Polyaniline/TiO_2 nanocomposite thin films prepared by microwave plasma

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تحضير أغشية رقيقة لمتراكب البولي أنيلين/ أوكسيد التيتانيوم ببلازما الميكروويف

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المستخلص

حُضرت أغشية رقيقة للبولي أنيلين (PANI)ولمتراكب البولي أنيلين/أوكسيد التيتانيوم PANI/TiO_2 بطريقة البلمرة بالبلازما المحتثة بالمايكروويف. وكان معدل حجم جسيمات أوكسيد التيتانيوم المستخدمه 50 نانومتر. وتم توصيف الأغشية الرقيقة الناتجة بوساطة UV-VIS,FTIR,AFM,SEM لدراسة تأثير أوكسيد التيتانيوم على الخواص البصرية وشكل سطوح وتركيب الأغشية الرقيقة. بينت دراسة الخواص البصرية ان فجوة الطاقة البصرية للمتراكب قلت من3.58 إلى 3.38 إلكترون فولت مع زيادة تركيز جسيمات أوكسيد التيتانيوم من 1 إلى 5 نسبه وزنيه%. قياس الطيف للغشاء الرقيق بالأشعة تحت الحمراء بين إن هناك إزاحة في قمم الامتصاص مع إضافة جسيمات اوكسيد التيتانيوم. كما بينت صور AFM و SEMتوزيعاً منتظماً للجسيمات النانوية في مصفوفة غشاء البولي أنيلين. ويمكن الأستنتاج بأن هناك إمكانية للسيطرة على فجوة الطاقة البصرية للأغشية الرقيقة للمتراكب النانوي PANI/TiO_2المحضر بطريقة البلازما المحتثة بالمايكروويف.

Abstract

Polyaniline (PANI) and PANI/TiO_2 nanocomposite thin films were prepared by microwave plasma. The TiO_2 powder of average particle size of 50 nm was used to prepare PANI/TiO_2 nanocomposite thin films. The PANI/TiO_2 nanocomposite thin films prepared by polymerization in plasma and characterized by UV-VIS, FTIR, AFM and SEM to study the effect of titanium oxide nanoparticles on the optical properties, morphology and structure of the thin films. The optical properties studies showed that the optical energy band gap of the PANI/TiO_2 decreased systematically from 3.58 eV to 3.38 eV with increasing TiO_2 nanoparticles concentration from 1 to 5 wt%. The FTIR measurement showed a shifting in the FTIR absorption peaks with TiO_2 concentration. AFM and SEM images indicated a uniform distribution of the TiO_2 nanoparticles in the PANI matrix. It can be concluded that PANI/TiO_2 nanocomposite thin films with controlled optical energy band gap can be prepared by microwave plasma technique.

Keywords: **Plasma polymerization, polyaniline nanocomposite, titanium oxide, microwave induced plasma**.

Introduction

In recent years, the development of inorganic/polymer hybrid materials on nanometer scale have been receiving significant attention due to their wide range of potential applications in optoelectronic devices and in field effect transistors (1). TiO_2 is one of the typical n-type semiconductors, while polyaniline is one of the typical conductive polymers, which is usually considered as p-type materials (2).Inorganic nanoparticles such as TiO_2 have so far been encapsulated into the shell of conducting polymers giving rise to a host of nanocomposite(3).Polymers are usually polyconjugated structures which are insulators in their pure state; but when treated with oxidizing or reducing agents they can be converted into polymer having reasonable electrical conductivity. Nanoscale particles are more attractive due to intriguing properties arising from the nanosize and large surface area. The insertion of nanoscale fillers may improve the electrical and sensing properties of the polymers (4). The conducting polyaniline polymer has reasonable electrical conductivity (5).In a polymer, the σ and π-bonded systems lead to the conduction in a π conjugated polymer, the bond between adjacent carbon atoms alternate between single and double bonds (6). In 1950 Rudolf Peierls found that it is energetically favorable for such a chain to distort spontaneously, creating a gap between the filled valance and the unfilled conduction band and converting a chain from a conductor to a semiconductor (6).The reason for the wide application range of high frequency (HF) plasmas is that they have good power efficiency, in direct current plasma the charges are always accelerated to the opposite electrode and are eventually lost there but in an oscillating field with an alternating polarization, it is clear that it is possible to contain charges for a much longer time. Moreover, high frequency plasma can be electrode contact-free. The latter is essential for high-purity deposition systems, because no sputtering products from the electrodes are present in the process plasma (7).

