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Highly crystalline uniform nanostructured polyaniline doped with H₂SO₄

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ABSTRACT

In this contribution, highly crystalline, uniform rod-like nanostructured polyanilines, ca. 100–150 nm in diameter and 500–900 nm in length were successfully synthesized by chemical polymerization by both stirring and without stirring the reaction system at 0°C and room temperature in acidic medium (H_2SO_4). Resulted polymers were characterized by UV-Vis, Fourier transform infrared (FT-IR), proton-nuclear magnetic resonance (^{1}HNMR) and X-ray diffraction (XRD) techniques. Two distinctive morphologies, rod like and grain like structures were observed as confirmed unambiguously by scanning electron microscopy (SEM) by stirring and without stirring the reaction respectively. We have evaluated their conductivity by dc electrical conductivity measurements and thermal properties by thermogravimetric analysis (TGA).   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

Recently, nanoscience and nanotechnology getting its own place in both academia and industry. Nanomaterials have attracted widespread attention since the 1990's because of their specific features that differ from common materials[1,2]. Nanomaterials have wide-ranging applications in a variety of areas, including chemistry[3], physics[4], electronics[5], optics[6], biomedical science[7] and the materials sciences[8]. Therefore, increasing research interests have been focused on nanomaterials[9]. Polymers are becoming the most promising new materials for next generation electronic devices[10]. Polyaniline (PAni) is one of the most attracted

conducting polymers (ICPs). Nanostructured conducting polyanilines especially nanofibers/nanotubes/nanowires/ nanorods have been extensively studied because of their unique properties and promising applications as nanomaterials and in nanodevices[11] as solid state devices using as sensors, optoelectronic devices, energy storage devices, metallization of printed circuit boards, radiation shielding materials has been established[12]. Polyaniline nanomaterials are found to have higher performance over their bulk counterparts. Various PAni nanostructures (nanofibers/tubes/wires/rods) have been prepared by some usual techniques, such as micro-emulsions[13], freeze drying[14], electrospining[15], hard and soft templates[16-18], interfacial polymeriza-

tion[19,20], dilute polymerization[21,22] and seed polymerization[23] and enzymatic polymerization technique, etc. Though the various approaches have been established, the preparation of nanostructured PAni with uniform sizes and morphologies is still a major challenge. Furthermore, the formation mechanisms of the nanostructures are still not wholly understood. Polyaniline is known to exhibit a variety of supramolecular morphologies, such as thin films on various substrates[24,25], colloidal particles[26-29], nanotubes[30-33], nanowires[34-36], sometimes referred to as nanofibres[37,38], and hollow PAni microspheres[38]. It is likely that PAni morphology, based on the self-assembly of PAni chains, will also be affected by the liquid or solid state of the medium in which the polymerization takes place. It has already been shown that the polymerization of aniline in the presence of hydroxypropylcellulose yields colloidal particles[39,40]. In the similar polymerization carried out in ice, a sponge-like macroporous composite has been obtained instead[39]. Granular morphology of PAni is typically obtained when the polymerization takes place at 20 °C in solutions of strong acids[41], such as 0.1M sulfuric acid. At -5 °C, some indications of extended nanostructures are observed .If the similar reaction takes place in the solutions of weak acid[42], 0.4 M acetic acid, PAni nanotubes are the dominating product, A rough nanogranular "dotted" surface of the nanotubes, occasionally reported in literature[39,43,44], should be noted. The morphology after polymerization in ice is different, irrespective of acid, and is constituted by particles of submicrometre size, mutually connected by nanofibres of *ca.* 20 nm thickness. In this paper, PAni doped with inorganic acid, H_2SO_4 was synthesized by liquid state polymerization by stirring and without stirring the reaction system at 0 °C and room temperature. The results were explained on comparative basis. In this contribution, highly crystalline, uniform rod-like nanostructured polyanilines, ca. 50–130 nm in diameter, and 130–260 nm in length were successfully synthesized by chemical polymerization in acidic (H_2SO_4) medium. Resulted polymers were characterized by ultraviolet-visible (UV-Vis), Fourier transform infrared (FTIR), proton-nuclear magnetic resonance (^{1}HNMR) and X-ray diffraction (XRD) techniques. We have also evaluated their conductivity (dc electrical conductivity), thermal (thermogravimetric analysis (TGA)), and morphological (scanning electron microscopy (SEM) properties.

