Effect of TiO_2 on the Optical Properties of PANI/TiO_2 Nanocomposite Thin Films

Wasan Adeeb Fadhil [a] **Dr. Tariq Jaffar Alwan [b]**

Mustansiriyah University, College of Education, Physics Department

[a)] wasanalhasnawi@gmail.com [b)] tariq@uomustansiriyah.edu.iq

Abstract:

The effect of TiO_2 nanoparticles (NPs) weight ratio on the properties of PANI/TiO_2 nanocomposite thin films deposited via chemical polymerization onto glass substrates at 0°C were reported. Optical properties studies were carried out in the wavelength region (300-900) nm, optical parameters such as absorbance and transmittance spectra, band gap energy, absorption coefficient, were calculated from the optical data. The results have shown that all optical parameters were affected by increase the TiO_2 NPs weight ratio.

Keywords: Polyaniline (PANI), PANI: TiO_2 thin films, optical parameters, nanocomposite.

تأثير ثاني اوكسيد التيتانيوم على الخواص البصرية للأغشية الرقيقة للمركبات النانوية PANI/ TiO_2

وسن اديب فاضل **أ.د. طارق جعفر علوان**

الجامعة المستنصرية، كلية التربية، قسم الفيزياء

الملخص

تم دراسة تأثير النسبة الوزنية للحبيبات النانوية لثنائي أكسيد التيتانيوم على خصائص الأغشية الرقيقة للمتراكب النانوي PANI:TiO_2 المرسبه عبر البلمرة الكيميائية على ركائز زجاجية عند درجة الصفر مئوية. أجريت دراسات الخصائص البصرية في منطقة الطول الموجي (٣٠٠-٩٠٠) نانومتر، وتم حساب المعلمات البصرية مثل أطياف الامتصاص والنفاذية، وفجوة الطاقة البصرية، ومعامل الامتصاص، بالاعتماد على البيانات البصرية. أظهرت النتائج أن جميع المعلمات البصرية قد تأثرت بزيادة النسبة الوزنية للحبيبات النانوية لثنائي أكسيد التيتانيوم.

الكلمات المفتاحية: بولیانیلین (PANI)، أغشية PANI: TiO_2 الرقيقة، المعلمات الضوئية، المركب النانوي.

Introduction

Hybrid materials (organic/inorganic) based on inorganic nanostructures as well as organic conducting polymers (CPs) have been at the forefront of research as well as development (R & D) [1]. An expansive assortment of combinations have been acknowledged, which include the hybridization of nanostructured carbon, metal, and metal chalcogenides nanoparticles. Oxide semiconductor are astoundingly attractive materials on the grounds that the correlative attributes of the natural equal can be joined with a wide scope of properties [2]. Accordingly, p/n intersections were shaped by joining various polymers (essentially thiophene subordinates) with Titanium dioxide, Tungsten trioxide, or Zinc oxide and conveyed in sun powered cells, electrochromic gadgets, or for photocatalysis. Molybdenum trioxide and Iron (II, III) oxide are coordinated into conducting polymers and brought about high detecting, attractive, and synergist crossover content. The embedding of Vanadium (V) oxide, Ruthenium (IV) oxide, and Manganese (IV) oxide in conducting polymer matrixes such as polypyrrole, polyaniline, and PEDOT was used to prepare composite materials with improved load storage ability [3]. These materials can be performed in different synthetic rows, from mixing the mechanical components to the co-electrochemical polymer coding of polymers, from chemically polymerized monomers to electrochemically polymerized monomers in the presence of nano parts and oxide (nano) particles. The 3 generally significant of these methodologies were the conceivable aggregation of inorganic particles, bringing about a moderately little p/n interface zone; (ii) electrical loss of cooperation between the inorganic issue with the supporting anode; and in conclusion (iii) unregulated irregular dispersion of the particles in the polymeric network [4, 5].

