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EFFECT OF THICKNESS ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF POT/MgO NANOCOMPOSITE THIN FILMS

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Abstract

The properties of amorphous poly(o-toluidine)/magnesium oxide (POT/MgO) nanocomposite films with different thicknesses (t= 107, *191*, and 30*9* nm) deposited via chemical polymerization onto glass substrates at 0°C were investigated. FE-SEM images revealed that POT/MgO thin films have nanorod structures with diameters in the range of 93.13-204.65 nm. The increase in the thickness leads to an increase in the nanorod diameters. The samples were characterized through fourier transform infrared spectroscopy to examine the effect of the increase in the thickness on the functional group of POT/MgO nanocomposite thin films. X-ray diffraction showed that the POT/MgO thin films have an amorphous structure. Conductivity measurements indicated that conductivity is 3.85 $S.cm^{-1}$ at 309 nm film thickness, increases to 6.98 $S.cm^{-1}$ when thickness decreases to a nano range.

Key words: POT/MgO thin films, electrical conductive, structural properties, nanocomposite.

1. Introduction

Conductive polymers (CPs) are considered one of the most important materials in the 20th century because they possess metallic properties and other unique properties, such as optical, electronic, and mechanical characteristics. CPs were first prepared in 1958; in particular, by Natta et al. prepared polyacetylene as a black powder and found that it can function as a semiconductor with conductivity of 10^{-11} to 10^{-3} $S.cm^{-1}$ [1]. Similar to polyacetylene, poly(o-toluidine) has been broadly studied to search for commercially viable materials. POT is a CP that has unique properties and can vary its electrical and optical properties; therefore, it is an excellent material for many applications [2,3]. POT can be prepared through several methods, including polymerization (chemical or electrochemical) in the form of bulk powder or films.

Hybrid materials (organic conductive polymer/inorganic nanostructures) have been extensively developed. Various kinds of composites, such as hybridized carbon nanostructures, metal nanoparticles, oxide semiconductors, and metal chalcogenides, have been registered. Oxide semiconductors are attractive materials because their features can be mixed with the additional characteristics of their organic counterparts. Accordingly, hybrid nanocomposite is shaped by joining various polymers with Tungsten trioxide WO_3, Magnesium Oxide MgO, or Zinc oxide ZnO and prepared through different methods and techniques. MgO nanoparticles (NPs) have favorable properties; as such, it is one of the structures studied most closely in this material class. A large number of proposed uses, such as electrocatalyst photocatalysis, charging batteries, drug delivery, electrochromism, sensing, electrochromism and, water divisions [4,5]. The development of hybrid materials focused on the nano-oxides and conductive polymers ordinarily preparaed by spin coating of a polymer that is solved by organic solvents, and then thermal treatment. However, this strategy has a limited scope. Therefore, these composites have been prepared by other methods and techniques to expand their practical applications [4,6].

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In this work, POT/MgO thin films were prepared through in situ polymerization, and the effects of film thickness on the morphological characteristics, structural properties and electrical conductivity of the samples were investigated.

2. Experimental

POT/MgO thin films were chemically synthesized using O-toluidine monomer, ammonium persulfate (APS), and hydrochloric acid through in situ polymerization in accordance with previously described methods in Ref. [7]. MgO nanoparticles (10 wt%) were mixed with o-toluidine, and POT/MgO thin films were deposited on glass slides. The slides are immersed in an o-toluid/MgO/HCl solution, and an oxidant APS was added under constant stirring to start polymerization. After 5, 15, and 20 min, the slides were pulled out of the beaker, rinsed with acetone and distilled water. After different deposition times, POT/MgO films with different thicknesses formed. The samples were morphologically analyzed with TESCAN MIRA3 FE-SEM. The thicknesses of the samples were calculated on the basis of cross-section imaging. The POT/MgO were subjected to FTIR spectroscopy by using a Shimadzu FTIR-8400S spectrometer. The thin films were structurally characterized using a Philips X-ray diffractometer with the following lines: Cu source, 30 mA current, 40 kV voltage, and 1.5405 A^o wavelength. The range of scanning was $2\theta = 10°–80°$.

3. Results and Discussion

The FE-SEM images Figure (1) present the morphological characteristics of POT/MgO thin films with different thicknesses t =107, 191, and 309 nm, from this images noted that the samples have formational like nanorods for all the samples, the images also showed the random interconnection of POT/MgO nanorods. The average diameter of nanorods at t =107 nm thin film was about 93.13 nm, this value increased to 204.54 nm at t=309 nm thin film (Table 1), nanorods become agglomerated, and their surface becomes rough with increased thickness of thin films, therefore, the better the results at thinner sample. Figure (2) shows the FE-SEM cross-section of the POT/MgO thin films deposited on a glass substrate at different deposition times. The thicknesses of the films are about 309, 191, and 107 nm corresponding to the deposition times of 20, 15, and 5 min, respectively, these results are consistent with a lot of previous research [8], which noted that, in the chemical deposition process, the thickness of the samples increases with increasing deposition time.

