International Journal of Bio-Inorganic Hybrid Nanomaterials

Modification Conductivity of Emeraldine Base form of Polyaniline-Cobalt Sulphate Nanocomposite Synthesis by Chemical Method

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ABSTRACT

The structural and electrical properties of polyaniline-cobalt sulphate nanocomposite prepared by chemical method. Polyaniline-cobalt sulphate nanocomposites were synthesized by the cobalt sulphate and ammonium persulphate and aniline. This paper reports on chemical technique using for synthesis of cobalt nanoparticles in the composite bridge is aniline. Electrical conductivity of polyaniline with cobalt sulphatena noparticles measured. Increasing amounts of cobalt nanoparticles in the sample equivalent to the highest electrical conductivity. We also studied morphology of polyaniline-cobalt sulphate nanocomposite. Size of cobalt nanoparticles, is ~ 65-75 nm.

Keyword: Polyaniline-CobaltSulphate; Conductive polymer; Electricalconductivity; Nanocomposites Chemical method; Properties of cobalt.

1. INTRODUCTION

Electrical properties of conducting polymers have been researched due to its application in molecular sensors, optical device and microelectronic devices. Polyaniline have relatively higher conductivity, better environmental stability, good processibility, cost effectiveness and can be easily synthesized in the catalysis, biosensors, batteries, and electronic technology. Apart from the above studies several works describing the preparation of metallic ions or particles dispersed in polyaniline have been reported. PANI is unique becauseof its high electrical conductivity, good environmental stability, and easy preparation [1-8].

A major study than to its successful utilization lays in its poor mechanical properties and processibility due to its insoluble nature in common organic solvents. The preparation method of PANI involves chemical and electrochemical polymerization techniques using suitable protonation media. A number of publications are available reporting the synthesis of PANI with different dopants and its characterization. Cobalt composite is a

Int. J. Bio-Inorg. Hybr. Nanomater., Vol. 3, No. 2 (2014), 125-130

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mixture of polyaniline and cobalt particles, long chain polymers and cobalt or any other form of metal ions the best material of chains the polyaniline. Many studies on the use of polyaniline as the sensor methanol vapors, gases like NH_3, SO_2, CO have been done [9]. This paper synthesis of cobalt compounds obtained polyaniline with chemical process and trying to improve electrical conductivity is aniline polymer.

2. EXPERIMENTAL

For the preparation of polyaniline-cobalt sulphate nanocomposite using chemical method. We synthesis this product used to 1 mol aniline and (10^{-1}-10^{-3} mol) cobalt sulphate ($CoSO_4$) solution mixture with 0.1 M ammonium peroxodisulphate (APS) [$(NH_4)_2S_2O_8$] and 1 molar HCl and stirred to prepare product. It is then centrifuged at 8000-10000 rpm for few minutes. After removed all product, the filtrate become green and dried in an oven at 40ºC for over night.

The size of the particles were studied by using transmission electron microscope (TEM), model ZEISS, CEM 902A operating at 100 KV. Fourier transform infrared (FTIR) spectra of the samples were measured with a Bruker IF5 66/5 in the region of 400 to 4000 Cm^{-1} using KBr pellet. The direct current electrical transport properties of polyaniline-cobalt nanocomposites are investigated in the present article. The dc transport properties of the sample have been measured within temperature range 77-300K in absence of a magnetic field. Electrical conductivity polymers are temperature dependent.

3. RESULTS AND DISCUSSION

3.1. Polymerization
The ANI oxidation of in strong acid (HCl) solution

has become preparing conductive polyaniline (PANI) [10-12]. The oxidation processes shown in Scheme 1 [13-16]. ANI molecules react with H^+ to form anilinium cations, because the aniline moleculeis weak base (pK_a = 4.6 at 25°C). Two imines nitrogen's have involve pKa_1 = 1.05 and pKa_2 = 2.55. The principal factor of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong coordination bond. Pure PANI is a poor semiconductor with conductivity of about 10^{-8} S/cm. Its conductivity could increase by a factor of 10 S/cm or more depending on the dopant used. The polymerization reaction starts from residual aniline molecules. With the proceeding of oxidation, the released protons increase the acidity. After the reduction by the residual aniline, the desired product, the green form of polyaniline are achieved. The oxidation of aniline with Ammonium persulfate in water yields PANI hydrogen sulfate. The para addition of constitutional units is shown but ortho addition can also be important [16-23].