In this research, Add TiO_2 to Polyaniline (PANI) was investigated by synthesis of PANI/TiO_2 nanocomposite thin films using a polymerization method at 0^oC temperature. The effects of add TiO_2 to PANI/TiO_2 on optical parameters are also discussed.

Experimental

The PANI and 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 [6]. The 0, 2, 4, 6, 8 and 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 done in ph 1M of HCl. 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.

Results and Discussion

Figures (1), show the UV-VIS absorbance spectra in the range of (300-900) nm for a all samples. From these spectra it can be observed that there are three absorption bands for each sample, at 340, 420 and 850 nm, which attributed to $\pi - \pi^*$ transitions, transitions π to polaron, and polaron to π^* respectively [7]. The obtained absorption bands are in good agreement with that reported in the literature [8].

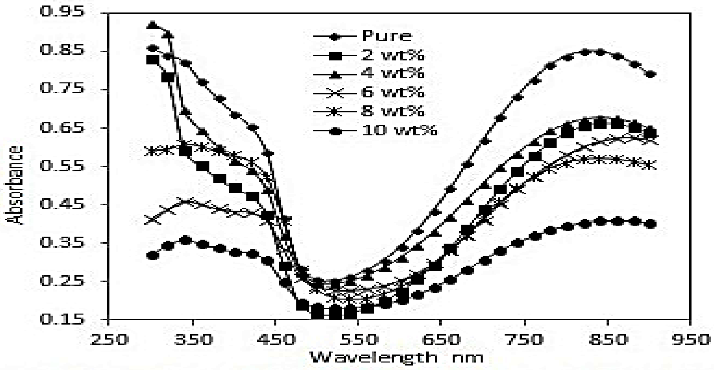

Fig. (1) Absorbance spectra of PANI/TiO_2 nanocomposite thin films at different TiO_2 weight ratios.

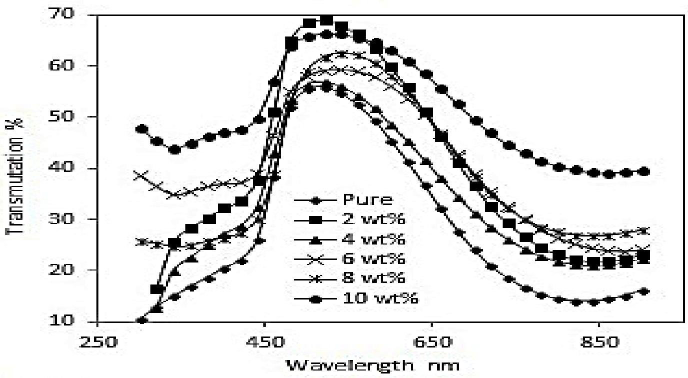

Fig. (2) Transmittance spectra of PANI/TiO_2 nanocomposite thin films at different TiO_2 weight ratios.

The UV-VIS absorbance spectra of the PANI and PANI/TiO_2 nanocomposite thin films at different TiO_2 NPs weight ratio is shown in figure (1), the influence of increasing TiO_2 NP weight ratio on PANI bands is shift the (850 nm) to higher wavelengths and from another hand decrease the absorbance with TiO_2 NPs weight ratio, this is probably due to coordinate complex formation between TiO_2 n NPs and PANI chains on absorbance [9].

Figures (2), show the UV-VIS transmittance spectra of PANI and PANI/TiO_2 nanocomposite thin films under the influence of increasing of TiO_2 NPs weight ratio, which exhibit opposite behavior to absorbance spectra for all the films.

Figures (3), show the absorption coefficient ln α of PANI and PANI/TiO_2 nanocomposite thin films under the influence of increasing the TiO_2 NPs weight ratio.

The absorption coefficient was calculated using the following equation [10]:-

$$\alpha = 2.303\frac{A}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where A :- absorbance and t :- thickness.

It is obvious that the values of α in the visible region are much greater than 10^4 cm^{-1} [11], indicating that the kind of transition occurs in all thin films is the allowed direct transition.