Figure (3) shows the X-ray diffraction patterns of the POT/MgO thin films at different thicknesses 107, 191, and 309 nm, From the figure it is clear the samples have amorphous structures, and a broad peak stretching is observed at $2\theta = 18°$ to 33°; the intensity of this peak slightly increases and growth peaks at $2\theta = 31°$ and 43°, with increase the thickness, possibly because of the tendency of the samples to shift toward a polycrystalline structure [9-11].

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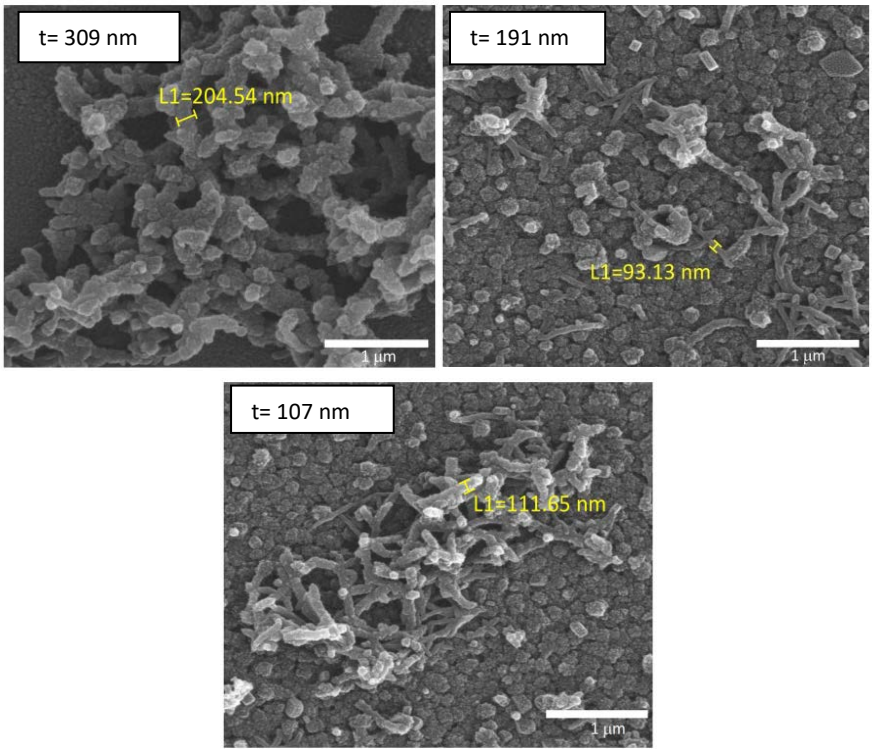

Fig 1. FESEM images for the POT/MgO thin films at different thickness.

