

Enhancing the adsorption of CdSe quantum dots on TiO₂ nanotubes by tuning the solvent polarity



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ABSTRACT

The aim of this work is to report the effect of the solvent polarity on the adsorption of CdSe quantum dots (QDots) over the surface of TiO₂ nanotubes and the influence of the coverage gained on the efficiency of photoanodes based on these materials. Particularly, it is shown that the amount of QDots adsorbed on TiO₂ nanotubes can be tuned by using solvent mixtures of different polarity and volume ratios. An increase on QDots coverage was found when the polarity increases. What is noticeable is that the photoanode efficiency increased at a higher rate than the QDots coverage. For instance, a two-fold increase of coverage at a 50% acetone – 50% toluene ratio induces up to a seven-fold increase of the photocurrent values with respect to those obtained when the adsorption is performed from toluene. This effect is explained in terms of a different distribution of QDots along the nanotube walls depending on the solvent polarity used for the adsorption.

1. Introduction

Quantum dots (Qdots) sensitized solar cells are a variation of Grätzel solar cells (Dye sensitized solar cells) [1]. In the first case the photoanodes are based on wide band gap nanostructured semiconductors such as TiO₂ or ZnO optically sensitized with Qdots instead of dyes. In this work, photoanodes made of TiO₂ nanotubes sensitized with CdSe Qdots are studied. The nanocrystalline wide band gap semiconductor fulfills two roles simultaneously. On one hand, because of its semiconductor nature, it absorbs light in the ultraviolet range generating electrons with this radiation. On the other hand, it serves as a large surface area support for quantum dots which are responsible for the generation of electrons due to the absorption of the visible fraction of solar light.

This type of device has potentially higher efficiencies in comparison with the Silicon based ones, i.e. their efficiency can go beyond the Shockley and Queisser thermodynamic efficiency limit. The main reason comes from the distinctive quantum confinement effects of quantum dots [2]. Since the beginning of the 90's and until today, nanocrystals synthetic methodologies have notably improved so nowadays it is possible to control the properties of these materials. Probably, the most studied nanocrystals are CdS, CdSe, CdTe, InP, GaAs, GaP, GaN, GaInP, core-shell InP/ZnCdSe₂, Ge and Si because their synthesis is easier than others and they also have peculiar photonic properties

[3].

Two of the methods used to achieve optical sensitization of wide band gap semiconductors are Successive Ionic Layer Adsorption and Reaction (SILAR) [4] and Chemical Bath Deposition (CBD) [5]. In spite of the poor control on the shape and size of deposited Qdots, these methods allow a more intimate contact between wide band gap semiconductors and Qdots, improving the electronic transfer between them. High coverage degrees can also be obtained using “linker” molecules [6] to attach previously synthesized Qdots but the photo-conversion efficiency reached is low because the linker molecules can act as recombination centers; thus electron lifetimes result shorter than those measured when a direct adsorption method is employed for optical sensitization [7,8]. Direct adsorption of previously synthesized Qdots allows a better control of the shape and the size of Qdots adsorbed. The main challenge of a direct method consists in reaching higher coverage degrees, without aggregation of Qdots. To improve the adsorption, a better understanding of the nature of the adherence forces of Qdots attached to TiO₂ nanotubes involved in this process is necessary.

The process through which Qdots (adsorbates) are attached to TiO₂ nanotubes surface (adsorbent) is physisorption (dispersion or dipole-dipole interactions) [9]. A major problem with direct adsorption is the irreproducibility caused by:

Abbreviations: Qdots, quantum dots; SILAR, Successive Ionic Layer Adsorption and Reaction; CBD, Chemical Bath Deposition

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- Variable coverages of Qdots surface with capping molecules that depends on the quantity of cleaning steps during the purification process [6],
- The solvent used for redispersing Qdots,
- Morphology and porosity of substrates.

Besides the adsorbate-adsorbent interactions, the solvent-adsorbate and solvent-adsorbent interactions must also be considered to analyze the adsorption process [10]. In other words, the solvent can compete with the adsorbate for the adsorption sites or avoid the adsorption of the adsorbate, maintaining it soluble in the liquid phase. For example, in reference [11] it was found that the amount of organic hydrophobic pollutants adsorbed on activated carbon, increases with the increasing polarity of the solvent because of the “hydrophobic interactions” that arise. From a thermodynamic point of view, the adsorption of hydrophobic compounds from polar solvents becomes favorable as solvent molecules structured around the adsorbates are released after the adsorption process, increasing the systems entropy.