3.2. Electrical conductivity property
Now polyaniline has becomethe most extensively studied conducting polymer because of its ease of preparation and processing, its richness in chemistry and physics, and its technological applications. It has been commercialized on a relatively large scale owing to it srelatively good environmental stability. It is in fact, the first commercially available conducting polymer. Figure 1 shows a conductivity ladder locating the conductivity of polyaniline with that of other conducting polymers and copper metal [22, 23].

Polyaniline is a typical phenylene-based polymer having a chemically flexible -NH group flanked on either side by phenylene rings. The protonation and deprotonation and various other physico-chemical properties of polyaniline can be related to the presence of the -NH- group. Polyaniline can be considered as being derived from apolymer, the base form of which

$$Ar-NH_2 \xrightarrow[Ar-NH_2]{Ar-NH_2} Ar-NH-Ar-NH_2 \xrightarrow[2e,\ -2H^+]{Ar-NH_2}$$

$$Ar-NH-Ar-NH-Ar-NH_2 \xrightarrow[coupling]{Further\ oxidative} Polyaniline$$
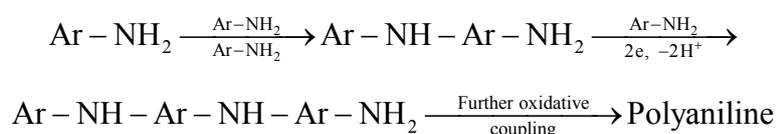
Scheme 1: *Mechanism of Polymerization and the oxidation of aniline with APS.*
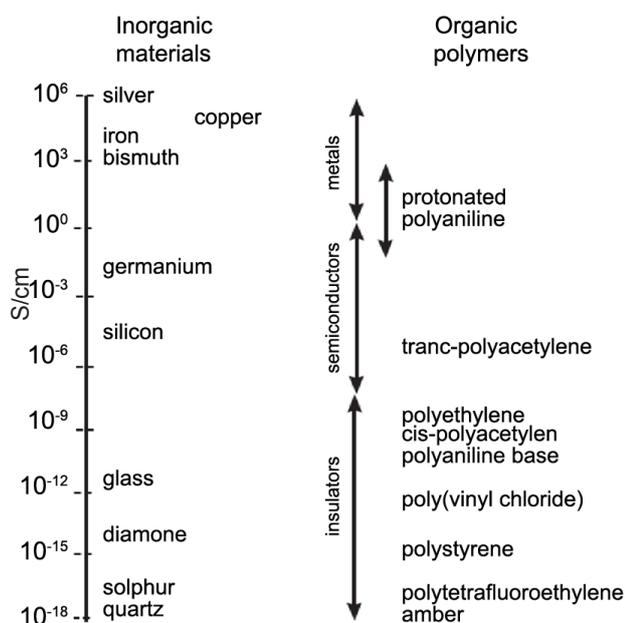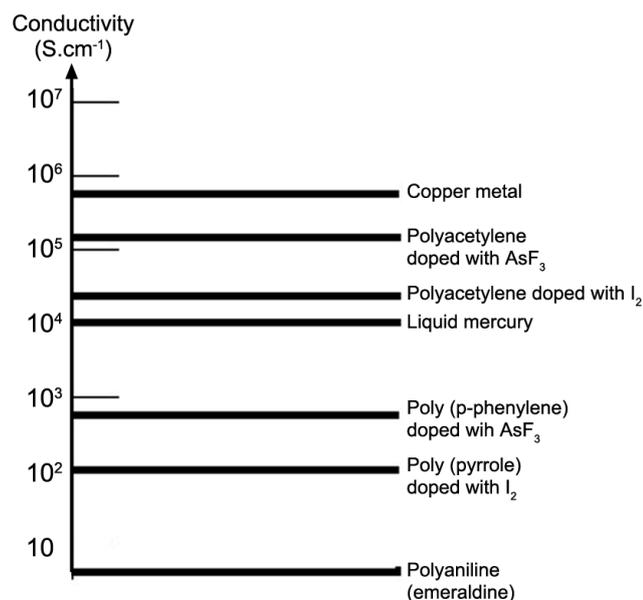
Conductivity
(S.cm^{-1})