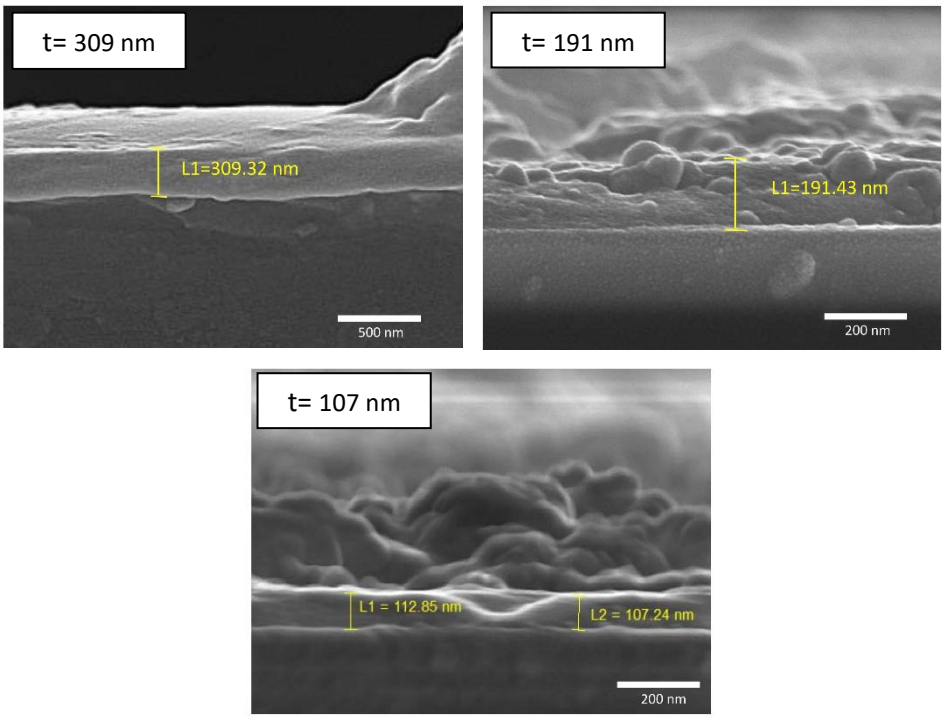

Fig. 2. FESEM cross section image at of some samples on glass substrate.

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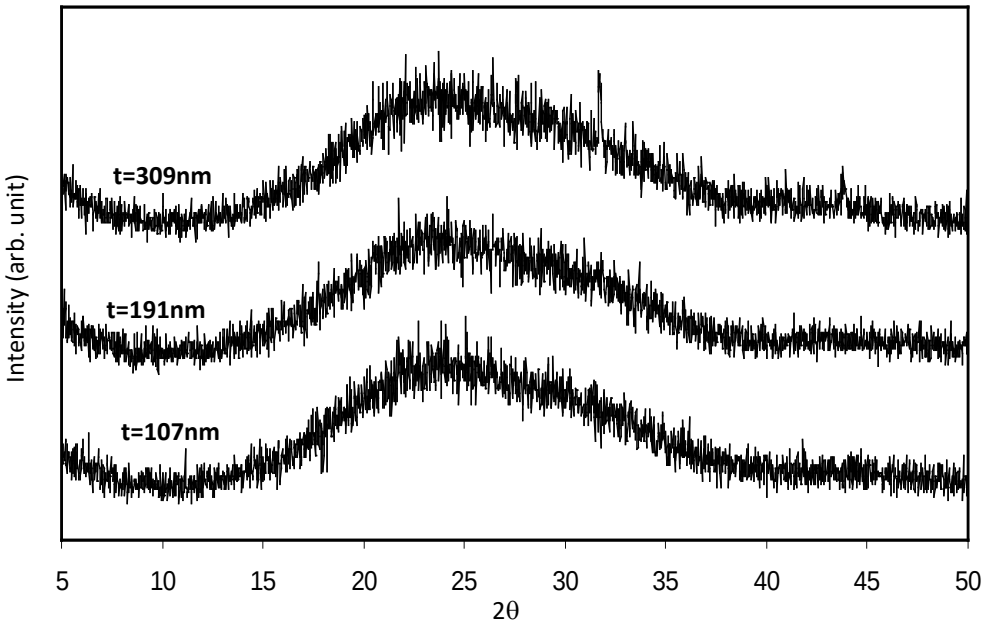

Fig 3. The XRD spectra of POT/MgO thin films at different thickness

Figure (4) illustrates the FT-IR spectra of POT/MgO thin films with different thicknesses. The spectra of the samples indicate strong IR absorption peaks at wavenumbers that refer to the POT bands. From the FTIR spectra for the POT it can be noticed that the bands at 1581, and 1511 cm^{-1} were attributed to the C=N and C=C stretching modes for the quinoid (Q) and benzoid (B) rings. The peak around 1306 and 1261 cm^{-1} are corresponds to the C–N stretching mode [12]. The peak at 1388 cm^{-1} is attributed to the symmetric deformation for -CH_3 group. And the peak at 1159 cm^{-1} is assigned to the C–H bond [13,14]. The pack at 715 $cm^{-}1$ corresponds to the stretching vibrations of the overtone for MgO [15]. Nevertheless, the strength (intensity) of the above bands increases as the thickness of the thin film increases possibly because of an increase in the amount (per unit volume) of the functional groups.

