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Optical Properties Study of Polypyrrole doped with TiO2, WO3, Fe2O3 and SnO2 Nanoparticles

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Abstract

The study involves the synthesis of PPy and PPy loaded with various metal oxides TiO2, WO3, Fe2O3, and SnO2 with different ratios by polymerization procedure. The UV-Visible analysis was carried in the wavelength range (300-1100nm) to determine the optical parameters like optical energy gap and optical constants. From the analysis of absorption spectra, the band gaps of polypyrrole undoped are 1.85eV While the samples of PPy/SnO2 composite gained the highest values 2.2eV at weight Percentage (5%) but with PPy/Fe2O3 gained lowest values 1.5eV at weight Percentage (1%).

Keywords: Polypyrrole, Polymerization, Metal Oxides, UV-Visible, optical constants

1-Introduction

Conducting polymers (CPs) have historically been synthesized by polymerisation with chemical or electrochemical oxidation. Chemical polymerization is fine at low cost for large-scale manufacturing, while electrochemical polymerization provides the option of in-situ formation[1] Polypyrrole has an advantage among various CPs because of its chemical stability to atmospheric situations and ease of synthesis by electrochemical and chemical methods [2]. PPy has been widely studied due to its ease of preparation, superior redox properties, stable oxidized form, high conductivity quality, water-soluble, commercially available and useful electrical and optical properties[3]. because of a simple Polypyrrole deposition from aqueous and non-aqueous media its remains one of the most studied, its adherence to a wide variety of substrates, its high electrical conductivity and its stability in air and aqueous media[4]. Extremely conductive and extremely stable CP films can be prepared either by chemical oxidation from a pyrroleum solution in the presence of a salt[5]. PPy films were prepared using the electrochemical process by choosing appropriate polymerisation conditions. Additionally it has been determined that the method of preparation also affects the properties of the films made. The polymer can be deposited in a solvent, where the polymer is insoluble, as a

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continuous film on the electrode surface. Such a synthesis needed a conductive substratum on which to grow the polymer film[6]. The important features of polypyrrole, It is electronic conductors through a p-type (oxidative) doping cycle, it is electroactive, which means that they can be oxidized and reduced and that the application of an electrical potential can affect their chemical structure and properties[7]. CPs contain π -electron backbone which accounts for their unusual electronic properties such as controllable electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity. Such materials are especially attractive due to the fact that they exhibit electrical, magnetic and optical properties of metals or semiconductors while retaining the attractive mechanical properties and the advantages of polymers in processing[8]. CPs have been synthesized in powder and film form respectively using chemical and electrochemical polymerisation methods. It is important to monitor precisely the structure and morphology of conducting polymers during the synthesis process, because most of them are insoluble in common solvents and not in thermoplastics. Notable progress has been made in the synthesis of nanomaterials over the past few decades. In particular, a number of metallic and inorganic semiconductor nanostructures were developed, with special electrical, optical, and chemical properties[9]. PPy nanoparticles have a good adhesion substratum, very high surface area and thus exhibit good electrocatalytic behavior. Examined the influence of PPy thickness on efficiency of the cells. PPy layer thickness increased with an increase in deposition time, but a thicker layer has poor adhesion which results in poor performance[10]. The preparation of hybrid nanocomposites used techniques in that regard is the most common. Organic-inorganic nanocomposites are the latest class of materials that in recent years are attracting increasing research interests due to their improved optical and electrical properties. Because of its remarkable electrical and optical properties, extensive research was carried out on organic materials such as polypyrrole (PPy), polyaniline (PANi), and polythiopene (PTh)[11]. Inorganic materials such as ZnO, Fe2O3, SnO2, WO3 were studied, due to simple preparation methods, long-term stability, high carrier mobility, band gap tunability, thermal and mechanical stability[12]. Nevertheless, polymers are unstable at the nanometer scale due to the presence of covalent interactions, making their nanostructures unstable too. Because of this, progress has been fairly slow in the synthesis of polymer nanomaterials so far, and only small work has been carried out into what fascinating properties polymer nanomaterials possess, as opposed to inorganic nanomaterials[13]. UV – VIS spectroscopy provides details about the electronic transitions of a solid's different orbitals via the absorption spectra. The optical excitation of the electrons from the valence band to the conductive band is demonstrated by an increase in the absorbance at a given wavelength corresponding to the size of the band gap[14]. The goal of the present research in this context is to investigate the effect of the doped nanoparticles on the efficiency of polypyrrole's optical properties.

