



## Electrical Conductivity Property Study of Polyaniline–Cobalt Nanocomposite

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### Abstract

Polyaniline-cobalt nanocomposites were synthesized by salt of cobalt with ammonium persulphate as an oxidizing agent and aniline. This paper reports on hydrothermal technique using for synthesis and size control of cobalt nanoparticles in the composite bridge is aniline. Electrical conductivity of polyaniline alone in acidic environments, without and with cobalt nanoparticles measured. Increasing amounts of cobalt nanoparticles in the sample equivalent to the highest electrical conductivity. We also studied morphology of polyaniline-cobalt nanocomposite. Size of cobalt particles were conformed ~33 nm in the structure of nanocomposite..

**Key words:** *Nanocomposites, Polyaniline-Cobalt, Electrical conductivity.*

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### Introduction

Conductive polymeric materials containing conjugated  $\pi$  bonds have attracted much interest in scientific and technological areas in recent years. Conducting polymers such as polypyrrole, polythiophene, poly (p-phenylene), and polyaniline (PANI) have commonly been used in scientific and industrial studies and in various applications such as rechargeable batteries [1, 2] sensors [3-6] diodes, transistors, and microelectronic devices [7]. Among these polymers, PANI is unique

because of its high electrical conductivity, good environmental stability, and easy preparation [8, 9]. As a result, it has been studied extensively and has emerged as the most promising candidate for commercial applications.

Nanocomposites are hybrid materials of the two phases are continuously formed and dispersed. If the dispersed phase was used in nanoparticle composites will be composed of a nanocomposite. Use of nanoparticles in composite materials can increase their strength or reduce their weight, their

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chemical and thermal resistance increases and new features such as electrical conductivity increase. However, a major problem related to its successful utilization lies in its poor mechanical properties and processibility due to its insoluble nature in commonorganic solvents. The preparation method of PANI involves two main techniques (chemical and electrochemical polymerization) using suitable protonation media. A number of publications are available reporting the synthesis of PANI with different dopants and its characterization [10, 11]. Polyaniline is one of conductive polymers [12, 13, 14, 15]. Characteristics of the polymer can be easy and cheap to make it pointed [16]. Cobalt composite is a mixture of polyaniline and cobalt particles, long chain polymers and cobalt or any other form of metal ions on the fine points of chains in which the composite polymer is polyaniline, amorphous are [17, 19]. Many studies on the use of polyaniline as the sensor methanol vapors, gases like NH<sub>3</sub>, SO<sub>2</sub>, CO have been done [12,13 and 18,19]. Some applications of polyaniline-cobalt: Corrosion-resistant agents, moisture-sensitive sensors, solar cells, microelectronics, semiconductors can be outlined [20, 24]. According to this paper synthesis of cobalt compounds obtained polyaniline with hydrothermal process and trying to improve electrical conductivity is more aniline polymer.

### **Experimental**

For preparing polyaniline–cobalt nanocomposites using hydrothermal methods. Ammonium persulphate (APS) [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], hydrochloric

acid and sulfuric acid (HCl, H<sub>2</sub>SO<sub>4</sub>), and cobalt nitrate were analytical reagent - grade and were used as received. The first step for chemical polymerization of aniline, it was distilled and the middle fraction polyaniline was collected and added solution of ammonium persulphate of 0.1M was taken in around bottom flask and concentrated HCl(H<sub>2</sub>SO<sub>4</sub>) was added drop-wise to it, so that keeping the total volume of the reaction mixture at 100 cc. During the addition of Ammonium persulphate the temperature of reaction mixture was maintained within 0–4 °C. The precipitated PANI–HCl (or PANI- H<sub>2</sub>SO<sub>4</sub>) salt and it was dried at room temperature for a period of 72 h. After conversion of the polymer to form emeraldine base of PANI with ammonia, starts second step. The second step cobalt nitrate solutions of various concentrations (5×10<sup>-4</sup>-5×10<sup>-1</sup> M) were prepared. About 1 gm of the PANI Emeraldine base was added to 100 ml Co(NO<sub>3</sub>)<sub>2</sub> solutions of different concentrations. The Co(NO<sub>3</sub>)<sub>2</sub> solutions containing PANI-base were kept in a 100 ml Teflon lined reaction vessel autoclave, to allow diffusion of Co<sup>+2</sup> ions to every part of the polymer. These solutions were then filtered and the samples were dried under vacuum for 72 h. The size of the particles were investigated by using transmission electron microscope (TEM), model ZEISS, CEM 902A operating at 100 KV. The morphology of the particles were investigated by using scanning tunneling electron microscopy (STEM) Phillips, model XL 30 WOX-3PC. Fourier transform infrared (FTIR) spectra of the samples were measured with a Bruker IF5 66/5 in

the region of 400 to 4000  $\text{Cm}^{-1}$  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. The conductivity values were obtained by using 4-point CDC 565 with epoxy body in the constant temperature.