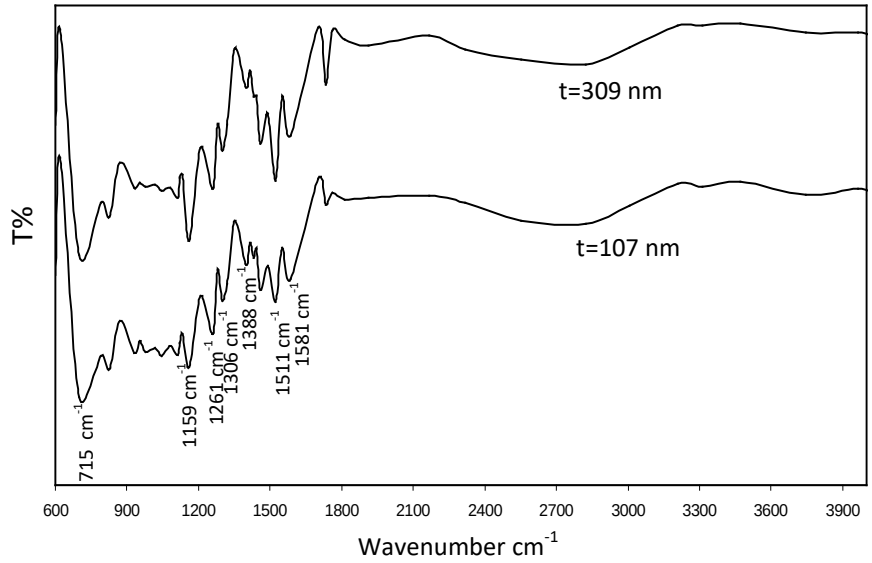

Fig 4. FTIR spectra of POT/MgO thin films.

Figure (5) presents the I–V curve of the POT/MgO thin films, which have an ohmic behavior. Conductivity measurements (Table 1) indicate a lower conductivity value of 1.33 $S \cdot cm^{-1}$ at 191 nm

ISSN 1512-1461

thickness. This value increases to 3.85 $S \cdot cm^{-1}$ at 309 nm thickness because of the improvement in the structure of the film yielding more packing density, therefore, charge carriers move easily [16]. However, conductivity increases to 6.98 $S \cdot cm^{-1}$ at a 107 nm thickness, and this may be attributed to the improved advantages that occur in the properties of a material when the thickness of films is in the nanoscale range, in this range, the mechanisms underlying the improved electrical properties can be ascribed to the intriguing molecular orientation. Similar results were obtained by Chin-Chiuan Kuo et al. [17] and Il Young Choi et al. [18].

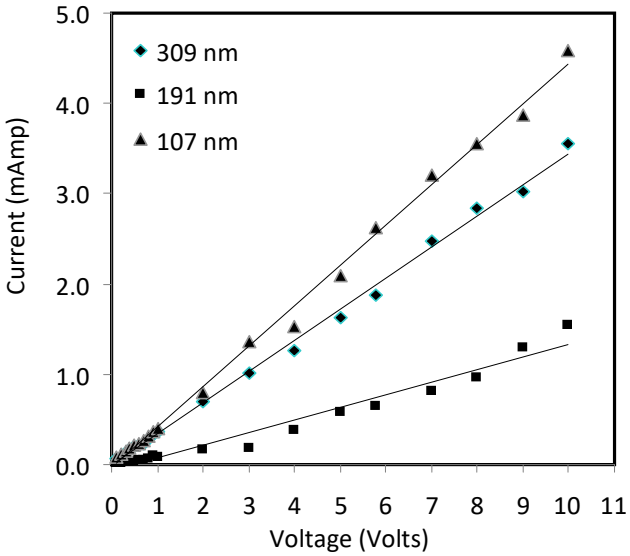

Fig. 5. The I-V curves for POT/MgO thin films.

Table1. Effect of thickness on structural, electrical parameters of the POT/MgO thin films.

Thickness nm	Nanorods Diameters nm	σ (S.cm-1)
107	93.13	6.98
191	111.65	1.33
309	204.65	3.85

4.Conclusion

Chemical oxidation polymerization is an effective method to deposit POT/MgO thin films on glass substrates. FE-SEM images show that the POT/MgO thin films have nanorod structures, whose diameters increase as film thickness increases. X-ray diffraction reveals that the films have an amorphous structure. FTIR measurement indicates that POT/MgO forms, and the thickness of the films does not affect the function group of POT/MgO thin films. The electrical conductivity measurements of POT/MgO thin films demonstrate that conductivity increases with film thickness. However, when thickness decreases and reaches the nanoscale, conductivity improves further.

ISSN 1512-1461

References:

[1]. Michael S. Freund, "**Self-doped conducting polymers**", John Wiley & Sons Ltd, 2007.
P. Savitha, D. N. Sathyanarayana, "**Synthesis and characterization of electrically conducting poly(o/m-toluidine-co-o-/m-aminoacetophenone) copolymers**", Polymer Science Part A Polymer Chemistry, 42(17), 4300 – 4310, 2004.