From figure (3), it is clear that all films have high absorption coefficient values at 2.28 eV corresponding to a wavelength of 520 nm shifted to high photon energy (short wave length) with increase TiO_2 NPs weight ratio, and also, in general note increases the absorption coefficient with increasing TiO_2 NPs weight ratio.

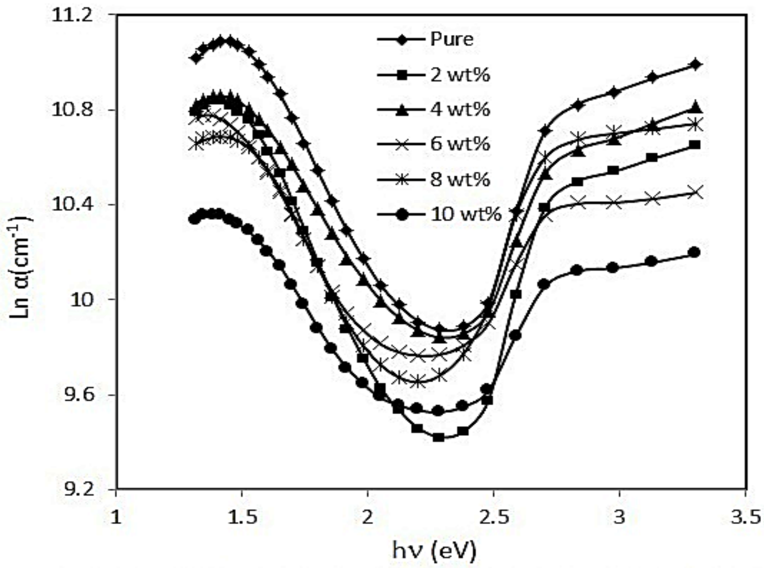

Fig. (3) Absorption coefficient of PANI/TiO_2 nanocomposite thin films at different TiO_2 weight ratios.

The optical energy gap is considered one of the most important physical constants that depend on it for making many electronic devices such as solar cells and detectors. All samples for prepared PANI/TiO_2 nanocomposite thin films are subject to the rule of allowed direct transition. The optical energy gap of PANI and PANI/TiO_2 nanocomposite thin films was calculated using equation [12] :-

$$\alpha h\nu = \acute{B}(h\nu - E_g)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where: $\acute{B}$ is constant.
hυ: is the photon energy.
E_g : is the band gap.

and then the relationship between $(\alpha h\nu)^2$ and photon energy (hυ) is plotted, the straight line extends from the curve to cross the photon energy axis at point $[(\alpha h\upsilon)^2 = 0]$ represents the E_g value, as shown in the Figures (4). Where these figures shows the optical energy gap of the PANI/TiO_2 nanocomposite thin films under the influence of increasing the TiO_2 NPs weight ratio. From the calculations of the optical energy gap of the PANI/TiO_2 nanocomposite thin films at different TiO_2 NP weight ratios shows that the values of the optical energy gap increase from 2.31 eV at 0 wt% TiO_2 NPs weight ratio to 2.4 eV at 10wt% TiO_2 NPs weight ratio As the indicator in the figure (4), which means that values of the energy gap increase when the TiO_2 NPs weight ratio is increased, this attributed to the quantum confinement of the particle size, this is consistent with R. K. Hasibur, et al., 2020 and [13] and Y. Wang,, et al., 1987 [14].

