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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND ELECTRICAL STUDY OF PPY/PHOTOPRODUCT NANOCOMPOSITE

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ABSTRACT

This paper deals with synthesis of nanocomposite of PPY with photoproduct of ferricyanide and piperazine. The synthesized photoproduct and nanocomposite material is characterized by standard analytical techniques like FTIR, X-ray diffraction (XRD), UV-Vis spectroscopy, scanning electron microscopy (SEM). The XRD analysis confirms two things; first synthesized nanocomposite shows crystalline nature, secondly, the phase structure of composite remains unchanged during doping of photoproduct in the polymer matrix. The dielectric property is strongly affected by the presence of photoproduct in the PPY matrix. The dielectric constant (ε) and dielectric loss (tan δ) factors decrease with the increase in frequency only up to a certain limit. The a.c. conductivity also increases with increase in frequency. The current-voltage characteristic of synthesised PPY nanocomposite is completely symmetrical with respect to the polarity of the applied voltage and shows non-linear ohmic behaviour.

INTRODUCTION

In recent years, both fundamental and applied research in intrinsically conducting polymers like polyaniline, polyacetylene, polythiophene and polypyrrole has grown widely (Jangida *et al*., 2014). The intrinsically conducting polymers have conjugated double bonds and are regarded as striking advanced materials for various applications like electronic devices, electrochromic displays, chemical and biochemical sensors, drug release systems, rechargeable batteries and many other applications (Barnoss*et al.,* 2003*;* Moosvi *et al.,*2016*;* Irfan *et al.,* 2014). In addition to this the conducting polymers offer various advantages like ease of synthesis, environmental stability and simple doping/dedoping chemistry (Zanganeh *et al*., 2008). The electrical properties of conducting polymers can be improved by the formation of composites with various types of dopants/fillers (Singh *et al*., 2014). It has been reported that the conductivity of these heterogeneous systems depend on many factors such as the degree of doping, nature of the dopant, their shape, size, orientation and interfacial interaction between dopant and polymer matrix (Marquez *et al*., 2007). A vast literature is available on the studies of electrical conductivity and dielectric properties of composites of conducting polymers (Islam *et al*., 2014). One of the most intensively investigated conducting polymers is polypyrrole (PPY) (Jiwei*et al*., 2008).

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This material combines several advantages. It is stable under ambient conditions when highly doped and can be synthesized via both chemical and electrochemical polymerization method (Barnoss *et al*., 2009). Though, a good deal of work has been done on polypyrrole doped with various types of dopants/fillers (Dai *et al.,* 2007*)*. However, a very few attempts have been made to study the properties of polypyrrole doped with transition metal complexes (Ferooze *et al.,* 2013*)* and quest about other electrical properties which will be very helpful to understand the study relating to the improvement of other physico-chemical characteristics are missing. This study will also give a new outlook in the exploration of material suitable for high frequency micro/nano electronics. Therefore we have synthesized PPY nanocomposite with a uniform morphology and good structural stability by oxidative chemical polymerisation method. In this work, we focus on the electricalproperties of nanocomposite of polypyrrole (PPY) and inorganic filler (photoproduct of ferricyanide and piperazine).

Experimental details

Reagents and Chemicals

Pyrrole, potassium ferricyanide, anhydrous ferric chloride and piperazine were obtained from Himedia, India. All the chemicals used were of analytical grade.

Synthesis of photoproduct: The photoproduct of $K_3[Fe(CN)_6]$ and piperazine was synthesise by irradiating an equimolar

mixture of $K_3[Fe(CN)_6]$ and piperazine for some time using Osram photolamp till the color of the mixture changed from yellow to reddish. The product was then isolated through crystallization technique and was subjected to various characterization techniques.

Synthesise of PPY/ photoproduct nanocomposite

The nanocomposite of PPY with photoproduct was synthesised via oxidative chemical polymerisation method. 0.055M $FeCl_3$ in 180 mL of chloroform was added drop wise to the stirred solution of 0.022M (in 70 mL chloroform) of distilled pyrrole monomer containing one gram of homogenised photoproduct. The mixture was on stirring for 12 hours. After 12 hours, product was filtered and washed several times. The material was then dried at room temperature.

Apparatus

The structural characterization of PPY/photoproduct nanocomposite were performed by XRD (PW 3050) in the 2 θ range of 20-60 degree with Cu Kα radiations (λ = 1.5418 Å) operated at a voltage of 40 kV and current of 30 mA. The UV-Vis spectrum was recorded using double beam UV-Vis spectrophotometer (Model PG instruments T80). FTIR spectra were recorded on Perkin Elmer RX – 1 FTIR spectrophotometer using KBr pellets. The morphology was observed by Hitachi SEM (Model S-3600N). Electrical properties were measured using computer control LCR meter analyzer (Model Agilent 4285). For the analysis of electrical properties a pellet of 10 mm in diameter and thickness of 2.35 mm was made by applying pressure up to 10 ton/cm^2 on the powder sample.