## Results and discussion

### *Polymerization*

The oxidation of ANI in strong acid (HCl,  $\text{H}_2\text{SO}_4$ ) solution has become a standard method for preparing conductive polyaniline (PANI) [14, 23]. The all oxidation is an interaction of oxidation and protonation processes (Figure 1a) [17, 25]. When the oxidation of ANI molecules react with  $\text{H}^+$  to form anilinium cations (Figure 1b) because the aniline molecule is weak base ( $\text{pK}_a=4.6$  at  $25^\circ\text{C}$ ) [25]. The acid dissociation constant ( $\text{pK}_a$ ) is an important aspect of PANI synthesis, because in PANI, protonation equilibria involves exclusively the quinone diamine segment, having two imine nitrogen's with  $\text{pK}_{a1} = 1.05$  and  $\text{pK}_{a2} = 2.55$  [26]. Therefore, any acid whose  $\text{pK}_a$  value falls within this range would be suitable as a dopant whereas the anilinium ion has a  $\text{pK}_a$  of 4.60 and the ammonium ion 9.24. Acids having  $\text{pK}_a$  values around that of an anilinium ion would be suitable as solvents if they are liquids and can also be used to prevent over-oxidation of

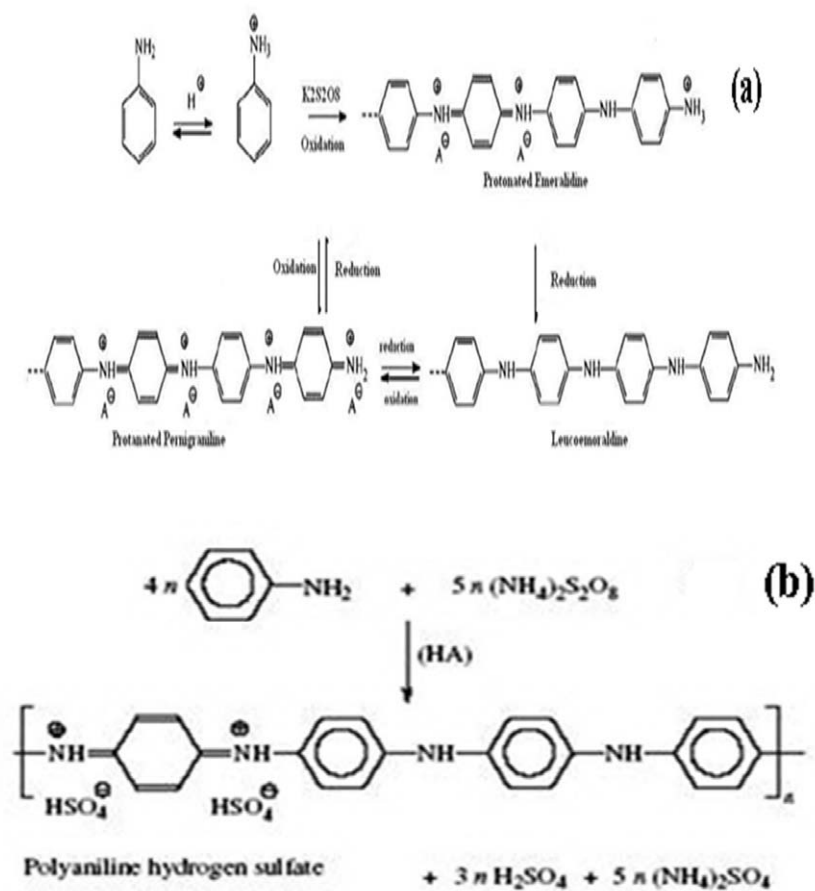
PANI. A simple oxidizing agent like ammonium persulfate yields a polymer of better quality than oxidizing agents containing metal ions. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong coordination bond with either substrate/intermediate or with the final product. Pure PANI, in the undoped state, is a poor semiconductor with conductivity of about  $10^{-8}$  S/cm. However, once it is doped, its conductivity could increase by a factor of 10 S/cm or more depending on the dopant used. Polyaniline holds a special position amongst conducting polymers in that its most 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 [27, 28]. The aniline molecules and anilinium cations have different electron density distributions. 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 [24, 30]. 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. Sulfuric acid and ammonium sulfate or ammonium hydrogen are the by-products.

