ISSN 1512-1461

STUDY THE EFFECT OF HCL MOLARITY ON X-RAD DIFFRACTION SPECTRA AND OPTICAL PROPERTIES OF PANI/TIO_2 NANOCOMPOSITE THIN FILMS

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Abstract: *The PANI/TiO_2 nanocomposite thin films have been synthesized by a chemical polymerization method. The PANI/TiO_2 nanocomposite thin films was doped under different HCl molarity. The samples were characterized by X-ray diffraction (XRD) in order to know the effect of the increase in HCl molarity on the structural properties of the prepared samples. Optical studies were carried out in the wavelength region (300-900) nm, optical parameters, band gap energy, absorption coefficient, a refractive index were calculated from the optical data. The results have shown that all optical parameters were affected by increase the HCL molarity.*
Keywords: PANI/TiO_2 thin films, optical properties, structural properties, nanocomposite.

1. Introduction

In the past decades, conducting polymers had been considered an important organic material for various fields of research due to their wide range of applications. Among conducting polymers, PANI has been extensively studied due to its excellent conductivity, ease of synthesis, environmental stability, low cost, and highly reversible redox properties. These properties are beneficial for many applications such as rechargeable batteries, sensors, anticorrosion coatings,photovoltaic cells, and light emitting diodes (LED) [1–3]. New materials with exceptional properties are urgently needed to satisfy the increasing demands coming from the electronic, photoelectronic and nanoelectronic industries. The combination of organic and inorganic materials with different nature has been proposed as an effective approach to access complementary properties and synergetic effects [4-6]. Hybrid materials based on organic conducting polymers (CPs) and inorganic nanostructures have been at the leading edge of research and development. A wide range of composites has been realized, including the hybridization of metal nanoparticles, carbon nanostructures, and metal chalcogenides (specifically quantum dots with CPs). Oxide semiconductors are remarkably attractive materials in this regard because a wide range of properties can be combined with complementary features of the organic counterpart. Therefore, p/n junctions were formed by combining various polymers (dominantly thiophene derivatives) with TiO_2, WO_3, or ZnO and deployed in solar cells, electrochromic devices, or for photocatalysis. Incorporation of MoO_3 and Fe_3O_4 into CPs has led to hybrid materials with superior sensing, magnetic, and catalytic properties. Composite materials with enhanced charge storage capacity were prepared by embedding V_2O_5, RuO_2, and MnO_2 into thematrix of CPs such as polypyrrole, polyaniline(PANI), and PEDOT. Such hybrid materials can be obtained by different synthetic routes ranging from simple mechanical mixing of the components, through chemical and electrochemical polymerization of the monomer in the presence of the inorganic nanoparticles, to simultaneous electrochemical codeposition of the polymer and the oxide (nano) particles [7]. In this research, HCl at different molarity was investigated in synthesis of PANI/TiO_2 nanocomposite thin films using a polymerization method at 0^oC temperature. The effects of HCl molarity on PANI/TiO_2 structural and optical properties are also discussed.

ISSN 1512-1461

2. Experimental

The PANI/TiO_2 nanocomposite thin films was chemically synthesized by in-situ polymerization method, where using aniline monomer and ammonium persulfate and hydrochloric acid, accordance to a method similar to the described by Tariq J. Alwan and Zian M. 2020 [8]. The 10 wt% of TiO_2 nanoparticles was mixed with aniline were used. PANI/TiO_2 nanocomposite thin films was deposited on glass slides. The slides are dipped in aniline/TiO_2/HCl solution then the oxidant agent (APS) was added under constant stirring to start the polymerization process, after 20 min, all the slides are removed from a baker, then rinsed acetone, finally left to dry in air at room temperature. This proceses rpeted for different HCl molarity (1M, 2M, 3M). Structure characterization of the thin films is investigated by the use of Philips X-ray diffraction diffractometers with the following lines: Source Cu, the current was 30 mA, the voltage was 40 KV and the wavelength was 1.5405 A. The range of scanning was between 2θ = 10-80^o. The optical measurements were calculated for thin films prepared on glass substrate by using UV-VIS spectrophotometer type (SHIMADZU)(UV-1600/1700 series) in the range (300-900) nm.