EXPERIMENTAL PART

Materials

Aniline [E. Merck] was distilled prior to use. Analytical grade (99% pure) reagents such as ammonium persulfate (APS), H_2SO_4 and sodium hydroxide were used as received. Double distilled water was used for the preparation of required solutions.

Synthesis of polyaniline (PANI)

In a typical experiment, aqueous solution of 0.1 M oxidizing agent, ammonium per sulfate was added dropwise into 1.0 M H_2SO_4 solution containing 0.1 M aniline at a temperature of 0–5 °C/room temp. The oxidation of aniline is highly exothermic and therefore, the rate of addition of the oxidant was adjusted to prevent any increase in the temperature of the reaction mixture. After the addition of oxidant, the reaction mixture was stirred at constant temperature for 5 minutes and then reaction system kept stirring/left still without shaking for 4 hours. The obtained green precipitate, polyaniline was filtered and then washed with distilled water until the washing liquid was colourless. In order to remove oligomers and other organic byproducts, the precipitate was washed with methanol until the methanol solution was colourless. Finally, the resulting polymer salt was dried at 100 °C until a constant mass. Polyaniline base was prepared by dedoping polyaniline-sulfate salt (1 g), with constant stirring at ambient temperature in 100 mL NaOH solution (1 M) for 12 h. The resultant solid was filtered and washed with water, followed by acetone and finally dried at 100 °C until a constant mass.

Characterization techniques and studies used

A weighed amount (10 mg) of polymer was added to 2 mL of the solvent with stirring. Additional solvent was added at the rate 1 mL per 10 min till the polymer was completely dissolved. This procedure was continued for next 30 min and left for 3 h and then filtered. The polymers, which don't dissolve completely during this period, were taken as "partially soluble".

The morphologies of the polymers were studied by

using coupling JSM-840A scanning electron microscope. The electron microscope was operated at 20 kV. The FT-IR spectra of the polymers were recorded on a JASCO FTIR-5300 instrument in the range 4000-400 cm^{-1} at a resolution of 4 cm^{-1} by making KBr pellets. For UV-vis, the samples were prepared by dissolving the polymers in the dimethylsulphoxide (DMSO). The UV-Vis spectrum was recorded using a UV-visible 5704SS ECIL spectrophotometer operated at 1 nm resolution from 200-800 nm. ^{1}HNMR spectra were recorded with a Bruker AMX 400 MHz instrument using DMSO as an internal reference. The XRD patterns were obtained employing a JEOL JDX-8p spectrometer using Cu Kα radiation ($\lambda = 1.54$ Å). The X-ray generator was operated at 30 kV and 20 mA. The scanning range, $2\theta/\theta$ was selected.

The thermogravimetric analysis (TGA) measurements were made using a Mettler Toledo Star System at a heating rate of 10 °C per min under nitrogen atmosphere. Conductivity measurements were done at room temperature by two-probe method on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The error in resistance measurements under galvanostic conditions with a Keithley model 220 programmable current sources and a Keithely model digital 195A voltammeter was less than 2%.

RESULTS AND DISCUSSION

Solubility

PANI is soluble with dark bluish violet colour in polar solvents like dimethyl sulphoxide (DMSO), N-methyl pyrolidine (NMP), dimethyl formamide (DMF), and tetrahydrofuran (THF), partially soluble with light bluish colour in less polar solvents like chloroform and insoluble in ethyl alcohol and benzene.