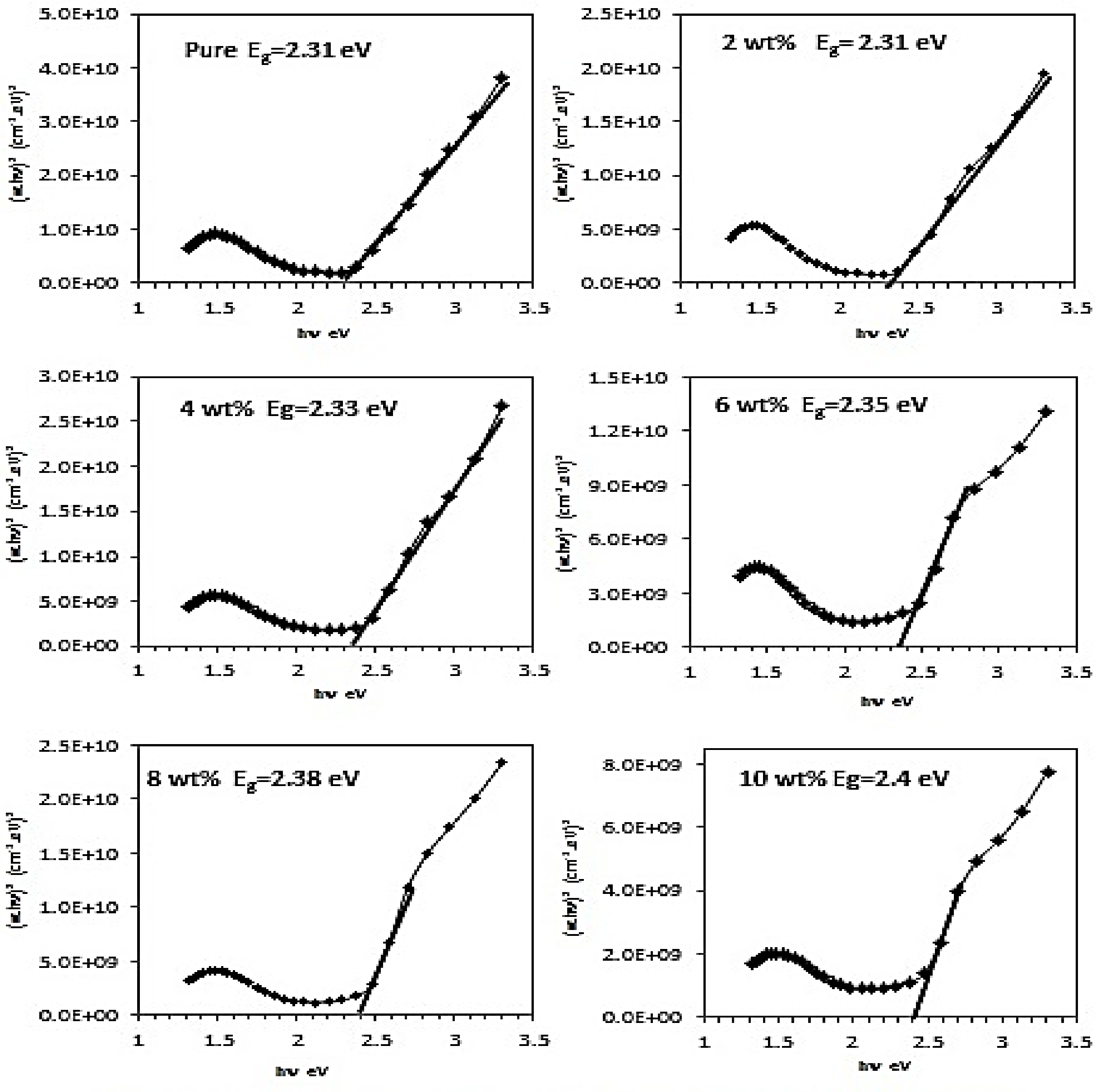

Fig. (4) The dependance of $(\alpha h\nu)^2$ on photon energy for PANI and PANI/TiO2 nanocomposite thin films at different TiO_2 weight ratios.

