



Effect of LiCl on conductivity of polyaniline synthesized via *in-situ* chemical oxidative method

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ABSTRACT

An *in-situ* chemical oxidative method has been exploited for the synthesis of polyaniline (PANI) using HCl as a dopant, LiCl as a co-dopant and ammonium persulfate (APS) as an oxidizing agent at room temperature. The monomer to oxidant ratio has been optimized as 1:1.125 and the concentration of LiCl was varied from 0.0625 to 3 M. The synthesized polymer (PANI-LiCl) was characterized by Fourier transform infrared (FTIR) spectroscopy, Ultraviolet–Visible (UV–Vis) spectroscopy, X-ray diffraction (XRD) studies, Scanning Electron Microscopy (SEM) X-ray Photoelectron Spectroscopy (XPS) and Electrical conductivity measurements. The thermal properties of the synthesized PANI-LiCl have been characterized by Differential Scanning Colorimetry (DSC). The conductivity of the synthesized PANI-LiCl increases with the increasing concentration of LiCl from 0.0625 to 2.5 M. Further increase of LiCl concentration (3 M) drastically decreased the conductivity of PANI due to the saturation or over oxidation. The maximum electrical conductivity of 25.01 S cm⁻¹ was realized for 2.5 M LiCl doped PANI.

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1. Introduction

Polyaniline (PANI) is one of the most widely used Intrinsic Conducting Polymers (ICP) for various applications such as light emitting diode (LED), supercapacitors, biosensors, electromagnetic shielding, and electronic sensors, due to its outstanding qualities of good environmental stability, excellent electrical and optical properties, etc. [1]. Especially, PANI can be modified for specific functions towards the application and the electrical conductivity of PANI can be controlled by both charge transfer and protonation. Moreover, secondary and tertiary amines present in PANI chain have the ability to bind metal ions [2]. In the real sense, the electrical conductivity of polyaniline makes it a promising candidate for the above said applications. But, the electrical conductivity of PANI depends on many factors such as the method of synthesis, dopant and temperature. Chemical oxidation is one of the best and easiest methods to synthesize PANI with high electrical conductivity. On other hand, various dopants have been used to enhance the electrical conductivity, magnetic, structural properties of PANI [3]. Especially, Li salt doped PANI such as LiBF₄, LiAsF₆, LiCF₃SO₃, and LiCl have attracted the researchers for supercapacitor application. Among them, Lithium chloride can act a better dopant due to the presence of the Cl⁻ ion as dopant [4,5]. In some cases, LiCl induces the degree of protonic acid doping on PANI due to Li⁺ binding with the imine site present in PANI. This causes the structural changes of PANI and resulted in enhanced electrical conductivity [6,7]. As per the existing

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literature, LiCl doped PANI can be synthesized at zero and sub-zero temperature conditions and moreover LiCl doping can be achieved by *ex-situ* method [8].

Very few work has been carried out on LiCl doped PANI. In the present study, PANI-LiCl was synthesized by an *in-situ* chemically oxidative method using HCl as a dopant, LiCl as co-dopant and ammonium persulfate was used as an oxidizing agent at room temperature. During the synthesis, the LiCl concentration was changed from 0.0625 to 3 M. The synthesized PANI-LiCl was duly characterized and the results are presented in this paper.

2. Experimental

2.1. Materials

Aniline (AR grade) was obtained from Sigma Aldrich. Ammonium persulfate (APS) and LiCl were purchased from Merck, India. Hydrochloric acid was purchased from SDFCL, India. Aniline was vacuum distilled before use. All other chemicals were used as received. All reactions were carried out using milli-pore water.