Figure 1: *The conductivity ladder.*

has the generalized composition (Scheme 2):
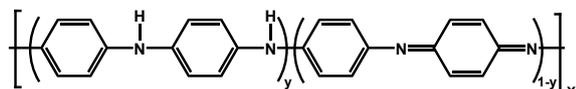
Scheme 2: *Polyaniline.*

And which consists of alternating reduced:
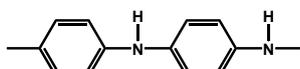
And oxidized:
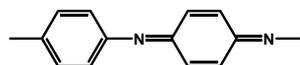
Repeat units [23-26]. The average oxidation state (1-y) can be varied continuously from zero, to give the completely reduced polymer:
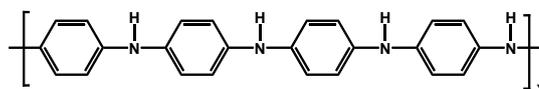
To 0.5, to give the "half-oxidized" polymer:
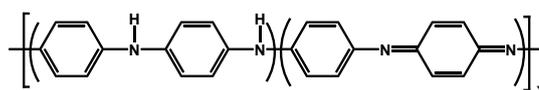
To one, to give the completely oxidized polymer:
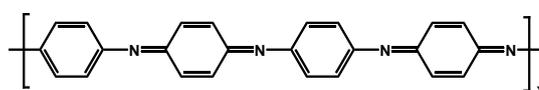
Scheme 3: *Completely oxidized polymer.*

The terms "leuco-emeraldine", "emeraldine" and "pernigraniline" refer to the different oxidation states of the polymer where (1-y) = 0, 0.5, and 1, respectively, either in the base form e.g., emeraldine base, or in the protonated salt form, e.g.,emeraldine hydrochloride [24, 25]. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on the pH ofthe aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base by aqueous HCl, for example, results in the formation of a delocalized polysemiquinone radical cation and is accompanied by an increase in conductivity of ~1010 [27]. The partly protonated emeraldine hydrochloride salt can be synthesized easily by either the chemical or the electrochemical oxidative polymerization of aniline [28]. It can be deprotonated by aqueous ammonium hydroxide to give emeraldine base powder (a semiconductor). The protonated emeraldine is green in color and conducting, emeraldine base is blue and nonconducting, protonated pernigraniline is blue in color, pernigraniline base is violet and non-conducting. The leuco-emeraldine is colorless and non-conducting. The emeraldine base form of PANI is the most stable of the three states because, leuco-emeraldineis easily oxidized when exposed to air and pernigraniline is easily degraded. Doping is the process by which
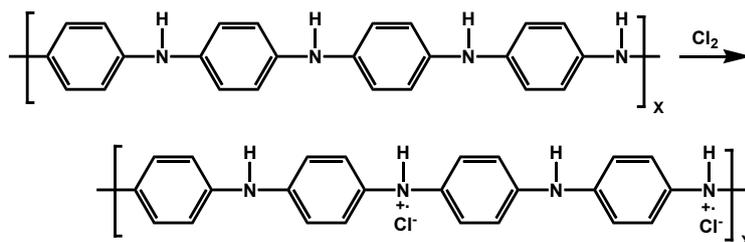
Scheme 4: Emeraldine hydrochloride PANI.

polymers that are insulators or semi-conductors as synthesized are exposed to charge transfer agents (dopants) in the gas or solution phase or through appropriate electrochemical oxidation or reduction. This process will increase the polymer's ability to conduct electricity because of the increased concentration of charge carriers [26]. Pure PANI, in the undoped state, is a poor semi conductor. However, once it is doped, its conductivity could increase by a factor of 10 S/cm or more depending on thedopant used. Polyaniline holds a special position amongst conducting polymers in that it'smost highly conducting doped form can be reached by two completely different process-protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base units with, for example, 1 M aqueous HCl results in complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt [25, 26]. The protonation is accompanied by a 9-10 order of magnitude increase in conductivity reaching a maximum with ~ 1 M aqueous HCl. The same doped polymer can be obtained by chemical oxidation (p doping) of leuco-emeraldine-base [28]. This actually involves the oxidation of the σ/π system rather than just the π system of the polymer as is usually the case in p-type doping. Its reaction with a solution of chlorine in carbon tetrachloride pro-

ceeds to give emeraldine hydrochloride (Scheme 4).