RESULTS AND DISCUSSION

UV–Visible Absorption Spectra

UV-Vis spectroscopic technique was used to confirm the synthesis of photoproduct of $K_3[Fe(CN)_6]$ and piperazine. Two peaks at 241 and 465 nm were observed in the absorption spectrum of the mixture before irradiation as depicted in Fig.1(a). However, a change in absorption spectrum was observed after irradiation of mixture as is depicted in Fig.1(b). Thus, incorporation of piperazine into the coordination complex has been found to shift the absorption edge from 465 nm towards longer wavelength (red shift) side (530 nm).

XRD Analysis

The XRD analysis of photoproduct and PPY nanocomposite material was studied and shown in Fig. 2. Photoproduct and PPY nanocomposite material showed intense peaks indicating crystalline nature. The lattice parameters of the synthesized photoproduct and nanocomposite indicated that the monoclinic phase structure remains unchanged during doping of photoproduct in the polymer matrix. The average crystallite size of nanocomposite was calculated by Scherrer equation (Deivanayaki *et al*., 2013)

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where D is the crystallite size, k the shape factor, λ the wavelength, θ the diffraction angle and β is the full width at half maximum (FWHM). The average crystallite size of nanocomposite and was found to be 23 nm.

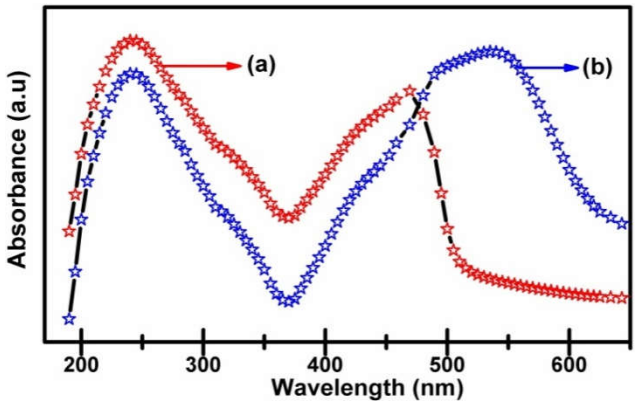

Fig. 1. UV-Visible spectra of aqueous solution of $K_3[Fe(CN)_6]$ and piperazine (a) before irradiation and (b) after irradiation

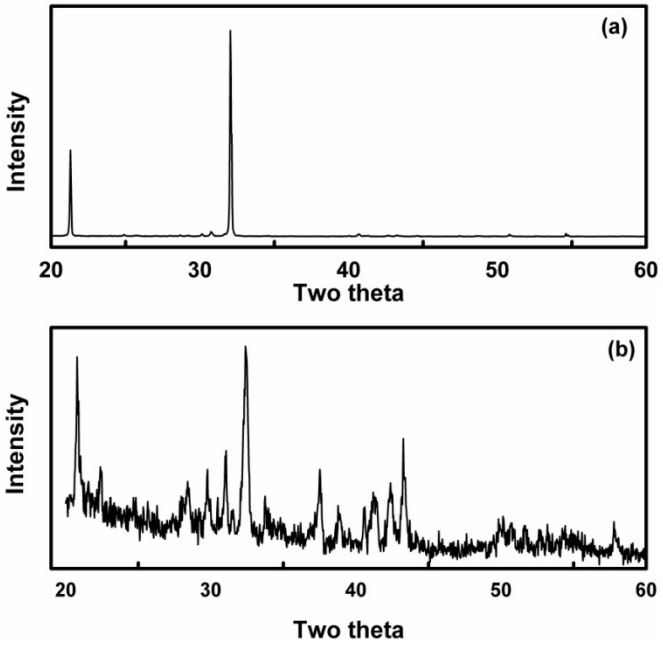

Fig. 2. XRD of (a) photoproduct, (b) nanocomposite

FTIR Characterization

FTIR spectra of photoproduct and PPY nanocomposite are presented in Fig. 3(a, b) respectively. The synthesis of photoproduct is clear by the presence of many different vibrations of both ferricyanide and piperazine (Moosvi *et al*., 2017). The insertion of photoproduct in the PPY matrix is evident by the presence of C≡N stretching frequency at 2070 cm^{-1} in the nanocomposite. Thus, the vibrational analysis of photoproduct and nanocomposite indicate their successful synthesis.

SEM Analysis

Fig. 4(a, b) presents the morphology of photoproduct and PPY nanocomposite respectively. SEM micrograph of photoproduct shows agglomerated crystals. The presence of photoproduct can be seen in the SEM image of composite material confirming the formation of composite.