2-Experimental

2-1 Material

A suitable solution for electropolymerization of polypyrrole was prepared using 0.1 M of pyrrole monomer and was doping with oxalic acid (0.1M) as oxidized with the presence of 150 ml distilled water as well. A two-electrode electrochemical cell was used in all cases. The working electrode was an Indium doped Tin Oxide (ITO) (area of 4 cm²) and the counter-electrode was a platinum sheet(area of 6 cm²). All electrochemical experiments were carried out at room temperature (293 K). Pyrrole was from Cheng Du Micxy Chemical Co. (article 161208002, \geq 98% pure) and was

distilled before use. Oxalic acid was from BHD Chemical Ltd. Nanoparticles (TiO₂, Mgo, WO₃, ZnO, Fe₂O₃, SnO₂) are used in the working as doping.

2-2 PPy Synthesis

1.35 g Of Oxalic acid ($C_2H_2O_4$) was added into 150 mL of distilled water and stirred for about 5 mint until it was completely dissolved and a clear aqueous solution was achieved. 1.036 mL of pyrrole monomer was added drop wise into the solution while stirring for about 5 mint. After obtaining the mixture of aqueous Oxalic acid solution and the monomer potential is applied(1.6V)

between the ITO and platinum by the power supply for about 5 mint with continuous stirring until complete the polymerization, Black film of PPy pure precipitate on ITO glass substrate. Nanoparticles with different weight percentages (0.01, 0.03 and 0.05) % were added to the pyrrole monomer when added the Nanoparticles using ultrasonic homogenous to get homogenous solutions. Black film of PPy with additive Nanoparticles precipitates on the ITO glass substrate.

3-Results and discussion

The transmittance (PPY) films prepared with different ratios, undoped and doped with TiO2, WO3, Fe2O3 and SnO2 Nanoparticles are shown in Fig.1. the transmittance pattern of all deposited thin films aberrance high transmittance at a low wavelength and decrease between 300-350nm and take straight line after 350nm. On other hands, the transmittance change in a non-systematic manner with increase of weight percentages of different Nanoparticles, i.e. higher transmittance aberrance at 1% of TiO2 and 5% of WO3 and SnO2 but with Fe2O3 higher transmittance aberrance at 3% whereas the PPy undoped showed low transmittance of all samples result from the black color of PPy when added the Nanoparticles lead to decreases the opaque of PPy, for this reason, the transmittance increase of doping sample.

The Variation of $(\alpha hv)^2$ with photon energy (hv) for thin films of PPy undoped and doped with TiO2, WO3, Fe2O3 and SnO2 Nanoparticles were plotted in Figure 2 and the optical energy gap are determined and listed in the table1. The results showed that the value of Eg of PPy undoped is 1.85 eV. Energy gap change in a non-systematic manner with increase of weight percentages of different Nanoparticles, the resulting exhibit red shift for PPy composites films doped with TiO2, Fe2O3, and SnO2 at weight percentages 5% where Eg equal to 1.8, 2 and 2.2 eV respectively while the blue shift take place for PPy composites films doped with WO3 at 3% where Eg equal 2.05 eV. It obvious from Figure 2, that doping with four metal oxides with different weight percentages Nanoparticle declares different.

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Fig.1:Transmittance spectra of PPy undoped and doped with TiO2, WO3, Fe2O3 and SnO2 Nanoparticles.



Fig.2 Variation of $(\alpha hv)^2$ with photon energy (hv) for thin films of PPy undoped and doped with TiO2,WO3,Fe2O3 and SnO2 Nanoparticles.

The wavelength (λ)dependence of the refractive index (n) for PPy thin films undoped and doped with different weight percentages of Nanoparticles (1%,3% and 5%) are shown in Figure 3. It obvious that (n) values increase vertical at wavelength 300nm but not exhibit constant manner with an increase of wavelength from 300nm to 350 nm of the incident photon when increasing wavelength up 350 nm all samples take straight line likeness constant. It can be attention from the table(1) that the refractive index higher value at weight percentage 1% for all samples doping with different Nanoparticles and equal likeness 7.26 but the other samples of weight percentage don't exhibit constant manner with different the Nanoparticles type. It is obvious that the refractive index grows as any type of metal oxides added to the host polymer. On the other hand the refractive index tends to decrease by the increase of loading ratio and then gets to grow by a further increase of loading ratio for all composites samples. The reduction of the refractive index reflects the growing of the transmittance i.e. the sample becomes more transparent to the incident wavelength as expected from the simultaneous increase of the energy gap.

