Synthesis and Characterization of Polyaniline/Gold Nanocomposites

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Abstract

Conductive polymers are a new class of materials, which exhibit highly reversible redox behavior and unusual combination of properties of metals and plastics. The conductivity of a polymer can be increased several-fold by doping it with a suitable dopant. Doping plays a very important role to convert the polymer into conductive form. In this work an attempt has been made to synthesize polyaniline chemically with various types of dopant acids such as inorganic acids like sulphuric acid , organic acids like p-Toluenesulfonic acid, Camphorsulfonic acid and metal Lewis acids like Auric acid which act as an oxidative agent as well as a secondary dopant to result in a Polyaniline/Gold nanocomposite. Polyaniline (PANI) was chemically synthesized by oxidative polymerization of aniline in different acid dopants. The influence of concentration of dopant acids during polymerization of aniline was studied. The level of doping and nature of the polymer formed was studied using UV-Visible Spectroscopy. FTIR spectra show that the incorporation of Au seems to be effective for better conductivity of the polymer samples. XRD study confirms the presence of Au in the polymer sample in nanometer scale.

Keywords: Polyaniline; PANI; dopant; nanocomposite; gold.

1. Introduction

Composites are a special class of materials originating from combinations of two or more compounds by a suitable technique, which results in materials having unique physiochemical properties and large potential for application in diverse areas. Novel properties of composites can be derived from the successful combination of the characteristics of the parent constituents into a single material. Conventional polymers usually serve as the matrix, which result in a special class of hybrid materials termed “polymeric nanocomposite”. This composite material differs from the pure polymer in respect to some of the physical and chemical properties and hence it is useful for many applications in different fields [1].

Nanocomposites of conducting polymers and metal nanoparticles have received considerable attention due to the potential possibilities to create suitable materials for electrocatalysis, chemical sensors and microelectronic devices [2]. The incorporation of metallic or semiconducting nanoparticles in conducting polymers such as polyaniline (PANI) is of interest because of the strong electronic interaction between the nanoparticles and the polymer matrix [3, 4]. Metal nanoparticles incorporated into conducting polymers are also known to enhance the conductivity of the polymers.

Therefore, the fabrication of novel nanocomposites based upon metal nanoparticles and conducting polymers would provide various interesting characteristics and new features in nano-technological applications [5]. Among the nanomaterials used, gold nanoparticles have received great interest because they have several kinds of intriguing properties such as excellent biocompatibility, conductivity, catalytic properties, high surface-to-volume ratio and high density. Several reports on the synthesis of polyaniline using various oxidizing agents are available like, Chattopadhyay *et al.* [6] have reported on the preparation of gold-PANI composite material using H_2O_2 as both the oxidizing and reducing agent. The synthesis of PANI gold composites using HBF_4 as oxidizing agent has been reported by Smith *et al.* [7]. The conductance of the resultant PANI-Au composite doped with HBF_4 was higher when compared to an undoped composite.

In the present work, synthesis of PANI with various primary dopant acids such as Sulphuric acid, p-Toluenesulfonic acid, Camphorsulfonic acid and Auric acid as the oxidizing agent which also acts as a secondary dopant has been reported for the first time and characterized using various techniques.

2. Methods

2.1. Chemicals and Solutions

Aniline ($C_6H_5NH_2$, M.Wt -93.13) was distilled and used. Sulphuric acid (H_2SO_4, M.Wt 98.08), p-Toluenesulfonic acid (PTSA) ($C_7H_8O_3$, M.Wt - 190.22), Camphorsulfonic acid (CSA) ($C_{10}H_{16}O_4S$, M.Wt - 250.32), Auric acid ($HAuCl_4$), Acetone (99.8%) were used as received. All the chemicals used were of analaR Quality. All solutions were prepared using Millipore water obtained from a MILLIPORE water purifying system (Elix 3).