In this work nanocomposite thin films of polyaniline with titanium oxide nanoparticles were deposited on glass substrates by microwave plasma polymerization of aniline. The effect of titanium oxide nanoparticles on the optical properties, morphology and structure of the thin films were studied.

Experimental set-up

Our home-built microwave plasma system consisted of cylindrical stainless steel vacuum chamber of 10 cm inner diameter and 30 cm length. The cylindrical chamber have many ports, one port was coupled with double stage rotary vane vacuum pump, pumping speed of $8m^3/h$ from L.H., to maintain a vacuum of about 10^{-3} mbar. The other port was used to introduce the sample (aniline with TiO_2 nanoparticles) which was injected to the plasma chamber using electrical car injector nozzle. The quantity of the injected liquid can be controlled by special electrical circuit that controlling the injector output. Also, there was a view window that fixed at the side port. The two axial end ports of the cylindrical chamber were closed with two flanges that have circular holes at their centers and there was quartz glass tube passing through these two holes along the cylindrical chamber axis. The inside of the tube is at atmospheric pressure whereas the outside is at low pressure. After proper evacuation time, Argon was fed to the chamber, as a working plasma gas, through a needle valve to control the gas flow precisely. The filling pressure in the chamber was monitored using Pirani gauge. To avoid the heat that was generated by the plasma in the chamber, air blower cooling was fixed at the one end of the quartz pipe. The microwave was generated by means of 750

Watt magnetron working at frequency of 2.45GHz. The microwave output was transmitted through arectangular waveguide which hold a TE_{10} transmission mode. A copper pipe of diameter 6 mm was inserted at the other end of the glass tube through the waveguide at a certain position that represented a maximum of the standing wave oscillating in the waveguide, this copper pipe working as an antenna that transmitting the microwave radiation from the waveguide to the vacuum chamber when passing through the quartz tube along its axis. In fact this configuration can be considered as a coaxial cable transmission line where the copper pipe represents the central conductor of the cable, while the glass tube represents its outer insulator and the generated plasma which is a conductive medium replaces the missing outer conductor of the coaxial cable. When the electric field strength, which transmitted through the copper antenna, exceeds the breakdown field strength the discharge ignites in the outer low pressure regime inside the chamber. By increasing microwave power the plasma grows along the tube and axially homogeneous plasma is formed, the space occupied by the plasma is proportional to many factors such as microwave power and working gas pressure.

The glass substrate after proper cleaning procedure, were fixed at certain positions just below the plasma, as we avoid putting the substrate within the plasma directly because the polymer films burned at this position. The polyaniline nanocomposite thin films were deposited on the glass substrates by using different concentrations of TiO_2 nanoparticles of 1, 3 and 5 wt% with aniline. Thicknesses of the deposited films depend on the quantity of the injected mixture in the Ar plasma as pulses of controlled duration. This control of pulse duration and number of pulses was necessary to keep the pressure in the chamber within certain range that was 0.5-1.0 mbar which is of great importance to maintain the plasma working. Schematic diagram and a photograph of the experimental arrangement are shown in figures (1) and (2) respectively.

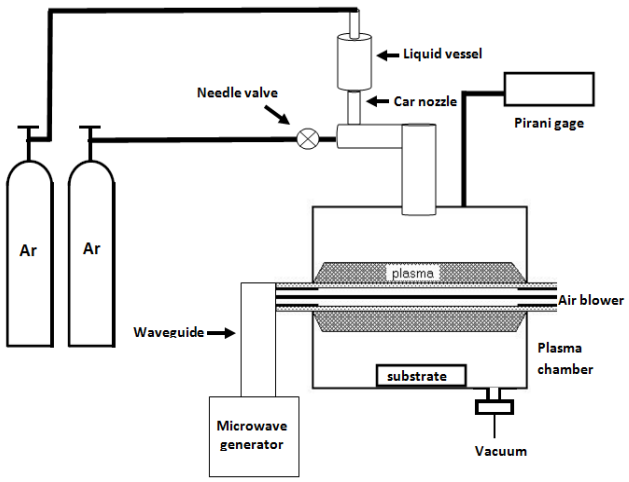
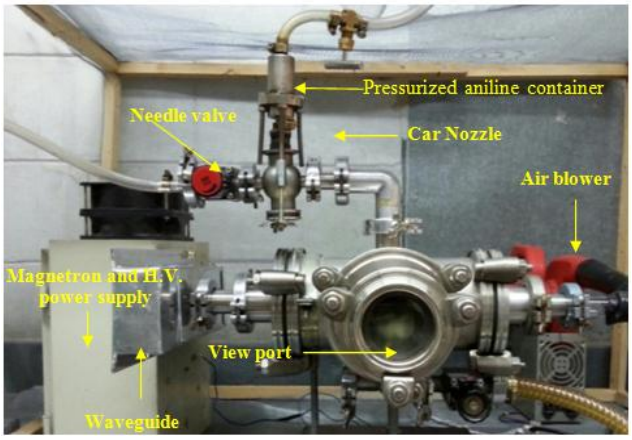


Figure (1):Schematic diagram of the experimental arrangement.



