

# Synthesis of copper chloride doped in polyaniline and its characterization

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**Abstract :** In this present work, doping effect of transition metal ion (Cu) in polyaniline thin film investigated. Polyaniline (PANI) composites containing copper chloride (CuCl<sub>2</sub>) were prepared by HCl and ammonium persulphate. The chemical polymerization of aniline hydrochloride using ammonium persulfate as an oxidant in the presence of copper chloride. Polyaniline-Copper (PANI-Cu) composite was prepared by the chemical oxidative polymerization method. The formation of Polyaniline-Copper (PANI-Cu) composit was characterized by various methods like UV-Vis spectroscopy; Fourier transforms infrared (FT-IR) spectroscopy, Energy dispersion X-ray (EDX-ray), Transmission electron microscopy (TEM), and electric conductivity.

**Keywords:** Polyaniline, conducting polymer, chemical synthesis, doping.

## I. Introduction

During the last thirty years, the conducting polymer like polyaniline, polythiophene, polypyrrole polyacetylene, etc. was extensively studied by polymer researchers. It is an important class of hybrid materials. Due to its high electro-active surface area, high specific capacitance, electrical conducting capacity, a high degree of stability is used in the laboratory instead of the metal conductor all over the world.<sup>[1]</sup> It belongs to the class of conjugated conducting polymer. This feature polyaniline (PANI) originates from  $\pi$ -electron. polyaniline has a  $\pi$ -conjugated backbone structure with imine groups by this structure and group, it can stabilize the metal ion in an aqueous medium as well as polymer by  $\pi$ - $\pi$  interactions, steric effects, and hydrophilic interaction. polyaniline has received much attraction in the last ten years due to its properties like intrinsic electrical conductivity, simple and easy synthesis method, excellent environmental stability, cheap and easy availability of monomer, and behavior redox properties. It remains stable at a long time in the presence of a large range of humidity, hot and cold air. <sup>[2-4]</sup> Besides these properties, polyaniline (PANI) has much practical application such as chemical sensor device,<sup>[5]</sup> light-emitting devices,<sup>[6-7]</sup> electromagnetic interference shielding materials,<sup>[8-9]</sup> electrode, <sup>[10-12]</sup> molecular sensors, lightweight batteries, and surgical instrument,<sup>[13]</sup> for making important constituent of solar cells, electrochromic displays <sup>[14]</sup> and as corrosion protecting agent in the paint industry, polyaniline exists in various oxidation states fully oxidized pernigraniline, fully reduced leucoemeraldine and half oxidized emeraldine base. PANI-Cu composite has high electrochemical properties and excellent antibacterial activity. <sup>[15]</sup> The main aim of this research work is to develop high-performance and high conductive Copper doped polyaniline for the to improve the electronic conductivity of polyaniline thin films and comparing their properties. The physical properties of PANI depend on the choice of the counter metal ion called dopants. In this research paper, we report the synthesis, the characterization of Copper doped polyaniline prepared by chemical methods.

## 2 Experimental Details

### 2.1 Materials

All chemical were supplied by Merck (Extra Pure) and were used without further purification.

### 2.2. Chemical Polymerization

The monomer Aniline, oxidizing agent Ammonium persulphate (APS) and Hydrochloric acid used as received without further treatment. Polyaniline was synthesized by the chemical oxidation method at lower temperatures (0-2°) C. APS (Merck, Germany) was used as an oxidant. Five ml aniline was first dissolved in 1.5 M, 70ml HCl (Merck, Germany). After this process, this solution was kept in an ice bath maintaining temperature below 5° C. Ten gram ammonium persulphate dissolved double-distilled deionized water. The solution of APS was added drop by drop into monomer solution and stirred at a constant speed. The polymerization process was performed for four to five hours. At the end of polymerization reaction, final green color polyaniline was formed, washed with dilute hydrochloric acid solution and dried at 70°C in hot air oven, for 10-12 hours. After forming polyaniline, an appropriate amount of Copper chloride solution 0.2 M was dissolved in the Polyaniline solution. Doping of Cu in polyaniline was done by chemical doping method. In order to obtain the uniform distribution of Cu ion in the polyaniline solution, the mixture was stirred for 1 hour. The surface morphology of the doped polyaniline film was examined by FTIR, SEM, TEM, TGA methods, UV/VIS spectroscopy, X-ray diffraction and conductivity measurement.



