Optical properties for TiO_2 / PMMA nanocomposite thin films prepared by plasma jet

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Abstract

PMMA/TiO_2 homogeneous thin films were deposited by using plasma jet system under normal atmospheric pressure and room temperature. PMMA/TiO_2 nanocomposite thin film synthesized by plasma polymerization. Titanium oxide was mixed with Methyl Methacrylate Monomer (MMA) with specific weight ratios (1, 3 and 5 grams of TiO_2 per 100 ml of MMA). Optical properties of PMMA/TiO_2 nanocomposite thin films were characterized by UV-Visible absorption spectra using a double beam UV-Vis-NIR Spectrophotometer. The thin films surface morphological analysis is carried out by employing SEM. The structure analysis are achieved by X-ray diffraction. UV-Visible absorption spectra shows that the increasing the concentration of titanium oxide added to the polymer leads to shift the peak position (λ_{max}) toward the infrared region of the electromagnetic spectrum. Also the peak width increases when the concentration of TiO_2 increases. It can be controlled optical energy band gap of PMMA/TiO_2 nanocomposite thin films by changing concentration of TiO_2. SEM indicate a uniform distribution of titanium oxide particles in PMMA matrix. The x-ray diffraction pattern indicated that the thin films have amorphous structure.

Key words
Optical properties, plasma jet, PMMA/TIO_2 nanocomposite, plasma polymerization.

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الخواص البصرية لأغشية رقيقة للمتراكبات النانوي PMMA/TIO_2 المحضرة باستخدام بلازما النفث

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الخلاصة

تم ترسيب أغشية رقيقة متجانسة لمتراكبات إلـ PMMA/TiO_2 تم باستخدام تقنية بلازما النفث العاملة تحت الضغط الجوي الاعتيادي وعند درجة حرارة الغرفة. كما أجريت عملية البلمرة لغشاء PMMA/TiO_2 موضعيا بالبلازما. تمت عملية التحضير بخلط اوكسيد التيتانيوم مع مونمر المثيل ميتاكريلايت بنسب وزنيه محددة وهي (1 و 3 و 5) غرام من اوكسيد التيتانيوم لكل 100ملتير من المثيل ميتاكريلايت). وتم توصيف الخواص البصرية للأغشية الرقيقة النانوية لمتراكب إلـ PMMA/TiO_2 بواسطة إلـ UV-Visible absorption spectra. وباستخدام تقنية إلـ SEM تم تحليل مورفولوجية السطح. بينما تمت دراسة التركيب البنائي بواسطة حيود الأشعة السينية. أظهر طيف الامتصاص إن زيادة تركيز اوكسيد التيتانيوم المضاف إلى البوليمر يؤدي إلى إزاحة موقع القمة الامتصاص العظمى باتجاه المنطقة تحت الحمراء من الطيف الكهرومغناطيسي. كذلك يظهر زيادة في عرض القمة عند زيادة تركيز اوكسيد التيتانيوم. يمكن التحكم بعرض فجوة الطاقة البصرية لأغشية إلـ PMMA/TiO_2 المحضرة بتغيير تركيز إلـ TiO_2. كما بينت صورة إلـ SEM توزيعا منتظما للجسيمات في مصفوفة غشاء PMMA. بينما اظهر حيود الأشعة السينية التركيب العشوائي للغشاء المحضر.

