XRD pattern of the polymer generally differs because of uncertainty in the polymeric chains. It depends on the synthetic routes, solvent and ionized state [5]. The

crystal structure for PANI is reported to be orthorhombic. The XRD pattern reveals the structure of these materials is polycrystalline because of some reflections and diffused background. The value of d -spacing in the materials concludes that local chain arrays are similar. The XRD of the self-doped PANI prepared by using *o*-aminobenzenesulfonic acid have peaks at $2\theta = 23, 26$ and 28° [25]. The XRD spectra of self-doped PANI synthesized in this study by using oxalic acid (OA)/ acetic acid (AA) at different concentrations are shown in Fig. 2 and the values d_{obs} , d_{cal} , 2θ and % relative peak intensity are tabulated in Table 1. It can be seen from the figures and the table that PANI-AA (0.4M) is more crystalline as compared to PANI-AA (0.1M), indicating the nanotubes structure of PANI-AA (0.4M) and microsphere structure of PANI-AA (0.1M). On the other hand PANI-OA(0.1M) and PANI-OA(0.4M) are crystalline, indicating nanotube structure and the diameter depends on their concentration. The peaks in all PANIs are attributed to the diffraction along periodicity perpendicular to the self-doped PANI Chain [26, 27]. The results indicate that the microsphere structure PANI shows an amorphous morphology, while high crystalline morphology occurs in nanotube structure PANI. This result also supports from SEM of the synthesized PANIs. The d -spacing calculated (d_{cal}) from the angular positions of the reflections and from the reflection broadening (2θ), the inter-chain lateral distance a , b and c for these synthesized self-doped PANIs are reported in Table 2. From the values of inter-chain lateral distance, it is confirmed that the crystal structure for the synthesized polyaniline is orthorhombic and the larger values of c confirms that the C-N-C angle is larger. This increase may be due to steric interaction between H and substituted group of benzene ring.

Table 2. Inter-chain lateral distance of self-doped PANIs.

SD-PANI	a (Å)	b (Å)	c (Å)
0.1M (OA)	3.4	6.1	15.2
0.4M (OA)	3.5	6.2	15.8
0.1M (AA)	4.5	7.8	17.0
0.4M (AA)	4.4	7.6	16.8

Fig. 3 (a) and (b) shows SEM images of 0.1M and 0.4M concentration of OA and figure 3 (c) and (d) shows SEM images of 0.1M and 0.4M concentration of AA respectively. In case of Aniline–OA, nanotubes are observed in 0.1M concentration, but as the concentration increases, the diameter of tubes increases. In case of Aniline–AA, as the molar ratio of aniline to AA increased, tubular structure changes into bundle structure at 0.4M. In this polymerization process, AA or OA plays the roles of surfactant and dopant for the self-doping PANIs. First, AA and aniline cations form micelles in aqueous solution. The aniline cations can appear in the interface of micelles and water. The polymerization initially occurs at the surface of the micelles as the oxidant APS is added [28]. In addition, the micelles tend to aggregate and react along the direction

of the polymer chain in the polymerization process. The micelles act as the template in the self-assembly of PANI to form nanotube structures. The nanotubular structure aggregates to form a bundle structure as the concentration increases as seen in SEM images. This is schematically represented in **scheme I**. More uniform structure is observed in case of OA than that of AA, which may be due to the bulky structure of OA than AA.