Conclusion

The PANI and PANI:TiO_2 nanocomposite thin films are successfully synthesized using polymerization method, optical characteristics of prepared samples have been studied. The optical constants (optical energy gap, and absorption coefficient) of PANI and PANI:TiO_2 nanocomposite thin films were determined by simple calculations using the absorption and transmittance spectra. Absorbance spectra reveal that PANI and PANI:TiO_2 nanocomposite thin film has bands located at 340, 420, and 850 nm, and those bands are the characteristics of one state of PANI which is known as conducting emeraldine salt state. A high change in optical constants is observed when increasing weight ratios of TiO_2 from 0 to 10 wt %.

References

1. Sajjad H. M., Larry A. N., Thomas T., Parvaneh M.-T., Hidemitsu F., and Ajit K., Review-Organic-Inorganic Hybrid Functional Materials: An Integrated Platform for Applied Technologies, Journal of The Electrochemical Society, Vol. 165, No. 8, pp. B3137- B3156, 2018.
2. H. Dong, Y.-C. Chen and C. Feldmann, Polyol synthesis of nanoparticles: status and options regarding metals, oxides, chalcogenides, and non-metal element, Green Chem, Vol, 17, No 8, pp. 107-4132, 2015.
3. F. M. El-Hossary , A. Ghitas , A. M. Abd El-Rahman, A. A. Ebnalwaled, M. Abdelhamid Shahat and M. H. Fawey, Effect of UV-activated TiO_2 Nanoparticles on the Properties and Performance of PAni-TiO_2 Nanocomposite Films for Solar Cell Applications, IOP Conf. Series: Materials Science and Engineering, Vol. 956, pp. 1-9, 2020.
4. Csaba J., Norma R. de Tacconi, Wilaiwan C., and Krishnan R., “Bringing conjugated polymers and oxide nanoarchitectures into intimate contact: light-induced lectrodeposition of polypyrrole and polyaniline on nanoporous WO_3 or TiO_2 nanotube array”, J. Phys. Chem. C, Vol. 116, pp. 19145−19155, 2012.
5. Zang J., Bao S. J., Li C. M., Bian H., Cui X., Bao Q., Sun C. Q., Guo J. and Lian K. J., Phys. Chem. C, Vol.112, pp.14843. 2008.
6. Tariq J. Alwan and Zain A. Muhammad, “Effect of f-SWCNT on the structure, electrical and optical properties of PANI thin films”, Optoelectronics and Advanced Materials–Rapid Communications, Vol. 14, No. 9-10, pp. 421-426, 2020.
7. Patil. R. B, Jatratkar. A. A, Devan.R. S, Ma. Y. R., Puri. R. K., Puri. V and Yadav. J. B., “Effect of pH on the properties of chemical bath deposited polyaniline thin film,” Appl. Surf. Sci., Vol. 327, pp. 201–204, 2015.
8. M. Trchová, I. Šeděnková, Z. Morávková and J. Stejskal, “Conducting polymer and ionic liquid: Improved thermal stability of the material - A spectroscopic study,” Polym. Degrad. Stab., Vol. 109, pp. 27–32, 2014.
9. M. Sasikumar and N. P. Subiramaniyam, “Microstructure, electrical and humidity sensing properties of TiO_2/polyaniline nanocomposite films prepared by sol–gel spin coating technique”, Journal of Materials Science: Materials in electronics, Vol. 29, pp. 7099–7106, 2018.
10. R. J. E. and A. I. Gibson, An Introduction to Solid State Physics and Application, 1st editio. Macillian Inc., 1974.
11. R. S. Ali, “Effect of substrate temperature on structural and optical properties of CdO thin films,” Int. Lett. Chem. Phys. Astron., Vol. 8, pp. 47-55, 2014.
12. L. K. and A. H. Clark, Polycrystalline and Amorphouse Thin Films and Device. New York: Edited by Lawrence Academic Press, 1980.
13. Rahman K. H. and Kar A. K., “Titanium-di-oxide (TiO_2) concentration-dependent optical and morphological properties of PAni-TiO_2 nanocomposite”, Materials Science in Semiconductor Processing, Vol. 105, pp 1-11, 2020.