2.2. Chemical Synthesis of PANI

The chemical polymerization of aniline with different dopants was done as follows:

In a 250ml round bottom flask, Aniline (3.4mM), Sulphuric acid (3.4mM) and dopant acid (3.4mM) was added into a 25ml of Millipore water and stirred for two hours to form a homogeneous aqueous dispersion. When CSA and PTSA were used as the dopants, drop wise addition of the acid was carried out with suitable concentration and the mixture was stirred in a magnetic stirrer for 30 minutes. To this mixture Auric acid was added drop wise to the reaction mixture for about 30 minutes under ice-cold condition and constant stirring. The polymerization started with the slow addition of Auric acid as indicated by the colour change of solution from blue emeraldine base form to dark green emeraldine salt form immediately. The precipitated PANI was washed repeatedly with acetone to remove the water and to get the PANI powder. The solution was filtered and dried under vacuum for 3-4 hrs. The same procedure was employed for all the syntheses done with different dopants (Table 1).

2.3. UV-Visible Spectroscopy

The UV-Visible spectra of the synthesized PANI Emeraldine salt powder in N-methy 2-pyrrolidone (NMP) were recorded on a Hitachi (model U - 2001) UV- Visible spectrometer. All measurements were performed in a single; teflon capped quartz cuvette with a 1cm path length. NMP was used as a blank for taking each spectrum.

2.4. FT-IR Spectroscopy

The FT-IR spectra of the PANI powder were taken on a JASCO FT-IR 460 blue model. Pellets of samples with KBr were used to take the spectrum.

2.5. X-Ray Diffraction

Powder X-ray diffraction (XRD) patterns of prepared PANI-Au composite was recorded by diffractometer (Rigaku) using Cu Kα radiation (= 1.54 A°).

Table 1: Chemical Synthesis of Polyaniline/Gold composites.

Samples	Aniline (mM)	H_2SO_4 (mM)	PTSA (mM)	CSA (mM)	Auric acid (mM)
PANI 1	3.4	3.4	-	-	3.4
PANI 2	3.4	3.4	3.4	-	3.4
PANI 3	3.4	3.4	-	3.4	3.4

3. Results and Discussion

3.1. UV-Visible Spectroscopy

The UV-Vis spectra taken for all the chemically synthesized PANI Samples are presented in Figure 1. All the spectra in the Figure 1 show three characteristic absorbance peaks. They are the π-π^* transition located between 240 to

280 nm, the polaron-π^* transition at ~ 340 nm and polaron-π transition around 620 nm and the intensity of the peaks are same for all the polymer samples. This indicates that the synthesized polyanilines have been effectively doped with the primary and secondary dopants.

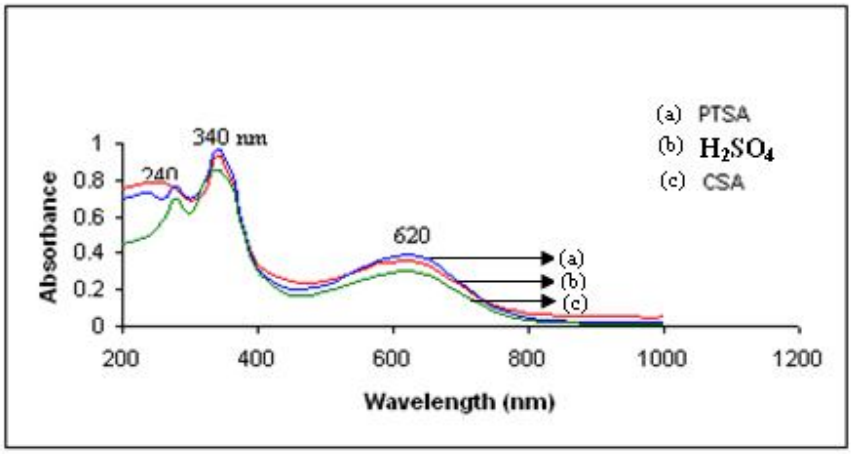

Figure 1: UV-Vis spectra of PANI/Au composites with different dopant acids.