In this work, the effect of the polarity of the Qdots dispersion solvent the adsorption equilibrium was analyzed. The amount of Qdots adsorbed onto TiO₂ nanotubes from colloidal dispersions using solvent mixtures of increasing polarity was compared and the efficiency of the resulting photoanodes was tested.

2. Experimental section

2.1. TiO₂ nanotubes synthesis

The chemicals used for TiO₂ nanotubes synthesis were Titanium foil, Ethylene glycol (Pro analysis, Dorwil) and ammonium fluoride (NH₄F Pro analysis, Ciccarelli).

Anodization was carried out following a procedure previously reported in [12], which is based on methods described in [13] with slight changes. Briefly, before anodization was carried out, Ti foils were polished and ultrasonically cleaned in isopropyl alcohol, acetone, ethanol, deionized water (MILLI-Q) and dried with nitrogen. A two-electrode cell employing Ti foil as working electrode and Au foil as counter electrode was used for the anodization. The electrolyte solution was 4%w/w deionized water and 0.3%w/w NH₄F in ethylene glycol. 40 V were applied between the electrodes for 2 h, at 24 °C and under constant stirring. After anodization the Ti/TiO₂ nanotube surface was rinsed and ultrasonically cleaned for 2 min with ethanol and left drying in air. Finally, to convert TiO₂ crystalline structure to anatase, thermal annealing treatment in a furnace was carried out in air at 400 °C during 4 h.

TiO₂ nanotubes were morphologically characterized by Scanning Electron Microscopy (See Fig. S1 in Supporting Information). The SEM images show that the TiO₂ nanotubes formed were closely packed hexagonal arrangements. The image analysis indicates that the average diameter of nanotubes was (85 ± 5) nm and their average height, resulted in (4.7 ± 0.1) μm.

2.2. CdSe Qdots synthesis and characterization

The chemicals used for CdSe Qdots synthesis were Cadmium oxide (CdO 99,5%, Aldrich), Selenium powder (99,5%, Sigma Aldrich), Trioctylphosphine (TOP 90%, Technical grade, Sigma Aldrich), Myristic Acid (98%, Fluka) and 1-Octadecene (90%, Technical grade, Aldrich).

CdSe Qdots, capped with myristic acid and trioctylphosphine (TOP) were synthesized by the “Hot injection method”, following a methodology previously described in [12] based on [14]. Briefly, the Se-precursor (TOP-Se) prepared under N₂ atmosphere, at room temperature and dissolved in 1-octadecene was rapidly injected into a flask containing the Cd-precursor (Cadmium myristate) dissolved in 1-octadecene previously heated at ~230 °C under N₂ atmosphere. After

75 s the reaction vessel was removed from the hot plate and cooled down to quench the reaction. After the synthesis, the Qdot sample was purified by several washing cycles dispersing it in ethanol, followed by centrifugation and extraction of the ethanolic phase which became enriched with 1-octadecene and the excess of precursors. Finally, the CdSe Qdots were dispersed in toluene and characterized by UV–Vis absorption (UV 1700, Shimadzu) and fluorescent emission. With this synthetic method, a good quality Qdots dispersion, with a small size distribution evidenced by the small Full Width at Half Maximum (FWHM ~30 nm) of the fluorescence emission spectrum signal was obtained. The average diameter, 3.3 nm, was determined from the absorbance spectrum using the Brus model [15].

2.3. Preparation and characterization of the photoanodes

Photoanodes were prepared with TiO₂ nanotubes sensitized with previously synthesized CdSe Qdots by direct adsorption. This method simply consists in the immersion of TiO₂ nanotubes for different periods of time into colloidal dispersions of variable concentration of CdSe Qdots in toluene and acetone mixtures of different proportion. This adsorption was followed using absorption spectroscopy. The Ti/TiO₂ nanotubes foil was placed against the side wall of the cuvette so as not to disturb the passage of light (see Fig. 1).

Besides, direct adsorption was monitored in time measuring the photocurrent produced by the photoanodes were illuminated with white light as it is described in the next paragraph.

Photoelectrochemical experiments were performed in a three electrode cell built in a standard spectrophotometric cuvette with 1 cm path length. The photoanode was the working electrode, a Pt wire the counter electrode and Ag₂S/Ag the reference electrode (see Fig. 2). An aqueous 1 M sodium sulfide (Na₂S.xH₂O 60–62%, Riedel-de Häen) solution was used as electrolyte.