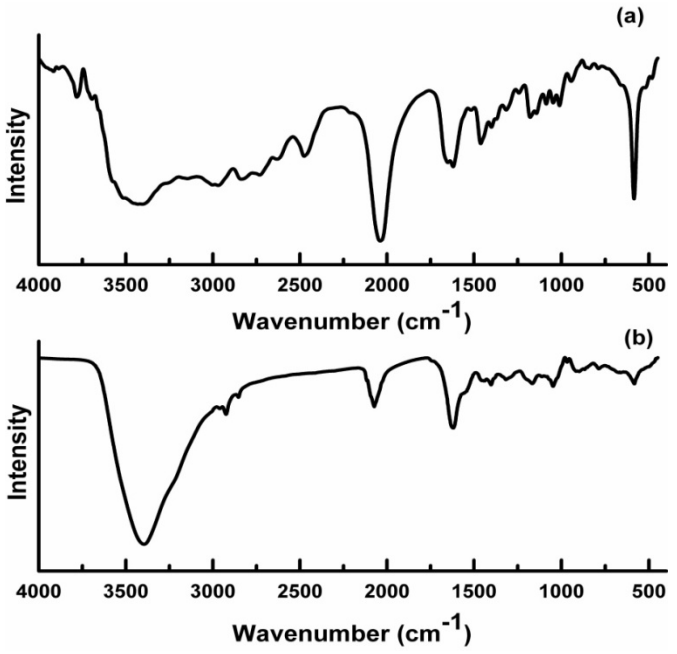

Fig. 3. FTIR spectra of (a) photoproduct, (b) nanocomposite

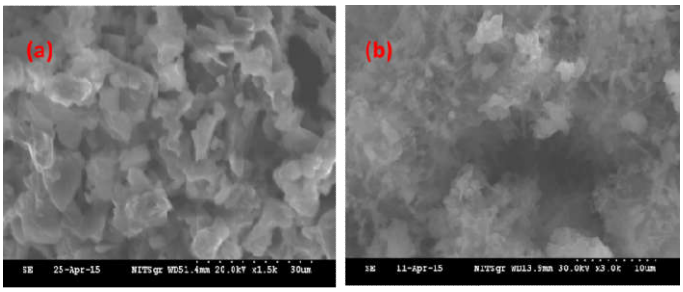

Fig. 4. SEM micrographs of (a) photoproduct (b) PPY nanocomposite

Electrical Properties

Dielectric Studies

Dielectric studies were carried out to find out the suitability of the synthesized nanocomposite for high frequency microelectronic device application. The variation of real part of dielectric constant (ε) and imaginary part of dielectric constant (έ) with frequency of nanocomposite are shown in Fig. 5 (a, b) respectively, at room temperature. These figures are found to exhibit the same behaviour as described by Hanief et al in the study of dielectric properties of PPY nanocomposite as a candidate for capacitor and a sensor for HF radio wave detection (Najar *et al*., 2014). The dielectric properties of a material is contributed by various types of polarization viz dipolar, electronic, atomic and space charge polarization. Fig.5 (a, b) show that the magnitude of ε andέ decreases with an increase in frequency. At low frequency, the dielectric constant is high due to the accumulation of charge at grain boundary, and space charge polarization (Devikala *et al*., 2013). As the frequency increases, the dielectric constant decreases. The decrease in the dielectric constant with increasing frequency is due to dielectric relaxation (Fatima *et al*., 2015). The dielectric constant is independent at higher frequency which indicates the domination of electronic and atomic contribution. The more dielectric constant was observed in synthesise nanocomposite than reported in pure PPY (Moosvi *et al*., 2017). This is due to accumulation of charge carriers in the internal surface of PPY matrix which can be explained by Maxwell-Wagner-Sillars affects (Psarras *et al*., 2002). According to the Max- well–Wagner–Sillars model a dielectric medium consist of double layers having well conducting grains that are separated by poorly conducting grain boundaries. The external electric field application provokes the charge carriers that can easily migrate to the grains, but these grains accumulate at the grain boundaries resulting large polarization and high dielectric constant. The higher value of dielectric constant is also due to inhomogeneous nature of nanocomposite.

