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PREPARATION AND CHARACTERIZATION OF TiO₂ FILMS OBTAINED BY ELECTRODEPOSITION ON ITO AND ANNEALING TREATMENT

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Abstract

Due to the growing demand for renewable energy sources, the development of new materials for use in solar cells is of critical importance. Titanium dioxide (TiO₂) is a n-type semiconductor and is a low-cost alternative for use in solar cells. This study presents the feasibility of using TiO₂ films electrodeposited on indium–tin oxide (ITO) as an electron acceptor in hybrid photovoltaic cells. Results obtained by X-ray diffraction show that all films exhibited the anatase phase at 600 °C. Fluorescence measurements were performed using confocal microscopy laser scanning fluorescence. It was observed that the polyfluorene light-emitting *polymer*, when used in conjunction with TiO₂, showed a decrease in the emission ratio as compared with the film in the absence of TiO₂. This result shows that TiO₂ films prepared using the approach described in this study can effectively act as electrons acceptors.

Introduction

Solar energy is a form of clean renewable energy¹⁻⁴ with great potential. Results show that the energy generated by the Sun during a day can satisfy the energy needs of the Earth for a year¹. Despite the research progress made regarding the use of solar energy, this fact is still rarely exploited, and this is largely due to the high cost of producing high-efficiency photovoltaic cells. Thus, it is necessary to develop new types of materials that have low production cost but high performance during the manufacture of photovoltaic cells, thus achieving economical but significant energy conversion.

Currently, 90% of the photovoltaic cells used in the world are composed of silicon². Cells made of silicon are known as the first-generation photovoltaic cells, and their operation is based on the p-n junction of the material. The second-generation photovoltaic cells have silicon as a base, but they are composed of other semiconductors and even amorphous silicon. Another essential characteristic of these second-generation cells is the use of thin films, which reduce the material used in the composition of the cells, thus cutting the manufacturing cost. However, there is a decrease in yield obtained from these cells as compared to the first-generation cells, though reduction in production cost is achieved^{2,5}.

In recent decades, new alternatives, such as organic semiconductor materials, have been studied to further reduce the cost of producing photovoltaic cells. However, photovoltaic cells that use these materials have low efficiency; therefore, much research is still necessary to achieve their commercial viability^{6,7}. The solar cells that use organic semiconductors are the third generation of photovoltaic cells. Those that use only organic materials are called polymer cells, and those that use organic and inorganic materials are called hybrid cells^{5,6}. Among all the inorganic semiconductor materials that can be used in the production of this type of photovoltaic cells, TiO₂ stands out due to its unique properties, such as a full band gap (approximately 3.2 eV), high absorption in the ultraviolet range, excellent chemical stability, and low cost of sourcing^{8,9}.

To production TiO₂ thin films for use in solar cells, the electrodeposition technique is a convenient and versatile route. Compared with other methods^{10,11} has different advantages: low process temperature, low cost for raw materials and equipment, the capability of controlling composition and morphology by electrochemical parameters, and the ability to deposit films on the substrates with large dimensions and complicated shapes. However, this process usually involves a solvent and an organic stabilizer that can lead to contamination of the film with carbonaceous material after heat treatment. The presence of contaminants can reduce the efficiency of TiO₂ as a non-fullerene electron acceptor. Therefore, in this study, a new technique is using for the preparation of TiO₂ films electrodeposition on ITO from aqueous solution without the use of organic stabilizers. To investigate

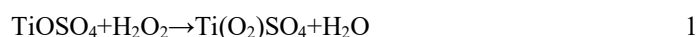


the TiO₂ films as electron acceptors, we used confocal microscopy laser scanning fluorescence to perform the necessary measurements.

Materials and methods

For the preparation of the solution, 0.002 mol/L titanyl sulfate (TiOSO₄) (Sigma Aldrich), 0.12 mol/L hydrogen peroxide (H₂O₂) (Sigma Aldrich), 0.40 mol/L potassium nitrate (KNO₃) (Sigma Aldrich), and deionized water (H₂O) were mixed. The resulting solution was placed in an ice bath and maintained at a temperature of approximately 10 °C. This procedure increases the viscosity of the solution by delaying the precipitation process, which, according to Karuppachamy et al., improves the quality of deposited films⁶.