The cell was illuminated using a focused beam from a 150 W Xe lamp and photocurrent was measured using a potentiostat (PGSTAT-101, Autolab).

Diffuse reflectance measurements of the obtained photoanodes were carried out using a white LED and an Ocean Optics HR2000+ spectrometer.

Electron Dispersive Spectroscopy (EDS) of the obtained photoanodes was performed employing a Sigma FE-SEM to map the distribution of Qdots along the nanotubes. The analysis of the distribution map of Cd and Se along nanotubes was carried out with Aztec Software which divides the corresponding micrographs in smaller areas and reconstructs the spectra in each of those portions. Cd La1 and Se La1_2 signals were normalized by Ti La1_2 signal which was uniform in each point of the analyzed micrographs.

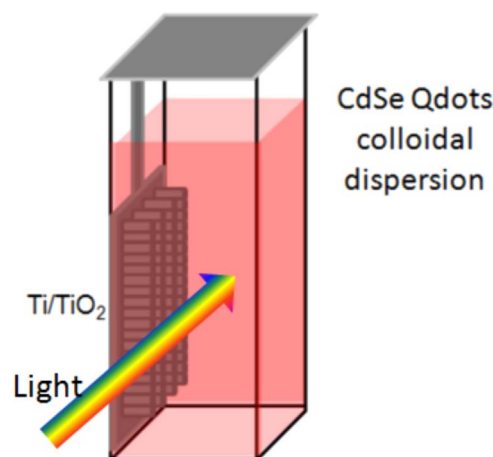


Fig. 1. Glass spectrophotometric cuvette with a stopper to prevent solvent evaporation employed to track direct adsorption of Qdots on TiO₂ nanotubes.

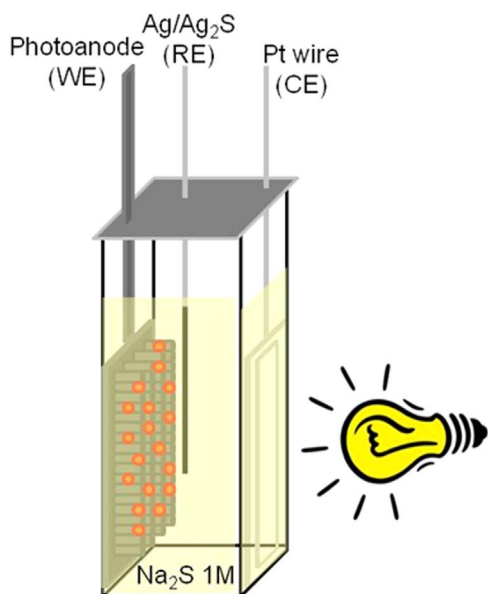


Fig. 2. Electrochemical cell assembly used to characterize the photoanode [12].

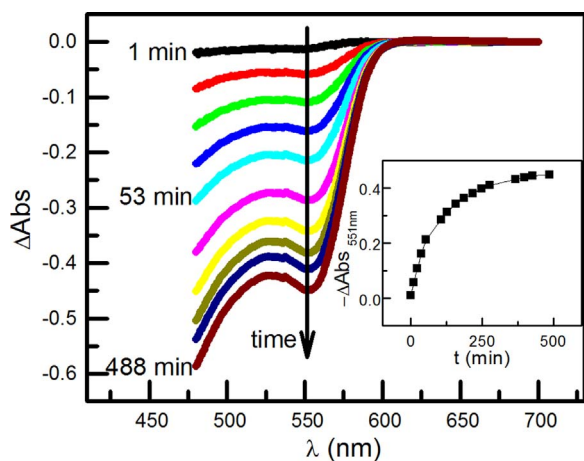


Fig. 3. Change of the absorption spectrum with time during the adsorption of Qdots on TiO_2 nanotubes. Reference spectrum was taken at the beginning of the adsorption process. Inset: Change of optical absorption at 551 nm (excitonic peak) with time during the adsorption process.