Figure(2):Photograph of microwave plasma system for PANI/TiO_2 nanocomposite thin films deposition.

Plasma parameters, electron temperature and density were measured using optical emission spectroscopy. Electron temperature was determined by two lines ratio method (8), the twoAr spectral lines chosen were 750.34 and 811.5 nm, while the electron density was determined by Stark broadening effect method (9). These measured values were T_e=0.5 eV and n_e=1.75x 10^{17} cm^{-3}. The

film thickness was measured using the optical interferometer method employing laser of (532nm), the films thickness (t) was determined using the formula (10):

$$t = \frac{\lambda}{2} \cdot \frac{\Delta X}{X} \qquad (1)$$

where ΔX is the width of the fringe, x is the position of the fringe and λ is the wavelength of the used light. A double beam UV-VIS-NIR 210A Spectrometer was used to measure the absorption spectrum of the PANI/TiO_2 thin films. The absorption data with films thicknesses can be used to calculate absorption coefficients of the films at different wavelengths which have been used to determine the optical energy band gap.

FTIR spectra were recorded using solid KBr discs and testing all samples by Shimadzu Co. FTIR 8000 series Fourier transform infrared spectrophotometer in the wavelength range 400-4000 cm^{-1}. The morphological surface analysis was carried out employing an atomic force microscope (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS) from Angstrom Ad-Vance Inc.

Results and discussion

FTIR analysis

FTIR spectra of PANI/TiO_2nanocomposite is shown in figure (3), while the assignment of the FTIR absorption bands for different concentrations of PANI/TiO_2 is given in table (1). The bands related to N-H stretching of in aromatic amine appear at 3498 cm^{-1} for film of 1wt% TiO_2 and 3440 cm^{-1} for film of 5wt% TiO_2. The peaks at 2929 cm^{-1} is due to C-H stretch. The bands corresponding to quinoid (N=Q=N) and benzennoid (N-B-N) ring stretching modes were observed at 1539 cm^{-1} for film of 1wt% TiO_2, and 1516 cm^{-1} for film of 5wt% TiO_2, 1456 cm^{-1} for films of 1wt% and 5wt% TiO_2 respectively. Another characteristic band in the FTIR is C-N band at about 1315 cm^{-1} for all concentrations, and for C-H bending vibration the peaks observed at 1168cm^{-1} and 1166 cm^{-1} for 1 and 5wt% TiO_2. The peaks appeared at 439 cm^{-1} for 1wt% and 451 cm^{-1} for 5wt%. These changes suggest that C=C and C–N bands become weaker in PANI/TiO_2nanocomposite, while the N–H band becomes stronger. This is probably because of the action of hydrogen bonding between the surfaces of TiO_2 nanoparticles and the N–H groups in PANI macromolecules. The results confirm that there is strong interaction between PANI and TiO_2.