Introduction

Recently, there are significant interest in TiO_2 Nano- thin films because it has so many potential applications, in chemical sensors, biomedical material and solar cells.TiO_2 also are the most commonly used coatings because of their attractive properties, like good transmission in the visible and near infrared regions, good cohesion, and high constancy against mechanical scratch, and high temperatures [1-3]. so that it used regularly as single -layer or multilayer optical coatings. TiO_2 is also cost effective and chemically stable, with good optical properties, thermal stability, high refractive index, and a deficiency of absorbance of visible light [4, 5]. TiO_2 is one of the typical of n-type semiconductor with wide bandgap (3.03 eV for rutile and 3.18 eV for anatase) and can absorb 5% of incident sun light in the ultraviolet region [6, 7]. Selected PMMA because of its simple synthesis procedure, good environmental, thermal stability, good optical and chemical properties [8]. Organic-inorganic mixture materials have been widely investigated. Its core reason is to supposed to be obtained new type composite materials with complementary behaviors, and be used in electronic or nanoelectronic devices [6]. However, the characteristics of PMMA/TiO_2 films are strongly dependent on the preparation methods and the deposition parameters. Many methods is used to prepare PMMA/TiO_2 thin films like ion beam method, evaporation, and reactive sputtering [7]. In this work, the plasma jet technique is used to synthesize PMMA/TiO_2 nanocomposite films.

The goal of this research is prepared nanocomposites thin films of PMMA with titanium oxide nanopaticales with a high homogeneous distribution of titanium oxide nanoparticles within the polymer and then, these thin films were characterize. Polymerization is done using localized plasma jet under atmospheric pressure. The other aim is controlled optical energy band gap of PMMA/TiO_2 nanocomposite thin films by altering concentration of TiO_2.

Experimental work

In this work, Titanium dioxide nanocomposites thin films (PMMA/TiO_2) were prepared on glass substrates via a plasma jet. The plasma was generated downstream to the substrate which was positioned at fixed distance from the plasma torch end. The torch was generated via Argon gas flow through a nobilizer which contained mixed of TiO_2 and MMA (methyl methacrylate). The mixed (1, 3 and 5 grams of TiO_2 per 100 ml of MMA) was transformed into aerosol, the aerosol was guided by the Argon gas throught tephlon tube to the plasma jet. The plasma was ignited by using an electric source at a fixed frequency (28.0 kHz). The thin films deposition was carried out for 10 minte. In oredr to obtain a homogeneous films thickness a long the substrat area, the substrateswere monted on a movable x - y stage. The film thickness was measured using the optical interferometer method employing laser of (532 nm), the films thickness (t) was determined using the formula [9]:

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

where ΔX is the width of the fringe, x is the position of the fringe and λ is the wavelength of the used laser light. Structural analysis of PMMA/TiO_2 thin films performed by (Shimadzu XRD-6000 Japan) diffractometer with CuK_α radiation (λ=1.5418 Å) at 40 kV and 30 mA in the scanning angle (2θ) from 20^o to 70^o with the scanning speed of 0.05 deg/s. The surface morphology were examined by Scanning electron microscopy (SEM) under ambient condition. The optical transmission spectra of the deposited films were recorded using UV-VIS double-beam spectrophotometer in the wavelength range 200-1100 nm.

Results and discussion

The UV–Visible absorption spectrum of the PMMA/TiO_2 nanocomposite thin films is shown in Fig.1. A Layer of PMMA/TiO_2 deposited on glass substrates with a thickness of 200, 250 and 265 nm at the concentration of TiO_2 is 1, 3 and 5 gram per 100 ml of MMA, respectively. The mean absorption appears around 350, 367 and 387 nm at the three concentration. Figure note that the increase in the concentration of TiO_2 lead to displace the peak position (λ_{max}) toward the infrared region of the electromagnetic spectrum. Also the peak width increases when the concentration of TiO_2 increases.