Dielectric losses

The analysis revealed that the PPY nanocomposite exhibited the frequency dependent dielectric losses, however, the synthesised nanocompositewas found to show constant behaviour of dielectric losses at higher frequency (Fig.5 (d)).The high value of dielectric losses at lower frequency may be due to the high resistivity caused by grain boundary (Raghasudha*et al*., 2013). The low value of dielectric loss at higher frequency indicates the possible application in high frequency devices.

a.c-conductivity

Fig. 5(c) shows the variation of a.c conductivity with frequency of synthesized nanocomposite at room temperature. Generally, the total conductivity is the summation of band and hoping parts which is given by

$$\sigma = \sigma_o (T) + \omega\varepsilon_o\varepsilon_r \tan\delta$$

Where ω is the angular frequency, and ε_o is the permittivity of free space, σ_o (T) is the d.c. conductivity and independent of frequency and $\omega\varepsilon_o\varepsilon_r\tan\delta$ is the a.c. conductivity, which depends on frequency. It was observed that the ac-conductivity of PPY nanocomposite slowly increases with an increase in the frequency of ac field and at higher it increases rapidly. This is due to the fact that on increasing the frequency, the electron hopping frequency enhances. PPY nanocomposite was noticed to exhibit higher ac conductivity than that reported for pure PPY (Moosvi *et al*., 2017).

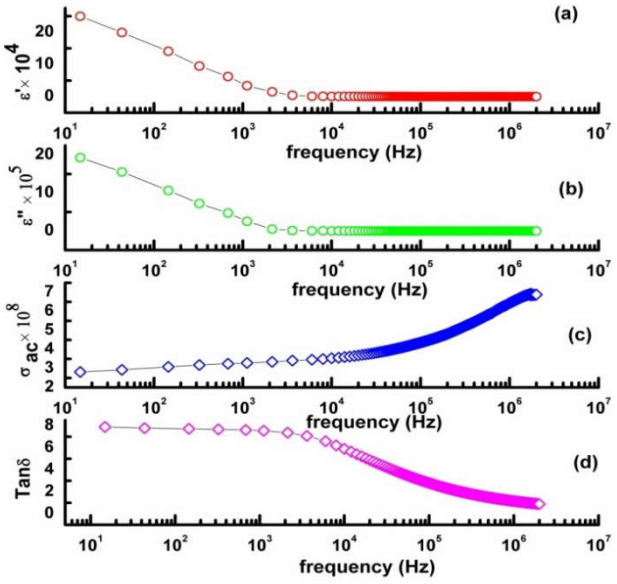

Fig. 5. Variation of (a) real permittivity (b) imaginary permittivity (c) ac-conductivity (d) tangential loss with frequency

I-V Characteristics

The electrical conductivity of the synthesised nanocomposite was measured at room temperature using a four probe technique. The conductivity (σ) was calculated using the following equation (Ting *et al.,* 2009).

$\sigma = Ln2/(\pi.R.d)$
$R = V/I$

where I is the set current (A) , V the measured voltage (V) and d the thickness (cm) of the sample. The dc conductivity of the PPY nanocomposite is in the order of $1.05 \times 10^{-3} Scm^{-1}$, which is higher than reported for pure PPY (Moosvi *et al*., 2017). The current–voltage characteristic of the nanocomposite was measured at room temperature and is depicted in Fig. 6(a).

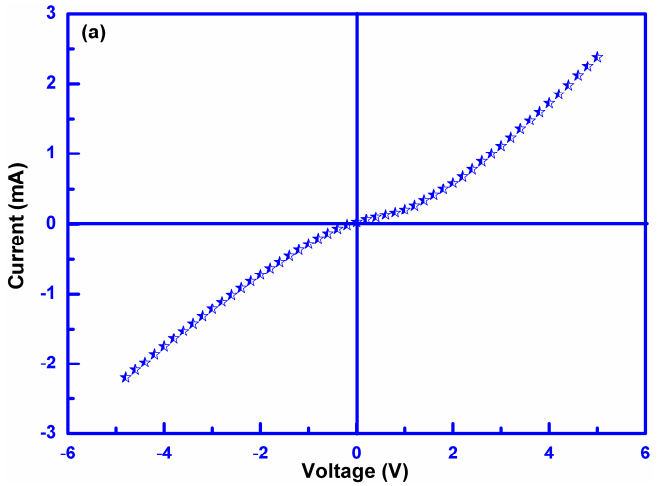

Fig. 6. I-V characteristics of PPY nanocomposite

It is evident that the current-voltage characteristics of synthesised PPY nanocomposite is completely symmetrical with respect to the polarity of the applied voltage and shows non-linear ohmic behaviour. This nonlinear increase in current with applied voltage is related to the conduction mechanism of PPY nanocomposite. Indeed, unlike semiconductors the current is not only carried by free carriers (electrons and holes) but also by the formation of polarons and bipolarons. As the applied voltage is increased, the formation of polarons and bipolarons increases rapidly, contributing to higher values of current through the sample (Belaabed*et al*., 2010).

Conclusion

The synthesis of nanocomposite of PPY and photoproduct was confirmed from FTIR, XRD and SEM characterization techniques. Nanocomposite exhibited high value of dielectric constant and ac-conductivity. I-V characteristic of nanocomposite shows non-linear ohmic behaviour.

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