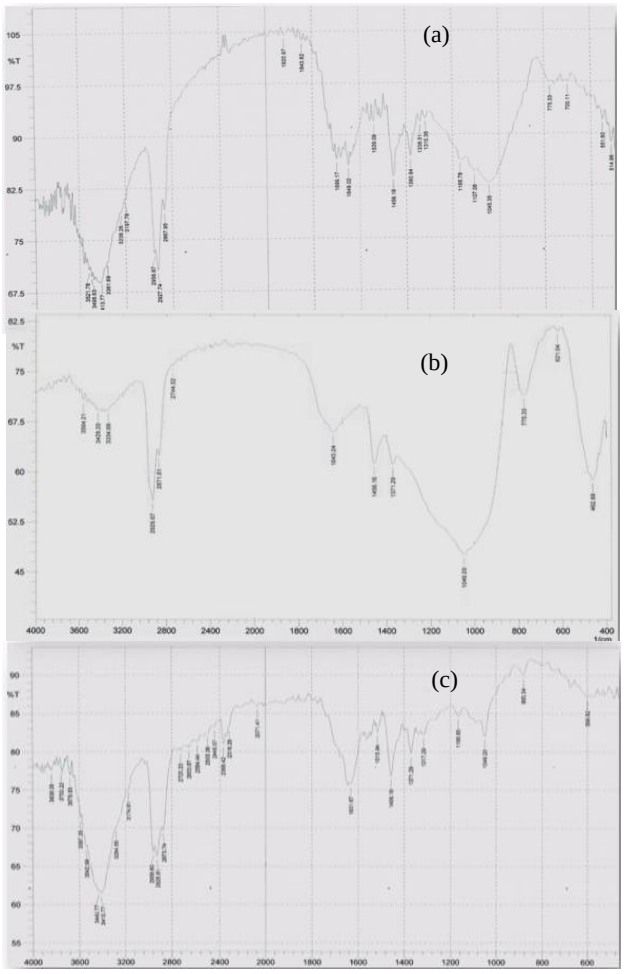


Figure (3): FTIR spectra of (a) pure polyaniline, (b) PANI/TiO_2nanocomposite with 1wt% TiO_2, (c) PANI/TiO_2nanocomposite with 5wt% TiO_2.

Table (1): FTIR common band for pure polyaniline and polyaniline with different concentrations of TiO_2.

Bond range(cm^{-1})	Polyaniline	1wt% TiO_2/Polyaniline nanocomposite	5wt% TiO_2/Polyaniline nanocomposite	Expected vibration
3100-3500	3429	3498	3440	N-H stretching
2923-3017	2927	2929	2929	C-H stretching of aromatic ring
1500-1600	1575	1539	1516	C=C stretching of quinoid ring (N=Q=N)
1400-1480	1456	1456	1456	C=C stretching vibration of benzennoid ring (N-B-N)
1200-1300	1334	1315	1315	C-N stretching of primary aromatic amines
1100	1161	1168	1166	C-H bending vibration
400-700		439	451	TiO_2/PANI

The optical band gap (E_g)

The plot of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ for PANI/TiO_2nanocomposite thin films at different concentrations of TiO_2, (pure polyaniline, polyaniline/$TiO_2$of 1wt%, 3wt% and 5wt% TiO_2), is shown in Fig. (4).

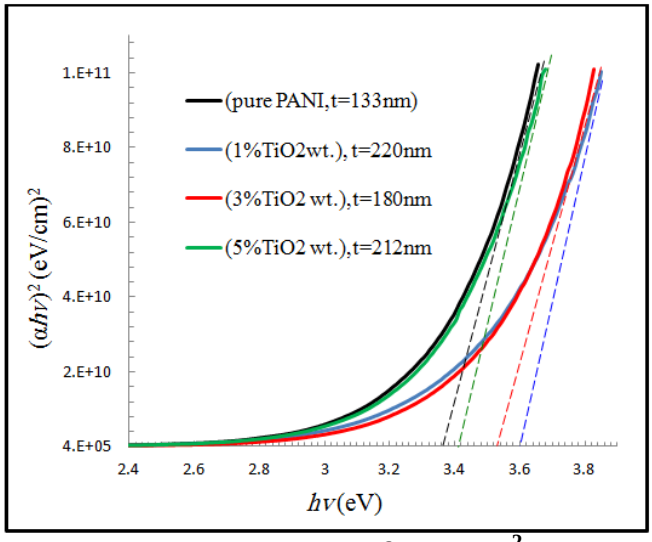


Figure (4): Variation of $(\alpha h\upsilon)^2$ with photon energy (hυ) of pure PANI and PANI/TiO_2nanocomposite thin films of different concentrations of TiO_2.

The increasing of the weight percentage of titanium oxide in the nanocomposite thin films lead to a decrease in the optical energy gap from 3.58 to 3.38 eV. This reduction in the optical energy gap is probably due to the modification of the polymer structureand this can be identified through the changes that happened in the FTIR spectrum of many bonds due to the change in TiO_2 concentration.

Atomic force microscopy (AFM)

The morphological characteristics of the pure polyaniline and PANI/$TiO_2$of (5wt% TiO_2) thin films have been studied by atomic force microscopy (AFM). The surface roughness average of the pure polyaniline film is 2.45 nm and the average particles size is 100.78 nm, while for PANI/TiO_2film the roughness average is 2.06 nm and the average particles size is 94.61 nm. These results can be shown in Figures(5) and (6).

