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Investigation on optical, electrical, morphological and structural properties of micro and nano copper blended Polyaniline

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Abstract

Polyaniline (PANI) is one of the unique conducting polymers due to its potential applications. PANI based metal composites are a special class of hybrid materials which have obtained complementary behaviors such as high performance of electrical conductivity. This study is based on the system consisting of conducting polymer PANI doped with micro and nano copper particles which were prepared by the chemical oxidation polymerization method separately. The structural, morphological characteristics and electrical conducting properties of PANI ,micro copper doped polyaniline (µ-CuPANI) and nano copper doped polyaniline (n-CuPANI) have been investigated by FT-Raman, SEM-EDX and conductivity measurements. FT-Raman spectra confirmed the formation of PANI and show the characteristics peaks of PANI. The surface morphology of the samples was investigated by SEM and its compositional analysis has been studied by energy dispersive X-Ray spectroscopy. The conductivities of PANI and its composites after doping have been compared. The results revealed that nano composite (1.49 x 10^{-2}S/cm) and micro composite (1.09 x 10^{-2}S/cm) have an increased electrical conductivity than PANI (5.03 x 10^{-5}S/cm) at room temperature. A feasible mechanism for the formation of micro and nano composite is presented. This new type of hybrid materials may have enormous application.

Keywords: Polyaniline doped with micro /nano copper metal, Electrical conductivity

1. Introduction

In recent years conducting polymers have been the main focus for the active research in many areas and fields such as energy storage, sensors, anticorrosive materials, solar cells ,organic light emitting diodes and electromagnetic interference shielding[1-8].Among the conducting polymers polyaniline (PANI) has been extensively studied due to ease synthesis, good environmental stability, economical synthetic cost ,high conductivity in doped state, special electronic ,optical ,magnetic and mechanical properties. So PANI is a promising material for various

techno-commercial applications[9-11]. PANI can be synthesized by chemical oxidative polymerization[12, 13] and electrochemical polymerization [14, 15]. Chemical oxidative polymerization method for preparing PANI has been used since it allows mass production in a short duration. Various physical and chemical properties can be enhanced by making blends or composite with metal particles[16, 17].Thus the combination of organic-inorganic hybrid materials possess the properties of both the constituents. This new kind of composite materials with synergistic performance can be utilized in various fields such as rechargeable batteries, nanoelectronic devices and biological sensors[18-21] etc. They can be synthesized either by electrochemical or by chemical oxidation polymerization. The possibility of synthesizing and making a composite of conducting polymer with metal particles provides a versatile class of polymers. This metal particle which is an additive increases the electrical conductivity of conducting polymer[22, 23]. In the present work we report the synthesis of PANI, µ-CuPANI and n-CuPANI by chemical oxidation polymerization method separately. We present the structural and electrical properties of pure PANI, micro and nanocomposite. The structural and morphological properties were analyzed by FT-Raman and SEM-EDX. The conductivity measurements were studied using two probe methods.

2. Experimental

2.1Materials

Aniline (C_6H_7N) monomer, sulphuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), micro copper particles (sigma Aldrich, 99%) and nanocopper particles (nanoshell LLC, USA) were obtained and used as received.

2.2synthesis of polyaniline

PANI was prepared by the chemical oxidation polymerization method. $K_2Cr_2O_7$ is used as an oxidant. H_2SO_4 is used as a dopant. 1M of H_2SO_4 was added drop wise into 1M of the aniline monomer solution. This reaction mixture was placed on a magnetic stirrer for 1hourat constant RPM value. The solution of 0.5M of $K_2Cr_2O_7$ was added drop wise into the mixture. This reaction mixture was stirred continuously at constant RPM value for 24hours under ice cold temperature. The precipitate was separated out by filtering. The final suspension was dried in oven at 100ºC for 90 minutes. The final product was grounded into a fine powder.

2.3 Preparation of Polyaniline/ Micro/Nano Copper composites

100 mg of PANI powder was mixed with 100ml of distilled water.100mg of micro/nano copper particles was added to this mixture and stirred for 12 hours continuously. Then the precipitate was separated out by filtering. The final product was dried in oven at 100ºC for 60 minutes.

3. CharacterizationTechniques

FT-Raman spectrum was recorded on a BRUKER RFS 27: Stand alone FT-Raman spectrometer in the range of 4000 cm^{-1} – 50 cm^{-1} using Nd: YAG laser source operated at 1064 nm . The SEM –EDX images were recorded using S-3000H with an accelerating voltage of 0.3-30kV**.** Th**e** conductivity measurements were performed by a typical two probe method with PSM 1735 Frequency response analyzer employing the pressed pellet method over the frequency range from $1H_Z$ to $10MH_Z$ at room temperature.

4. Results and discussion

4.1 FT-Raman spectroscopy

Raman spectroscopy is a major tool for characterizing conducting polymers. The FT-Raman spectra for PANI, µ-CuPANI and n-CuPANI are shown in the figure in 1(a), (b) & (c).