### 3.2. Fourier Transform Infra-Red (FT-IR)

Fourier Transform Infra-Red spectra were recorded in a region ranging from 400 to 4000  $\text{cm}^{-1}$ , for this analysis IR prestige-21 FT-IR spectrophotometer Shimadzu, Japan was used. Figure shows the FT-IR spectra of undoped Polyaniline (a), copper doped polyaniline (b). In Figure 2 (a)–(b) the peaks at around 1510 and 1582  $\text{cm}^{-1}$  are related to the benzenoid and quinoid unit of PANI. The peaks at 830 and 1140  $\text{cm}^{-1}$  are related to the C-H out-of-plane and in-plane bending mode. The bands at 1305 and 1232  $\text{cm}^{-1}$  are related to the C-N and C=N stretching modes. Figure 2 b shows the peak for a quinoid unit at 1582 indicating the interaction of Copper chloride with the nitrogen atom of the quinoid unit of polyaniline.

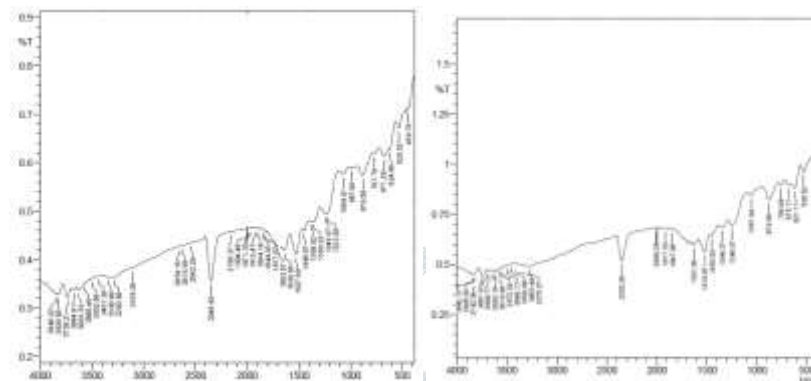


Figure 2 (Left) FTIR Spectra for Pure PANI and (Right) FTIR Spectra for Cu- doped PANI

### 3.3. Scanning electron microscopy (SEM)

The SEM images of undoped Polyaniline and copper doped polyaniline are shown in Figure 3(a) and (b) respectively. Figure 3a shows an uneven irregular morphology. But in the Figure 3b of polyaniline-Cu composite the irregularity increases than the pure polyaniline. When  $\text{CuCl}_2$  is added in polyaniline, the pore size of the mixture or composite becomes larger, which leads to the change in the morphological structure of polyaniline and manganese bind to various sites of polyaniline to form interchain linkage among several adjacent polyaniline chains by coordination bond. It also indicates that the surface of doped polyaniline is more porous than undoped polyaniline.

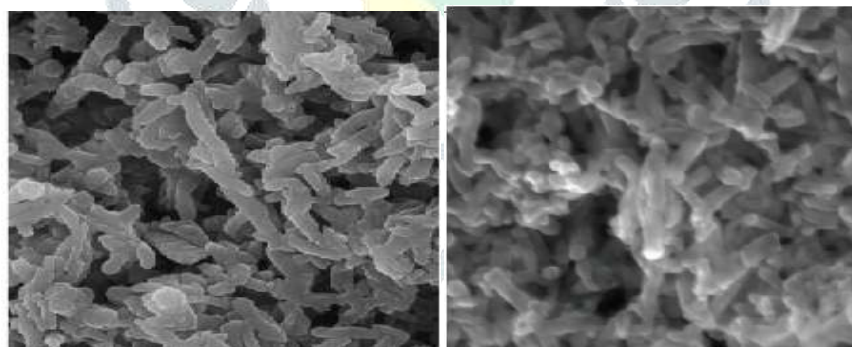


Figure 3a (left) SEM Image for Pure PANI and (Right) 3b SEM Image for  $\text{CuCl}_2$ - doped PANI

### 3.4. TEM analysis

Figure 4a and 4b shows the TEM image of pure polyaniline (PANI) and copper chloride-polyaniline (PANI) composite obtained at 100 nm and 200 nm respectively. Figure 4a shows  $\text{CuCl}_2$  attached to the PANI composite. It also shows spherical-particle like structures with dark and gray regions but in pure polyaniline it does not show any spherical-particle. The diameters of these granular black and gray spherical structures are between 10–20 nm. The morphological characteristics of  $\text{CuCl}_2$  doped in polyaniline (PANI) were investigated by TEM and images are shown in figure 4b. It represents  $\text{CuCl}_2$  doped in polyaniline (PANI). However, uniform doping of polyaniline (PANI) by  $\text{CuCl}_2$  is observed in figure 4b. So, we can expect that due to uniform doping, composite polyaniline show more electrical conductivity and low resistivity.

