Anatase titania nanoparticles for covering P3HT microfibers: Morphological properties

Evelyn B. Díaz-Cruz¹, Diego Hernandez², M.E. Nicho-Díaz², Omar Martínez-Alvarez³, Hailin Zhao-Hu⁴, Claudia Martínez-Alonso⁴, M.C. Arenas-Arrocena⁵*

¹Posgrado en Ciencia e Ingeniería de Materiales, Universidad Nacional Autónoma de México, UNAM, México
²Centro de Investigación en Ingeniería y Ciencia Aplicadas, UAEM, Cuernavaca Morelos, México
³Universidad Politécnica de Guanajuato, Cortazar Guanajuato, México
⁴Instituto de Energías Renovables, UNAM, Temixco Morelos, México
⁵Escuela Nacional de Estudios Superiores, Unidad León, UNAM, León Guanajuato, México
* Corresponding Author

ABSTRACT

Anatase titania has been widely used for several applications such as photocatalysis and solar cells. Sol-gel is a conventional route to obtain amorphous titania and, either post-annealing or a post-hydrothermal treatment are necessary to obtain anatase crystalline phase. It is well known that the synthesis conditions affect in the particle size, surface area and grain size of the titania. In this work regular nanoparticles of anatase titania (TiO₂) were obtained by an easy ultrasound-assisted synthesis; the nanoparticles were undergone to either a hydrothermal treatment at 130 ºC and/or to an annealing at 450ºC. Nanoparticles powder with a crystal size of about 8-10 nm were re-dispersed in aqueous solution at different concentrations (5 to 20mg/mL). Poly (3-hexylthiophene) (P3HT) microfibers were immersed into the TiO₂ nanoparticles solution for 24 h and they were dried at 80°C for 1 h in order to form the bulk heterojunction. P3HT:TiO₂ heterojunctions were characterized by SEM and EDS. According to SEM results at low concentration (5 mg/mL), the covering of the P3HT microfibers is poor and at high concentration (20 mg/mL) the microfibers were seen cracked. The best homogeneous covering onto the P3HT microfibers was obtained at 10mg/mL of titania nanoparticles; it could be the optimal concentration to build bulk heterojunction for hybrid solar cells.

INTRODUCTION

Anatase titania is a stable crystalline phase at atmospheric pressure and at room temperature, it is a n-type semiconductor widely used in photocatalytic and photovoltaic applications due to its optoelectronic properties [1, 2]. In solar cells, it works like an electron acceptor and like a window layer due to its large Eg (3.2 a 3.4 eV) [3]. Sol-gel is a conventional route to obtain amorphous titania and, either a post-annealing or a post-hydrothermal treatment are necessary to obtain anatase crystalline phase [2].

Bulk heterojunction is one of the engineering strategies to increase the interfacial area and to improve the exciton dissociation. Inorganic nanostructures have been included in this type of heterojunction due to its high mobility and physical stability [4, 5].

Physical mixture is the main process used to form the bulk heterojunction; usually the electron donor and acceptor are blended in organic solvents, but the segregation of phases in the
blend remains a challenge to overcome, it also plays an important role in the final performance of the device. Currently, a report about the solventless processing of conjugated polymers could be a new way to avoid or diminish the segregation and also improve the molecular order [6]. The melting processing, processing of bulk solids and, post processing of the solution cast films are discussed by Brandão et al. [6]. They include the mechanical rubbing, stretching and template wetting of the conjugated polymer, so that one-dimensional polymers could be also considered a good option to obtain bulk heterojunctions in solid-stated.

The highlight of this work is the synthesis of regular nanoparticles anatase titania from an easy sol-gel assisted with ultrasonic action during the hydrolysis process in order to form bulk heterojunctions based on microfibers of poly(3-hexylthiophene). The influence of the titania concentration and the post-treatment in the morphological properties of the heterojunction are made.

**EXPERIMENTAL**

**Synthesis of titania by sol-gel assisted with ultrasound (UT)**

A mixture of deionized water (0.90 mL), 2-propanol (5.4 mL), nitric acid (0.090 mL) and titanium (IV) isopropoxide, was putted in an ultrasound bath (145 W, 40kHz ± 6%) for 1 h. The white paste product was kept overnight and then it was washed with ethanol several times under centrifugation at 3000 rpm for 10 min. Then, post treatments at different conditions were made such as seen in the scheme 1. The product depicted as UTT was prepared under ultrasonic action and was annealed at 450°C for 1 h; the UTH product was prepared under ultrasonic action and received a hydrothermal treatment in a Teflon autoclave at 130°C for 3 h. The UTHT product was prepared under ultrasonic action, received a hydrothermal treatment in a Teflon autoclave at 130°C for 3h and it was annealed at 450°C for 1 h. A conventional synthesis was realized, which consisted of the procedure described elsewhere [7].

Titania solution was casted on Corning substrate for X-ray characterization (Rigaku DMAX-2200, Cu Kα1.54 Å, 2θ= 5-70°, 2°/min each 0.06 s).

