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Complex optical studies on conducting polyindole as-synthesized through chemical route

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ABSTRACT

This research article reports the novel UV-vis spectroscopic studies on as-synthesized conducting polyindole (PIn) through chemical polymerization route at room temperature using anhydrous ferric chloride as an oxidant. The complex optical properties of derived samples were studied by using UV-vis spectroscopy. The as-synthesized polymeric samples exhibited absorption around 220–300 nm. The optical band gap was found to ranges over 4.630–5.224 eV. The maximum optical conductivity for 0.6 M FeCl₃ was found to be 7.93 × 10⁸ S cm⁻¹ at 275 nm. The estimated optical band gap accomplished that this material has potential applications in optical devices.

1. Introduction

Now days, in the development of new efficient and enhanced materials, there was rising research focus towards the synthesis of conducting polymers like polyaniline (PANI), poly-pyrrole (PPy) and polythiopene (PTh) due to their high electrical conductivity, interesting electrochemical properties, and easy processability [1–3]. These electrical and electrochemical properties of such conducting polymers show much assurance for commercial applications in battery materials [4], electrochromic devices [5], sensor technology [6], and nonlinear optics [7]. However, among various aromatic-compound-based conducting polymers, polyindole (PIn) has received excellent research interest due to its close structural similarities with the polymers mentioned above [8–10]. PIn is electroactive polymer, which can be derived either by chemical oxidation or by electrochemically oxidation of monomer using FeCl₃ or CuCl₂ as an oxidant [11]. PIn shows good thermal stability, high-redox activity and stability, and slow degradation rate in comparison with PANi and PPy [12-14].

The available literature reported that, PIn has been derived chemically by oxidation of indole using a supramolecular assembly of chloroauric acid as an oxidant [15]. PIn shows good thermal stability, high-redox activity and stability, and slow degradation rate in comparison with PANi and PPy [12-14].

The available literature reported that, PIn has been derived chemically by oxidation of indole using a supramolecular assembly of chloroauric acid as an oxidant [15]. The formation of nanorods and microspheres of PIn conducting polymer based on chemical synthesis using two miscible and two immiscible solvents respectively without surfactant and supported by UV-vis spectrum [16]. Joshi et al. focused on indole polymerization governed by chloro-auric acid also reduction of Au³⁺ ions occurred simultaneously in a single step, was monitored using UV-vis absorption spectroscopy [17]. There are various techniques of polymerization, but chemical polymerization is
easier than other techniques. The synthesis of conducting polymers through chemical oxidative polymerization route offers mass production at sensible cost.

This research article is intended by presenting a more systematic report on the novel complex optical study of as-synthesized PIn through chemical route using oxidant FeCl₃ at room temperature. From the literature of materials science, not a single report present on the complex optical study of PIn synthesized using an oxidant FeCl₃. The as-synthesized materials were characterized through X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) analysis, and ultra violet-visible (UV-vis) spectroscopy.

2. Experimental

2.1. Materials

All chemicals, such as monomer indole, oxidant anhydrous iron (III) chloride (FeCl₃), hydrogen peroxide (H₂O₂) used as catalyst, were of analytical grade and procured from SD Fine Chemicals, India. The indole monomer was used as received for synthesis of PIn without further purification. The polymeric materials were prepared via chemical oxidative technique using FeCl₃ as an oxidant. In the typical procedure, monomer and oxidant in stoichiometric ratio were dissolved in deionized water. Consequently, H₂O₂ (0.1 M) was added into the reaction mixture, which was to enhance the rate of reaction and jointly yield. The reaction mixture was allowed for constant stirring for 12 h to complete polymerization reaction with a magnetic stirrer at 30 °C. The precipitate was washed with copious amounts of triply distilled water until the washings were clear and then kept for overnight at room temperature. Subsequent to this step, sample was sintered at 60 °C for 30 min. By adopting same route, successful synthesis of five samples of different wt. % was carried out.

3. Results and discussion

The XRD pattern of powder sample was recorded on Rigaku miniflex-II X-ray diffraction using CuKα radiation (λ = 1.54 Å) in the range 10°—70°. The XRD pattern for PIn powder sample with 0.6 M of FeCl₃ is depicted in Fig. 1. The pattern shows the broad hump appears at 2θ region of 18°—28° and absence of well-defined peaks clearly pointed out that the as-synthesized material is purely amorphous.