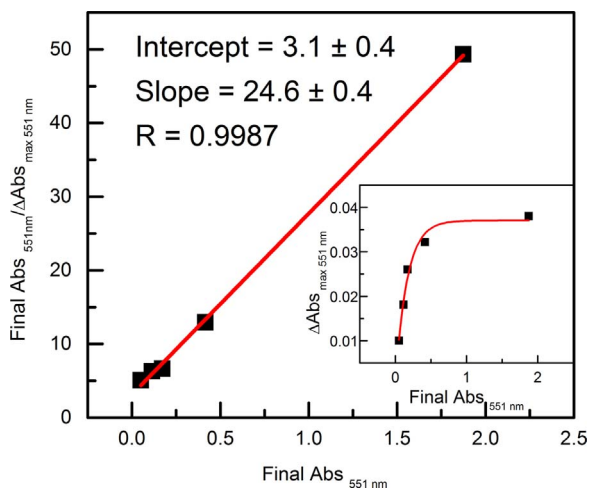


Fig. 4. Fitting of the results obtained of adsorption isotherm of Qdots from toluene colloidal dispersions on TiO_2 nanotubes based on the Langmuir model. Inset: Adsorption isotherm of Qdots from toluene colloidal dispersion on TiO_2 nanotubes.

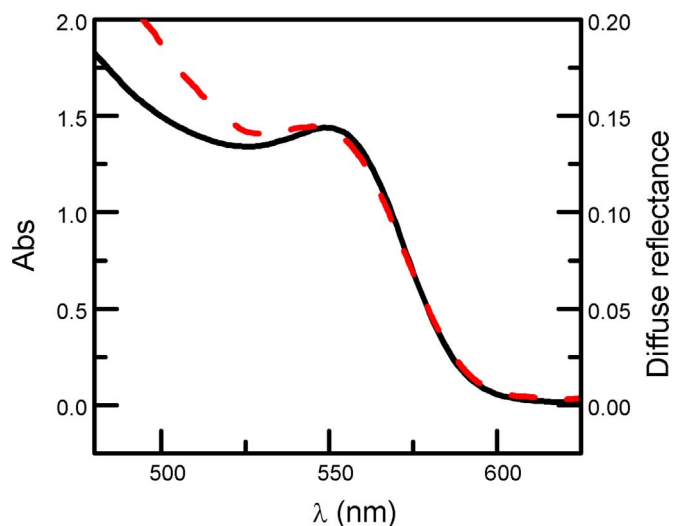


Fig. 5. Absorption spectrum of colloidal CdSe Qdots (black line) and diffuse reflectance spectrum of Ti/TiO_2 foil after Qdots direct adsorption (dashed red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

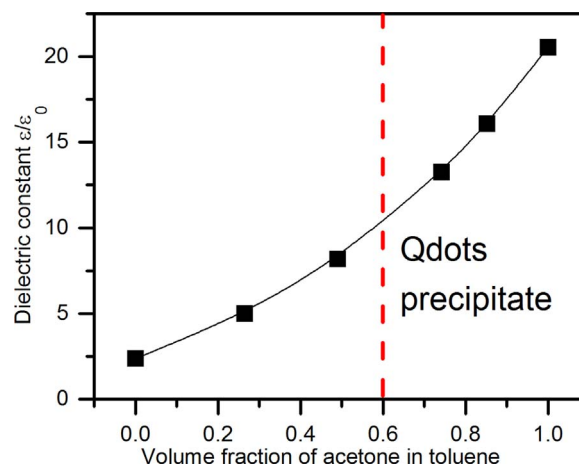


Fig. 6. Dielectric constant of mixtures of toluene/acetone with different volume fractions. Dashed red line indicates the approximate value of volume fraction of acetone in toluene from which CdSe Qdots precipitate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The transient photocurrent technique was performed exposing the photoelectrochemical cell to a 400 nm Led pulsed by a waveform generator in series with a constant voltage source. The light perturbation consisted of square wave modulation pulses (100 ms) superimposed on constant illumination intensity measured employing a photomultiplier tube connected to an oscilloscope. The decay of transient photocurrents was recorded using a potentiostat (PGSTAT-101, Autolab) connected to the oscilloscope. The oscilloscope measurement of photocurrent transient was triggered by the light signal of the photomultiplier tube and averaged for about 3 min.

Ti/TiO_2 nanotube foils were reused several times after removing the adsorbed Qdots immersing them in a 1 M HNO_3 solution for 2 h approximately followed by a thermal treatment at 400 °C during 2 h.