3. Results and Discussion

Figure (1) shows the X-ray diffraction patterns of the PANI/TiO_2 nanocomposite thin films at different HCL molarity. X-ray diffraction revealed that all the films are of amorphous nature. It can be observed from the figure, the increasing the molarity of HCL 1, 2, 3 M, showing the presence of broad a low angle asymmetric scattering peak stretching from 2θ between 12^o and 39o, also decrase the peak intensity with the molarity, this indicates that the increase in molarity has a negative effect on the structure of samples [9, 3]. The UV-Visible absorption spectra of PANI/TiO_2 nanocomposite thin films are shown in Figure (2). From the figure it can be seen that the absorption of the all prepared sample have two peaks, one at 390 nm and the other at 880 nm, as expected these two bands should appear in the UV-Vis spectrum of the conducting emeraldine salt polymer [10]. Also it can be observed that the increase in HCL molarity lead to increases the absorption of the prepared samples at 2M, than decrease at 3M, where the reason for these changes is due to the change in polymer chain structure and doping degree.

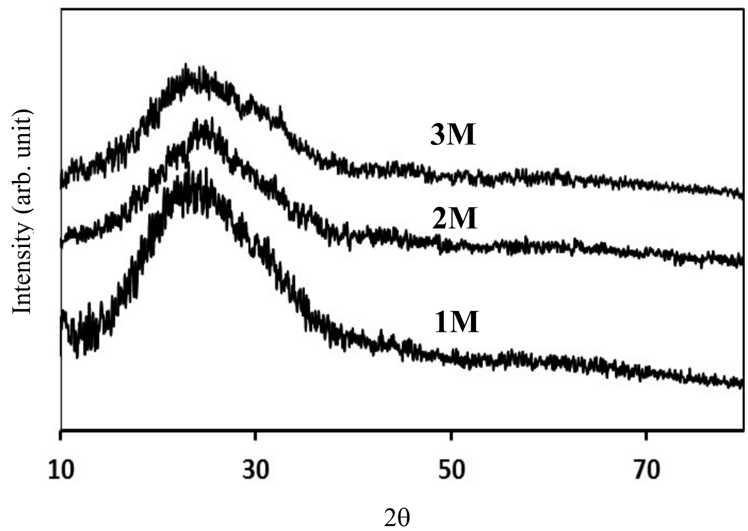


Fig. 1 The XRD spectra of PANI/TiO_2 nanocomposite thin films at different HCl molarity.

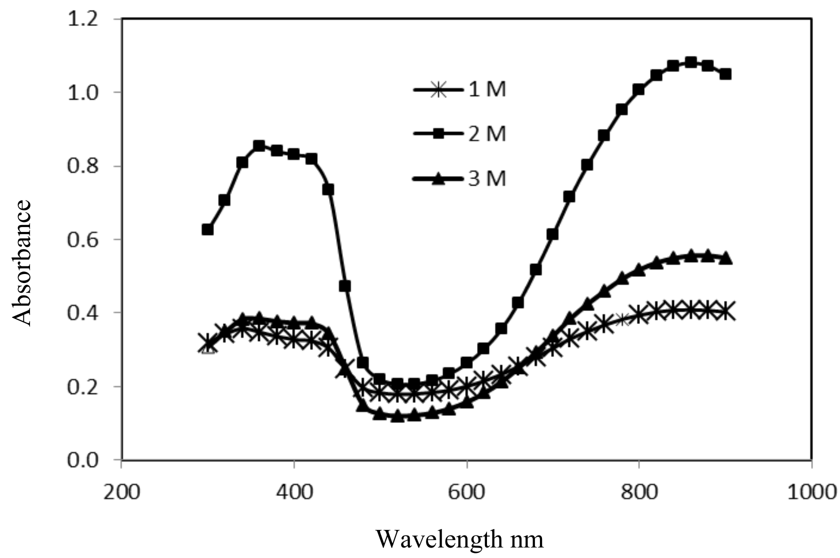


Fig. 2 Absorbance spectra of PANI/TiO_2 nanocomposite thin films.