Morphological study

The reaction solution without stirring yield uniform morphologies (Figure 1). Figure 1a shows the SEM images of polyanilines synthesized at room temperature without stirring, which reveal that the resulting polyaniline salts are composed of a large quantity of uniform rod-like nanostructures with diameters of 100-150 nm and length up to 500 nm-900 nm. It was found that obtained rod-like PAni morphology was obviously differ-

ent with that of PAni salts prepared under stirring (Figure 1b), are grains like structures with size 400-800 nm. In this figure, the particles are agglomerated to form giant like structure and may be due to the moisture content in the sample. This is consistent with the result in literature[45,46] in which the morphology of the PAni nanofibers was strongly dependent on the disturbance and the concentration of both monomer and oxidant. Indeed, changing the molar ratio of APS to Ani would change the morphologies of resulting PAni salts. On the other hand, the reaction temperature has little influence on the formation of uniform rod-like PAni nanostructures. The reaction systems of APS:Ani: = 0.5:1 at 0 °C or 35 °C without stirring also yielded nano rod-like PAni salts (Figure 1c). In other words, we believe that the formation of uniform rod-like nanostructured PAni is related to the reaction condition like stirring, low molar ratio of aniline to oxidant and the low concentration of aniline in the reaction system.
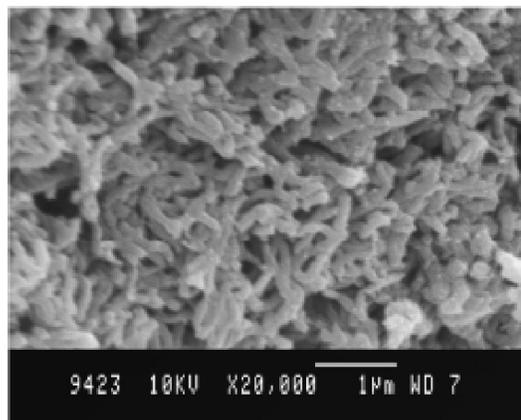
Figure 1(a) : SEM image of rod like PANI prepared at room temperature without stirring.
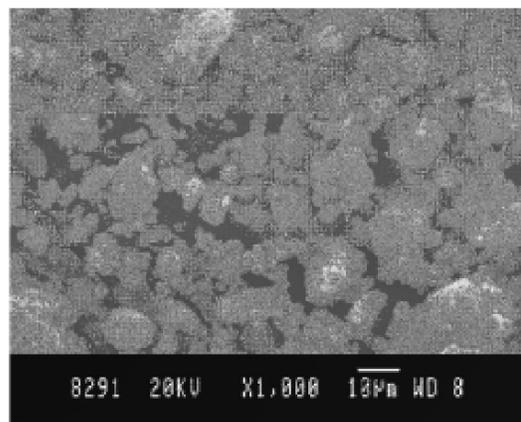
Figure 1(b) : SEM image of PANI prepared at room temperature with stirring.
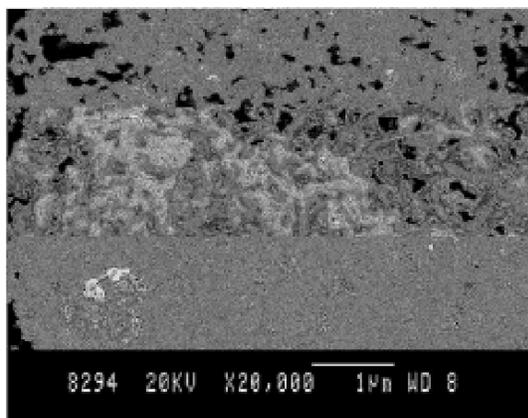
Figure 1(c) : SEM image of PANI prepared at room temperature without stirring.

FT-IR spectroscopy studies

Figure 2 shows the FT-IR spectra of PAni. It was found that the FT-IR spectra of both PAni were similar. The characteristic bands of nanostructured rod like PANI (Figure 2) in the IR spectrum occurs at 1562, 1487, 1302 1240, 1107 and 798 cm^{-1}. Identifying the resulting rod-like PAni salts were well-doped[47]. The appearance of the intense broad band at about 1107 cm^{-1} was associated with high electrical conductivity and a high degree of electron delocalization in PAni salts. The band at about 507 cm^{-1} can be assigned to the absorptions of the sulfonate anion[48]. A broad band at 3440 cm^{-1} was assigned to the free N-H stretching vibration. The bands at 2920 and 2850 cm^{-1} was assigned to vibration associated with NH part in $C_6H_4NH_2C_6H_4$. The high-frequency bands at 1562 and 1487 cm^{-1} are assigned to the C=C ring stretching vibrations of the benzenoid ring and the C–N stretching of the quinoid ring, respectively. The bands at 1302 and 1240 cm^{-1} correspond to the N–H bending and symmetric component of the C=C (or C–N of the benzenoid ring) stretching modes. The remaining bands at
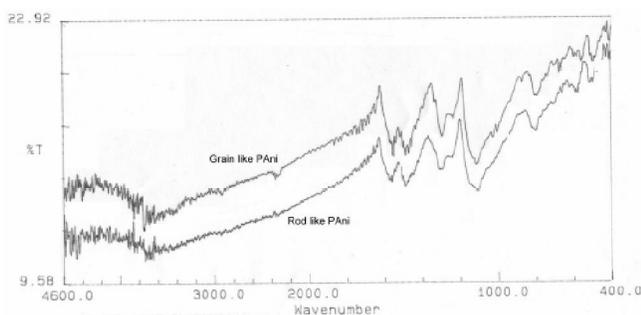
Figure 2 : FTIR spectra of PANI.