When TiOSO₄ was initially added to the aqueous solution of H₂O₂, an orange solution was obtained^{6,7}. After five minutes of stirring, the solution's color changed from orange to reddish, and this occurred as a result of increasing the pH (from 1 to approximately 2) of the solution. The process is expressed by equation (1):



When a potential is applied between the electrodes, ions K⁺ and NO₃⁻, that are present in the solution in an already dissolved state because of being present in aqueous solution, generate OH⁻ ions. The presence of OH⁻ ions increases the pH of the solution near the electrode, which is essential for the formation of titanium peroxide complex (Eq. 3). The reduction reaction of NO₃⁻ occurs according to equation (2)¹²:

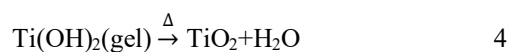


In the electrodeposition process, an electrochemical cell with three electrodes, namely, a platinum counter electrode (Pt), a saturated calomel reference electrode and the working electrode, made use of the ITO films. The electrodeposition process was performed in the potentiostatic mode at the values of -0.95, -1.00, -1.10, and -1.20 V. Three samples of TiO₂ were electrodeposited at each potential.

The films electrodeposited onto the ITO are amorphous and are known as titanium peroxide complex (in gel form before heat treatment)¹². The chemical process involved in the deposition and formation of this gel is described by equation (3).



For the crystallization of the complex, heat treatment was carried out at a temperature of 600 °C for 4 h. In this process, the temperature gradient employed was 3 °C/min. In the descent, the thermal inertia obtained with the oven switched off was used. The treatment process can be represented by equation (4)¹².



Results and discussion

The results obtained upon using X-ray diffraction (XRD) to analyze the TiO₂ films deposited on the ITO substrate at different potentials and heat-treated at a temperature of 600 °C are shown in Figure 1. In all the diffractograms, the characteristic peaks of ITO and TiO₂ are observed.

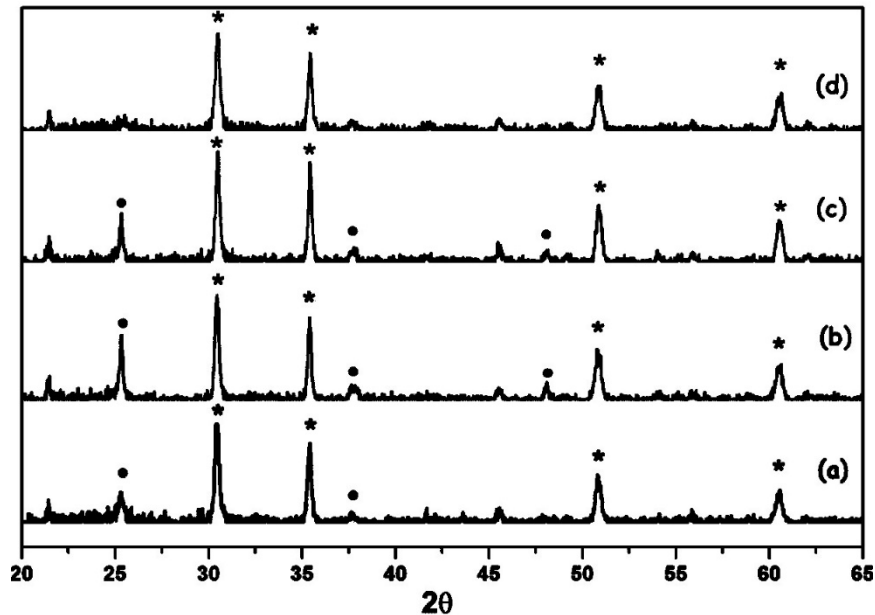


Figure 1: Diffractogram of the electrodeposited films in different potentials: (a) -0.95 V; (B) -1.0 V; (C) -1.1 V and (d) -1.2 V treated at 600 °C, where (*) ITO peaks and (•) anatase phase peaks [NBSMA6,782 (1969)] ($2\theta = 25.304^\circ$).