The optical reflectance spectra of of PANI/TiO_2 nanocomposite thin films under the influence of increasing HCL molarity are shown in Figure 3. The reflectance behavior of PANI/TiO_2 nanocomposite thin film with the increase of HCL molarity, it depends on the range of the wavelength. Figure 4. shows the absorption coefficient (α) of the PANI/TiO_2 nanocomposite thin films with different HCl molarity, the absorption coefficient could be calculated using the following relation [11]:-

$\alpha=2.303\ (A/x)$

where A , x are the absorption and thickness respectively.

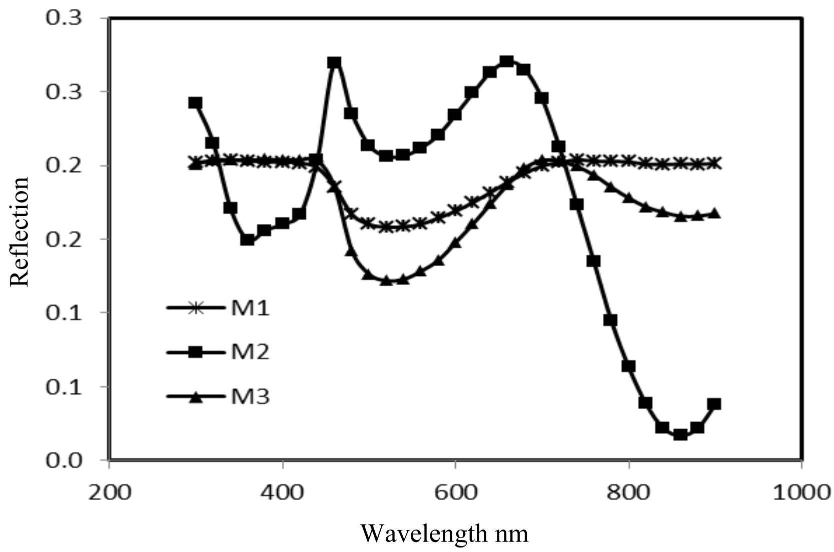


Fig. 3 reflectance spectra of PANI/TiO_2 nanocomposite thin films.

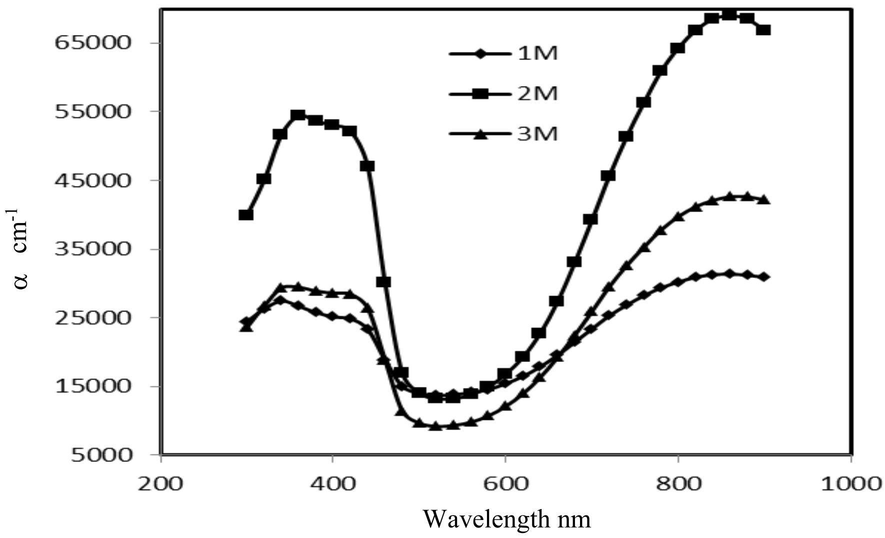


Fig. 4 The absorption coefficient of PANI/TiO_2 nanocomposite thin films.