3. Results and discussion

3.1. Langmuir-like adsorption isotherm of CdSe quantum dots on TiO_2 nanotubes from colloidal dispersions with toluene as the solvent

Direct adsorption of Qdots was followed using absorption spectroscopy. To start monitoring this process a baseline was taken with Qdots

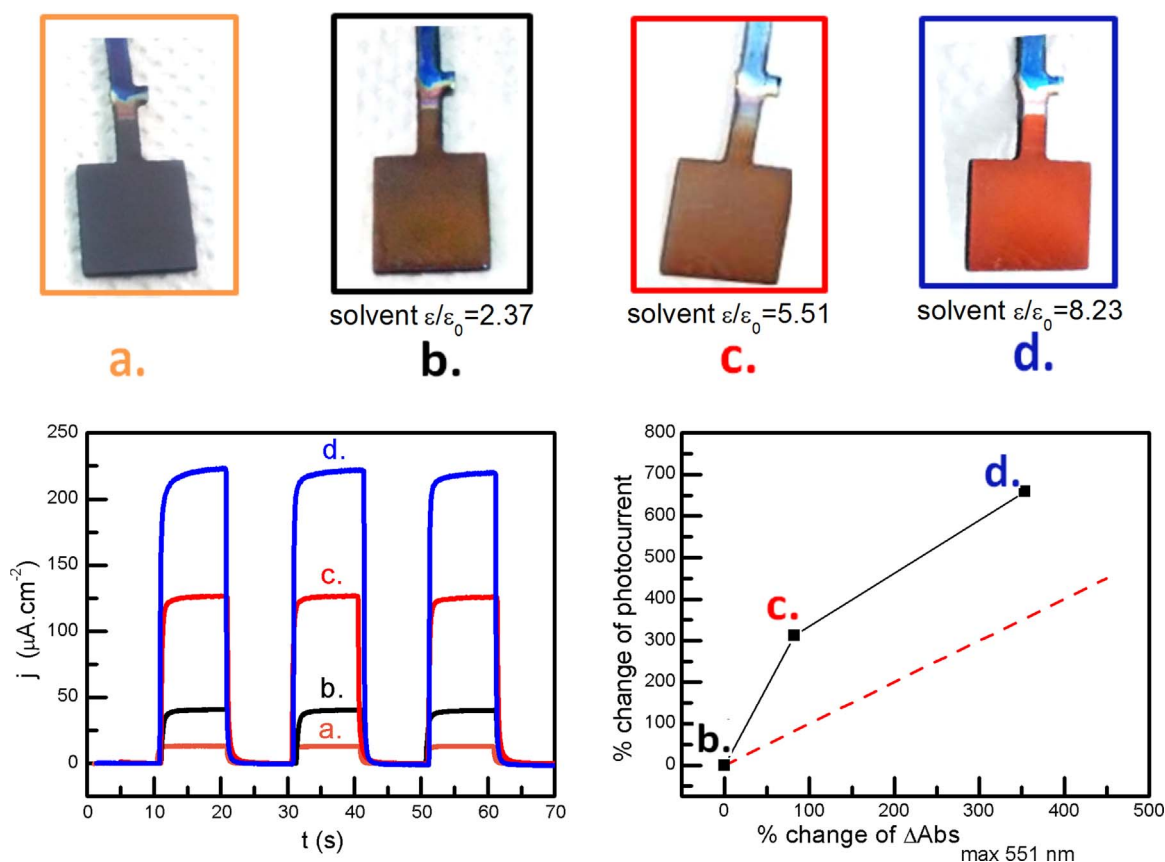


Fig. 7. Above: Photographs of a) TiO₂ nanotubes and of photoanodes obtained by adsorption of CdSe Qdots on TiO₂ nanotubes from colloidal dispersions using as solvents: b) 100% toluene ($\epsilon/\epsilon_0=2.37$), c) 70% toluene – 30% acetone ($\epsilon/\epsilon_0=5.51$) and d) 50% toluene – 50% acetone ($\epsilon/\epsilon_0=8.23$). Below: Profiles of photocurrent development of each photoanode while illuminating with white light (left) and percentage change of photocurrent density vs. percentage change of $\Delta\text{Abs}_{\text{max } 551 \text{ nm}}$ (right). In the last graph, a red dashed line with a slope equal to one indicates the trend for a linear correlation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

colloidal dispersion employing toluene as the solvent. Then, the Ti/TiO₂ nanotube foil was immersed in the colloidal dispersion and the negative absorption spectra registered with time showed the decrease of Qdots concentration in the colloidal dispersion while adsorption on nanotubes surface was taking place (Fig. 3). This procedure was carried out for various Qdots colloidal dispersions of different concentrations. The change of the optical absorption (ΔAbs) with time at 551 nm is proportional to the amount of adsorbed Qdots. ΔAbs eventually reached a constant maximum value after 7 h (3–7 h depending on Qdots concentration). With the results of the maximum ΔAbs at 551 nm and the final Absorbance at 551 nm of the colloidal dispersions of different concentrations, the corresponding isotherm was obtained and adjusted with the Langmuir model (Fig. 4). This result is supported by previous work in [16].

