Organic-inorganic hybrid solar cells based on 1D ZnO/P3HT active layers and 0D Au as cathode

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Abstract

In this paper two different methodologies for the assembling of organic-inorganic hybrid solar cells in 1D are presented: conventional and inverted. The conventional solar cell has the configuration of ITO/P3HT/ZnO/Au, while the inverted of ITO/ZnO/P3HT/Au. The active layers are composed of ZnO nanorods and P3HT nanorods. P3HT was synthesized by chemical oxidative polymerization and the nanorods were obtained by template assisted method. ZnO nanorods were synthesized by electrochemical method on ITO glass. The influence of the arrangement of the semiconductors was studied. The cathode of both solar cells was formed of gold nanoparticles (0D), synthesized by microwave method. The active layers were analyzed by UV–vis spectrophotometry, FTIR and SEM. Results of J-V curves indicate that the conventional solar cell has the highest current density due to the higher contact between the layers.

1. Introduction

In the last years, the synthesis of hybrid solar cells (HSC) has become a trending topic due to the low manufacturing costs, flexibility and ease to produce. The active layer is composed of organic and inorganic semiconductors, with the aim to take advantage of the properties associated with the two types of materials [1–5]. The inorganic semiconductor act as an electron acceptor material providing additional benefits to the active layer, compared to organic solar cells. The energy conversion efficiency of HSC is still low compared to that of organic solar cells based on fullerenes and conjugated polymers, however, efforts are still being made to address this problem [6, 7].

One of the research lines that has gained strength in recent years is that of nanostructured cells. It has been reported that the incorporation of organic and inorganic semiconductor in nanorod shape can improve the performance of HSC. The explanation lies at this nanoforms act as ‘free-path’ for the charge carriers, transferring them direct to the electrodes, reducing the losses by recombination [8–12].

ZnO is a n-type semiconductor with a wide band gap of 3.37 eV and an exciton binding energy of 60 meV. Is highly used in hybrid solar cells due to its stability, high electron movement and high transparency. Its anisotropic nature and polar surface allow it to be easily controlled to crystallized in many different nanostructures, such as wires, flowers, tetrapods, tubes, nanorods of hexagonal prisms, among others. This last one nanostructure is particularly useful for solar cells because they provide a large surface area and a direct path for the electrons [13]. P3HT is a p-type semiconductor highly used for its ability to collect photons from sunlight and to work as a hole transport material with a high hole mobility and excellent thermal stability; its electrical conductivity is around $10^{-10}–10^5$ S cm$^{-1}$ [14]. In contrast with a metal, an organic semiconductor cannot crystallized in nanorod shape, therefore, the template-assisted method is used to obtain a polymer oriented film [15–17]. It has been reported that the incorporation of these two semiconductors can increase the performance of solar cells compared to those that are synthesized with only one of the semiconductors. The explanation lies in the nature of both semiconductors, ZnO (n-type semiconductor) allows the transport of electrons, while P3HT
(p-type semiconductor), allows the transport of holes towards the electrode and therefore losses due to electron-hole recombination are reduced [18, 19].

According to the arrangement of the semiconductors in the active layer, hybrid solar cells are classified into two types: conventional and inverted. In a conventional solar cell, the transparent conductive oxide (TCO) act as the positive electrode and is in direct contact with the organic semiconductor; under this configuration, the holes travel towards the TCO and the electrons towards the negative electrode. In an inverted solar cell, an inverse process is carried out, the TCO act as the negative electrode because is in direct contact with the inorganic semiconductor, this allow that the electrons travel towards the TCO and the holes towards the positive electrode [20–22].

In the present studio, conventional and inverted solar cells were synthesized and characterized to compare the optical properties. The configuration of the conventional and inverted solar cells were ITO/P3HT/ZnO/Au and ITO/ZnO/P3HT/Au, respectively.

To the best of our knowledge, this is the first time that a hybrid solar cell of P3HT/ZnO in nanorod shape is synthesized using a cathode of gold nanoparticles, as an economic alternative for the use of thermal evaporation. Besides, the use of nanoparticles substantially increases surface area compared to thin films, which could be beneficial to the performance of the solar cell due to the increased area of interaction between gold and semiconductors.

2. Experimental

The hybrid solar cells were fabricated on indium tin oxide (ITO) coated glass substrates which were first wash with soap and cleaned in acetone, isopropanol and distilled water in ultrasonic bath.