In the diffractogram, it is observed that the electrodeposited film at the potential of -0.95 V presents the anatase phase, which can be identified by the diffraction peak $2\theta = 25,304^\circ$. This peak has a lower intensity when compared to the same peaks found at potentials -1.00 and -1.10 V. This difference could be attributed to the lower film thickness obtained in the electrodeposition potential of -0.95 V. At the potentials of -1.00 and -1.10 V the peak ($2\theta = 25,304^\circ$) becomes more evident, showing a higher crystallinity of the film and, possibly, a larger thickness. At -1.20 V, it is not possible to detect any remnants of the anatase phase or any other phase. Instead, only the characteristic peaks of the ITO are observed, because in this case, the deposition efficiency is reduced by the overpotential, leading to a reduction in the film thickness. This reduction in thickness makes it difficult to detect any crystallographic phase. This fact demonstrates that for high potentials, the deposition practically does not occur; one reason may be the high mobility of the OH^- groups, which could lead to the decanting of the precipitate before it is deposited^{12,13}.

Figure 2 shows the scanning electron microscopy (SEM) images of the electrodeposited film at the potential of -0.95 V (a) without heat treatment, and (b) after the heat treatment at 600 °C.

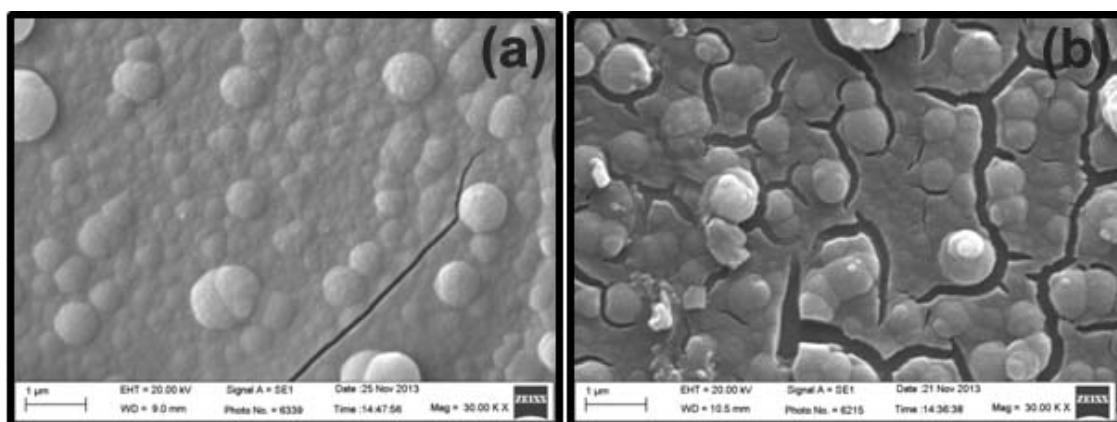


Figure 2: SEM images of the electrodeposited films at a potential of -0.95 V, without heat treatment (a) and treated at 600 °C (b).



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In Figure 2(a), it is observed that the initial formation of the film (amorphous state) is continuous with a granular formation spaced as if they were grain sites. Figure 2(b) shows that after thermal treatment, there is an increase in grain size as a consequence of crystallization, and that there are cracks in the film.

Figure 3 shows the film deposited at the potential of -1.00 V. Figure 3(a) shows the film without heat treatment, and Figure 3(b) shows the film after the heat treatment at 600 °C.