The chemical technique using for synthesis and size control of cobalt nanoparticles in the composite bridge is aniline. This method is much faster and more pure product was obtained. Upon oxidation, an electron is removed from the system of the backbone producing a free radical and a positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. This cation radical possesses spin = ½ and a unit charge [29]. This combination of a charge site and a radical is called a 'polaron'. Thus, a polaron is either a positively charged whole site (radical cation) or a negatively charged electron site (radical anion). This creates new localized electronic states in the gap with the lower energy states being occupied by single unpaired electrons. Up on further oxidation, the free radical of the polaron is removed creating a new spineless defect called 'bipolaron', which is a dictation or a dianion, which accounts for spineless conductivity in polyaniline. Theoretical models demonstrate that two radical ions i.e. polarons on the same chain react exothermically to produce a bipolaron. A bipolaron has a charge = 2e and spin = 0. The polaron and bipolaron structures of polyaniline are shown in Scheme 5.

The main mechanism used is by movement of
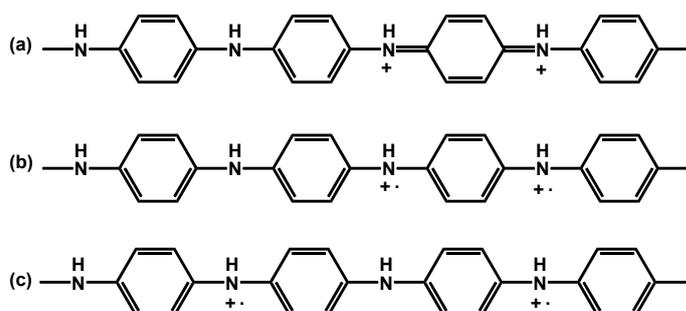
Scheme 5: Polaron and bipolaron lattice, (a) Emerladine salt in bipolar form. (b) Dissociation of the bipolaron into two polarons. (c) Rearrangement of the charges into a polaron lattice [29, 30].

Table 1: Electrical Conductivity.

EC (S/cm)	Sample
7.5	PANI-HCl
1.3×10^{-1}	PANI- Co-1V
6.2×10^{-2}	PANI- Co-111
2.1×10^{-3}	PANI- Co-11
4.5×10^{-4}	PANI-Co-1

charge carriers between localized sites or between polaron and bipolaron states. Electrical conductivity of polyaniline alone in acidic environments, without and with cobalt nanoparticles by the conductivity meter device measured [11, 12]. The results have been showed in Table 1.

Conductivity of polyaniline synthesis in the using hydrochloric acid measured. PANI-Co-1 sample with the lowest minimum conductivity equivalent 4.5×10^{-4} S/cmfor fewer amounts of cobalt nanoparticles and with increasing amounts of cobalt nanoparticles in the sample PANI-Co-1V equivalent to the highest electrical conductivity: 1.3×10^{-1} S/cmis reached. In comparison with polyaniline-cobalt nitrate nanocomposite, in the high acidity same as HCl, we find same result.

3.3. Characterization

The FTIR spectra of polyaniline-cobalt sulphate nanocomposite are demonstrated in Figure 2. The peak at 807.67 cm⁻¹ is the characteristic of Para distributed aromatic rings indicating polymer formation. C-H in plane and out of plane, bending vibrations appear at 1208.50 cm⁻¹ and 891.50 cm⁻¹, respectively. Aromatic C-N
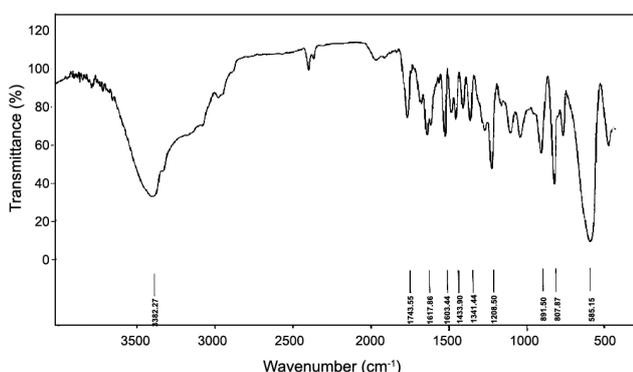