It is worth noting that when the excitonic peaks of diffuse reflectance spectrum of TiO₂ nanotubes after Qdots adsorption and the absorption spectrum of the colloidal dispersion of Qdots are compared, there are no perceptible changes so the optical properties of Qdots after adsorption are retained (Fig. 5).

The adsorption of Qdots on nanotubes over time was also followed by measuring the photocurrent generated by illumination of the photoanode with white light after different immersion times of TiO₂ nanotubes in the concentrated colloidal dispersion of Qdots in toluene (see Fig. S2 in Supporting Information). After 7 h, a constant photocurrent value is achieved as well. This result has been previously reported in [7], where the authors found that after long adsorption times of Qdots on TiO₂ nanotubes a constant photocurrent is reached unlike what happens when conglomerated TiO₂ nanoparticles are employed.

Previous works [6,9,17], reported a poor adsorption uptake of

quantum dots onto TiO₂ nanoparticle conglomerates when toluene is employed as the solvent of colloidal Qdots dispersions, so it was replaced by chloroform or dichloromethane without convincingly explaining the cause of solvent change. In the next section, the results of direct adsorption of CdSe Qdots on TiO₂ nanotubes employing colloidal dispersions with solvents of different polarity are presented.

3.2. Enhanced uptake of CdSe quantum dots adsorbed on TiO₂ nanotubes from colloidal Qdots dispersions with solvents of different polarity and the synergistic effect resulting on the photoanodes efficiency

To study the influence of the polarity of the solvent used to disperse Qdots on the adsorption equilibrium, mixtures of toluene and acetone of different proportions with increasing dielectric constants were employed. The Qdots concentration employed was the value corresponding to the plateau of the isotherm in toluene (see previous section).

First of all the range of polarity of the solvent in which Qdots could still be redispersed was determined (Fig. 6). Qdots are redispersible in 100% toluene up to 40% toluene – 60% acetone and precipitate in mixtures of a higher amount of acetone. In reference [18], a contraction of capping molecules occurring when Qdots are in contact with polar solvents is evidenced. This effect causes a decrease in the distance between capped Qdots, which is enough to overcome the steric repulsion forces between capped Qdots, causing flocculation. Therefore the useful range of solvent polarity that could be studied was from dielectric constant ($d=\epsilon/\epsilon_0$) of 2.5 up to approximately 8. The values of d in the different mixtures of toluene/acetone and acetonitrile/acetone were taken from bibliography [19,20].