The dependence of extinction coefficient (k) upon the wavelength (λ) of PPY undoped and doped with TiO2, WO3, Fe2O3 and SnO2 Nanoparticles are shown in Figure 4. It is remarked that (k) get to decrease as different types were added to the host polymer, indeed (k) increases from 1.57×10^{-2} to 6.79 $\times 10^{-3}$, 8.58×10^{-3} , 8.52×10^{-3} and 6.68×10^{-3} for PPy doped with TiO2, WO3, Fe2O3, and SnO2 Nanoparticles respectively. On the other side (k) tend to change in non-systematic sequence with the increase of loading ratio (i.e. increases and decreases).Maximum (k) value 3.6×10^{-2} obtained from PPy doped (3%)SnO2, see table1. The behavior of the extinction coefficient (attenuation in the intensity of the incident photon) is related to the scattering event that probably take place in the composites.

The real ε_r and imaginary part ε_i of the dielectric constant a function of wavelength are shown in Figures (5 and 6) for thin films of PPy undoped and doped with various Nanoparticles. It is clear that the variation of ε_r mainly depends on the values of (n^2) as a result of small (k^2) comparison with (n^2) , while ε_i mainly depends on the(k) values which are related to the variation of the absorption coefficient. It is remarked that the values of doped values are different with different weight percentages and with the type of Nanoparticles.



Fig.3:Variation of refractive index versus wavelength of PPY undoped and doped with TiO2,WO3,Fe2O3 and SnO2 Nanoparticles.



Fig.4: Variation of extinction coefficient versus wavelength of PPY undoped and doped with TiO2,WO3,Fe2O3 and SnO2 Nanoparticles



Fig.5: Variation of real dielectric constant versus wavelength of PPY undoped and doped with TiO2,WO3,Fe2O3 and SnO2 Nanoparticles.



Fig.6: Variation of imaginary dielectric constant versus wavelength of PPY undoped and doped with TiO2,WO3,Fe2O3 and SnO2 Nanoparticles.

Type of Sample	Mixture percentages	Eg (eV)	Т%	k	n	¢r	¢i
PPy	pure	1.85	1.9041	0.015769	4.5318	20.53719	0.14292
PPy +NPs TiO ₂	0.01%	1.7	18.155	0.006793	7.19477	51.7647	0.09775
	0.03%	1.72	3. 9151	0.01289	5.6961	32.4455	0.14695
	0.05%	1.8	0.11906	0.026804	1.3688	1.87297	0.07338
PPy+ NPs WO ₃	0.01%	1.95	11.5877	0.00858	7.2097	51.9806	0.12373
	0.03%	2.05	13.0870	0.008095	7.2697	52.8484	0.1177
	0.05%	1.85	45.8077	0.003108	4.79578	22.999	0.02981
PPy+ NPs Fe ₂ O ₃	0.01%	1.5	11.64	0.008529	7.2127	52.02298	0.12303
	0.03%	1.9	37.0614	0.00395	5.5992	31.3516	0.00442
	0.05%	2	18.8742	0.006638	7.16104	51.2804	0.09506
PPy+ NPs SnO ₂	0.01%	1.85	18.8364	0.006687	7.16279	51.2944	0.09578
	0.03%	1.65	0.01175	0.03602	3.5105	12.3226	0.02529
	0.05%	2.2	53.759	0.00247	4.1332	17.0845	0.02042

Table 1: Values of optical energy gap and optical constants at λ =500nm of PPy undoped and doped with Nanoparticles metal oxides.

4-Conclusions

From this work, the following points may be concluded:

- 1. The addition of NPs WO3 to PPy makes the composites sample more transparent While the addition of NPs (1% Fe2O3) to PPy make the composites sample more opaque .
- 2. Minimum energy gap value obtained (1.5) (eV) for PPy doped 1% Fe2O3.
- 3. The growth of the refractive index results from the increase of opacity while the reduction of the refractive index results from the increase of transparency.

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