The morphology and structural features of the material studied by FE-SEM (JEOL JSM-6360). The surface morphology of PIn powder sample with 0.6 M of FeCl₃ was analyzed by FE-SEM and the micrograph is displayed in Fig. 2. The FE-SEM micrograph represents the macro-granular structure formed by the aggregation of small globular structures. The nature of particles has irregular in structure which reflects definite amorphous morphology. The micrograph depicts the presence of aggregation up to some extent as well as an agglomeration of particles.

In order to study the complex optical properties of as-synthesized PIn materials, the UV-vis spectroscopic analysis were carried out through Agilent Technologies, Cary 60 UV-vis. Fig. 3 shows UV-vis spectrum of PIn with different concentration of FeCl₃. To investigate the optical parameters of as-synthesized material, the analysis of the spectrum was carried out. From the plot, it is observed that, the % absorption is higher on the lower wavelength side. The spectrum of as-synthesized material exhibits absorption around the 220—300 nm. The two different absorption peaks, at 225 nm and 280 nm grew due to wide chain length distribution of polymer [18].

The optical band gap of PIn (0.3—0.7 M of FeCl₃) was calculated by using the plot between \(\alpha h\) and photon energy \(h\nu\) as depicted in Fig. 4 (a—e). The material has many applications depend upon its optical band gap. The relation between absorption coefficient (\(\alpha\)) and incident photon energy (\(h\nu\)) can be expressed as in Equation (1) [19—21];

\[
\alpha = \frac{A(h\nu - E_g)^n}{h\nu}
\]

where, \(A\) is constant and \(E_g\) is optical band gap of material.

The values of the optical band gap of PIn with different concentration of FeCl₃ have been determined in the energy range 4.630—5.224 eV. The optical band gap energy values obviously concluded that, this material has potential
application in optoelectronics devices. Fig. 4 clearly represents that, PIn with 0.6 M of FeCl₃ oxidant has least optical band gap energy value, which was found to be 4.630 eV, which has been evaluated by extrapolation of a linear plot of the graph. It is also observed that, the optical band gap energy values decreases with increase in concentration of oxidant up to 0.6 M of FeCl₃, thereafter increases with further increase in concentration of oxidant.

Fig. 5 (a–e) represents the extinction coefficient as a function of photon energy for PIn (0.3–0.7 M) of FeCl₃. The extinction coefficient indicates the amount of absorption loss when electromagnetic wave propagates through a material, which is a measure of fraction of light lost owing to scattering and absorption per unit distance of penetration medium. The extinction coefficient is directly related to the absorption of material and is related to the absorption coefficient. Extinction coefficient has been estimated by the relation (2) [22];

\[ K = \frac{\alpha \lambda}{4\pi} \]  

where, \( K \) is extinction coefficient, \( \alpha \) is % absorption coefficient and \( \lambda \) is wavelength. It can be seen from Fig. 5 that, up to 5.1 eV, extinction coefficient decays exponentially and remains almost constant with humps at 4.5 eV. Beyond 5.1 eV, extinction coefficient shows a steep rise. As shown in Fig. 5, the exponentially decrease in extinction coefficient with an increase in photon energy represents that, the fraction of light lost owing to scattering and absorbance increases. Also, the loss factor decreases with increase in photon energy.

Fig. 5(a–e) shows, the plot of refractive index (n) as a function of wavelength (\( \lambda \)) for PIn samples with different (0.3–0.7 M) concentration of FeCl₃. The refractive index (n) has been computed using relation (3) [23];

\[ n = \left( \frac{1}{T_s} + \frac{1}{1 - T_s} \right)^{1/2} \]  

where, n is refractive index and T_s is % transmission coefficient.

It can be observed that, the refractive index of as-synthesized material decreases with increase in photon energy; it reflects that, the synthesized polymeric samples represent normal dispersion behaviour. The variation in n values with photon energy shows the interaction takes place between photon and electrons. Thus, we can attain the desired material for fabricating the optoelectronics devices by estimating the photon energy as internal energy of device depends on the photon energy. The decrease in extinction coefficient and refractive index with increase in photon energy may be correlated with an increase in absorption coefficient and decrease in the transmittance.