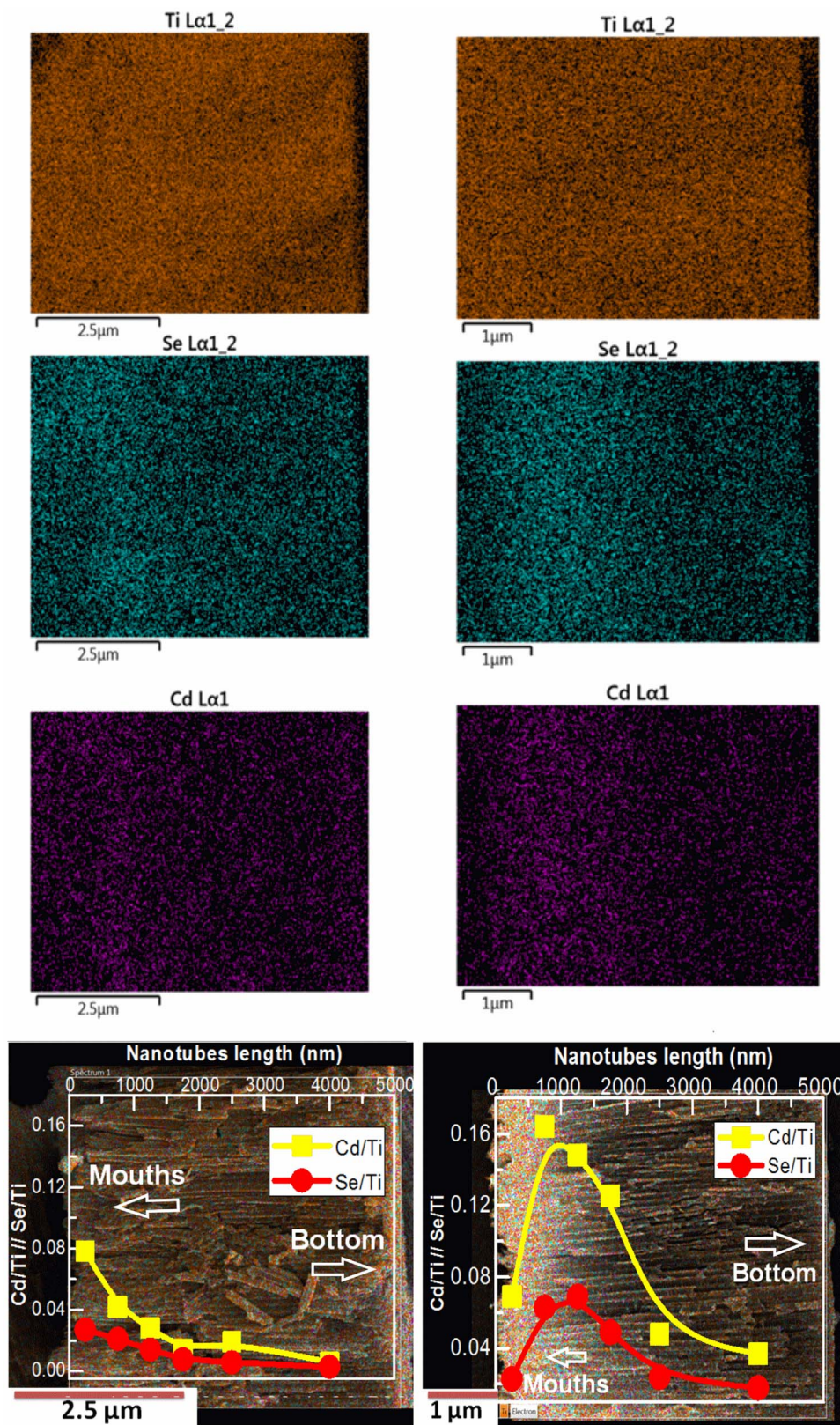


Fig. 8. Mapping of Cd La1, Se La1_2 and Ti La1_2 EDS signals along nanotubes of photoanodes obtained using 100% toluene (left) and 50% toluene – 50% acetone (right) as solvents after achieved maximum adsorption on TiO₂ nanotubes. Below: Normalized signals of Cd and Se with Ti in different portions along nanotubes length to show the distribution trend of Qdots across nanotubes while employing solvents of different polarity in the adsorption.

We found that the polarity of solvents in which Qdots are dispersed plays a major role in the equilibrium of Qdots adsorption onto nanotubes. At first sight it is observed that higher solvent polarity

causes a significant enhancement on the amount of adsorbed Qdots (Fig. 7). This behavior has also been corroborated by using acetonitrile/toluene mixtures, obtaining the same results as with acetone/toluene

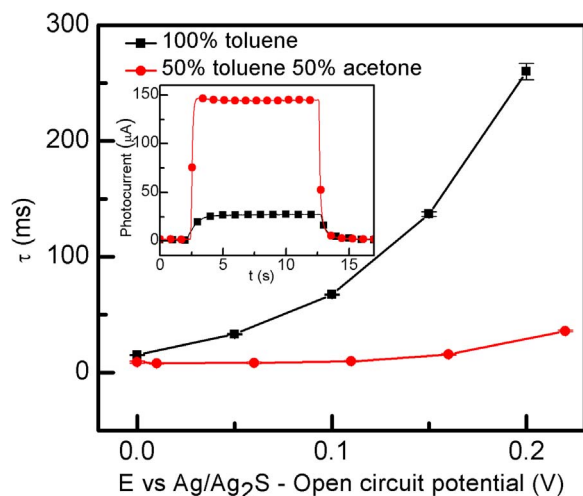


Fig. 9. Electron transport time vs. voltage when Qdots are adsorbed onto TiO_2 nanotubes from 100% toluene (black squares) and from 50% toluene – 50% acetone (red points). These results were obtained by transient photocurrent technique. Inset: Photocurrent development profiles obtained by direct adsorption from both solvents when illuminating photoanodes with white light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mixtures. (see Fig. S3 in Supporting Information).