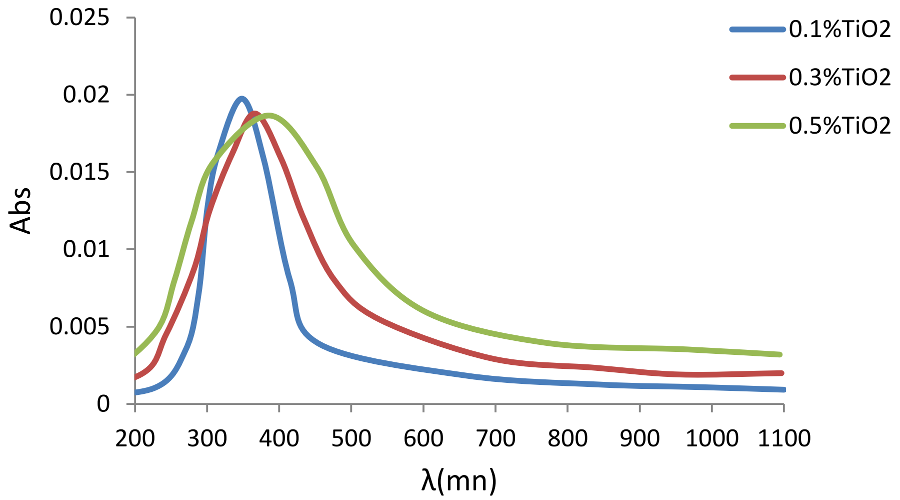

Fig. 1: UV-Visible absorption spectrum of TiO_2 nanocomposite thin film.

The type of transition was directly allowed transition as the dependence of (α) on the photon energy ($h\nu$) was found to follow the subsequent relationship [10]:

$$\alpha h\nu = \beta\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (2)$$

where β is a constant and E_g is the optical band gap.

Fig. 2 shows a plot of $(\alpha h\nu)^2$ as a function of $h\nu$ illustrates the optical band gap of PMMA/TiO_2 nanocomposite thin film with direct transition. The value of the optical energy gap as shown in Figures are 2.9, 2.74 and 2.6 eV at the concentration of TiO_2 is 1, 3 and 5 gram per 100 ml of MMA respectively. It can be observed that (E_g) is decreasing slightly and shifting towards the Infrared region with increasing concentration of TiO_2. This is because the effect of adding the semiconductor to the polymer moreover the effect of disorder. So can be concluded that the optical energy gap can be controlled by the control of TiO_2 ratios.

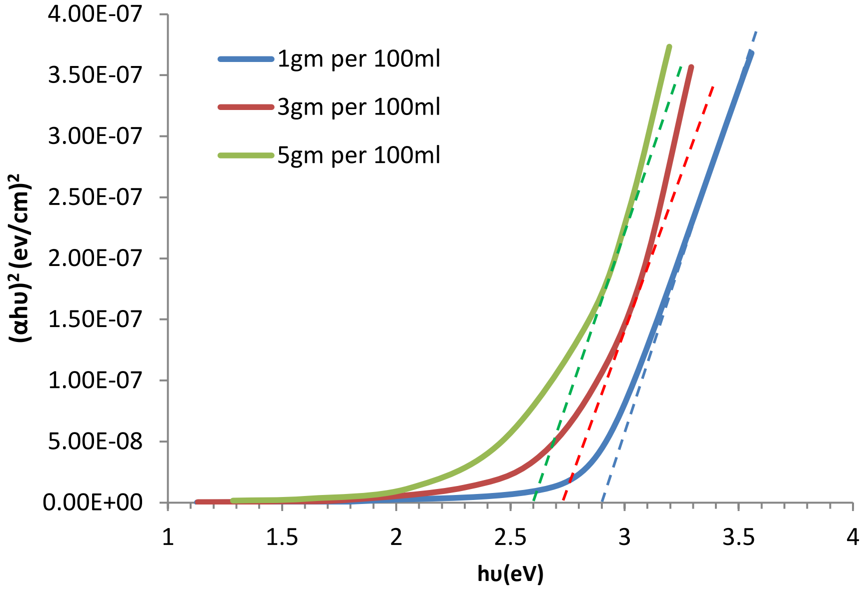

Fig. 2: The Varaition of $(\alpha h\upsilon)^2$ versus the photon Energy $(h\upsilon)$ of PMMA/TiO_2 film thin film at diffenent concentrations of TiO_2.

The scanning electron microscope analysis

The morphology of the nanocomposites' fracture surface and distribution of the PMMA/TiO_2, nanocomposite were determined by SEM and show in Fig. 3. This figure illustrates that the fracture surface of the treated PMMA/TiO_2 nanocomposite to be mostly a homogeneous rough surface in which the nano- PMMA/TiO_2 are evenly distributed and can be found that the PMMA/TiO_2 exhibit spherical morphology.