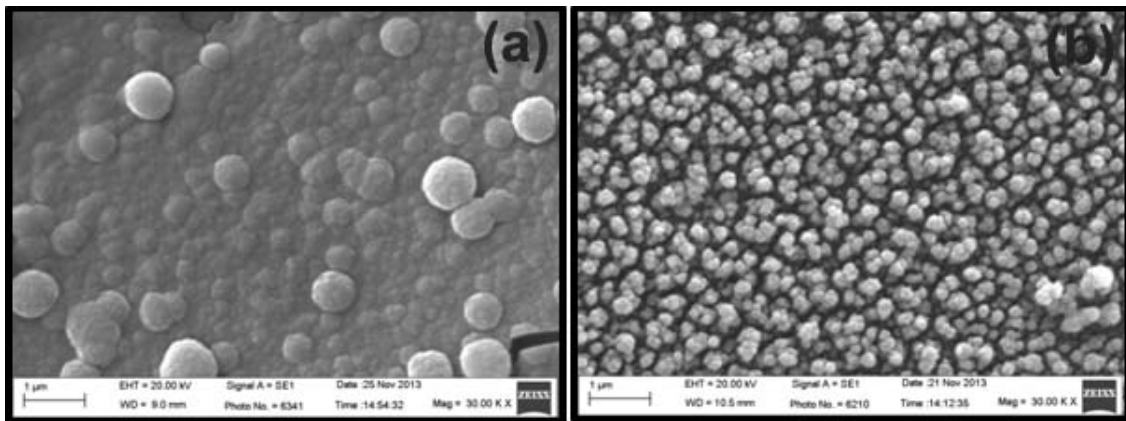


Figure 3: SEM images of the electrodeposited films at the potential of -1.0 V, without heat treatment (a) and treated at 600 °C (b).

In Figure 3(a), we observed continuous film with the presence of solitary nodules distributed in a more spread out manner, as observed in Figure 2(a). After the heat treatment (Figure 3(b)) only the formation of granular agglomerates was observed. Figure 4(a) shows the formation of granules that were maintained after the heat treatment, Figure 4(b).

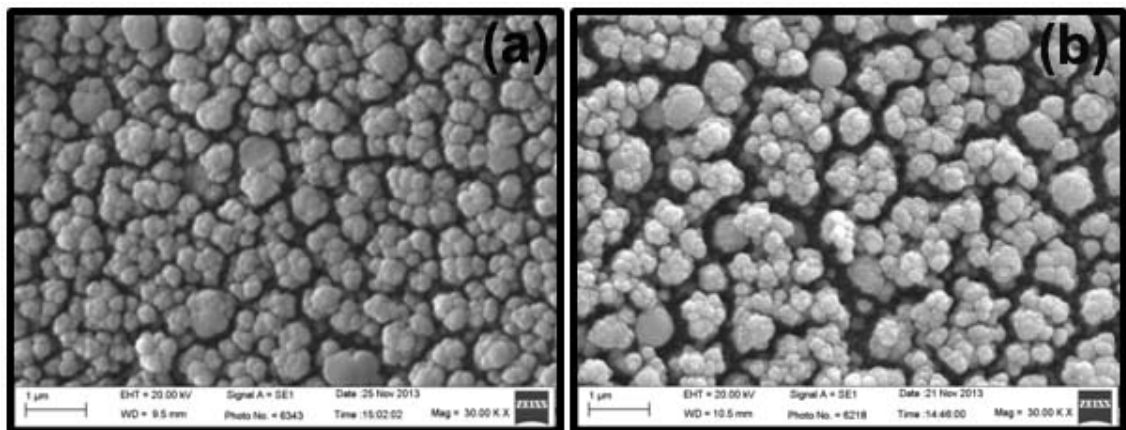


Figure 4: SEM images of electrodeposited films at a potential of -1.1 V without heat treatment (a) and treated at 600 °C (b).

It can be seen in Figure 5 (a) and (b) that the film obtained at the potential of -1.20 V does not exhibit the formation of agglomerates either before or after the heat treatment. The absence of the formation of the anatase phase and the presence of only the ITO, shown in Figure 1 (d), may be indicative of the presence of a very thin film, possibly due to the evolution of hydrogen due to the overpotential of -1.20 V used for electrodeposition.