Considering that the adsorption phenomenon is governed basically by the interaction between the adsorbent (TiO_2 nanotubes), adsorbate (CdSe Qdots) and solvent, an enhancement of the amount of Qdots adsorbed can be due to 3 probable causes:

- Increase of attractive forces between adsorbate and adsorbent,
- Decrease of the solubility of adsorbate in the solvent,
- Decrease of the affinity between solvent and adsorbent.

In this study, we propose that b) is the most plausible cause of the enhancement on the adsorption. Considering that CdSe Qdots are capped with myristic acid and Trioctylphosphine which are mainly non-polar, an increase on the solvent polarity may produce the decrease of its solubility. There is no evidence that supports that cause a) is occurring and cause c) can be also disregarded because the interaction between acetone and toluene (organic aprotic solvents) with TiO_2 cannot be considered important [21].

An interesting fact appears when the proportion of enhancement in the photocurrent produced with white light illumination of the photoanodes of TiO_2 nanotubes and the amount of Qdots adsorbed from colloidal dispersions with solvents of different polarity are correlated (Fig. 7). We found that the increase of the photocurrent is much larger in comparison with the amount of Qdots adsorbed. In other words, there is a non-linear dependence of the photocurrent produced and the quantity of adsorbed Qdots. Employing a mixture of 50% toluene – 50% acetone as solvent, it was found that the 2–3-fold increase on the amount of Qdots adsorbed corresponds to a 7-fold enhancement in the photocurrent produced i.e. an important synergistic effect is observed.

A possible explanation of this effect could arise from the distribution profiles of Cd and Se along the nanotubes obtained by Electron Dispersion Spectroscopy technique. When CdSe Qdots are adsorbed from a colloidal dispersion of 50% toluene – 50% acetone, the maximum of the distribution of Qdots extends deeper in the nanotubes than when the adsorption is performed from 100% toluene colloidal dispersions in which case, the maximum Qdots distribution is located near the mouth of the tubes (Fig. 8). Besides, it is worth mentioning that the information extracted by EDS technique and absorption spectroscopy is the same, i.e. that the amount of Qdots adsorbed from the acetone-toluene mixture is about 2–3 times higher compared when pure toluene is employed (see Table S1 in Supporting information).

Therefore, the majority of electrons that are photogenerated in Qdots must travel a shorter distance across the nanotubes to reach the contact in the former case, reducing the likelihood of experiencing recombination reactions. In other words, electrons are generated closer to the electrical contact in order to arrive there quickly. This fact was supported by the results of transient photocurrent technique (Fig. 9). Electron transport time along the nanotubes in direction to the electrical contact is obtained by this technique [22–24] by adjusting the decay of the photocurrent produced by short pulses of light with a mono exponential decay function. This is valid only when electron recombination time is slower in comparison to electron transport time [23]. In our case, by previous studies using charge extraction method [12] electron recombination time was shown to be in the second time scale while the times obtained from transient photocurrent decays are in the millisecond time scale. Thus it is valid to associate these decay times with electron transport time across the nanotubes. It was found that when Qdots are adsorbed onto nanotubes from colloidal dispersions of 50% toluene – 50% acetone, electron transport is faster (lower transport times) than with 100% toluene colloidal dispersions, having in mind that electronic transport time also depends on the potential applied to the photoanode.

4. Conclusions

Direct adsorption method for the optical sensitization of TiO_2 nanotubes with previously synthesized CdSe Qdots to achieve more efficient photoanodes was studied. Particularly, it was found that the effect of the polarity of the colloidal dispersion solvent of Qdots proved decisive on the adsorption equilibrium on TiO_2 nanotubes and on the efficiency of the obtained photoanodes. It was found that increasing the polarity of the employed solvent, the amount of Qdots adsorbed is higher. The possible cause is that CdSe Qdots synthesized are capped with non-polar molecules so an increase on the solvent polarity may produce a decrease of its solubility. Moreover, the photocurrent generated by illumination of the resulting photoanodes is enhanced too. Nevertheless it was found that the photocurrent increase is much higher than that expected according to the increase in the amount of Qdots adsorbed. This synergistic effect could be explained by the analysis of the distribution profiles of Cd and Se along the nanotubes and transient photocurrent technique results. When direct adsorption occurs from colloidal Qdots dispersions employing more polar solvents, the maximum of the distribution of Qdots extends deeper in the nanotubes in comparison with the adsorption from 100% toluene colloidal dispersions. Therefore, the majority of electrons that are photogenerated in Qdots must travel a shorter distances across the nanotubes to reach the contact in the former case, increasing the efficiency of the photoanode.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2017.02.015.

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