Study of SnO_2 doped Polypyrrole Nanocomposites for AC Conductivity and Dielectric properties

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Abstract

Nanocomposites of Polypyrrole and Stannic Oxide (SnO_2-PPy) were synthesized by in-situ polymerization in different weight percentages using oxidation method. The structural properties of prepared sample was studied by using X-ray diffraction. The surface Morphology of prepared sample were studied by field emission scanning electron micrograph (FE-SEM).The AC conductivity and Dielectric properties of SnO_2-PPy nanocomposite of various compositions were investigated at different temperatures and frequencies(100Hz–1MHz). It shows that the dielectric constant decreased with increase in frequency and temperature. As the concentration SnO_2 nano particles increases in PPy the AC conductivity increased with frequency. Activation energy for conduction has been also determined. Activation energy of PS3 (60 % ppy + 40 % SnO_2) was maximum among the samples and it is 0.1062 eV, it has increased with increase in frequency and SnO_2 nanoparticles concentration.

Keywords: Polypyrrole, Stannic Oxide; Dielectric constant, AC conductivity

Introduction

Recently, the conducting polymers shows the great importance as this exhibit unique properties such as optical, electrical, thermal and chemical etc. Among these polymers, polythiohene, Polypyrrole (Ppy) received more attention due to its high conductivity and thermal stability [1-3]. Polypyrrole (Ppy) is one of the most striking polymers due to its special transport properties, facile synthesis, higher conductivity and good environmental stability. Polypyrrole has various advantages and applications in batteries, electronic devices, optical switching devices, functional electrodes, sensors etc.[4]. Tin oxide (SnO_2) has become the important functional material due to its large band gap and excellent optical and electrical properties. It can be used as transparent electrode in thin-film solar cells, liquid crystal displays, smart windows and anodes for lithium batteries [5-7]. The composite of SnO_2/polyaniline (PANI) by chemical deposition technique and found that the AC conductivity and dielectric properties was studied

Experimental

All the chemicals used in this study were of GR grade purchased from Sd-fine, India (purity 99.99%). In preparation of SnO_2, 2g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 h. Then it is filtered and washed with water 2-3 times by using de-ionized water. The obtained precipitate were mixed with 0.27g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70ºC for 24 h to obtain a dried powder. Then this dry product was crushed into a fine powder by grinder. Now the obtained product of fine nanopowder of SnO_2 was calcinated at 700^{o}C up to 6 h in the auto-controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from products will be completely removed.

- **Synthesis of Polypyrole (PPy)**

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used as received for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$)was in such a way to get maximum yield. The resulting black precipitates are filtered and washed with copious amount of distilled water until the washings are clear. PPy so obtained is dried by keeping in oven at 600^{o}C for 3 h. The synthesized material was characterized by using XRD, SEM.

- **Preparations of films**

The thick films were prepared by using screen printing techniques. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure and composite nano powder of SnO_2 and PPy in different weight percentage with a solution of ethyl cellulose (as 10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste was then used to prepare thick films of pure and composite materials of SnO_2 and PPy and it was screen printed on a glass substrate. The prepared films were dried at 90-100^oC in oven for 1 h, so that all the organic materials (in the form of binders) and organic impurities can be evaporated from prepared films. For the surface conductance measurement, the electrodes of silver paint were formed on adjacent sides of the films and again, the films were subjected to heating at 70^oC for 15 minutes for drying the silver paint. The series of samples are as shown in table 1.

Table 1

S.N.	Nano composites	Sample Code
1.	Pure Polypyrrole	P
2.	80 % PPy + 20 % SnO_2	PS1
3.	70 % PPy + 30 % SnO_2	PS2
4.	60 % PPy + 40 % SnO_2	PS3
5.	50 % PPy + 50 % SnO_2	PS4
6.	40 % PPy + 60 % SnO_2	PS5
7.	30 % PPy + 70 % SnO_2	PS6
8.	20 % PPy + 80 % SnO_2	PS7
9.	Pure SnO_2	S