The complex dielectric constant is the basic intrinsic property of materials. The real part of the dielectric constant represents how much it will slow down the velocity of light in the material. Whereas, the imaginary part of dielectric constant indicates how a dielectric material absorbs energy from an electric field owing to dipole motion. Fig. 7 (a–e) shows the real dielectric constant (\( \varepsilon_r \)) as a function of photon energy,
while Fig. 8(a–e) displays the imaginary dielectric constant ($\varepsilon_i$) as a function of photon energy of as-synthesized PIn (0.3–0.7 M of FeCl$_3$) samples. The real and imaginary parts of the dielectric constant evaluated through the relations [24];

$$\varepsilon_r = \frac{n^2 - K^2}{K} \quad (4)$$

$$\varepsilon_i = 2nK \quad (5)$$

where, $\varepsilon_r$ is real part of dielectric constant, $n$ is refractive index, $\varepsilon_i$ is imaginary part of dielectric constant and $K$ is extinction coefficient. The figures, 7 and 8 reveals that real and imaginary part of dielectric constant decreases with increase in photon energy. The data of real and imaginary part of dielectric constant provide knowledge concerning the loss factor which is the ratio of imaginary to real dielectric constant. These results indicate that in synthesized material loss factor increases with decrease in photon energy. The real part of the dielectric constant decreases a little-bit rapidly with increase in photon energy in higher region but in lower region it decreases gradually. However, the imaginary part of the dielectric constant decreases gradually with increase in photon energy.

The optical response of material is generally calculated in terms of optical conductivity ($\sigma$) can be estimated through relation (6) [25];

$$\sigma = \alpha n c/4\pi \quad (6)$$

where, $\alpha$ is absorption coefficient, $n$ is refractive index and $c$ is velocity of light. Fig. 9(a–e) represents the plot of optical conductivity versus wavelength for PIn (0.3–0.7 M of FeCl$_3$). From the figure, it can be observed that optical conductivity...
directly depends upon an absorption coefficient and refractive index of as-synthesized PIn with different concentration of FeCl₃. It can be noticed that optical conductivity increases rapidly over the range 260–290 nm. From Fig. 9, it is clearly observed that, optical conductivity increases with increase in concentration of oxidant up to 0.6 M of oxidant. Further, increase in concentration of oxidant results in decrease of the optical conductivity. The values of optical conductivity for all samples are calculated in the range 4.25–7.89 × 10⁸ S⁻¹ at 280 nm. The optical conductivity was found to be gradually increases after 260 nm, correlated with gradual increase in absorption coefficient for all samples. The optimum value of optical conductivity for PIn with 0.6 M of FeCl₃ at 275 nm is found to be 7.93 × 10⁸ S⁻¹ (Table 1).

4. Conclusions

In the summary of present work, we successfully made attempt to discuss the complex optical properties of as-synthesized PIn samples with different concentration of FeCl₃ as an oxidant through chemical polymerization method at room temperature. The amorphous nature of as-synthesized material confirmed through XRD as well as FE-SEM analysis. The absorption spectrum of as-synthesized PIn samples has been analyzed ranges over 200–500 nm for the determination of optical parameters. These as-synthesized polymeric samples show absorption around the 220–300 nm. The least optical energy band gap was found to be 4.6302 eV, which corresponds...
to PIn with 0.6 M of FeCl₃. With the help of UV-vis study, we have represented the optical constant i.e. extinction coefficient, refractive index, real dielectric constant, and imaginary dielectric constant. The optical conductivity increases with increase in wavelength and this can be attributed to increase in absorption. The as-synthesized PIn material with 0.6 M of FeCl₃ has maximum optical conductivity value, which was found to be \(7.93 \times 10^8\) S cm⁻¹ at 275 nm. The critical analysis of results shows that all complex optical parameters vary with the concentration of oxidant. The estimated optical band gap energy has accepted value for photovoltaic activities and has potential for application in solar cells and optical devices.

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REFERENCES:

[1] Stejskal J, Bober P, Trchova M, Horsky J, Pilar J, Walterova Z. The oxidation of aniline with p-benzoquinone and its impact on the preparation of the conducting polymer, polyaniline. Synth Met 2014;192:66–73.

[2] Xu JK, Shi GQ, Qu LT, Zhang JX. Electrosyntheses of high quality polypyrrole films in isopropl alcohol solution of boron trifluoro diethyl etherate. Synth Met 2003;135:221–2.