PANI-Au nanocomposites did not exhibit the surface plasmon resonance (SPR) absorption band of Au at 520 nm. This is because Au particles are deeply incorporated into the polymer chain and they are unable to exhibit the surface plasmon resonance band at 520 nm.

3.2. FT-IR Spectroscopy

The FT-IR spectra of PANI samples show specific stretching vibrations for the different structural forms of PANI. The specific groups of PANI and their IR vibrational frequencies from the literature are given below:

- N-H stretching of Benzenoid ring - 3380 cm^{-1}
- Quinonoid ring - 1587 cm^{-1}, Benzenoid ring - 1510 cm^{-1}
- C-N stretching - ~1380 cm^{-1}
- Combination modes of benzenoid and quinonoid unit - 1150 cm^{-1}
- SO_3 stretching frequency of the various dopant acids - 1100 cm^{-1}

In the present study, IR spectra were taken for all the samples (Figures 2-4). All the spectra show the characteristic absorption bands of PANI in conductive emeraldine salt form as indicated by the presence of relatively sharp peaks around 1500 and 1600 cm^{-1} corresponding to the benzenoid and quinonoid forms of Emeraldine Base. The Au incorporated samples shows sharp band at 1150 cm^{-1} and a very small band nearby this shows the presence of $-SO_3$ group. This indicates that gold is incorporated into the polymer matrix by expelling sulphonic acid groups away from the nitrogen sites. Thus, the IR study clearly indicates that metallic gold is definitely incorporated into the polymer matrix and the most probable site of interaction could be the amine and imine nitrogen sites of benzenoid and quinonoid moieties.

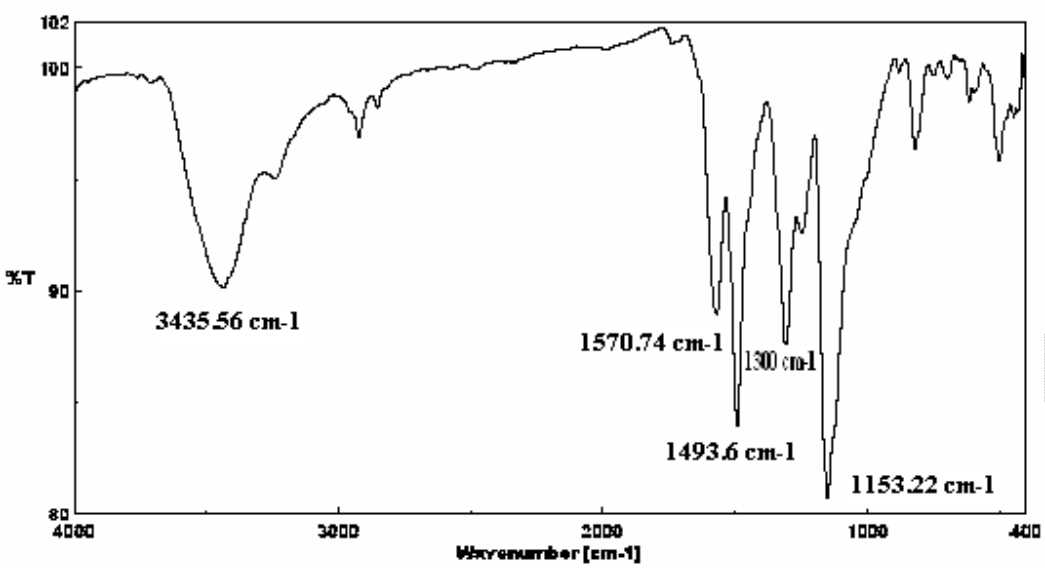

Figure 2: FT-IR spectrum of chemically prepared PANI/H_2SO_4/Au powder.