The absorption coefficient decreased sharply toward the middle of the visible spectrum, and then incresed gradually after 550 nm. It is clearly seen from Figure 4 that the absorption edges shift towards lower photon energy. This could be attributed to the increase of HCL molarity which creates a localized energy states in the forbidden band gap acts as a tail to the conduction band which reduced the energy gap [12].The optical band gap (E_g) of the PANI/TiO_2 nanocomposite thin films was evaluated from the absorption spectra and the optical absorption coefficient (α) near the absorption edge for allowed direct transitions is given by equation [13]:-

$$\alpha h\nu = B(h\nu - E_g)$$

Where the symbols hν stand for the photon energy, B is a constant depending on the material's properties and r is a constant which can take various values which depends on the kind of electronic transition, for the direct and indirect allowed transition = 1/2 or 2, respectively [13]. The best fit line is obtained for the direct allowed transition r = 1/2. The characteristics of $(\alpha h\nu)^2$ vs. hν (photon energy) were plotted for evaluating the band gap (E_g) of the PANI/TiO_2 nanocomposite thin films, and extrapolating the linear portion near the onset of absorption edge to the energy axis as shown in Figure 5. As can be seen clearly, E_g values of PANI/TiO_2 nanocomposite thin films are (2.4 , 2.5 , 2.45) eV corresponding to the HCL molarity (M=1, 2, 3) respectively. In another word, the optical band gap of thin films become wider as HCL molarity increases to 2M, the increase in the optical band gap is caused by doping degree and oxidation of PANI polymer as well as enhanced increase in polymer chain structure, while the dopant of 3M showed a decrease in optical band gap to 2.45 eV, this was caused by the destruction of the polymer chain structure when the molarity of acid given was too high resulting in a decrease in the optical bandgap of the PANI produced. Increased acid molarity was given up to a certain number resulted in an increase in optical bandgap, but the addition of subsequent molarity will decrease the optical band gap value [9, 3].

