Photovoltaic conversion of TiO$_2$ nanocrystals decorated with P3OT, Au nanocrystal or CdSe quantum dots

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In this work, the preparation and photovoltaic conversion characterization of 10 µm films of sensitized TiO$_2$ is reported. The 300 nm TiO$_2$ particles with anatase crystalline phase were deposited on an ITO substrate and decorated with Au nanocrystals, P3OT or CdSe Quantum Dots (QD’s). The photocurrent was measured in a three electrode electrochemical cell. The results exhibited that QD’s sensitized TiO$_2$ films have the largest photocurrent (237 µA/cm$^2$), giving a photo-conversion efficiency of 0.149%, more than fourfold the photocurrent of TiO$_2$ without sensitized (0.034%). These results are attributed to the ability of QD’s to photogenerate charge carriers efficiently giving a great amount of electrons to increase the photocurrent.

**Keywords:** Solar cells; nanoparticles; TiO$_2$; CdSe; P3OT; Au.

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1. Introduction

In the last years, there has been an increase in the research of sustainable alternative energy processes. It is a result of the reserve decrease of fossil fuels and its environmental effect. Photovoltaic Cells have received significant attention because the solar energy on the earth is 10$^{12}$ times more powerful than any other source in the planet. The most common solar cells, the silicon solar cells, have a photo-conversion efficiency of 20%, but the manufacturing process is very expensive and involves the use of toxic chemicals. The use of nanostructured materials allow reduce the cost of production due to the lower synthesis temperatures and deposition methods, although photoconversion efficiency ($\eta$) is today lower than the best silicon based solar cells. The advantage of nanostructured solar cells is the possibility to manipulate factors like shape and size of the particles to improve $\eta$ and make them commercially feasible. One of the most studied nanostructured solar cells are the Grätzel or dye sensitized solar cells (DSSC) [5]. This kind of cells consist in TiO$_2$ nanoparticles acting as a highly porous wide band gap semiconductor electron acceptor layer and a dye adsorbed onto the TiO$_2$ acting as sensitizer to harvest more of the solar flux. Under irradiation, the photo-exited dye molecules inject electrons into the TiO$_2$ layer and are transported through this layer to be collected by ITO film on the glass surface. The largest photovoltaic conversion efficiency of DSSC reported in literature is 11% [6]. The principal problem in DSSC is, the use of a liquid electrolyte, necessary to reverse the oxidation of dye, that evaporates at room temperature and reduces the life time of the cell. In addition, the largest conversion efficiency has been obtained with a dye based on Ruthenium that has a great photogeneration of charge carriers. However, is very expensive and require an increment of the charge carriers injection to avoid the recombination.

An alternative to DSSC is the use of CdSe Quantum Dots (QD’s) as sensitizer instead of the expensive Ru-complex Dyes. QD’s have a large extinction coefficient in the visible absorbing strongly that light and injecting electrons to the conduction band of metal oxides, contributing to increase the solar energy conversion. Attachment of QD’s to TiO$_2$ could be done by immersion method using a molecular linker. This kind of solar cells have a photoconversion efficiency of $\sim$3 %, however it presents a Quantum Efficiency (QE) of 12% [7,10]. In this kind of cells is necessary to improve the injection efficiency to increase $\eta$ and still having the problem of the liquid electrolyte.
Another alternative to DSSC are the solid-state hybrid organic-inorganic solar cells HSC. In these devices, the inorganic component is a metal oxide and a dye is used as light absorber like in DSSC. However, in this case, the regeneration of the dye is done for a hole injector-polymer. Thiophene derivatives seem to be the bests option for this purpose [1]. This configuration present less efficiency than the DSSC but present as advantage a longer life time due to polymer photostability. Cells made of metal oxides usually comprise a multilayer structure with metal oxide in the bottom layer and hole acceptor polymer in the top layer, so, the extent of the donor acceptor interface depends on the interpenetration of the polymer in the metal oxide, that implies the needed for a mesoporous metal oxide. This is the reason for the lower efficiency of HSC’s and a important topic of research in solar cells [4,9]. It is possible to use a polymer as sensitizer but the efficiency drops [1].

Semiconductor-metal nanocomposites have been widely studied in photocatalysis. The metal in contact with the semiconductor enhances the efficiency improving the charge separation process, the photocurrent and photovoltage [15]. Studies have shown a shift in the fermi level to more negative level by doping semiconductor with a metal ion. That shift enhances the efficiency of interfacial charge transfer process [2]. Gold nanoparticles have the ability to undergo quantized charging, that make them the best candidate to achieve Fermi-Level equilibration [3]. Gold have a size dependence conductance increasing by decreasing the size [15].