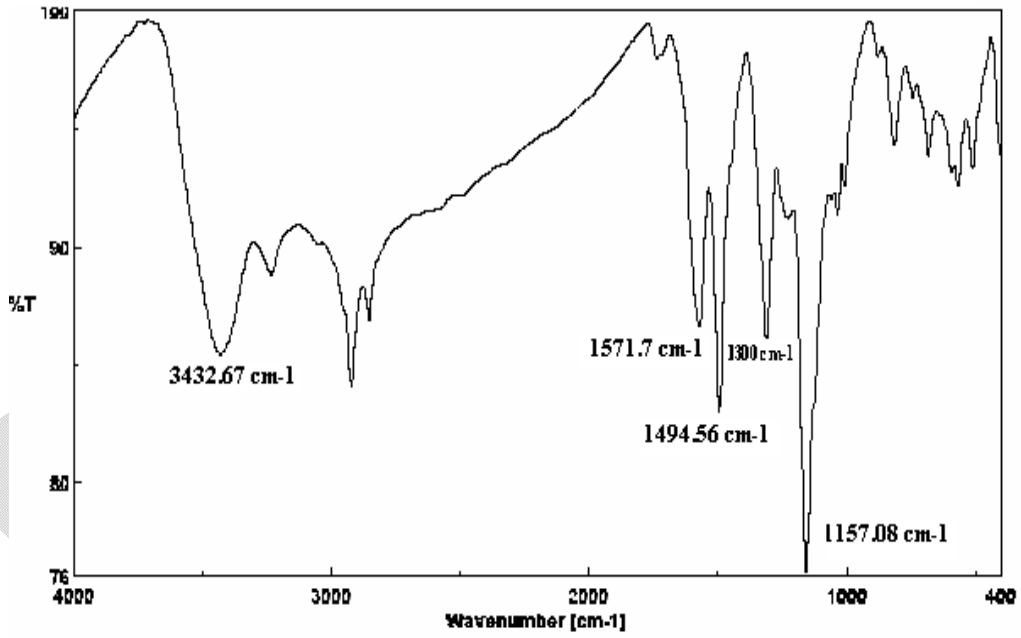

Figure 3: FT-IR spectrum of chemically prepared PANI/PTSA/Au powder.

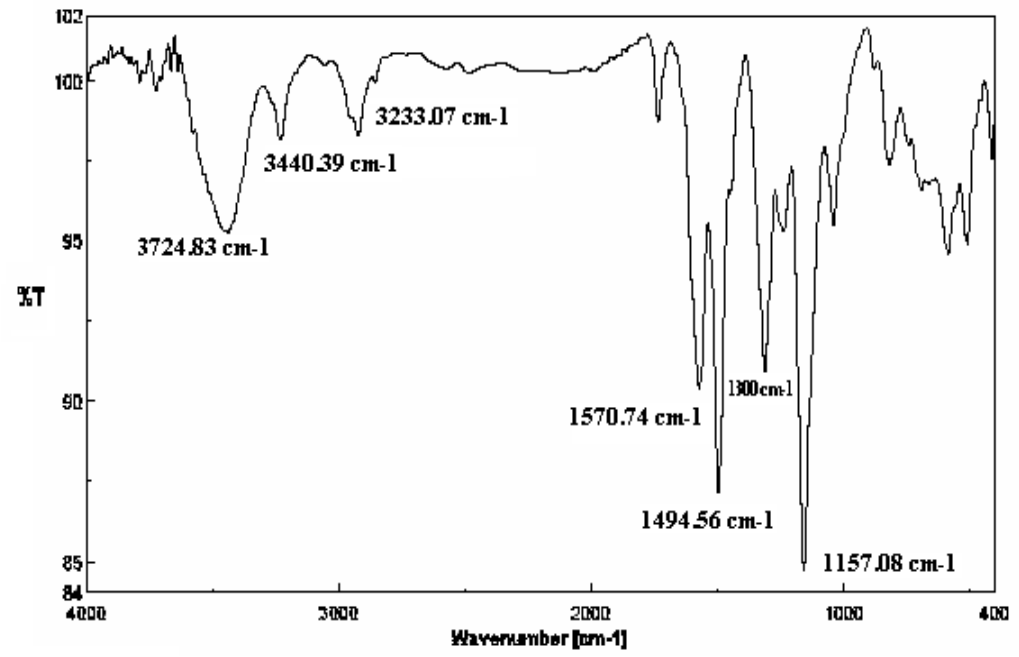

Figure 4: FT-IR spectrum of chemically prepared PANI/CSA/Au powder.