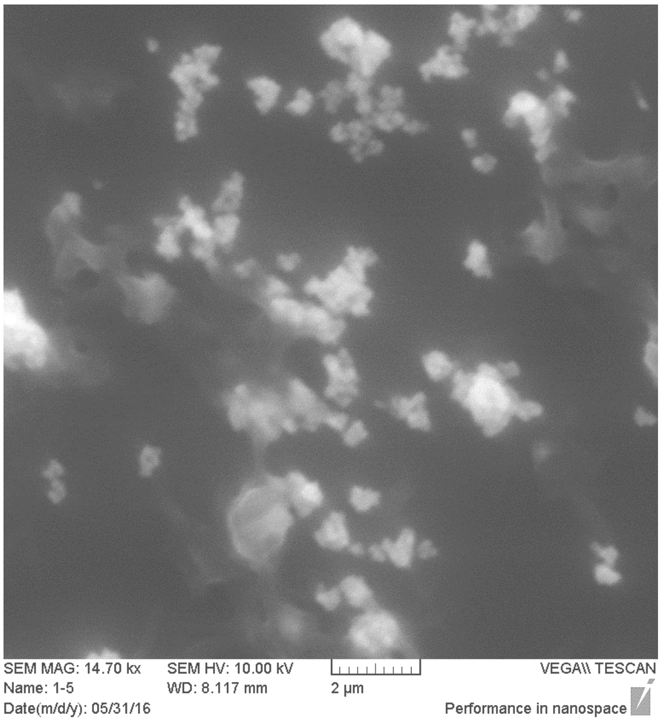

Fig. 3: SEM of fractured surface of PMMA/TiO_2 nanocomposite thin film.

X-ray diffraction patterns

Fig. 4 shows the x-ray diffraction pattern of the PMMA/TiO_2 nanocomposite thin film. The x-ray diffraction pattern indicated that the thin films have amorphous structure. Plasma polymer has short chains of building units and a high degree of cross-linking. Plasma polymers are usually amorphous in nature, where made of short chains of monomers characterized by a high degree of cross-linking and dangling bonds.

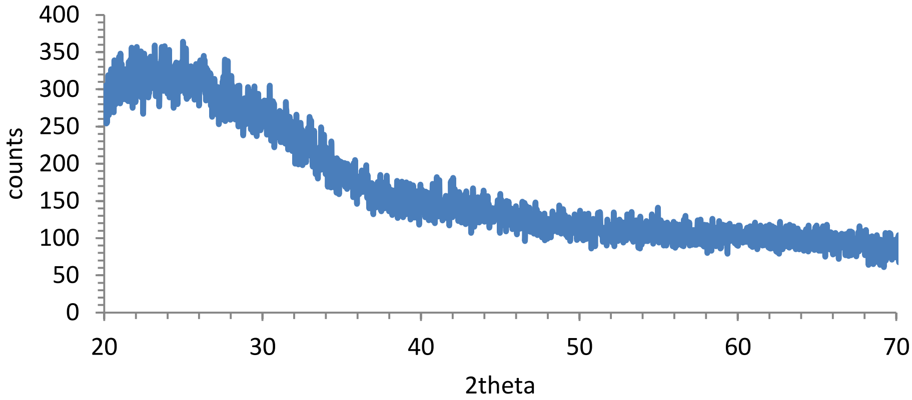

Fig. 4: X-ray diffraction pattern for PMMA/TiO_2 nanocomposite thin film.

Conclusions

1- Plasma polymerization can be employed to produce PMMA/TiO_2 nanocomposite thin films were the TiO_2 nanoparticles uniformly distributed in the PMMA matrix.

2- PMMA/TiO_2 nanocomposite thin film synthesized by plasma jet amorphous in nature.

3- The importance of this research comes from ability to modify optical properties of TiO_2 and PMMA by changing the concentration of TiO_2 added to the polymer.

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