Nanostructured TiO$_2$ have many features that can affect the photoconversion efficiency. Size affects the electron transport, by increasing the particle size defects and grain boundaries are reduced, consequently the charge carriers recombination decrease resulting in a fill factor gain [14]. In addition, the sensitizer metal-oxide interaction area is reduced that is expressed as photocurrent decrease. TiO$_2$ exists in three crystalline phase, anatase, rutile, and brookite; each phase presents different electrical propieties. Anatase and rutile have been used for photovoltaic cells, meanwhile brookite has no received similar attention because it is the most difficult to prepare as a thin film. A better crystallinity implies less defects and less recombination sites. The particle shape is an important factor in the efficiency of solar cells, some shapes foment a preferential flux of electrons “like nanorods” [16], and others give a major interaction area between polymer and metal oxide like nanotubes and mesoporous spheres. Particle connectivity plays an important role, a major connectivity gives better electron conduction but reduces polymer adsorption [1]. A major efficiency is achieved with a dual layer configuration, a compact layer in the bottom to obtain good contact with ITO, followed by a mesoscopic layer to obtain a good penetration of polymer [1].

Although these kinds of cells had been widely studied, there still unclear the optimal conditions to maximize its advantages, moreover there is no a systematic study to compare them in similar conditions. In this work, TiO$_2$ films were synthesized by sol-gel method, then were decorated with Au, P3OT or CdSe QD’s to compare the sensitizer photoconversion efficiency effect via electrochemical characterization.

2. Experimental

Preparation of TiO$_2$ sensitized films

**TiO$_2$ film preparation.** TiO$_2$ particles were made by sol-gel method. 3.75 mL of titanium isopropoxide (IV) and Pluronic F127 were added in a solution of 5 mL of H$_2$NO$_3$ in 50 mL of EtOH adding 2.5 mL of H$_2$O, the mixture was stirred one hour. The synthesis process was done in a glove box with N$_2$ atmosphere. The mixed solution was transferred into a teflon autoclave. The hydrothermal treatment was carried out at 70°C during 12 h outside the glove box. The resulting xerogel was washed three times with EtOH and annealed for one hour at 550°C. The TiO$_2$ powder was suspended in C$_6$H$_5$OH and deposited on ITO substrate by doctor blade method.

**CdSe QD’s Synthesis.** High-quality CdSe QD’s were synthesized. CdO is used as the Cd precursor and 1-Tetradecylphosphonic acid (TDPA, 99%) and trioctyolphosphine oxide (TOPO, 99%) are the ligands and coordinating solvents, respectively. The resulting CdSe nanocrystals were in the strong confinement size regime and were synthesized in normal air-free reaction conditions. The synthesis of the CdSe nanoparticle follows the procedure reported by Robel et al., wherein 0.05 g (0.39 mmol) of CdO, 0.3 g (1.1mmol) of TDPA, and 4 g of TOPO were heated to 110°C and degassed under vacuum and then heated to 300°C under a nitrogen flow [13]. A SeTOP (0.7% by weight) solution was obtained by adding 0.026 g of Se powder with 4.25 mL of TOP inside of a glove box and stirring for 1 h to ensure complete dissolution of the Se powder. After reaching 300°C, the Cd-TDPA-TOPO solution was cooled to 270°C prior to the injection of SeTOP. Under a nitrogen flow, 3 mL of SeTOP was injected, which resulted in the lowering of the temperature to 260°C. The temperature was then increased to 280°C to facilitate particle growth, and aliquots were removed and probed to track nanocrystallite growth via UV-vis absorption spectroscopy. The CdSe solution was cooled and removed from the reaction flask at around 80°C and dissolved into 10 mL of toluene. The QD’s in toluene were then cleaned twice through a precipitation and decantation regime using methanol and centrifugation at 3000 rpm, and the QD’s were ultimately redissolved in toluene prior to their use as a sensitizer.

**Au Nanocrystals Synthesis.** Au nanocrystals were synthesized mixing a 0.2 M dissolution of Cetyl trimethylammonium bromide (CTAB) with 5 mL of 0.0005 M dissolution of HAuCl$_4$. The mixture was stirred in ice bath and added 0.60 mL of 0.01M NaBH$_4$, as result a brown solution was obtained. The solution was stirred for 2 h to obtain a 4 nm particles. The size was proved via UV-vis absorption spectroscopy. Solution was stored avoiding light exposition until use as sensitizer.
PHOTOVOLTAIC CONVERSION OF TiO$_2$ NANOCRYSTALS DECORATED WITH P3OT, Au NANOCRYSTAL OR CdSe QUANTUM DOTS

P3OT Preparation. In this work, poly(3-octylthiophene) supplied by Sigma was used. A solution of $10^{-5}$ M in toluene of P3OT was made. The band gap of the P3OT was measured via UV-vis absorption spectroscopy derivate. The solution was stored in dark before its use as sensitizer.