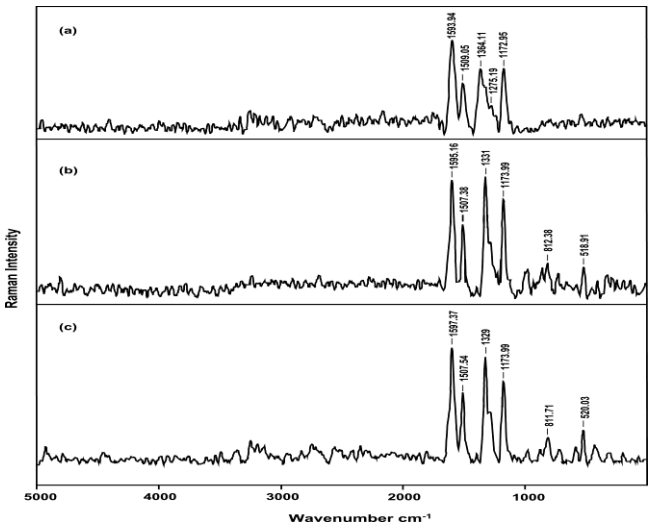

Fig. 1 FT-Raman spectra of (a)PANI (b) µ-Cu PANI (c) n-Cu PANI

The spectrum of PANI from fig.1(a) (b) &(c) shows the characteristic bands at 1172 cm^{-1} , 1275 cm^{-1} , 1364 cm^{-1},1509 cm^{-1} and 1593 cm^{-1}.The band at 1172 cm^{-1} is assigned to the in plane –CH bending. It is assigned to Q = $N^{+}H$ structure. The band at 1275 cm^{-1} is attributed to the –CN stretching. C=N stretching is seen in the band at 1364 cm^{-1}.The band at 1509 cm^{-1} indicates C=C stretching . The peak at 1593 cm^{-1} is due to C=C stretching of benzenoid rings of PANI[24-26]. FT-Raman spectra of micro and nanocomposites show the characteristic peaks of PANI. However a new band at 1331 cm^{-1} and 1329 cm^{-1} appears in µ-CuPANI and n-CuPANI which depends on the degree of the delocalization of π electrons along the polymeric chain. These Raman results indicate that PANI, micro copper particle and nanocopper particle have strong interaction with PANI and shows that there is a formation of µ-CuPANI and n-CuPANI composites.

4.2 SEM – EDX Analysis

The surface morphology of the prepared PANI, µ-CuPANI and n-CuPANI were analyzed using scanning electron microscopy (SEM) which is shown in fig.2(a) (b) & (c).

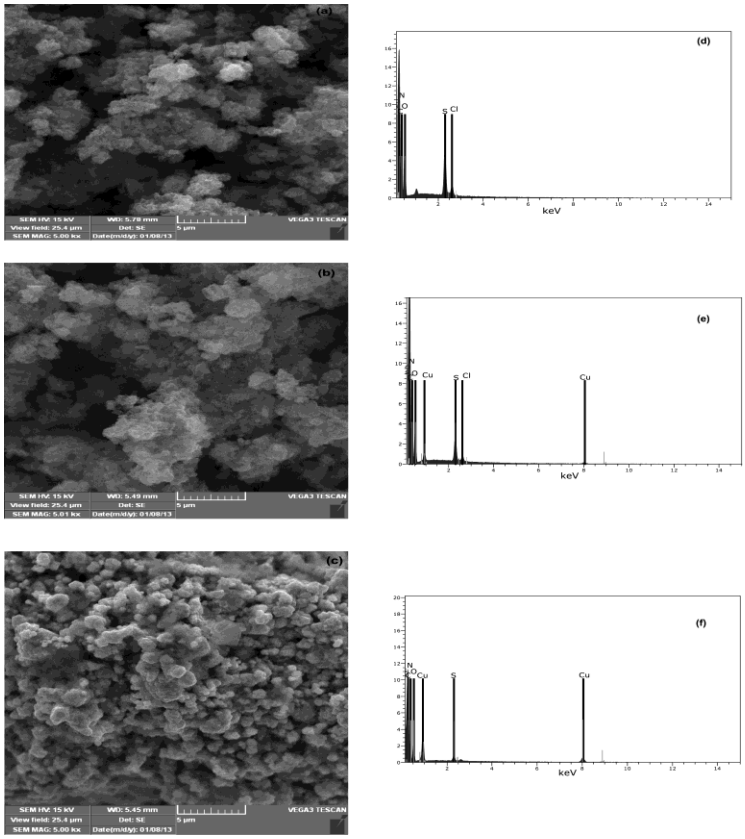

Fig. 2 (a-c) SEM images, (d, e & f) EDX spectrum of PANI, µ-Cu PANI and n-Cu PANI