[2]. Tariq Jaffar Alwan. "**Topography of electrospun nanofibers and its influence on (POT/PS)/Si hybrid solar cell parameter**". Turkish Journal of Physics, 34(5), 472 – 480, 2019.

[3]. Csaba Janáky, Norma R. de Tacconi, Wilaiwan Chanmanee, Krishnan Rajeshwar, "**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**", The Journal of Physical Chemistry C, 116, 19145−19155, 2012.

[4]. Nishigandh Pande, Adinath Jambhale, Viswas Purohit, Dipika Jaspal, Jalinder Ambekar and Narendra Pal Singh Chauhan, "**Poly(o-Toluidine)-Li nanocomposite: facile preparation and utilization in energy storage devices**", Polymer-Plastics Technology and Materials, 60 (2), 208-216, 2021.

[5]. Ran Liu, Jonathon Duay, Sang Bok Lee, "**Heterogeneous nanostructured electrode materials for electrochemical energy storage**", Chemical Communications, 47, 1384-1404, 2011.

[6]. Tariq J. Alwan, "**Improved electrical, structure, and mechanical properties of poly (o-toluidine) polymer by multiwalled carbon nanotubes**", Optoelectronics and Advanced Materials – Rapid Communications, 13(7-8), 472-476, 2019.

[7]. B. Abdallah, A. Ismail, H. Kashoua, W. Zetoun, "**Effects of deposition time on the morphology, structure, and optical properties of PbS thin films prepared by chemical bath deposition**", Journal of Nanomaterials, 2018, 1826959, 1-8, 2018.

[8]. Anand Kumar, Vazid Ali, Sushil Kumar and M. Husain, "**Studies on conductivity and optical properties of Poly(o-toluidine)-ferrous sulfate composites**", International Journal of Polymer Analysis and Characterization, 16(5), 298-30, 2011.

[9]. Rani Bushra, Mohammad Shahadat, A. S. Raeisssi, Syed Ashfaq Nabi, "**Development of nano-composite adsorbent for removal of heavy metals from industrial effluent and synthetic mixtures; its conducting behavior**", Desalination, 289, 1-11, 2012.

[10]. Maria Angela de Moraes Cordeiro, Débora Gonçalves, Luis Otavio de Sousa Bulhões, João Manuel Marques Cordeiro, "**Synthesis and characterization of poly-o-toluidine: kinetic and structural aspects**", Materials Research, 8 (1), 5-10, 2005.

[11]. Sudeshna Chaudhari and A. B. Gaikwad, "**Synthesis and corrosion protection aspects of Poly(o-toluidine)/CdO nanoparticle composite coatings on mild steel**", Journal of Coatings Technology and Research, 7(1), 119–129, 2010.

[12]. Pooja C. Yadav, Megha A. Deshmukh, Harshada K. Patil, Gajanan A. Bodkhe, Pasha W. Sayyad, Nikesh N. Ingle, Mahendra D. Shirsat, "**Copolymers of polyaniline and poly-o-toluidine: electrochemical synthesis and characterization,** AIP Conference Proceedings, 1953(1), 100058(1-8), 2018.

[13]. Tursun Abdiryim, Zhang Xiao-Gang, Ruxangul Jamal, "**Synthesis and characterization of poly(o-toluidine) doped with organic sulfonic acid by solid-state polymerization**", Wiley Periodicals, Inc. Journal of Applied Polymer Science, 96, 1630–1634, 2005

[14] K. Karthik, S. Dhanuskodi, C. Gobinath, S. Prabukumar and S. Sivaramakrishnan," **Ultrasonic-Assisted CdO–MgO nanocomposite for multifunctional applications**", Materials Technology Advanced Performance Materials, 34(7), 403-414, 2019.

ISSN 1512-1461

[15]. M. A. Momin, M. A. Islam, M. A. A. Azad, M. S. Ali, M. R. A. Bhuiyan. "**Influence of the thickness on the electrical properties of CdS thin films**". Journal of Applied Science and Technology, 7(1), 49-53, 2010.

[16]. Chin-Chiuan Kuo, Chi-Chang Liu, Shao-Chih He, Jing-Tang Chang, and Ju-Liang He, "**The Influences of thickness on the optical and electrical properties of dual-ion-beam sputtering-deposited molybdenum-doped zinc oxide layer**", Journal of Nanomaterials, 2011,1-5, 2011.

[17]. Il Young Choi, Joungphil Lee, Hyungmin Ahn, Jinho Lee, Hee Cheul Choi, Moon Jeong Park, "**High-conductivity two-dimensional polyaniline nanosheets developed on ice surfaces**", Angewandte Chemie International Edition, 54,10497–10501, 2015.

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