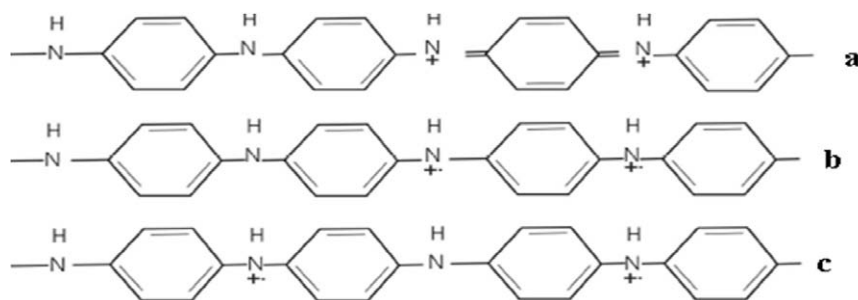
### Electrical Conductivity Property

The hydrothermal 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. The oxidative doping of polyaniline proceeds in the following way. 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 =  $\frac{1}{2}$  and a unit charge [31]. 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. Upon 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 [32]. A bipolaron has a charge =  $2e$  and spin = 0. The polaron and bipolaron structures of polyaniline are shown in Figure 2.



**Figure 1.** (a) Mechanism of Polymerization.(b) The oxidation of aniline with APS.



**Figure 2.** 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 [33, 34].

The main mechanism used is by movement of 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 [14, 15]. The results have been showed in Table 1.

**Table1.** Electrical Conductivity.

EC( $\Omega$ .Cm)	sample
0.07	PANI-HCl
0.102	PANI-H <sub>2</sub> SO <sub>4</sub>
$5.0 \times 10^{-5}$	PANI-Co-1
$3.3 \times 10^{-3}$	PANI- Co-11
$7.5 \times 10^{-3}$	PANI- Co-111
$1.5 \times 10^{-2}$	PANI- Co-1V

Conductivity of polyaniline synthesis in the using less sulfuric acid and choloric acid measured. PANI-Co-1 sample with the lowest minimum conductivity equivalent  $5 \times 10^{-5} \Omega$ .Cm for fewer

amounts of cobalt nanoparticles and with increasing amounts of cobalt nanoparticles in the sample PANI-Co-1V equivalent to the highest electrical conductivity:  $1.5 \times 10^{-2} \Omega$ .Cm is reached.

#### Characterization

Polyaniline -cobalt nanocomposites with different techniques were analyzed. Table 2 and figure 3, presents the experimental vibration spectrum of aniline in the liquid phase. NH<sub>2</sub> was bending or scissors mode which is attributed to  $1626 \text{ Cm}^{-1}$  a ring stretching with a contribution of the NH<sub>2</sub> scissoring band appeared at  $1604 \text{ Cm}^{-1}$ . A band at  $1498 \text{ Cm}^{-1}$  is characterized at typical ring stretching. The mode at  $1265 \text{ Cm}^{-1}$  is assigned as partly to C-N stretching and partly to the ring stretching vibration [35, 36].

**Table 2.** Experimental Vibration Frequencies ( $\text{Cm}^{-1}$ ) of Aniline.

Exp.	Assignment
1626	NH <sub>2</sub> sciss. ring str.
1604	Ring str., NH <sub>2</sub> sciss.
1497	C-H bend, ring str.
1264	C-N str., ring str.
1175	C-H bend, ip
1153	C-H bend
1030	Ring def., ip, ring breathing
792	C-N str., ring str.

