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Investigation of structural, thermal and dielectric properties of polypyrrole nanotubes tailoring with silver nanoparticles

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ABSTRACT

Polypyrrole nanotube–silver nanoparticles nanocomposites (PPy-NTs/Ag-NPs) have been synthesized by *in situ* chemical reduction of silver nitrate ($AgNO_3$) by sodium borohydride ($NaBH_4$) in the presence of pre-synthesized polypyrrole nanotubes (PPy-NTs) by varying the silver concentration. The nanocomposites have been investigated by HRTEM, SEM, XRD, TGA, UV–vis spectroscopy, impedance analyzer and *I–V* characteristics for their structural, thermal, optical, dielectric and electrical properties. The average diameter of PPy-NTs and silver nanoparticles (Ag-NPs) has been determined to be 130 and 25 nm, respectively. The thermal stability of the nanocomposites is enhanced, which may be attributed to suppression of the degradation of polypyrrole due to dispersion of silver nanoparticles. The enhanced dielectric properties of nanocomposites may be attributed to the interfacial space charge polarization. Significant increase in the ac conductivity of the nanocomposites is attributed to the extra contribution of conductivity from interfacial capacitive regions.

1. Introduction

Multifunctional materials having combination of properties such as magnetic, electrical, optical and biological are increasingly required in today's world. Nanocomposites have been gaining special attention because of their potential to combine desirable properties of different nanoscale materials [1]. The synthesis of metal nanoparticles–polymer nanocomposites has been the focus of intense research in the last few years from both academic and industrial point of view because of the unique and novel properties they acquire [2]. Conducting polymers are taken into consideration in nanobiotechnology, microelectronics, sensors, actuators due to their tuneable conductivity, good thermal stability, biocompatibility, low toxicity etc. [3,4]. Metal nanoparticles are gaining much interest because of their interesting properties which arises due to their quantum size effects and have potential applications in the technological field [5]. Silver and gold nanoparticles are of major research interest due to their significant optical, electrical and biological properties. At nanoscale, the ultra small particle size leads to ultra large surface area per unit mass where a large number of atoms are in immediate contact with ambience and readily available for reaction [6]. However, the aggregation of metal nanoparticles because of their high surface free energy, over time confined the nanoscale properties and limits their applications. Moreover they can be oxidized-contaminated by moisture, air, sulfur-dioxide (SO_2) etc. One of the possible prevention of the aggregation of metal nanoparticles is the use of polymer as a matrix. Conducting polymers such as polyaniline, polypyrrole etc. have redox properties and are excellent hosts for trapping metal nanoparticles such as silver or gold [7]. They allow incorporation and fine dispersion of nanoparticles because of their specific morphology and chemical and structural nature with long polymeric chains [8]. Moreover, combination of properties of conducting polymer and metal nanoparticles lead to improved or novel properties as compared to the parent counterparts. Recent report emerged that conducting polymers like polyaniline and polypyrrole exhibit antimicrobial property [9]. Likewise, silver (Ag) possesses antibacterial property to a broad spectrum of bacteria and is relatively non-toxic to human cells [10]. Thus conducting polypyrrole–silver nanocomposites can be considered as highly efficient multifunctional material for electrical, optoelectronics and biological applications. A few studies have been reported on the conducting polymer silver nanocomposites. Shi et al. [11] have reported facile fabrication of poly(tetrafluoroethylene)@polypyrrole/nano-silver composite membranes for antibacterial applications. Silver nanocables wrapped with polypyrrole have been reported by M.N. Nadagouda and R.S. Varma by wet chemical method [12]. The process involves direct polymerization of pyrrole by silver nitrate. Nanocomposites of polyaniline and silver were synthesised by *in situ* chemical

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polymerization of aniline in the presence of different concentration of silver nanoparticles (Ag-NPs) [13]. The nanocomposites exhibited excellent improvement in dielectric and electrical conductivity property as compared to that of pristine polyaniline. Furthermore, the ethanol sensing characteristics such as sensor response, response time, and reproducibility were found to depend on the Ag concentration in the sensor. Sensor containing 2.5 mol % of silver exhibited highest sensing capability along with better long term stability. Muñoz-Rojas et al. [14] investigated the effects of different parameter on the formation of PPy/Ag nanocomposites using Ag_2O. They reported that the formation of PPy cell around Ag_2O agglomerates was the key factor in the formation of PPy/Ag core cell structures.

In the present study we follow a chemical route to synthesize nanocomposites containing PPy-NTs decorated with Ag-NPs and investigate the effects of concentration of Ag-NPs on various properties of the nanocomposites. PPy-NTs/Ag-NPs nanocomposites have been synthesised by *in situ* chemical reduction of silver nitrate ($AgNO_3$) by Sodium borohydride ($NaBH_4$) in presence of pre-prepared PPy-NTs. We have investigated the effects of concentration of Ag-NPs on structural, thermal, optical, electrical and dielectric properties of the nanocomposites.