Sensitizers linkage to TiO$_2$. Sensitizers (Au, CdSe QD’s and P3OT) were linked to nanocrystalline TiO$_2$ thin films using TGA (HSCH$_2$COOH) as a molecular linker. TiO$_2$ has a strong affinity for the carboxylate group of the linker molecules (Fig. 1a), while the sulfur atom of TGA binds strongly to sensitizers through surface of these (Fig. 1b). The films were dried on a hot plate at 100$^\circ$C for 1 h to remove H$_2$O from the surface due to ambient humidity adsorption. The films were later immersed in TGA diluted at 70% in CH$_3$Cl for 12 h in a nitrogen environment in a glove box. The films were then immersed in toluene removing the excess TGA, and then immersed in a CdSe, P3OT or Au solution for 12 h inside the glove box. Four films of 3.2 cm$^2$ were immersed in 6 mL of sensitizers solution. The TiO$_2$ sensitized films were stored in a nitrogen-filled glove box and not exposed to light prior to Photoelectrochemistry (PEC) characterization. The TiO$_2$ functionalized cell in the electrolyte is very stable; however, when it is removed from the Na$_2$S electrolyte and are in ambient conditions, the thin film’s properties deteriorate after experimentation. Long-term stability needs to be further studied in future research.

Characterization

Raman Spectroscopy. The raman shift was measured exiting the TiO$_2$ powder with a HeNe Laser with 60 mW at 680 nm focusing the beam with a 40X microscope objective. The spectrum was measured from 200 to 1000 cm$^{-1}$. Morphological characterization. The shape and size of the TiO$_2$ particles was measured with a JSM-6390 series, JEOL Scanning Electron Microscope. Optical Absorption. The spectra were measured with a Perkin Elmer absorption spectrophotometer.


FIGURE 2. SEM image of TiO$_2$ particles.

FIGURE 3. Raman spectrum of TiO$_2$ aged at 70$^\circ$C for 12 hours and annealed at 550$^\circ$C for an hour, showing characteristic anatase crystalline phase peaks.

The TiO$_2$ spectra were measured via reflectance in tablets of compacted powder, scanning between 200 to 800 nm. Using the maxima of the first derivate of the spectra the threshold of the band gap was estimated. Electrochemical Characterization. The photocurrent was measured in a three electrode cell using the sample as work electrode, Statured Calomel Electrode (SCE) as reference, Pt wire as counter-electrode and Na$_2$S as electrolyte using a potensiosstat Gamry Reference 600. The work electrode was illuminated with 31.83 mW/cm$^2$ from a halogen lamp. Na$_2$S provide us NaS$^-$ and SO$_4^{2-}$ as redox couple with standard potential

$$E^0_{NaS^-\text{SO}_4^{2-}} = -0.618 \text{ volts vs NHE [12].}$$

3. Results and discussion

Structural and morphology characterization

Morphology. The morphology of the TiO$_2$ powder was studied by SEM. The average TiO$_2$ particle size was found to be around 300 nm in diameter see Fig. 2. This particles have a
quasi spheric shape and are composed for an agglomerate of many nanocrystals.

Raman Spectroscopy. Figure 3 shows raman spectrum for the TiO$_2$ powder. Raman spectrum has the well defined characteristic peaks of anatase crystalline phase of TiO$_2$ [17] indicating a high crystallinity. It can be seen that the characteristic peak for the anatase phase are centered at 395 cm$^{-1}$, 513 cm$^{-1}$ and 635 cm$^{-1}$.

Optical Absorption

The absorption spectra of TiO$_2$, P3OT, QD’s and Au are shown in solid lines in Fig. 4. The representative absorption peaks for TiO$_2$, P3OT and QD’s are centered at 3.69, 2.7, and 2.82 eV respectively. The first derivate of the absorption spectra evidence peaks centered at 3.34, 2.75 and 2.47 eV associated to the band gap of TiO$_2$, QD’s and P3OT, respectively, as is shown in Figs. 4a, 4b. The band gap of P3OT and QD’s are lower than the one of TiO$_2$. These materials spectra shows an obvious red shift of the absorption edge toward the visible region, allowing increase the photoconversion efficiency. P3OT have a wider absorption peak than QD’s. The Au nanoparticles present an absorption peak at 544 nm see Fig. 4c, corresponding to the plasmon resonance associated to the nanoparticle size (4 nm) [8].