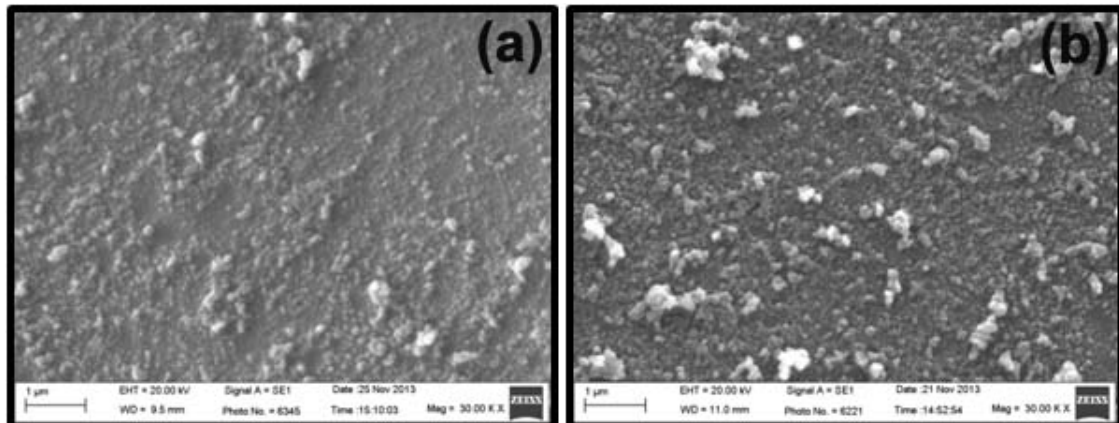


Figure 5: SEM images of the electrodeposited films at a potential of $-1,2$ V without heat treatment (a) and treated at 600 °C (b).

In this study, the Confocal Microscopy technique was used to: (i) excite the sample using a laser, (ii) to measure the emission of the photons generated, and (iii) to measure the time of decay. The emission of the photons generated, and the time of decay were used with an indication of the efficient or non-efficient of the dissociation of the exciton, and therefore, the transference of charge carriers from the PFO¹⁴ to TiO₂ film.

In order to achieve this objective, a PFO layer of approximately 10 nm thickness deposited by spin-coating in two different regions, namely, TiO₂ film (electrodeposited at -1.00 V) and glass, was used. The PFO was excited with 405 nm laser, and the resulting fluorescence map can be seen in Figure 6.

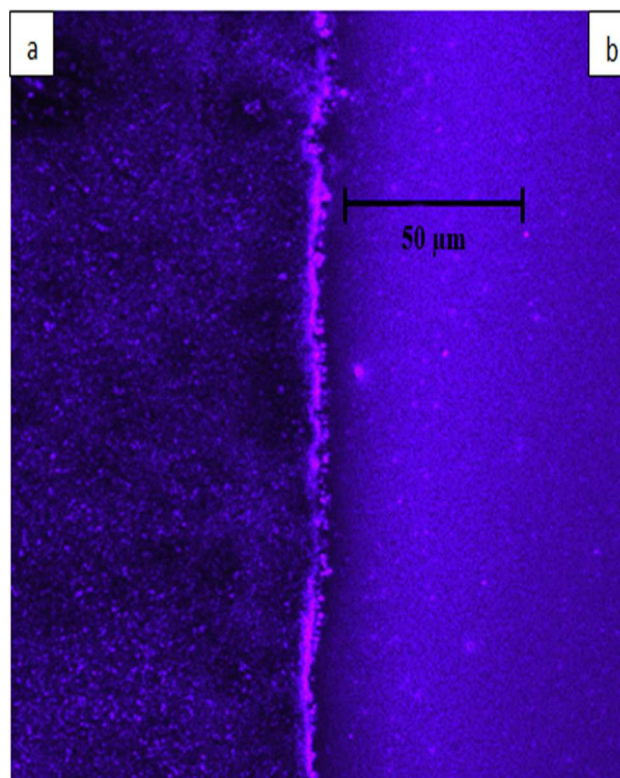


Figure 6: Image generated by confocal microscopy for the PFO film deposited on the TiO₂ film interface (a), and for the PFO film deposited on the glass (b).