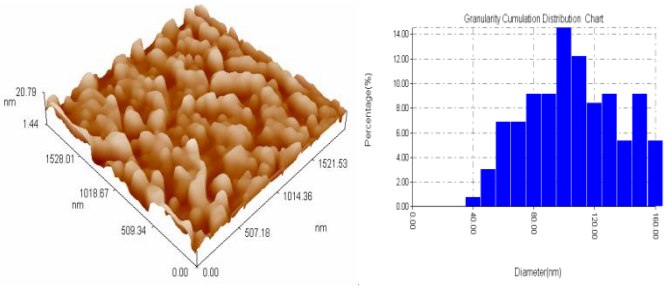


Figure (5): AFM photographs of pure polyaniline thin film surface, 3D image and size distribution of TiO_2/PANI.

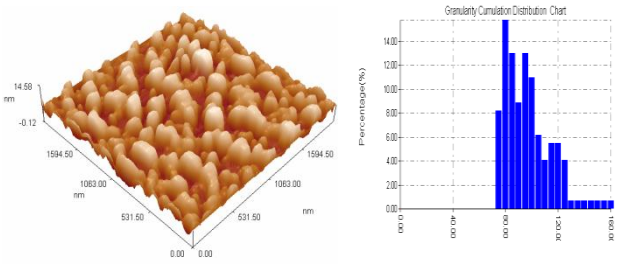


Figure (6): AFM photographs of 5wt%. of TiO_2 in PANI/TiO2 thin film surface, 3D image and size distribution of TiO_2/PANI.

Scanning electron microscopy (SEM)

The SEM images of the nanocomposite thin films of PANI/$TiO_2$are shown in Figures (7) and (8). As can be seen in this figure the TiO_2 nanoparticles attached with polyaniline during polymerization, the images also indicate that there is uniform distribution of the TiO_2 nanoparticles, which are spherical in shape, in the PANI matrix with few TiO_2 clusters of particles.

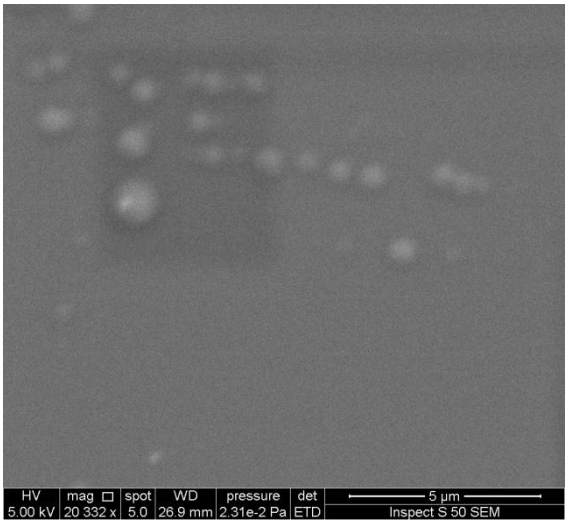


Figure (7): SEM image of 1wt% TiO_2 in PANI thin film.

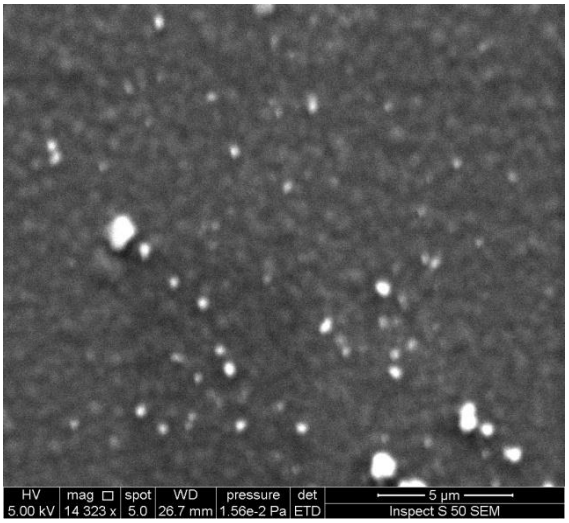


Figure (8): SEM image of 5wt% TiO_2 in PANI thin films.

Conclusion

Polymerization by microwave plasma technique can be employed to produce extremely smooth polyaniline/metal oxide nanocomposite thin films with very small surface roughness compared with films prepared by other techniques; the nanoparticles are uniformly distributed in the polyaniline matrix. PANI and PANI/TiO_2 nanocomposite thin films with controlled optical energy band gap were successfully prepared by plasma polymerization. Addition of TiO_2 nanoparticles in small concentration percentage increased the optical band gap to some extent and then decreased with increasing their concentration percentage; this may be due to the interaction between TiO_2 nanoparticles and PANI, moreover to the modification that happened in the polymer structure.

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