Electrochemical Characterization:

The current-voltage (I-V) profiles for solar cells fabricated with different sensitizers were obtained. In Fig. 5 can be appreciated that all decorated systems have a higher photocurrent than TiO$_2$ films without sensitizers. The highest photocurrent was achieved for the TiO$_2$-QD’s and the lower one for TiO$_2$-P3OT cell. The short-circuit current and open-circuit voltage found in Fig. 5 are summarized in Table I. The Fill Factor (FF) and power conversion efficiency ($\eta$) are also listed in Table I and were calculated by using the equations [11]

$$FF = \frac{P_{max}}{J_{sc} \cdot V_{oc}},$$

$$\eta = \frac{P_{max}}{P_l} = FF \frac{J_{sc} \cdot V_{oc}}{P_l},$$

where $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open-circuit voltage, $P_{max}$ is the maximum power density observed from the current density-voltage curve for each device, and $P_l$ is the incident light power density (31.83 mW/cm$^2$). It is clear than TiO$_2$-Au films exhibit the highest FF (51.8%) respectively.
PHOTOVOLTAIC CONVERSION OF TiO$_2$ NANOCRYSTALS DECORATED WITH P3OT, Au NANOCRYSTAL OR CdSe QUANTUM DOTS

FICURE 6. Schematic representation of the energy levels of TiO$_2$ decorated with a) QD's, b) Au, and c) P3OT.

followed for TiO$_2$-P3OT (46.6%) and TiO$_2$-QD's (44.4%). However, the highest photocurrent was achieved for TiO$_2$-QD's (237 $\mu$A), with the highest efficiency reported here ($\eta=0.14\%$).

**Discussion**

The efficiency of TiO$_2$-QD's films is due to QD's capacity to photogenerate charge carriers with a large QE ($\sim$12%) [7]. When this kind of cells is illuminated light excite electrons from the valence band (VB) of TiO$_2$ and QD's to their respective conduction band (CB), is shown in Fig.6a. Electrons in QD's CB are injected to TiO$_2$ CB due to the potential difference between bands. In TiO$_2$, electrons are transported to ITO substrate avoiding recombination process with the wide band gap of TiO$_2$. Even if Photogeneration of QD's increases the charge carriers population and consequently the photocurrent, QD's have small diffusion coefficient and relatively high resistance, that is the reason why many of the charge carriers recombine before be injected to TiO$_2$ limiting the FF parameter.

In the TiO$_2$-Au system (Fig. 6b), the increase in FF is due to Au conductive attributes. The work function of the Au moves to be at the same level than the fermi level of the TiO$_2$. When this kind of cell is illuminated, the photo-generation of charge carriers is done by the TiO$_2$ and the Au nanocrystals help to transport the electrons from the TiO$_2$ to the electrolyte increasing the injection rate and the photocurrent. The problem with this configuration is the depend of the UV light absorption of TiO$_2$. So, it have a poor photo-generation, but its injection rate is enough to give an important increment in the efficiency.

In the TiO$_2$-P3OT system (Fig. 6c), TiO$_2$ is again the responsible of the photo generation. But in this case, P3OT transports the holes from the TiO$_2$ to the electrolyte in contrast to TiO$_2$-Au system, P3OT can contribute with the photogeneration of charge carriers and it need lower excitation energies. But, P3OT have low electron transport efficiency to TiO$_2$, and only a small amount of the electrons generated in P3OT can arrive to TiO$_2$ and contribute whit the current. Additionally, the hole transport in P3OT is less efficient than the electron transport in Au in consequence the FF parameter and the photo conversion efficiency of P3OT decorated TiO$_2$ are minor than the Au decorated TiO$_2$.

**4. Conclusions**

The efficiency of TiO$_2$ films decorated with Au, P3OT and QD’s were compared. It was found that all systems increment the photo-conversion efficiency in different ways. Au increase the electron injection rate, P3OT increase the hole transport and CdSe QD’s increment the photo-generation of charge carriers. Also was found that each system have disadvantages. TiO$_2$-Au systems depends of the UV TiO$_2$ absorption, TiO$_2$-P3OT system partially depends of TiO$_2$ and have slow electron injection, and TiO$_2$-QD’s have slow charge carriers diffusion. It was found that the best efficiency was achieved with QD’s ($\eta=0.14\%$). According to the experimental results, this system could be improved using a conductor layer to increase the charge carrier diffusion.