1107 and 798 cm^{-1} could be attributed to the in-plane and out-of plane C–H bending modes respectively. The C–H out-of-plane bending mode has been used as a key to identify the type of substituted benzene. For polyaniline salt, this mode was observed as a single band at 798 cm^{-1}, which was almost nearer to the range 800–860 cm^{-1} reported for 1,4-substituted benzene[49].

UV-vis spectra

Absorption spectra were recorded in DMSO and NMP. Two main absorption bands were observed for polyaniline in both the solvents (Figure 3) one around 370 nm assigned to the $\pi-\pi^*$ transition of the phenyl ring and another around 620 nm assigned to the n–π^* transition. The absorption peaks in the 300–370 nm region and that at 550–610 nm region respectively correspond to excitation of amine nitrogen of the benzenoid segments and imine nitrogen of the quinoid segments[50].
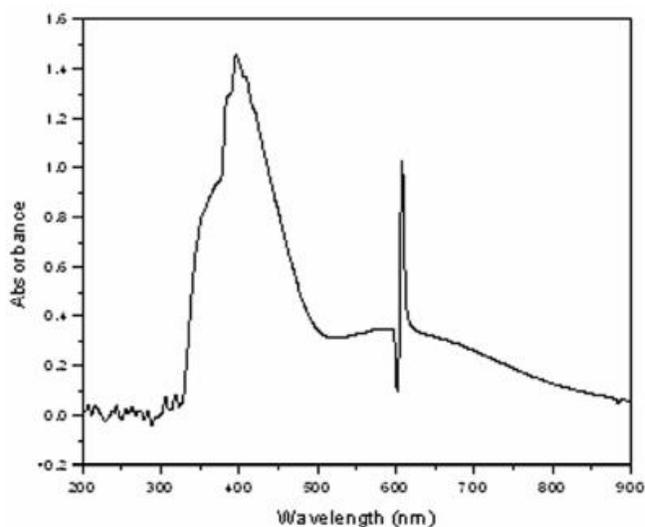
Figure 3 : UV-vis spectra of PANI.

X-ray diffraction studies

XRD pattern of rod-like PAni salt is depicted in (Figure 4). The peaks 2θ at 10.3°, 19.4°, 25.5°, 26.17°, 35.39° are the characteristic peaks of the PAni salts. The nicely sharp peak centered at 2θ=19.4⁰ may be ascribed to periodicity parallel to the polymer chain, while the latter peaks at 2θ = 25.5° and 26.16° are may be caused by the periodicity perpendicular to the polymer chain[51,52], presenting the resulting rod-like PAni salts are highly crystalline[53,54]. The chain length of PAni is about 4.355 AU[55].

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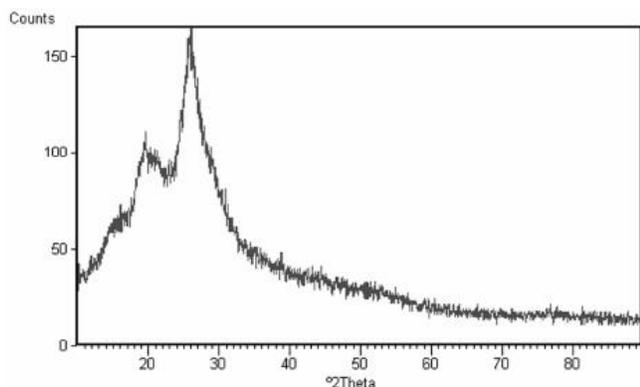
Figure 4 : XRD pattern of crystalline PANI.