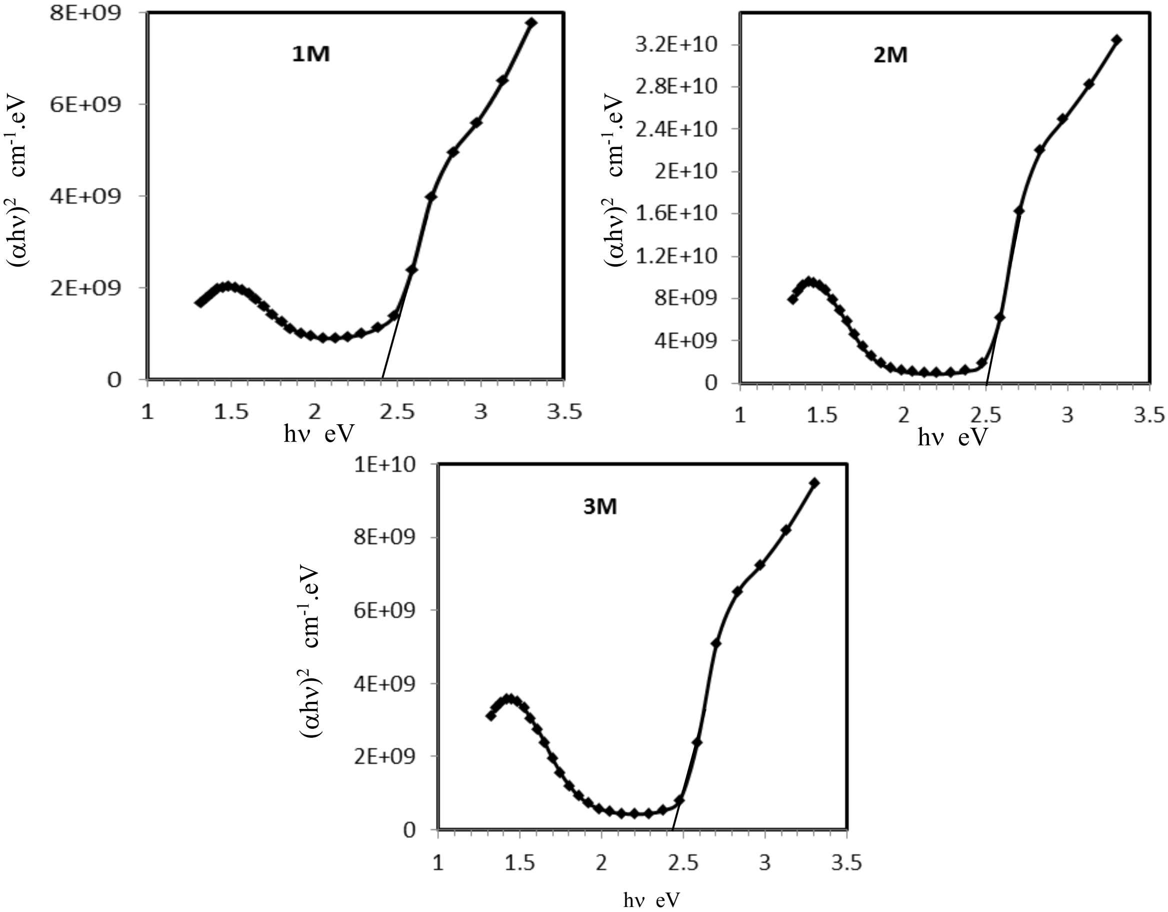


Fig. 5 The dependance of $(\alpha h\nu)^2$ on photon energy for PANI /TiO_2 thin films

The refractive indices (n) of the thin films were determined from equation [14]:-

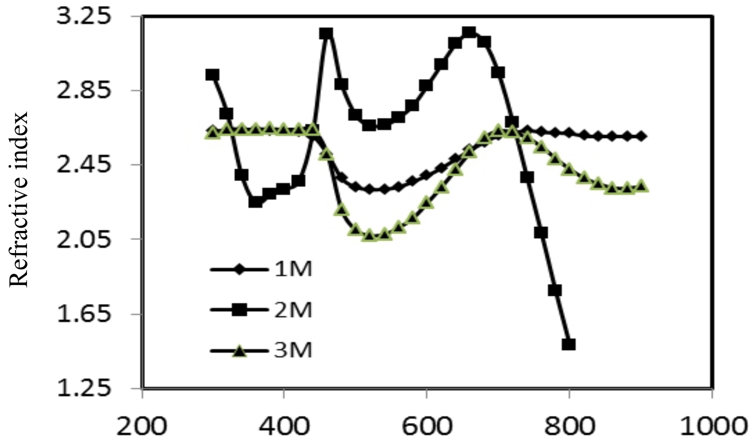
$$n = \sqrt{\frac{4R}{(R-1)^2 - k^2} - \frac{(R-1)}{(R-1)}}$$

Where R the reflectance, and k the extinction coefficient.
The extinction coefficient [15] , which calculated from the relation

$$k = \frac{\alpha \lambda}{4\pi} .$$

As shown in Figure 6, the refractive indices of the thin films are influenced by the HCL molarity. where noticed that the behavior of the refractive index with an increase in the wavelength and HCL molarity are irregular, same as this behavior for PAni is found by [16], and for organic semiconductor cobalt phthalocyanine (CoPc) by [17].

ISSN 1512-1461



Wavelength nm

Fig. 6 The refractive index of PANI/TiO_2 nanocomposite thin films.

4. Conclusion

The PANI/TiO_2 nanocomposite thin films are successfully polymerization method, structural and optical characteristics have been studied. The X-ray diffraction reveal that the films prepared possess an amorphous structure. The optical constants (optical energy gap, refractive index, and absorption coefficient) of PANI/TiO_2 nanocomposite thin films were determined by simple straight forward calculations using the absorption spectra. A high change in optical constants is observed when the HCL molarity increases from 1M to 3M.

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Article received: 2021-04-07