**Preparation of bulk heterojunctions**

The final titania products were re-dispersed in deionized water and they were used to cover microfibers of poly (3-hexylthiophene) as follows: microfibers were supported in a mesh and immersed in a solution of titania (5-20 mg/mL) for 24 h, then the microfiber/titania were dried at 80°C. The scanning electronic microscopy characterization was carried out in a HITACHI S-5500 equipment at 1kV.
RESULTS AND DISCUSSION

Titania obtained by sol-gel with and w/o ultrasonic action was analyzed by X ray diffraction to determine the crystalline structure (Figure 1). The conventional sample presents sharp peaks at 2θ≈25.28, 37.8, 48.04, 53.89 and 55.06°, which match very well to anatase phase (PDF#21-1272). Titania samples assisted with ultrasound (UTT, UTH, UTHT) present the same peaks, indicative that the anatase phase could be induced directly with ultrasonic action and the crystallinity can be improved either with a hydrothermal treatment or an annealing treatment [3]. At 2θ≈30.80° appear a peak in the preferential plane (1 2 1), which correspond to the PDF#29-1360 of brookite phase.

Figure 1. X ray patterns of titania samples obtained by sol-gel with different conditions. Conventional process; ultrasonic action and annealing (UTT); from an ultrasonic action, an hydrothermal treatment and annealed treatment (UTHT) and, ultrasonic action and a hydrothermal treatment (UTH).
The grain size of titania samples is displayed in Table 1. Titania obtained directly from an ultrasonic action and annealed at 450°C presents the similar crystal size of about 11nm that titania synthesized with the conventional process. The smaller grain size correspond to the UTH titania obtained from an ultrasonic action and a hydrothermal treatment (8 nm).

On the other hand, the atomic % ratio of oxygen/titanium from EDS analysis (Table 1) is about 1.6 to exception of the UTH sample (3.4), indicative there is remnants from the precursor reagents. The yield of the samples obtained with ultrasound (UTT, UTHT) is about 20% taken into account the conventional process as reference.

Table 1. Crystal size and atomic % of the titania samples obtained from a conventional synthesis and from an ultrasonic action.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystal size from X ray (nm)</th>
<th>Atomic % from EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Conventional</td>
<td>11.06</td>
<td>77.48</td>
</tr>
<tr>
<td>UTT</td>
<td>11.30</td>
<td>78.18</td>
</tr>
<tr>
<td>UTHT</td>
<td>10.7</td>
<td>65.76</td>
</tr>
<tr>
<td>UTH</td>
<td>8.01</td>
<td>84.63</td>
</tr>
</tbody>
</table>

Figure 2 shown the typical Tauc plot of the titania samples, which was obtained by using the diffuse reflectance data and Kabelka-Munk equation [8]. The estimated band gap value is about 3.2 eV, which is consist to the values previous reported for indirect transition [3].

Microfibers covered with titania nanoparticles were analyzed by SEM (Figure 3). According to SEM images (not show here) the morphology of the microfibers change as a function of titania concentration. At low concentration of titania (5 mg/mL) the covering is irregular; some zones of microfibers are not fully covered. At high concentration (20 mg/mL), granules and agglomerates are observed on the surface of the microfibers. The optimal concentration is 10mg/mL, therefore the following results are based on this concentration.

The SEM image of P3HT without covering is also included as reference (Inset of Figure 3A). Images shown that the covering of the P3HT microfibers is not fully homogeneous with titania nanoparticles obtained from a conventional process because some hole/porous are
observed (Figure 3A). The UTT and UTHT titania cover homogeneously the surface of the microfibers (Figure 3B, C), which could be used to the built of solid-state devices. The worst covering of the microfibers is with the smaller nanoparticles obtained from UTH because the microfibers are cracked (Figure 3D).

![Figure 3. SEM images of P3HT microfibers covered with titania obtained from conventional and ultrasound action.](image)

It is well known that the concentration of titania influences in the photovoltaic parameters [9], Kwong et al. found that 50% to 60% of titania are the optimal concentration in the bulk heterojunction based on blends, but this concentration could change in the hybrid heterojunction based on microfibers.

**CONCLUSIONS**

The homogeneous covering of P3HT microfibers depend on the crystal size and the concentration of titania. The best homogenous covering of the P3HT microfibers were obtained with a grain size of 10-11 nm and a concentration of 10mg/mL. These hybrid heterojunctions will be used to build solid-stated solar cells for the first time.

**ACKNOWLEDGMENTS**

This work was financed by CONACyT-México (CB176450) and SENER-CONACyT (CeMIE-Sol project No. 27). The authors are grateful for the technical support received from Gildardo Casarrubias, Rogelio Morán (IER-UNAM), Maria Luisa Ramon (IER-UNAM), Lourdes Palma (INB-UNAM) and Marina Vega-González (CGEO-UNAM).
REFERENCES