2.2. Synthesis of PANI and PANI-LiCl

Pure PANI doped with HCl was prepared as per the literature [9] and labeled as PANI. PANI-LiCl salt was synthesized by *in-situ* chemical oxidation method as follows: Aniline (0.25 M) was taken in a round bottom flask containing 100 mL of 1 M HCl. A varying amounts of LiCl such as 0.0625, 0.125, 0.75, 1.5, 2.0, 2.5 and 3.0 M were dissolved separately in aniline containing 1 M HCl and labeled as PANI-LiCl 1, PANI-LiCl 2, PANI-LiCl 3, PANI-LiCl 4, PANI-LiCl 5, PANI-LiCl 6, and PANI-LiCl 7 respectively. The oxidant APS (0.28 M) was dissolved in 100 mL of 1 M HCl and added dropwise to the above solution for 2 h under stirring. The system was kept under vigorous stirring for 6 h to complete the polymerization. Finally, PANI-LiCl salt was filtered and washed with 1 M HCl and diethyl ether until a colorless filtrate was obtained. The filtered PANI-LiCl salt was dried in a vacuum oven at 60 °C for 24 h.

2.3. Characterization

The UV-Vis spectroscopy was recorded using Perkin Elmer UV-630 spectrophotometer in the range of 1100–200 nm and DMSO was used as a solvent. Perkin Elmer 1600 was used to record FT-IR spectra of samples in the range from 4000 to 400 cm^{-1} . Van der Pauw four-probe method was followed to measure the electrical conductivity of samples. The XRD patterns were obtained using a Bruker binary V3 X-ray diffractometer in the 2θ range of 10–80° with Cu K α radiation (1.54 Å). The Differential Scanning Colorimetry (DSC) was performed using TA 2910 instrument. The heating rate was followed by 10 °C per minute and an inert nitrogen atmosphere was maintained during the experiments. The surface morphology of the polymers were studied by a TESCAN VEGA Scanning Electron Microscopy (SEM). The XPS measurement was performed with Carl Zeiss instrument. The spectra were acquired at a pressure using an ultra high vacuum with Al K α excitation at 250 W.

3. Results and discussion

3.1. Electrical conductivity

The electrical conductivity of PANI and PANI-LiCl salts were shown in Fig. 1. From Fig. 1, it is seen that the electrical conductivity of pure PANI is 12.99 S cm^{-1} , which is slightly decreased to 11.28 S cm^{-1} for PANI-LiCl 1 due to improper dispersion and entanglement of a small quantity of LiCl concentration. On further increase of LiCl concentration from 0.125 to 2.5 M, the conductivity increased from 14.96 to 25.01 S cm^{-1} for PANI-LiCl 2 to PANI-LiCl 6. The electrical conductivity was rapidly enhanced from PANI-LiCl 2 and reached a maximum electrical conductivity of 25.01 S cm^{-1} for PANI-LiCl 6. This might be due to the doping of LiCl on PANI. Further increase in LiCl lead to a drastic decrease in electrical conductivity of 13.8 S cm^{-1} for PANI-LiCl 7.

Scheme 1 represents the mechanism of lithium chloride doping in PANI. The Li^+ ions easily migrate towards doping site on the polymer chain and cause doping by nucleophilic reaction [10]. The counter ions effectively get doped on the surface of the polymers, enhancing its electrical conductivity up on increase of concentration of LiCl from 0.125 to 2.5 M. Further increase of LiCl concentration, decreased the conductivity due to the saturation (or) over oxidation of polyaniline backbone.

3.2. FT-IR spectroscopy

FT-IR spectra of pure PANI and PANI-LiCl salts were characterized to understand the interaction between PANI and LiCl salt. Fig. 2 shows the FT-IR spectra of pure PANI and PANI-LiCl salts. The pure PANI exhibited its characteristic bands at ~ 3455 , ~ 3323 , ~ 2925 , ~ 2880 , ~ 1570 , ~ 1482 , ~ 1142 and ~ 820 cm^{-1} due to asymmetric $-\text{NH}_2^+$ stretching, symmetric $-\text{NH}_2^+$ stretching, aromatic asymmetric C–H stretching, aromatic symmetric C–H stretching, quinonoid stretching,

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