The SEM images of PANI exhibits clusters of the spherical shaped nano polymers which are revealed in the fig. 2(a). The SEM images of the micro and nanocomposite shows that there is no agglomeration of micro and nanocopper particle in the PANI matrix and there is a uniform distribution of the copper particles in the PANI matrix. According to the SEM images we consider that the micro and nanocopper particles have been embedded with the netlike structure built by PANI chains. The chemical composition of the micro and nanocomposite with selective area analysis was done by energy dispersive X-Ray spectroscopy. EDX spectra for PANI, µ-CuPANI and n-CuPANI were shown in the fig.2(d), (e) & (f). The figure 2e&f reveals that the presence of micro and nano copper particles in the composites.

4.3 Electrical Conductivity Measurements

Conductivity measurements have been performed by a typical two probe technique using PSM 1735 frequency Response Analyzer at room temperature. Conducting samples of PANI, µ-CuPANI and n-CuPANI was formed as pellet by pressing the powder in a pelletizer. Now disc shaped specimens of 13 mm in diameter and about 2 mm thickness was formed for these samples. These samples were placed in between the probes in a sample holder

and the resistance is measured varying the frequency from 1 KHz to 10 MHz at room temperature. The A.C conductivities of PANI, µ-CuPANI and n-CuPANI were calculated using the formula[27].

$$\sigma_{A.C} = \varepsilon_o \varepsilon_r \omega \tan\delta \text{ ---------- (1)}$$

Where ε_o is the permittivity of free space, ε_r is the dielectric constant and $\omega = 2\pi f$ where f is the frequency and tan δ is the dielectric loss. Here the dielectric constant ε_r can be calculated using the formula[28].

$$\varepsilon_r = \left\{ \frac{\left[C_{Cry} - C_{air}\left(1 - \frac{A_{Crys}}{A_{air}}\right)\right]}{C_{air}} \right\} \left(\frac{A_{air}}{A_{Cry}} \right) \quad \ldots (2)$$

Where C_{cry} and C_{air} is the capacitance of the crystal and air, Ac_{ry} and A_{air} is area of the crystal and electrode which is in contact with the sample. The room temperature electrical conductivities of PANI, µ-CuPANI and n-CuPANI were 5.03×10^{-5}S/cm, 1.09×10^{-2}S/cm and 1.49×10^{-2}S/cm. When we compare the A.C conductivities of n-CuPANI and µ-CuPANI with pure PANI the conductivity have been increased by three orders.

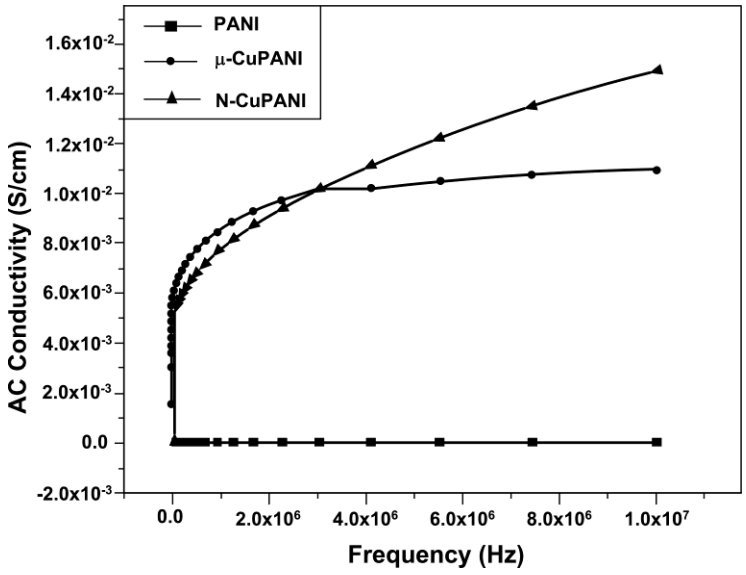

Fig. 3 A.C conductivity Vs frequency

Fig.3 shows the variation of AC electrical conductivity as a function of frequency for these samples. The result shows that micro and nanocomposite possess better electrical conductivity than PANI. This enhanced conductivity of n-CuPANI and µ-CuPANI is due to the incorporation of metal particles into the polymer matrix which favours electronic transport and due to the crystallinity in the composites as observed from EDX results.

5. Conclusions

In this communication PANI, µ-CuPANI and n-CuPANI were successfully synthesized by the chemical oxidation polymerization process. The structure of PANI and its composites have been confirmed by FT-Raman spectra and also showed that there exist a strong interaction between PANI and micro/nano copper. This was further proved by EDX analysis. AC conductivity results indicate a significant increase in electrical conductivity in the micro and nanocomposites compared to pure PANI. This may be due to the influence of copper particles on the PANI and it acts as inter crystallite networks and facilitate the conduction path for the flow of current.

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