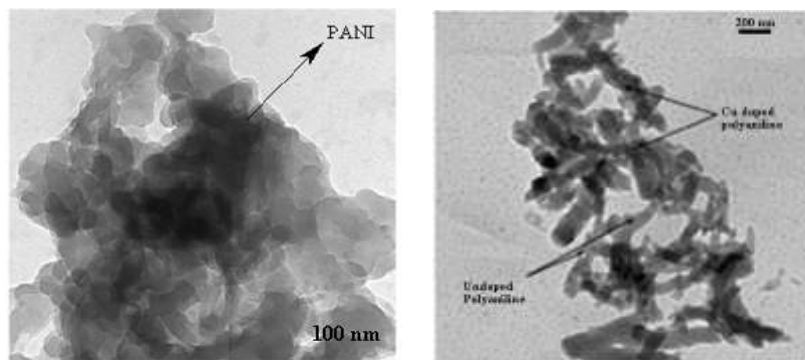


Figure 4a (left) TEM Image for Pure PANI and (Right) 4b TEM Image for  $\text{CuCl}_2$ - doped PANI

### 3.5 .X-ray diffraction (XRD)

In general, XRD characterization indicates the crystalline material structure with crystallite size, an atomic arrangement in the molecule, and imperfections in the molecule. It is also used to determine the prepared composite is amorphous or crystalline. In this case, it observed that undoped polyaniline and the composite has an amorphous form in nature. The X-ray diffractograms for Cu ion-doped polyaniline has been found to display at  $2\theta$  values of  $17.64^\circ$ ,  $18.15^\circ$ ,  $19.06^\circ$ ,  $20.040^\circ$ ,  $20.837^\circ$ ,  $23.446^\circ$ ,  $26.19^\circ$ ,  $26.910^\circ$ ,  $30.37^\circ$ ,  $32.58^\circ$ ,  $36.28^\circ$ ,  $40.56^\circ$  and  $48.11^\circ$ . The strongest peak is obviously for  $2\theta$  at  $17.764^\circ$ ,  $20.040^\circ$ ,  $20.837^\circ$ ,  $23.446^\circ$ ,  $26.19^\circ$ ,  $30.37^\circ$  and  $32.58^\circ$ . This entire strongest peak related to a pure Copper metal with face-centered cubic symmetry. Bragg's equation is used for the calculation of inter-chain distance. This strongest peak corresponding to the crystalline order of protonated Cu ion-doped polyaniline. The  $2\theta$  values of  $17.764^\circ$ ,  $20.040^\circ$ ,  $20.837^\circ$ ,  $23.446^\circ$ ,  $26.19^\circ$ ,  $30.37^\circ$  and  $32.58^\circ$  correspond to crystalline order in other ordered arrangements of oligomers.