*Figure 2: FTIR spectra of polyaniline-cobalt sulphatenano-composite.*
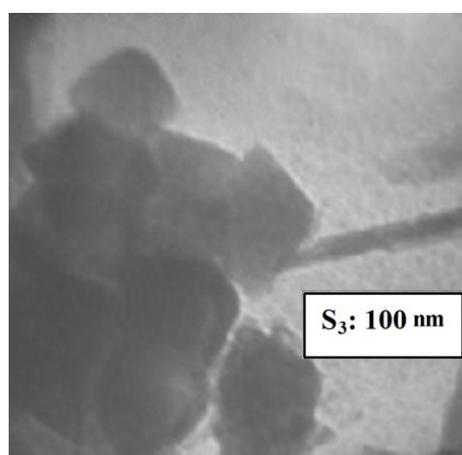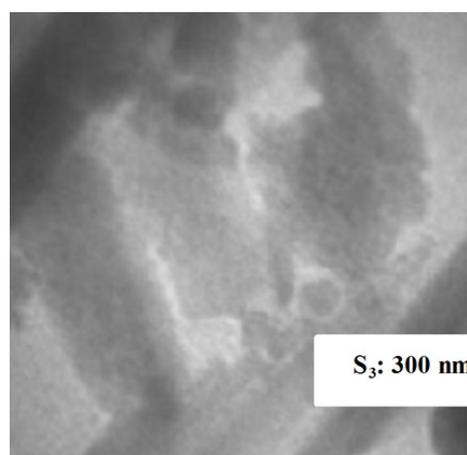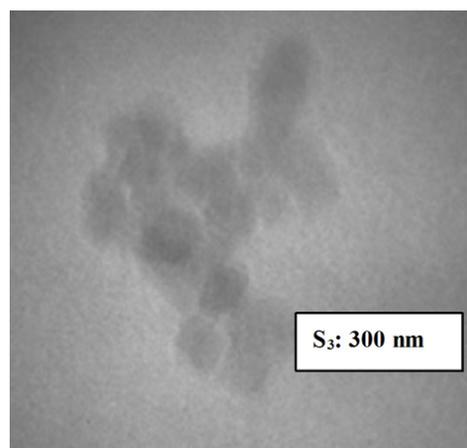
Figure 3: TEM of polyaniline-cobalt sulphate nanocomposite.

stretching indicates appearance of the secondary aromatic amine group at 1341.44 cm⁻¹. The bands in the vicinity of 1433.90 and 1617.86 cm⁻¹ corresponding to the benzoid ring and quinoid ring modes respectively are of particular interest. The presence of these bands clearly gives composition of insulating and conducting phase of the polymer. Band at 3382.27 cm⁻¹ is assigned to N-H stretching vibrations. Presence of these charac-

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teristics bands confirms the presence of conducting ES phase in the polymer. The metal oxygen stretching frequency of C-O is at 586.15-590 cm^{-1} [8].

3.4. Morphology

The average particle size calculated from the TEM image (Figure 3) confirmed that PANI-Co-1V pani chain width 40 nm and length in the range of 200 nm. PANI-Co-1V consists of elongated round shaped particles and size of cobalt nanoparticles prepared in presence of aniline and cobalt sulphate solution, is shown in Figure 3, and is ~65-75 nm.

4. CONCLUSIONS

Polyaniline-cobalt sulphate nanocomposite has been synthesized by chemical method. It is also confirmed from the above studies the shape and structure, conductivity of polyaniline-cobalt sulphate nanocompos ite synthesis in the using HCl. Sample with increasing amounts of cobalt nanoparticles equivalent to the highest electrical conductivity. Morphology of cobalt in the polyaniline-cobalt sulphate nanocompositeis spherical shaped and confirmed exist of polymer chain is observed TEM. The particle size is Pani Width 40 nm and length in the range of 200 nm and particle size of Cobalt metal dopant of pani, is ~ 65-75 nm.

ACKNOWLEDGMENTS

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