

Synthesis and characterization of polyaniline doped with Cu II chloride by inverse emulsion polymerization

Rizwan Ullah^a, Salma Bilal^b, Khurshid Ali^a, Anwar-ul-Haq Ali Shah^{a,*}

^a Institute of Chemical Sciences, University of Peshawar, 25120, Peshawar, Pakistan

^b National Centre of Excellence in Physical Chemistry, University of Peshawar, 25120, Peshawar, Pakistan

ARTICLE INFO

Article history:

Received 22 November 2013

Received in revised form 15 May 2014

Accepted 11 September 2014

Available online 15 October 2014

Keywords:

Polyaniline

Copper chloride

TGA

XRD

ABSTRACT

Polyaniline and its composites with Cu II chloride were synthesized by inverse emulsion polymerization. The synthesized composites were characterized with UV/vis, FT-IR, XRD and SEM. The results show the presence of polyaniline in the emeraldine base form doped with copper II chloride. The thermal properties of the composites were studied by carrying out TGA. The electrical transport properties were calculated from the conductivity measurement. The composites were found to be soluble in common organic solvents such as chloroform, NMP, DMSO, 1:2 mixture of 2-propanol and toluene and 1:2 mixture of 2-propanol and chloroform. Cyclic voltammetry was carried out to find out the redox properties of synthesized composites.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

During the last three decades the conducting polymers like polyacetylene, polypyrrole, polythiophenes, polyaniline, etc. were extensively studied by the scientist from all over the world. The major breakthrough in the field of conducting polymer was reported by Shirakawa et al. [1] in 1977 when they discovered polyacetylene. Later on other conducting polymers including polyaniline were synthesized by scientists. Polyaniline being one of the most recently studied intrinsically conducting polymer due to the exceptional properties like easy synthesis, extra stability, inexpensive monomer, excellent environmental stability [2], doping dedoping ability [3], etc. Beside these properties PANI has many important industrial applications such as removal of mercury from waste water [4], as a corrosion protecting agent in paint industry [5], an essential constituent of solar cell, light emitting diodes, surgical instruments and light weight batteries [6].

Recently the studies of PANI composites with other materials such as metals are gaining attention due to the diverse physico-chemical properties. PANI-silver nanocomposites with improved conductivity as compared to pure PANI were reported by Blinova et al. [7] in 2009. Kinyanjui et al. [8] reported the synthesis of PANI-gold composites with short chains and high yield of reaction. The gold microparticles were found to be embedded in the PANI resulting in the formation of composites; however, they did not report

any substantial change in conductivity. PANI-paratoluenesulfonic acid-gold (PANI-p-TSA-Au) composites were synthesized by Zhang et al. [9]. They reported high conductivity for the composites as compared to PANI-p-TSA. The oxidative polymerization of aniline by using copper II sulfate as oxidizing agent was carried out by Mallick et al. [10]. They reported PANI-Cu nanocomposites having flower like morphology with similar chemical structure like that of conventionally synthesized PANI. The conductivity of nanocomposites was of comparable to the emeraldine salt form of PANI. Le Cocq et al. [11] have reported the oxidative role of CuCl₂, CuSO₄, and CuBr₂ in the polymerization of aniline monomer. They reported the formation of less conductive copper-aniline complexes instead of copper-polyaniline composites. They reported that the oxidative polymerization of aniline by using CuCl₂, CuSO₄, and CuBr₂ did not result in the synthesis of polyaniline. Dimitriev [12] have added different concentrations of transition metals salts to the solution of already synthesized emeraldine base in N-methylpyrrolidone (NMP). The samples obtained were characterized by UV/vis, FT-IR and SEM. The conductivity was found to be dependent on the transition metal salt.

In the present work we have synthesized PANI-Cu composites by using inverse emulsion polymerization in the presence of benzoyl peroxide as oxidizing agent.

2. Experimental

2.1. Procedure

Aniline monomer reagent grade was purchased from Acros organics and distilled twice before use. Toluene (BDH), 2-propanol

* Corresponding author. Tel.: +92 91 9216652.