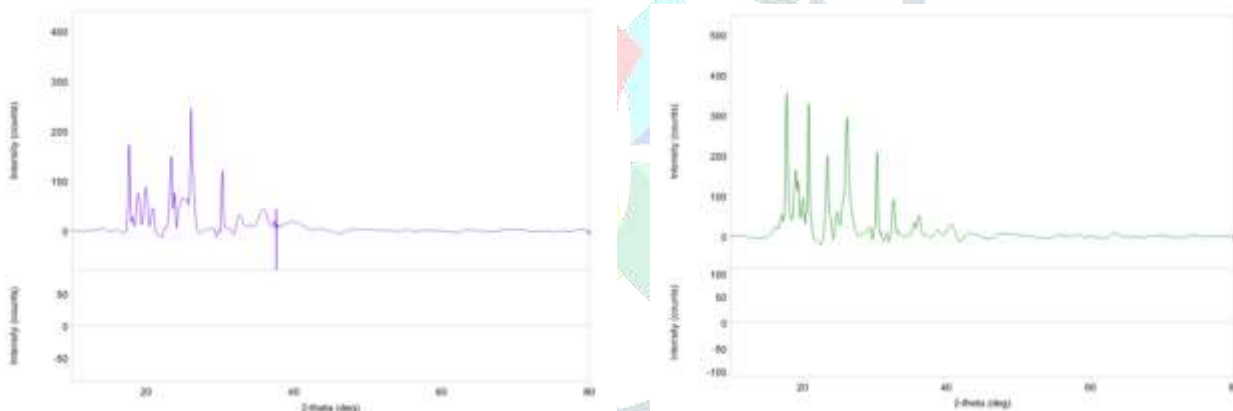
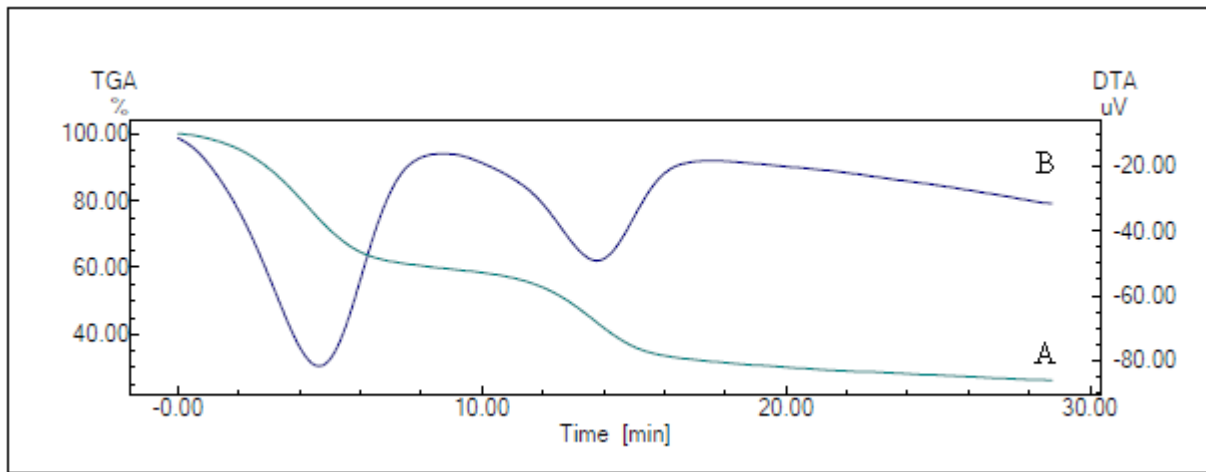


Figure 5a (left) xrd of pure pani and 5b (right) xrd for cu- doped pani

### 3.6. Thermo gravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed on polyaniline samples at a temperature range from  $0^\circ\text{C}$  to  $650^\circ\text{C}$  by using Diamond TGA/DTA Perkin Elmer, United States of America. The thermal stability of prepared Polyaniline and copper doped polyaniline was tested by using the thermogravimetric analysis (TGA) technique. The polyaniline samples were kept for one minute at  $30^\circ\text{C}$  and then heated from  $30$  to  $650^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . The loss in weight for polyaniline and copper doped polyaniline upon heating under an inert gas atmosphere is shown in figure 6 graph (a) and (b) respectively. Figure 6 graph (a) polyaniline and (b) copper doped polyaniline shows a steady mass decrease is found at the range  $280^\circ\text{C}$  to  $295^\circ\text{C}$ . It also shows a rapid change at range from  $295^\circ\text{C}$  to  $400^\circ\text{C}$ . The figure indicates polyaniline weight% is less than composite polyaniline. The weight loss of Polyaniline and Polyaniline-copper composite at  $650^\circ\text{C}$  was  $72.05\%$  and  $92.44\%$  respectively. Thermogravimetric analysis (TGA) indicates polyaniline-copper composite has less thermal stability because of the copper particle as dopant at the nitrogen sites of polyaniline.