2.1. Synthesis of P3HT nanorods

The organic semiconductor, poly 3-hexylthiophene (P3HT), was synthesized from its monomer 3HT by chemical oxidative polymerization. The synthesis was held in a 3-necked flask in which the necks were covered with rubber stoppers. First, 4 mmol of FeCl₃ were mixed with 50 ml of CHCl₃ and stirred for 1 h. After, 1 mmol of 3HT in 10 ml of CHCl₃ was added to the solution dropwise using a syringe. The mixture was left still under nitrogen atmosphere. After 24 h, the resultant black solution, was transferred to an equal volume of CH₃OH and stirred for 2 min. The final solution was filtered to separate the synthesized polymer.

To obtain vertically aligned nanorods, anodic aluminum oxide templates (Sigma Aldrich®) with 0.1 μm of pore size and 20 μm of thickness were used. For this, P3HT was dissolved in C₆H₅Cl in a concentration of 5 g ml⁻¹ and 60 μl of the solution were spin-coated onto the templates at 3500 rpm. After, the templates containing the polymer were immerse in a 3 M solution of NaOH for 45–60 min to dissolve the template and release the vertically aligned nanorods. Finally, these nanorods were attached to ITO glass, previously activated with CHCl₃.

2.2. Synthesis of ZnO nanorods

Vertically aligned ZnO nanorods were obtained by electrochemical method on ITO glass, previously activated with aqua regia. For this, a 0.005 M solution of Zn(NO₃)₂·6H₂O was used as electrolyte in a three-electrode cell. ITO was used as substrate, Pt as counter electrode and Ag/AgCl as working electrode. The electrodeposition was performed at 80 °C for 10 min at a voltage of −1 V. Under these specific conditions, ZnO tends to form nanorods.

2.3. Synthesis of Au nanoparticles

Spherical Au nanoparticles were obtained from the reduction of HAuCl₄. For this, a reactant solution was prepared mixing 1 ml of 5 mM HAuCl₄, 1 ml of 25 mM Na₂C₆H₅O₇ and 18 ml of H₂O. The reaction was performed by microwave synthesis (Whirlpool® WM1207D) during 10 min at 1275 W.

2.4. Assembling solar cell in configuration ITO/ZnO/P3HT/Au

First, ZnO was electrodeposited on ITO glass as was mentioned in section 2.2. Once the nanorods were obtained, P3HT was spin-coated on the ZnO/ITO substrate. Finally, the substrate was used as working electrode for the electrophoretic deposition of the Au nanoparticles, as described in section 2.6. See figure 1.

2.5. Assembling a solar cell in configuration ITO/P3HT/ZnO/Au

First, P3HT was spin-coated on ITO glass as was mentioned in section 2.1. Once the nanorods were vertically aligned on ITO glass, the substrate was submerged in a solution of Zn(NO₃)₂·6H₂O to perform the electrodeposition of the ZnO nanorods, under the same conditions that were already described. Finally, the
substrate was used as working electrode for the electrophoretic deposition of the Au nanoparticles, as described in the next section. See figure 2.

2.6. Electrophoretic deposition of Au nanoparticles
The electrophoretic deposition is a simple process that allows to deposit charged particles onto substrates without damaging the surface. This technique is suitable for depositing nanoparticles on the hybrid layers, since it prevents damage to the complex synthesized structures. The Au nanoparticles were electrodeposited on the P3HT/ZnO active layers as described below. For this, the substrate of ITO/P3HT/ZnO was used as working electrode, ITO glass was used as counter electrode (both with the same area size). The electrodes were immersed in the solution of gold nanoparticles synthesized, as was described in the section 2.3, and separated at a distance of 1 cm. Subsequently, a potential difference of 4 V was applied for 1 min. The same procedure was performed with the ITO/ZnO/P3HT active layer. See figure 3 for better reference.

3. Results

3.1. Characterization of P3HT
The polymer was characterized by spectrophotometry UV–vis to observe the two characteristic bands. As can be appreciated in figure 4, the first band is presented around 450 nm and the second band around 260 nm. The first of the bands is associated to the excitation of an electron from a pi bonding orbital to a pi antibonding orbital. The second band is associated to the movement of an electron from a non-bonding pair of electrons to a pi antibonding orbital [23].

The four characteristic bands of the semiconductor polymer in the infrared region were obtained by FTIR and are presented in figure 5. The first band (A) is correlated with the C–H vibration in the aliphatic chain. In the second band (B) the thiophene ring is identified. The third band (C) is associated to the C–H vibration of the aromatic ring and the fourth band (D) with the bond C–S [24, 25]. In table 1 are presented the details of these bands.

When the P3HT is spin-coated on the anodic aluminum oxide templates, the capillary forces allow pores to be filled. As can be appreciated in figure 6, some of the pores were filled with the semiconductor polymer. These pores have a width of around 100 nm.
Figure 7(a) show the P3HT nanorods, once the template was removed. It can be observed sizes between 100 nm and 1300 nm, approximately. The template pore size is 100 nm, however, when the polymer is released, tends to agglomerate with neighboring nanorods increasing their size. In figure 7(b), can be appreciated a single nanorod of P3HT.