E-mail address: anwhq.pk@yahoo.com (A.-u.-H.A. Shah).

(Merck), benzoyl peroxide (Merck) and dodecylbenzenesulfonic acid (DBSA) from (Acros) were used as received. The material was synthesized by slightly modifying the procedure mentioned in literature [3]. In a typical experiment 50 mL of toluene was taken in a 100 mL round bottom flask. Benzoyl peroxide 0.40 g was added to it under mechanical stirring. 10 mL of 2-propanol was added to the above solution. To the above mixture 1.5 mL DBSA, 0.2 mL aniline and 10 mL (0.6 M CuCl_2) solution in deionized water was added respectively to form a white milky emulsion. A greenish brown color appears after 7 h. The reaction was allowed to proceed for 24 h. In the end the mixture was transferred into a separating funnel there by separating the organic layer from the aqueous layer. The organic layer containing polyaniline was extensively washed with acetone and the product obtained was transferred in to a petri dish and dried in oven for 24 h at 40 °C. The polymer was broken in to flakes by the addition of small amount of acetone. The polymer was separated from the petri dish and was labeled as PANI-Cu. Different concentrations of CuCl_2 from 0.2 to 0.7 M were investigated.

2.2. Characterization

A four-point probe Jandel Model RM2 instrument was used to carry out the conductivity measurements of the PANI-Cu composites. The powder samples were compressed to form a solid pellet and four electrical contacts were made with the solid pellet to measure the conductivity.

A Shimadzu UV/vis 1700 spectrophotometer was used to record the UV/vis spectra. The spectra were recorded with a sampling interval of 0.5 nm in the spectral region from 900 to 200 nm.

FT-IR spectra were recorded in a region ranging from 400 to 4000 cm^{-1} by using IR prestige-21 FT-IR spectrophotometer Shimadzu, Japan. The number of scans for each sample was 10.

The TGA was performed on solid samples at a temperature range from 0 to 600 °C by using Diamond TG/DTA Perkin Elmer, USA.

The XRD of solid samples was carried out by using Siemens diffractometer D 5000.

The SEM was carried out by using scanning electron microscope Model JSM-5910 JEOL Japan.

Cyclic voltammetry (CV) was carried out by using ALS/DY 2323 Biopotentiostat. A gold coiled wire was used as counter electrode while gold sheet was used as working electrode. The calomel electrode was used as reference. On the gold sheet electrode a thin film of the polymer was deposited and the CVs were recorded with a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4 solution as supporting electrolyte.

3. Results and discussion

Table 1 shows the % yield of PANI and various PANI-Cu products along with their conductivities measured by four point probe instrument. The powder samples were compressed to form solid pellets and four electrical contacts were made with the solid pellet to measure the conductivity. Table 1 shows that the % yield of the composite PANI-Cu decreases as the molar concentration of CuCl_2 solution increases in the reaction mixture. This decrease in mass yield may be attributed to the formation of copper aniline complex [11] in addition to the formation of PANI-Cu products. The conductivity data shows the decrease in conductivity of the composite which could be attributed to the partial blocking of conductive path by Cu particle in the PANI matrix [13,14] however, these values are in good agreement with the data reported in [12]. Although the conductivity of PANI has been decreased by doping with Cu but, still it is significantly greater than the undoped emeraldine base form of PANI reported in literature [15].