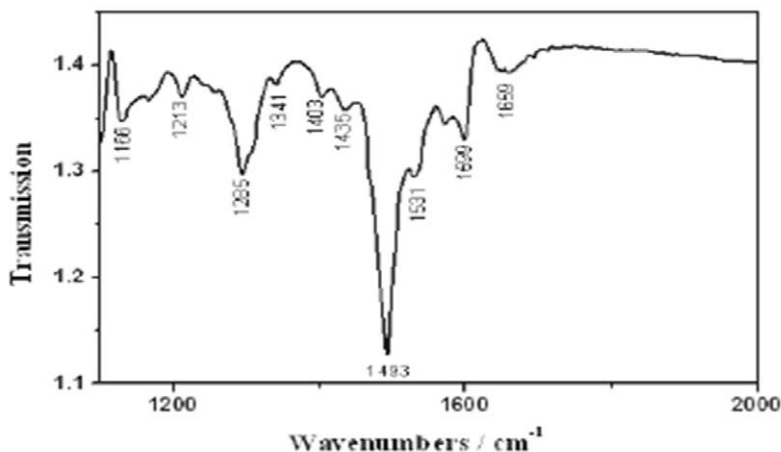


Figure 3. FTIR spectra of aniline.

Figure 4 is FTIR vibration spectrum of polyaniline. The vibration frequencies of C-N are obtained at 1145.00  $\text{cm}^{-1}$  corresponding to ring 3 and 4. Again at 1499.20  $\text{cm}^{-1}$ , this band corresponding to C-N of the ring 3. Finally the C-N of the ring 4 is

observed at 1499.20  $\text{cm}^{-1}$ . C=N of the ring 2 has one vibration modes at both 1588.33  $\text{cm}^{-1}$ . Another two vibrational modes were noticed for the ring 4 and the ring 1, 2, 3 and obtained at both of 1303.09  $\text{cm}^{-1}$  and 1588.33  $\text{cm}^{-1}$ .

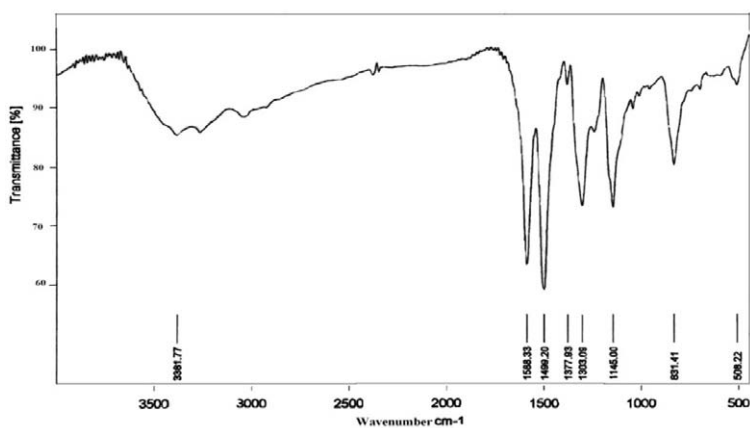
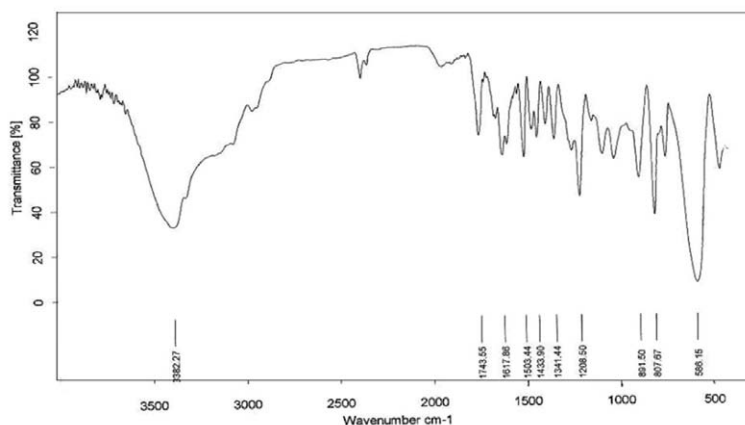


Figure 4. FTIR spectra of polyaniline.

The FTIR spectra of polyaniline-Co nanocomposite are demonstrated in Figure 5. The peak at 807.67  $\text{cm}^{-1}$  is the characteristic of paradi-substituted aromatic rings indicating polymer formation. C-H in plane and out of plane, bending vibrations appear at 1208.50  $\text{cm}^{-1}$  and 891.50  $\text{cm}^{-1}$ , respectively. Aromatic C-N stretching indicates appearance of

the secondary aromatic amine group at 1341.44  $\text{cm}^{-1}$ . The bands in the vicinity of 1433.90 and 1617.86  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  is assigned

to N-H stretching vibrations. Presence of these characteristics bands confirms the presence of conducting ES phase in the polymer. The metal oxygen stretching frequency of C-O is at  $586.15\text{ cm}^{-1}$  [37].