Characterization

- **XRD (X-ray Diffraction)**

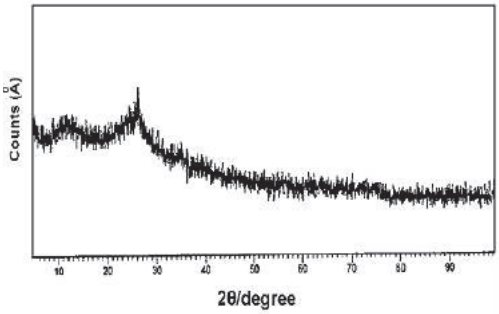


Figure. 1. XRD of pure PPy

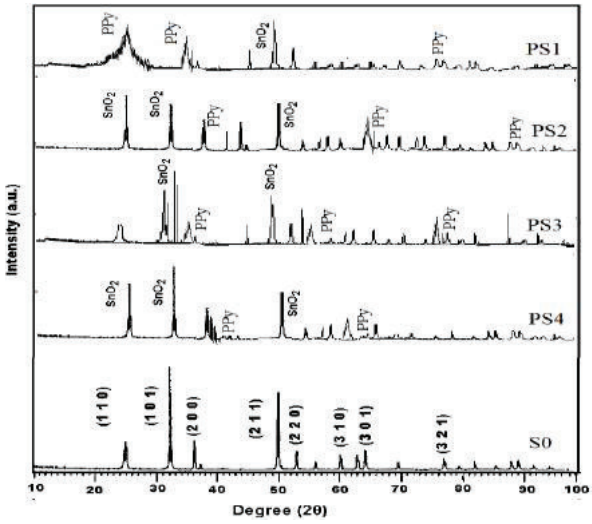


Figure.2.XRD of all composites sample

X-Ray diffraction pattern of pure polypyrrole (PPy) and their composites are as shown in figure (1 and 2). The pure PPy exhibited that, it was amorphous in nature. The broad peak occurred at 24^0 and it is characteristics of amorphous nature of polypyrrole. The broad peak occurs due to the scattering of X-rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio. The X-ray diffraction patterns of composites of PPy, SnO_2 and pure SnO_2, calcinated at 200^oC. Main peak, in case of pure SnO_2, is observed at 26.6^o and this peak corresponds to the plane (1 1 0) of SnO_2 in tetragonal structure (JCPDS Card No.3-1114) with 100% intensity and the average crystalline size by using Scherer's formula was found to be 147.31 nm [9,10]. All the peaks are for the composites materials for molar weight percentage of various samples that are perfectly matched.

- **Scanning Electron Microscope (SEM)**

Figure. 1.SEM of Pure PPy

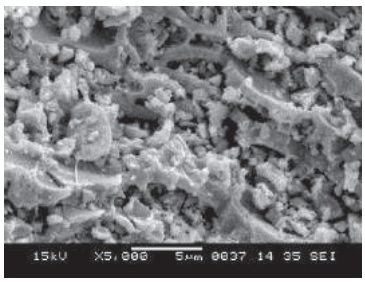


Figure. 2. SEM of PS3

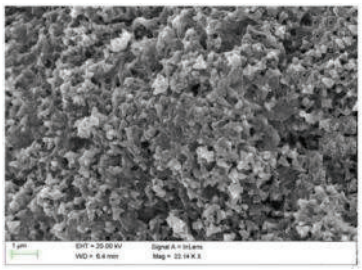
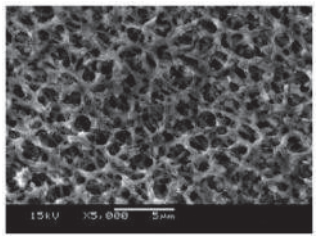