3.2. Characterization of ZnO
Figure 8 shows the micrograph of the nanorods synthesized, previous to polymer deposition by spin-coating method. It can be observed that these nanorods have a hexagonal shape of approximately 100 nm of diameter and are vertically aligned on the substrate.

3.3. Characterization of Au nanoparticles
As can be appreciated in figure 9, the synthesized gold nanoparticles have a spherical form. According to measurements made in an image analyzer, the synthesized gold nanoparticles have an average size between 20 nm and 30 nm. These nanoparticles were added by electrophoretic deposition to the hybrid active layers as a thin film to act as the cathode.
3.4. ZnO nanorods on P3HT nanorods

The ZnO nanorods formation on ITO glass was followed by a current-time curve as can be appreciated in figure 10. In the same figure it is shown the current-time curve of the ZnO nanorods formation on top of P3HT nanorods. Both curves have the same characteristic behavior, so the effective formation of ZnO nanorods on P3HT film can be confirmed.

![Figure 5. FTIR spectrum of P3HT.](image)

![Table 1. FTIR band assignment.](table)

| Band | Position (cm⁻¹) | Assignment          |
|------|-----------------|---------------------|
| A    | ~2918 y 2849    | Stretching C–H chain|
| B    | ~1458           | Stretching C=C      |
| C    | ~1121           | Stretching C–H ring |
| D    | ~820            | Bending C=S         |

![Figure 6. Surface electron microscopy of P3HT inside the pores of AAO template.](image)
Figure 7. Surface electron microscopy of P3HT nanorods, (a) multiples and (b) a single nanorod.

Figure 8. SEM image of ZnO nanorods vertically aligned in ITO glass.
3.5. Transmittance spectra

Figure 11 shows the transmittance spectra of ITO glass, ZnO nanorods and P3HT nanorods. As can be observed, the transmittance of the ITO is reduced by the P3HT and to a greater extent with the ZnO. These results are favorable for the layer because a reduction in the transmittance leads on an increase of the absorbance.

3.6. Current-voltage characteristics

3.6.1. Solar cell in configuration ITO/ZnO/P3HT/Au

Figure 12 shows the current density-voltage (J-V) curve in dark and light for the inverted solar cell. The maximum power was calculated from the data of J and V (P = J*V) and with this information, the rest of the basic parameters.

The parameters of J_{sc} and η present low values (table 2) probably associated with a little contact between the organic and inorganic semiconductor.

3.6.2. Solar cell in configuration ITO/P3HT/ZnO/Au

Figure 13 shows the current density-voltage curve in dark and light for the conventional solar cell. The obtained parameters are presented in table 3.

Comparing the parameters of both solar cells, the conventional solar cell presents an improvement in J_{sc} and FF. This increment is probably because there is more contact between the organic semiconductor, P3HT, and
the ITO glass, which act as positive electrode in this kind of configuration, causing the holes travel through the polymer.

The Voc of the conventional solar cell is lower than the inverted. The explanation lies at the fabrication process of both cells. In the inverted solar cell, the ZnO nanorods are formed directly over the ITO glass allowing a complete contact; while in the conventional solar cell, the P3HT nanorods are added by contact to ITO glass resulting in low contact.

The contact in hybrid solar cells can be increased by heat treatment, solvent annealing, vacuum deposit among other techniques. Increasing contact between layers could improve the parameters.
The cathode of both solar cells was formed by a thin film of the synthesized gold nanoparticles. With this method is avoided the use of thermal evaporation, however, it could be affecting the performance of the solar cells.

4. Conclusions

In summary, two different assembling of organic-inorganic hybrid solar cells in 1D were presented in this paper. Simple methodologies to obtained semiconductors organic and inorganic in nanorod shape and vertically aligned in ITO glass were developed, as well as synthesis of gold nanoparticles (0D) by microwave. Gold nanoparticles were used as cathode for the hybrid solar cells. The calculus of the parameters of the solar cells shows that the conventional solar cell has a higher current density, favored by the arrangement of the layers. The low efficiency in both cells is associated to the low contact between layer; this contact can be improved subjecting the solar cells to a heat treatment in a high vacuum oven.

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Table 3. Parameters of the conventional solar cell.

| Parameter | Value |
|-----------|-------|
| $V_{oc}$ (mV) | 200 |
| $I_{sc}$ (mA cm$^{-2}$) | $1.09 \times 10^{-7}$ |
| FF (%) | 30 |
| $\eta$ (%) | $6.53 \times 10^{-7}$ |

Figure 13. J-V curve of the solar cell with structure ITO/P3HT/ZnO/Au.
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