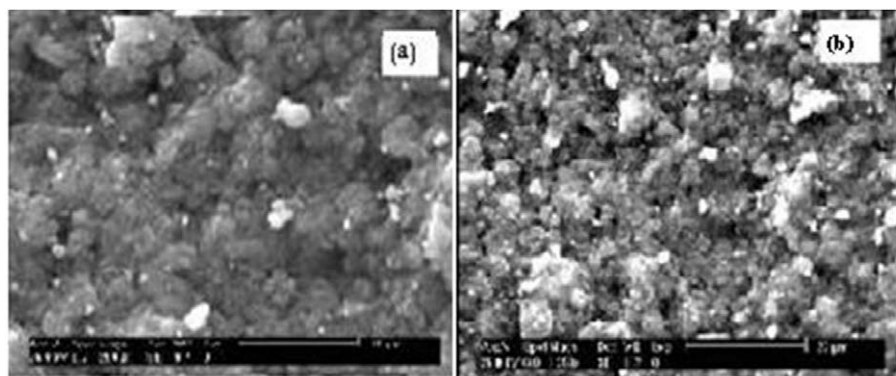


**Figure 5.** FTIR spectra of polyaniline-Co nanocomposite.

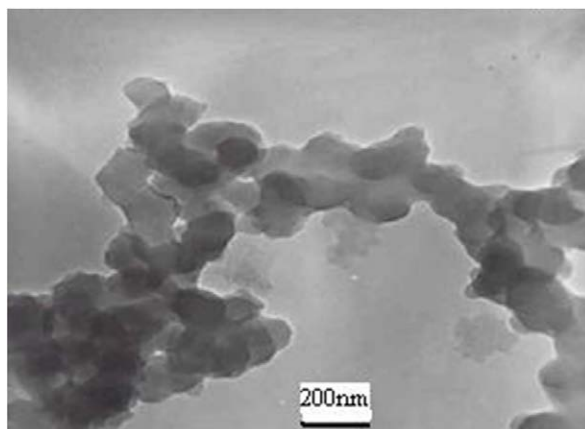
### Morphology

STEM for thicknesses variation from  $10\mu\text{m}$  to  $20\mu\text{m}$  are as shown in figure 6(a-b), respectively. Figure (6a) shown globular-like structures and lowest thickness of  $10\mu\text{m}$ . A globular-like with the instantaneous nucleation of the nanocomposite is observed at higher magnification figure (6b) for highest thickness of  $20\mu\text{m}$ . The composite shows agglomeration of polymer for highest thicknesses and porosity is seen for lower thicknesses. The pores facilitate adsorption of water vapours in such

composites. Spherical shaped Co is seen in lower thicknesses, formed spherical shaped. Figure (6b) polyaniline agglomerates and also forms spherical shaped and then platelet-like structures with increasing thicknesses [36-39]. We show brightness point in the figures 6(a-b) are cobalt nanoparticles, this figures confirmed by TEM micrograph of the cobalt nanoparticles prepared in presence of aniline and cobalt nitrate solution, is shown in Fig.7 the average particle size calculated from the TEM image is  $\sim 30\text{-}33\text{ nm}$ .



**Figure 6.** STEM of polyaniline-Co nanocomposite, (a)  $10\mu\text{m}$ , and (b)  $20\mu\text{m}$ .



**Figure 7.** TEM of polyaniline-CO nanocomposite.

### Conclusions

Polyaniline – cobalt nanocomposite has been synthesized by hydrothermal method. It is also confirmed from the above studies that not only the shape, conductivity of polyaniline - Co nanocomposite synthesis in the using acidic environments measured. Sample with increasing amounts of cobalt nanoparticles equivalent to the highest electrical conductivity. Morphology of polyaniline-cobaltis spherical shaped and confirmed exist of polyaniline-cobalt nanocomposite observed FTIR spectrum, such as aniline, polyaniline and polyaniline-cobalt. The particle size was 30-33 nm.

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