Thermogravimetric analysis

Thermogravimetric analysis of PANI performed in an air atmosphere, employing a heating rate of 10 ^{0}C min^{-1}. The TGA curve for the PANI salt shows (Figure 5) a three step weight loss. The weight loss of about 6% up to 150 °C was due to the loss of moisture. The 4.5% weight loss occurring up to 395 °C is attributed to the loss of the dopant H_2SO_4. The final step starts at around 400 °C, leads to the complete degradation of the polyaniline salt[56].
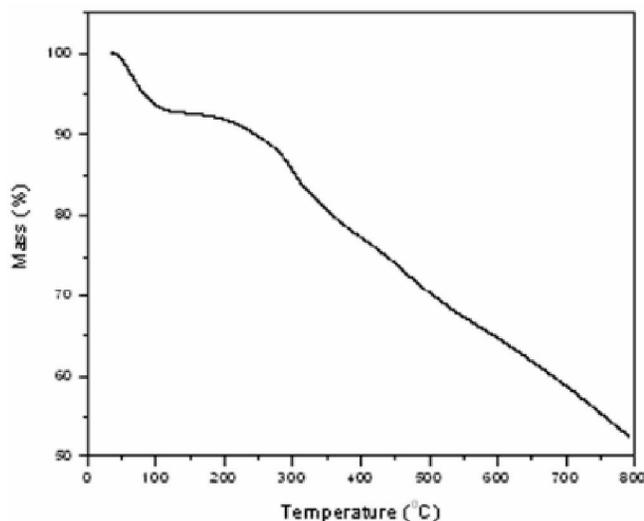
Figure 5 : TGA of PANI.

Conductivity

The conductivity of PAni depends on the degree of doping, oxidation state, particle morphology, crystallinity, interior intrachain interactions, molecular weight, etc.[57]. The conductivity of PAni salt is shown in Figure 6. The nanostructured uniform rod-like PAni produced without stirring at 0°C has a higher electrical conductivity than PAni prepared at room temperature. The dif-

ferences in the conductivities of the rod and grain like structures PAni is due to the change in the morphologies of PAni particles, which is evident by from the results of FT-IR, UV–vis spectra and SEM studies. One can see that the conductivity of polyaniline with grain morphology is the smallest in the two forms.
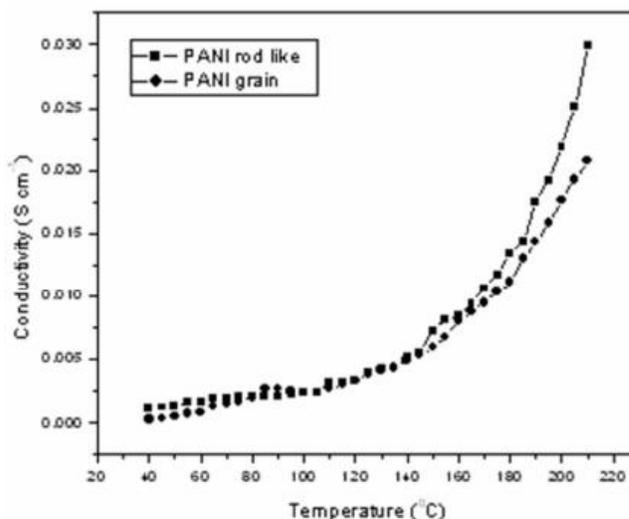
Figure 6 : Conductivity of rod like PANI and grain like PANI.

CONCLUSIONS

In summary, nanostructured polyaniline salts with uniform rod-like morphologies were prepared using ammonium peroxydisulfate as oxidant at room and 0 °C temperature without stirring. The obtained polyaniline rice-like nanostructures were well-doped characterized using FT-IR and UV–vis spectra, and composed of 100–150 nm in diameter and 500–900 nm in length with high crystallinity. It is believed that non-stirring condition play an important role in the formation of the uniform rod-like polyaniline nanostructures.

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