[3] Jeon SS, Yang SJ, Lee KJ, Im SS. A facile and rapid synthesis of unsubstituted polypyrrole with high electrical conductivity using binary organic solvents. Polym 2010;51:4069–76.

[4] Mermilliod N, Tanguy J, Petiot F. A study of chemically synthesized polypyrrole as electrode material for battery applications. J Electrochem Soc 1986;133:1073–9.

[5] MacDiarmid AG, Epstein AJ. Application of thin films of polyaniline and polypyrrole in novel light-emitting devices. ACS Symp Ser 1997;672:395–415.

[6] Xue HG, Mu SL. Bioelectrochemical response of the polypyrrole xanthine-oxidase electrode. J Electroanal Chem 1995;397:241–7.

[7] Lindenberger H, Schaferesiebert D, Roth S, Hanack M. Synthesis and properties of polypyrrole prepared by electrochemical polymerization of \(\alpha\)-bipyrrrole. Synth Met 1987;18:37–41.

[8] Sazou D. The dynamical behavior of the bioelectrochemical polymerization of indole on Fe in acetonitrile-water mixtures. Synth Met 2002;130:45–54.

[9] Ismail AA, Sanad SH, El-Meligi AA. Inhibiting effect of indole and some of its derivatives on corrosion of C-steel in HCl. J Mat Sci Technol 2000;16:397–400.

[10] Dudukcu M, Yazici B, Erbil M. The effect of indole on the corrosion behaviour of stainless steel. Mat Chem Phys 2004;103:138–41.

[11] Xu J, Hua J, Zhang S, Zhang R, Nie G, Pu S. Electrosyntheses of high quality poly[5-methylindole] films in mixed electrolytes of boron trifluoro diethyl etherate and diethyl ether. Eur Polym J 2006;42:1384–95.

[12] Pandey PC, Prakash R. Characterization of electropolymerized polypyrrole-application in the construction of a solid-state, ion-selective electrode. J Electrochem Soc 1998;145:4103–7.

[13] Billaud D, Maarouf EB, Hancourt E. Chemical oxidation and polymerization of indole. Synth Met 1995;69:571–2.

[14] Abthagir PS, Dhanalakshmi K, Saraswathi R. Thermal studies on polypyrrole and polycarbazole. Synth Met 1998;93:1–7.

[15] Kumar A, Prakash R. Synthesis of nano ground nutshell-like polypyrrole by supramolecular assembled salts of ss-DNA assisted chloroauric acid. Chem Phys Lett 2011;511:77–81.

[16] Gupta B, Chauhan DS, Prakash R. Controlled morphology of conducting polymers: formation of nanorods and microspheres of polypyrrole. Mat Chem Phys 2010;120:625–30.

[17] Joshi L, Prakash R. Polyindole-Au nanocomposite produced at the liquid/liquid interface. Mat Let 2012;66:250–3.

[18] Joshi L, Prakash R. One-pot synthesis of polypyrrole-Au nanocomposite and its nanoscale electrical properties. Mat Let 2011;65:3016–9.

[19] Nemade KR, Waghuley SA. UV-VIS spectroscopic study of one pot synthesized strontium oxide quantum dots. Results Phys 2013;3:52–4.

[20] Uma B, Murugesan KS, Krishnan S, Das SJ, Boaz BM. Optical and dielectric studies on organic nonlinear optical 2-furoic acid single crystals. Optik 2013;124:2754–7.

[21] Foroutani K, Pourabbas B, Sharif M, Fallahian M, Khademi S, Mohammadzadeh M. In situ deposition of polyphtiene nanoparticles on flexible transparent films: effect of the process conditions. Mat Sci Semi Process 2014;19:57–61.

[22] Dalal J, Sinha N, Kumar B. Structural, optical and dielectric studies of novel non-linear bisglycine lithium nitrate piezoelectric single crystal. Opt Mat 2014;37:457–63.

[23] Jenkins PA, White HE. Fundamentals of optics. New York: McGraw-Hill; 1957.

[24] Goswami A. Thin film fundamentals. New Delhi: New Age Int; 1996.

[25] Sharma P, Katyal SC. Determination of optical parameters of \(\alpha\)-(As₂Se₃)₉0 Ge₁₀ thin film. J Phys D Appl Phys 2007;40:2115–20.