Figure 6 Thermo gravimetric analysis of (a) PANI and (b) PANI-CuCl<sub>2</sub>

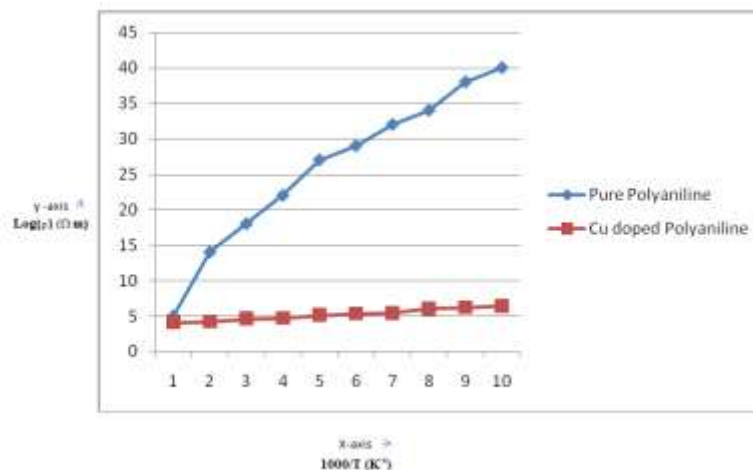
### 3.7. Electrical Resistivity

The DC electrical resistivity ( $\rho$ ) of the synthesized pure polyaniline and CuCl<sub>2</sub> Cu ion-polyaniline composite materials were measured by the four-point probe method at change temperature with the change in current. The temperature variation of voltage was determined. The DC electrical resistivity ( $\rho$ ) of the pure polyaniline and (CuCl<sub>2</sub>) Cu-polyaniline sample was determined from the range room temp. to 100°C temperature. It was observed that the resistance of Cu ion-doped polyaniline and pure polyaniline is different from each other. It depends on the dopant agent as well as the temperature of the sample. The DC electrical resistivity ( $\rho$ ) of the (CuCl<sub>2</sub>) Cu-polyaniline was calculated by using the following equations.

$$\text{Resistivity (r, } \Omega \text{ cm)} = \rho t / In2 (V/I) \quad (1)$$

$$\text{Conductivity (s, } S \text{ cm}^{-2}) = 1/r \quad (2)$$

Where  $I$  is the applied current, and  $V$  is the measured voltage and  $t$  is the thickness of pure polyaniline and (CuCl<sub>2</sub>) Cu-doped polyaniline. Maximum ten tests were performed for pure polyaniline as well as (CuCl<sub>2</sub>) Cu-doped polyaniline and finally, data were averaged. All the data was used for the calculation and graph. Knowing DC resistivity ( $\rho$ ) of the sample platinum probe was used. The frequency-dependent AC conductivity and dielectric permittivity of the pure polyaniline a flat, square shape thickness 0.46 and area  $1.9 \times 10^{-1} \text{ cm}^2$  (CuCl<sub>2</sub>) Cu ion-doped polyaniline flat, square shape thickness 0.47 and area  $1.9 \times 10^{-1} \text{ cm}^2$  were obtained by using a computerized impedance analyzer and using an alternating electric field amplitude 1.000 V across the pure polyaniline and Cu-doped polyaniline in the frequency region of 50 HZ to 10 MHZ. By using the formula and data plots is observed that conductivity increases with an increase in temperature. As the temperature increases, the mobility of electrons or ions also increases which results in a rise in conductivity in pure polyaniline availability of free electrons or ions is low but in (CuCl<sub>2</sub>) Cu ion-doped polyaniline composite availability of free electrons or ions is more than pure polyaniline. The curve is linear. The slope of the curve shows activation energy. DC electrical resistivity ( $\rho$ ) decreases with an increase in Cu-polyaniline samples. The decrease in resistivity and an increase in the conductivity of (CuCl<sub>2</sub>) Cu ion-doped polyaniline increased due to the mobility of electrons or ions. As the crystallinity increases and hydrogen bonding from FTIR confirmed which also shows increased conductivity.  $E_a$  value of Cu-polyaniline shows a low potential barrier than pure polyaniline. (CuCl<sub>2</sub>) Cu ion concentration increases the conductivity. The conductivities of the (CuCl<sub>2</sub>) Cu-polyaniline composites increased with increased temperature. At room temperature, DC electrical resistivity ( $\rho$ ) for pure PANI film observed at 0.025  $\Omega/\text{m}$  and it decreases with the presence of Cu. And resistivity of pure polyaniline is 40  $\Omega \text{ m}$  and Cu-doped polyaniline is 06.40  $\Omega \text{ m}$ .

Figure 7 Electrical resistivity of the a) pure polyaniline, (b) Polyaniline- CuCl<sub>2</sub> composite

## I. Conclusions

TGA shows polyaniline has more thermal stability than doped polyaniline. The SEM image shows the pore size in polyaniline-Cu is larger and uneven than polyaniline. TEM analysis shows uniform dispersion of the copper nanoparticles in the polyaniline. XRD which suggests that the polyaniline sample is more crystalline than copper doped polyaniline that's mean doped polyaniline has less crystallinity. Although the polyaniline-copper chloride composite is less resistivity than pure undoped polyaniline but still has high conductivity than undoped polyaniline.

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