3.3. X-ray Diffraction Studies

X-Ray diffraction study was carried out for one representative sample containing PANI/H_2SO_4/Au to confirm the presence of gold. XRD pattern for the sample polymer shows three intense absorption peak at 2θ values in 38.5, 44.3, 64.8 representing Bragg's reflections from (111), (200), (220) planes of Au. This is shown in Figure 5. This indicates that the gold-polymer matrix had grown in three different planes. An estimation of mean size of gold nanoparticles was performed for the width of (111), (200), (220) Bragg reflection using the Debye-Scherrer equation. The size of the nanoparticles thus estimated was found to be 12.8 nm, 16.42 nm and 14.75 nm respectively.

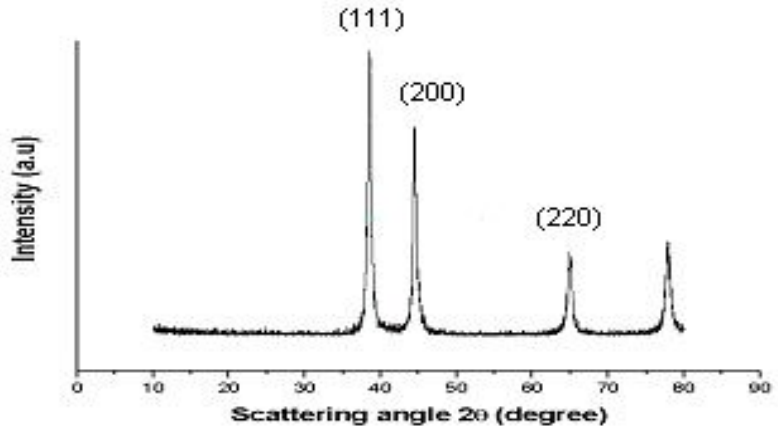

Figure 5: Powder XRD pattern of chemically polymerized PANI/H_2SO_4/Au sample.

4. Conclusion

PANI samples were chemically synthesized by using various dopants with gold. All the chemically synthesized PANI/gold composites have resulted in emeraldine salt form as indicated by dark green colour of the salt. Various characterization techniques employed were UV-Visible spectroscopy, FT-IR and XRD studies. All these techniques confirm the various properties of PANI. The characteristic peaks in UV-Visible spectra of the samples indicate that effective doping has occurred in the synthesized polymer. FTIR spectra show that the incorporation of gold seems to be easier and effective for sulphuric acid and PTSA than CSA due to steric reasons. Thus, the IR study indicates that metallic gold is definitely incorporated into the polymer matrix and the most probable site of interaction could be the amine and imine nitrogen sites of benzenoid and quinonoid moieties. The appearance of the intense broad band at about 1150cm^{-1}, in Au incorporated polymer samples have been associated with high electrical conductivity and a high degree of electron delocalization in PANI. XRD study confirms the presence of Au in the polymer sample in nanometer scale. The size of the Au nanoparticles thus estimated was found to be 12.8 nm, 16.42 nm and 14.75 nm for (111), (200), (220) Bragg reflection planes respectively. The synthesized polymer nanocomposites can be taken for further application studies depending upon their properties. Thus, the present work gives a simple and facile method of synthesis of polyaniline/gold nanocomposites.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

VSD developed the project and supervised the preparation of the manuscript; SM and CS assisted with the preparation of the manuscript, synthesis and characterization of nanomaterials.

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