Figure. 3.SEM of Pure SnO_2

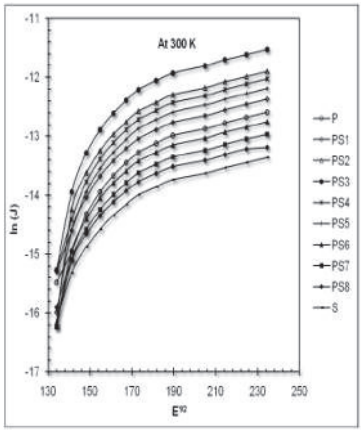


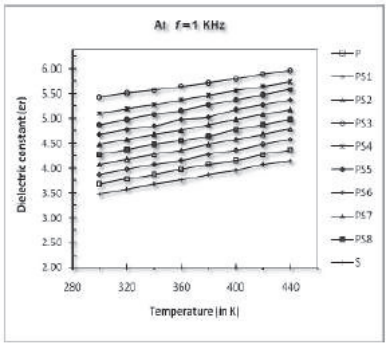
From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average number of pores was taken for comparative study. From every photo, porosity was calculated for one inch region and listed in the tabular form. From above figures, it is found that number of porosity of ($60PPy:40SnO_2$) PS3 composition is more among the prepared and pure samples. Due to high porosity, available area for the flow of ions and charges is more and conductivity enhances. High porosity reduces the obstacle to the flow of charges and ions as collisions reduce (relaxation time increases) and charges mobility increases. This tends to high electrical conductivity.

Result and Discussion

- **Schottky Plots**

In the given setting of applied sample holder assembly, area of cross section is fixed and thickness of the different fabricated pellets is different. Then by using different potential differences, current is measured and that current per unit area of cross section gives current density (J). Applied voltage per unit thickness of the sample gives electric field intensity (E). Then graphs are plotted between ln(J) and E1/2 at different temperatures viz ; 300 K, From graphs, it is observed that as electric field increases, current density increases more in the beginning and then shows saturation. Also ln(J) is maximum for PS3 sample, at constant temperature ln(J) increases and becomes maximum for PS3 sample and then decreases and remains minimum for pure SnO2 (S sample). This shows that with increase in doping of SnO_2 in PPy, ln(J) increases and maximum for PS3 (60% PPy + 40% SnO2). It is, also observed that as temperature increases, ln (J) increases [9-10] and becomes maximum for PS3 sample.





Dielctric constant

Dielectric constant was measured as a function of temperature at constant frequency and sketches are drawn between dielectric constant and different temperatures such as 300 K, . The graphs show variation of dielectric constant with temperature at constant different frequencies and variation of dielectric constant with frequency at different constant temperatures. As temperature increases, dielectric constant increases for all compositions of PPy and SnO2. As the temperature rises, the interfacial polarization increases due to creation of crystal defects [54-58], where the increase in dielectric constant with increase in temperature is thus expected. Also due to increase in temperature, free charges collide with atoms vibrating with large amplitude and thus refractive index (μ) increases as it is inversely proportional to temperature and hence according to relation, , dielectric constant increases. With increase in temperature and increase in doping percentage of SnO2 in PPY, dielectric constant increases and becomes maximum for 60 % PPy + 40 % SnO2 sample (PS3 sample). With further increase in doping of SnO2 in PPy, dielectric constant decreases and becomes minimum for pure SnO2 i.e. for S sample. This is because PS3 sample may have large number of free charges as compared to other compositions and their more collisions with vibrating atoms results in increase of refractive index of the PS3 sample and hence dielectric constant is high among the other compositions.

Conclusion

XRD pattern showed that the sample PS3 has smallest average crystalline size which is 96.01 nm. SEM study exhibited that the number of pores per inch for PS3 samples is more as compared to other compositions. Due to high porosity, available area for the flow of ions and charges is more and as such conductivity enhances (ac conductivity). High porosity reduces the obstacle to the flow of charges and ions as collisions reduce (relaxation time increases) and mobility of charges increases. This tends to high electrical conductivity. From dielectric constant study it is concluded that with the increase in temperature and increase in doping percentage of SnO_2 in PPy, dielectric constant increases and becomes maximum for PS3 sample. With further increase in doping of SnO_2 in PPy, dielectric constant decreases. This is because PS3 sample may have large number of free charges as compared to other compositions and their more collisions with vibrating atoms results in increase of refractive index of the PS3 sample and hence dielectric constant is high among the other compositions. From ac conductivity graphs, it is clear that with increase in frequency and temperature, ac conductivity (ac σ) increases continuously. With increase in doping of SnO_2 in PPy, ac σ increases and becomes maximum for PS3 sample (ac $\sigma = 1.072 \times 10^{-4}$ S/cm). Also it is recorded that ac activation energy of PS3 sample is more among the compositions of PPy and SnO_2 and this maximum value is 0.290 eV.

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