2. Experimental

2.1. Materials

Monomer (pyrrole, Sigma Aldrich) was vacuum dried prior to use. $AgNO_3$, methyl Orange (MO), $NaBH_4$ and ferric chloride ($FeCl_3$) from Sisco Research Laboratory were used as received.

2.2. Synthesis

PPy-NTs have been synthesized by reactive self degrade template method discussed elsewhere [15]. Definite amounts of the prepared nanotubes were dispersed in DD water and ultrasonicated for 20 min. Appropriate amount of $AgNO_3$ was dissolved in the polypyrrole solution with vigorous stirring. Solution of $NaBH_4$ with different concentrations was prepared in DD water so that the molar ratio of $AgNO_3$:$NaBH_4$ was maintained at 1:2. Finally, the $AgNO_3$ solution containing PPy-NTs was mixed drop wise in $NaBH_4$ solution and stirred for 24 h. The synthesized nanocomposite was washed with DD water to remove the impurities to obtain pure nanocomposites. Four different compositions were prepared by varying the Ag concentration 6, 9, 12 and 15 wt% with respect to polypyrrole.

2.3. Analysis and characterization techniques

Morphological analysis: HRTEM studies of the synthesized nanocomposites were performed with a HRTEM model JEOL JEM 2100 at an accelerating voltage 200 kV.

SEM analysis: The surface morphology was investigated by scanning electron microscope model JEOL JSM 6390 LV at 15 kV accelerating voltage.

X-ray diffraction: The X-ray diffraction analysis of the nanocomposites was performed with Rigaku miniflex X-ray diffractometer at 5°/min scan rate.

Current–voltage (I–V) characteristics: The current voltage characteristics of the nanocomposites were studied in the voltage range −10 V to 10 V. For this purpose the nanocomposites were compressed in the form of pellets.

UV–Vis spectroscopy: Absorbance from 200–800 nm was performed employing a Shimadzu 1700 UV–visible spectrophotometer using quartz cuvettes of 1 cm path length.

Thermogravimetric analysis: Thermogravimetric analysis (TGA) of the polymer nanocomposites was performed on a Perkin Elmer, model STA 6000 thermal analyzer with different heating rates of 5, 10, 15 and 20 °C min^{-1} with a dynamic nitrogen flow of 20 ml min^{-1} to diminish mass increase due to oxidation.

Impedance spectroscopy: The dielectric properties were evaluated by measuring the impedance and capacitance of the samples using Hioki 3532-50 LCR HiTester in the frequency range from 42 Hz to 5 MHz at room temperature. A two stainless-steel electrode system was employed for dielectric measurements, wherein the pellets of the samples were sandwiched between the electrodes. An ac sinusoidal signal of peak voltage 3 mV with varying frequencies was applied to measure the desired parameters.

3. Results and discussion

3.1. Morphological analysis

The distribution of Ag-NPs over PPy-NTs was determined using SEM and HRTEM and is shown in Fig. 1. It is observed from the figure that the distribution of Ag-NPs is uniform in the polymer matrix. It is also observed that the Ag-NPs are spherical shape and their concentration increases with increase in silver nitrate concentration. From the HRTEM micrographs the average diameter of PPy-NTs and Ag-NPs has been calculated to be 130 and 25 nm, respectively. Polypyrrole nanotubes function as capping agent in the formation of silver nanoparticles and also serve as matrix to stabilize them.

3.2. XRD studies

The XRD pattern of PPy-NTs/Ag-NPs nanocomposites (Fig. 2) confirms the incorporation of Ag-NPs within the polymer matrix. Polypyrrole exhibits a broad diffraction peak with 2θ around 25° which is due to the low crystallinity of polypyrrole. This is associated with the closest distant of approach of the face to face planar aromatic ring of pyrrole [16]. The XRD results also indicate the remarkably intensive diffraction of the characteristics peak at 2θ value 38.3°, 44.6° and 64.4° corresponding to the (111), (200) and (220) planes, respectively of face-centered cubic silver [17]. As expected the diffraction peaks assigned to the Ag-NPs appear with a higher intensity than that of the band of polypyrrole due to higher scattering intensity of the particles. The crystallite size (D) and microstrain (ε) of the silver nanoparticles have been calculated from the Williamson–Hall equation given by

$$\beta \cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin\theta \quad (1)$$

where β is full width at half maximum (FWHM) at Braggs angle 2θ and λ is the wavelength of Cu Kα radiation (~1.5406 Å). Eq. (1) is a straight line equation and one can obtain the microstrain and crystallite size from the slope and intercept, respectively. The Williamson–Hall plot for the sample with 6 wt% of silver is shown in Fig. 3. The calculated microstrain and crystallite size of Ag-NPs with different composition is given in Table 1. The lattice constant has been calculated to be 4.06 Å, in agreement with the value reported in literature [18].

3.3. UV–vis spectroscopy

A metal–dielectric when excited by light photons, coupled at the metal–dielectric interface causing an induced charge density oscillation that shows a strong absorption at a particular wavelength [19]. The UV–vis absorption spectrum of PPy-NTs/Ag-NPs nanocomposites is depicted in Fig. 4. The absorbance band at