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The intensity of the radiative emission of an organic semiconductor is directly proportional to the generation rate of the exciton. Thus, although photoluminescence is not a direct measure of the rate of exciton generation, a direct consequence of its quantity can be analyzed through the rate of radiative and recombination, in this case to photoluminescence. In Figure 6 it can be seen that there is a clear difference in the emission intensity between regions (a) and (b) containing and not containing the TiO₂ film, respectively. This difference is evident when observing the intensity of photoluminescence in the two distinct regions. As can be seen in Figure 7, there is a 2-fold difference in the peak-to-peak intensity of the PFO emission at 427 nm, indicating that the TiO₂ surface is effectively acting as an acceptor.

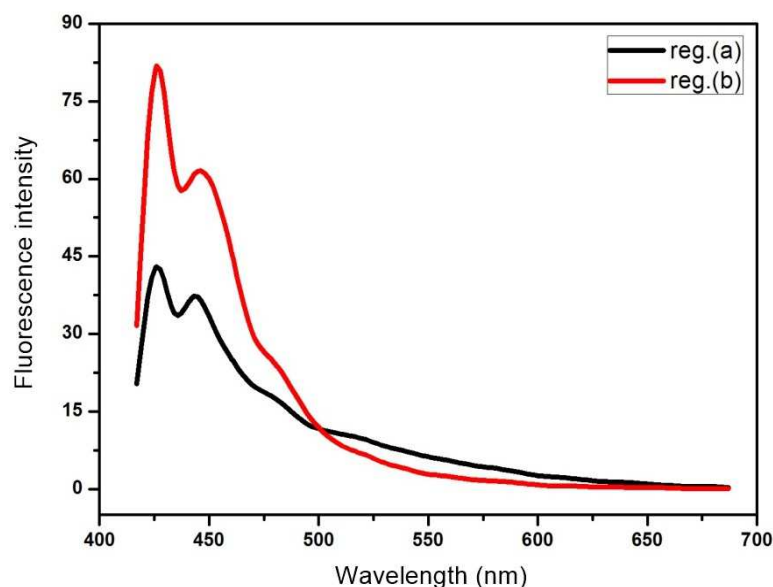


Figure 7: Result of the fluorescence intensity for the PFO film deposited on the TiO₂ film interface (a), and for the PFO film deposited on the glass (b).

Conclusions

In relation to the results obtained with the TiO₂ films, the objective was to analyze the morphology of the films with respect to the potential of electrodeposition and their viability as electron acceptors in solar cells. The results obtained through the XRD analysis showed that for potentials of deposition ranging from -0.95 to -1.10 V, all samples, after the heat treatment at 600 °C, presented the anatase phase with increased crystallinity and crystallite size with increase in potential. The crystallite size varied as seen in the narrowing of the peaks. In this same range of potential, the micrographs obtained by scanning electron microscopy (SEM) showed the formation of granular agglomerates that became more evident after the heat treatment. For the film obtained at -1.20 V, a small remnant of the anatase phase was observed, in which only the characteristic peaks of the ITO were more evident. At the potential of -1.20 V, the deposition efficiency is reduced by the overpotential, which leads to a reduction in the thickness of the film, thus making it difficult to detect any crystallographic phase. At this potential, the formation of agglomerates was not observed either before or after the heat treatment.

The results showed that the best electrodeposition potential of TiO₂ films was -1.00 V, wherein the anatase phase was obtained with films that had higher crystallinity and larger crystallite size.

Concerning the results of the confocal microscopy measurements obtained for the two regions, i.e., the region containing the TiO₂ film with one PFO layer and the other containing only the PFO film, a clear difference in emission intensity between the regions is observed (Figure 6). This difference was confirmed by the intensity of photoluminescence in the two distinct regions (Figure 7) which showed a 2-fold difference in peak-to-peak intensity of PFO emission at 427 nm. This difference indicates that the TiO₂ surface is effectively acting as an electron acceptor. This result shows the feasibility of the use of electrodeposited TiO₂ films in hybrid photovoltaic cells as an efficient electron acceptor.



Acknowledgments

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