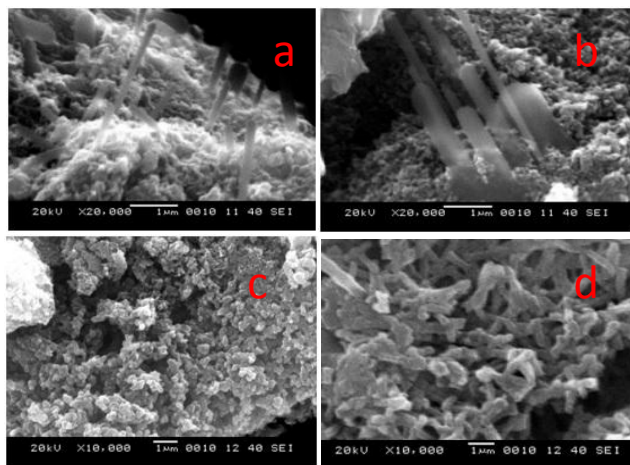
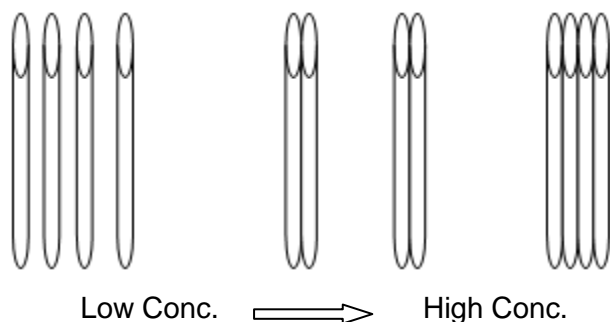


Fig. 3. (a) SEM image of PANI-OA (0.1M), (b) SEM image of PANI-OA (0.4M), (c) SEM image of PANI-AA (0.1M), (d) SEM image of PANI-AA (0.4M).



Scheme I. The nanotubular structure aggregates to form a bundle structure.

Fig. 4 (a) and **(b)** show thermal dependence dc electrical conductivity (σ) of self-doped PANI-OA and PANI-AA respectively. The dc electrical conductivity (σ) was measured by using four probe conductivity measurement technique. The increase in conductivity with increase in temperature is the characteristic of “thermal activated behavior” [29]. 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 [30]. It is also possible that the thermal curing affects the chain alignment of the polymer, which leads to the increase of conjugation length and brings about the increase of conductivity. There also had to be molecular rearrangement on heating, which made the molecular conformation favorable for electron delocalization [31].

Conductivity of PANI-OA increased significantly from 0.3498 to 0.8233 S/cm as concentration of OA increases from 0.1 to 0.4M. Similarly, conductivity of PANI-AA increased from 0.0120 to 0.0164 S/cm as concentration of AA increases from 0.1 to 0.4M. The origin of the lower conductivity for low degree of doping may be due to the presence of the side substitute group led to the separation enhancement of polymer main-chains and reduced inter-chain diffusion of charge carriers, subsequently resulting in lower self-doped PANI conductivity.

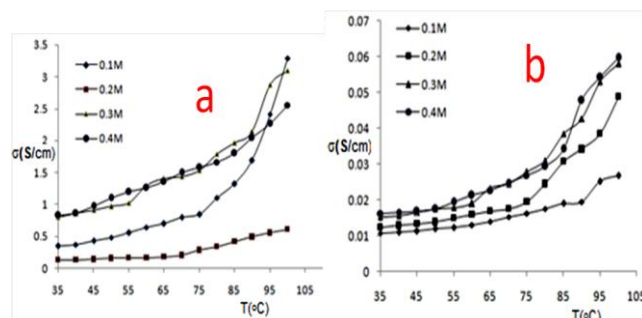


Fig. 4. (a) DC electrical conductivity (σ) of PANI-OA, (b) DC electrical conductivity (σ) of PANI-AA

Conclusion

Self-doping polyaniline was successfully synthesized by copolymerization of monomer aniline and oxalic acid (OA)/acetic acid (AA) via the self-assembly process. In this polymerization process, AA or OA plays the roles of surfactant and dopant for the self-doping PANIs. Depending on molar ratio of aniline to OA/AA, nanotubes structure of polyaniline (PANI) can be formed. Higher absorption intensity in UV-Vis spectra of self-doping PANIs was observed for lower concentration of OA/AA. The crystal structure for the synthesized self-doped PANIs is orthorhombic and the C-N-C angle is larger. High electrical conductivity of the self doped polyanilines was observed as a function of degree of doping.

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