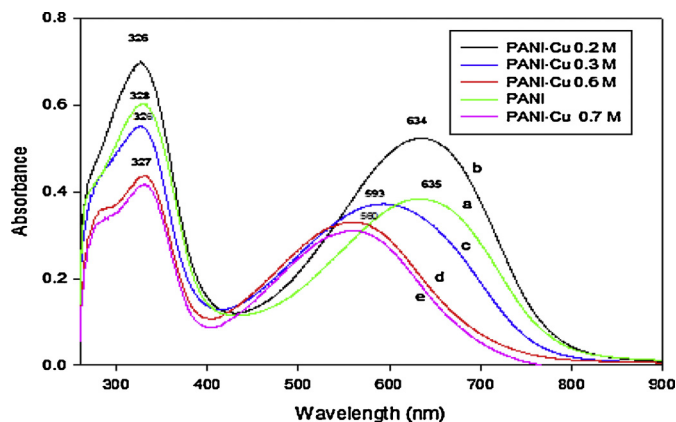


Fig. 1. UV/vis spectra of (a) PANI, (b) PANI-Cu 0.2, (c) PANI-Cu 0.4, (d) PANI-Cu 0.6, and (e) PANI-Cu 0.7 in N-methylpyrrolidone (NMP).

3.1. UV/vis spectroscopy

The UV/vis spectra of polyaniline show strong absorption in the region from 320 to 330 nm and 600–660 nm. These peaks are assigned to the $\pi-\pi^*$ and $n-\pi^*$ transition of the benzenoid and quinoid units of polyaniline respectively [16].

The UV/vis spectra of PANI, PANI-Cu 0.2, PANI-Cu 0.4, PANI-Cu 0.6 and PANI-Cu 0.7 in N-methylpyrrolidone (NMP) as solvent are shown in Fig. 1(a)–(e) respectively. The peaks 326–328 nm indicates the $\pi-\pi^*$ transition of benzenoid units of polyaniline [17]. In case of PANI-Cu 0.2, PANI-Cu 0.4, PANI-Cu 0.6 and PANI-Cu 0.7 the peak for the quinoid units of polyaniline has a blue shift. This blue shift may be attributed to the presence of Cu II chromophores. The spectra also indicate that the blue shift becomes more prominent with the increase in CuCl_2 concentration [18]. The energy gap of PANI [19] is estimated to be 1.95 eV while this gap increases about 0.26 eV for the PANI-Cu 0.6 composite (2.21 eV). This statement is in agreement with conductivity data (vide supra).

3.2. FT-IR spectroscopy

Fig. 2 shows the FT-IR spectra of PANI (a), PANI-Cu 0.2 (b), PANI-Cu 0.4 (c), and PANI-Cu 0.6 (d). In Fig. 2(a)–(d) the peaks at around 1508–1494 and 1581 cm^{-1} are attributed to the benzenoid and quinoid unit of polyaniline. The bands at 1232 and 1311–1303 are attributed to the C=N and C–N stretching modes. The peaks at 829 and 1139 cm^{-1} are assigned to the C–H out-of-plane and in-plane bending mode [9]. In Fig. 2(b)–(d) the peak for quinoid unit at 1581 gains intensity as the concentration of CuCl_2 increases in the reaction mixture indicating the interaction of CuCl_2 with the

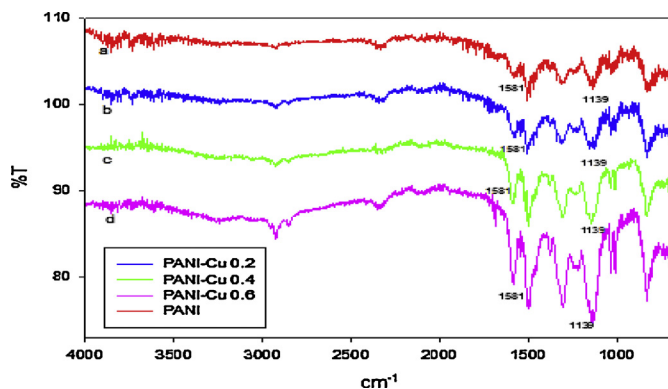


Fig. 2. FT-IR spectra of (a) PANI, (b) PANI-Cu 0.2, (c) PANI-Cu 0.4, and (d) PANI-Cu 0.6.

Download English Version:

<https://daneshyari.com/en/article/1440722>

Download Persian Version:

<https://daneshyari.com/article/1440722>

[Daneshyari.com](https://daneshyari.com)