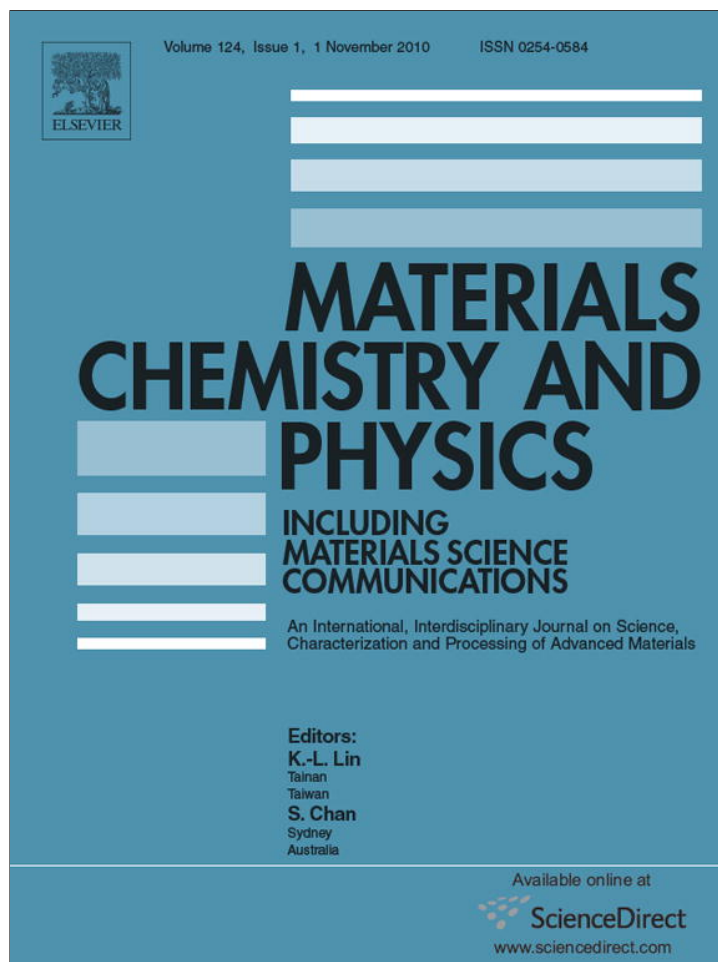


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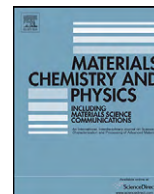
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Influence of cysteine adsorption on the performance of CdSe quantum dots sensitized solar cells

Xueqing Xu^{a,*}, Sixto Giménez^b, Iván Mora-Seró^{b,*}, Antonio Abate^b, Juan Bisquert^b, Gang Xu^a^a Guangzhou Institute of Energy Conversion, Renewable Energy and Gas Hydrate Key Laboratory of Chinese Academy of Sciences, Guangzhou 510640, China^b Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, Castelló 12071, Spain

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ABSTRACT

The surface of mesoporous TiO₂ electrodes has been functionalized with cysteine using different solutions for the subsequent attachment of colloidal CdSe QDs solved in toluene. The adsorption behavior of both cysteine and CdSe QDs on the TiO₂ nanoparticles has been investigated by Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy. The photoelectrochemical properties of the CdSe QDs sensitized TiO₂ electrode have been characterized by using UV–vis spectroscopy, photocurrent-potential measurement, open-circuit voltage decay, and cyclic voltammetry. It is found that the amount of adsorbed cysteine becomes excessive when highly concentrated aqueous solutions were adopted instead of toluene solutions, leading to a blocking for the diffusion and adsorption of the CdSe QDs. This is translated into a decrease of light harvesting and short circuit current (J_{sc}) in the solar cell devices. On the other hand, it is suggested that the large amount of adsorbed cysteine on the surface of the TiO₂ electrode could reduce the electron recombination at the interface between the TiO₂ electrode and the electrolyte. As a consequence, the charge transfer resistance and fill factor became larger, and the electron lifetime became longer.

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1. Introduction

Organic dye-sensitized Nano-crystalline TiO₂ solar cells (DSSCs) have attracted significant attentions as low-cost photovoltaic devices [1,2]. As inorganic light absorbers, semiconductor quantum dots (QDs) have drawn great interest as light sensitizers in QDSSCs for the following reasons: Firstly, its tunable band edge offers new opportunities for harvesting light energy in most of the visible region of the solar spectrum [3]. In addition, QDs exhibit a larger extinction coefficient than organic dyes [4]. It has been also suggested that QDs allow to utilize hot electrons or generate multiple charge carriers with a single photon [5,6]. Although the conversion efficiencies of QDSSCs are in this moment far away of the efficiencies of DSSCs, in the last 2 years the maximum reported efficiencies have increased in a factor 2–3, highlighting the enormous potentiality of this kind of solar device. Many authors consider QDSSCs as analogous to DSSCs, but this is not completely true. For the use of QDs as light absorber it is necessary to take into account the specific properties of QDs (role of surface states, stability, preparation, attaching mode to TiO₂, ...). In this sense the study of these specific properties of QDSSCs is very important in order to optimize

their performance. In this work we will focus in the role of the linker molecule used to attach colloidal QD to TiO₂ surface, showing that not only the linker molecule (we compare cysteine and MPA) but also the treatment (we compare adsorption from water and from toluene solutions) carried out to attach these molecules to TiO₂ influences the final performance of QDSSCs.

In order to study these properties colloidal CdSe QDs have been used as light sensitizers. CdSe QDs have received particular attention due to their relatively easy synthesis and also because of its suitable bandgap (1.7 eV for bulk material). The properties of the QDs can be carefully tailored in the colloidal synthesis, but in this case is necessary to develop a method to attach the colloidal QDs to the semiconductor nanostructured matrix. To assemble the CdSe colloidal QDs onto the large bandgap semiconductors such as TiO₂, ZnO, or SnO₂, bifunctional linkers of HS–R–COOH, such as mercaptopropionic acid (MPA), thiolacetic acid (TAA), mercaptohexadecanoic acid (MDA), and thioglycolic acid (TGA) have been adopted [7,8]. Recently, Mora-Seró et al. have shown that the incident photon to charge carrier generation efficiency (IPCE) can be improved by a factor of 5–6 if cysteine is used as a linker instead of MPA [8]. In this study, different cysteine solutions (varying both solvent and concentration) were adopted to improve the linkage between the TiO₂ electrodes and CdSe QDs. The light harvesting performance and the photoelectrochemical properties of the CdSe QDs sensitized solar cells (QDSSCs) previously functionalized by different cysteine solutions have been investigated.

* Corresponding authors.

E-mail addresses: xuxq@ms.giec.ac.cn (X. Xu), sero@fca.uji.es, sero@exp.uji.es (I. Mora-Seró).

Table 1

Description of the different cysteine solutions employed in the present study and MPA solution employed as a reference.

Solvent	Concentration (mol l ⁻¹)	Dipping time	Temperature (°C)
Toluene	Saturation (ca. 0.022)	12 h to 7 days	25
H ₂ O	0.4	1 h	70
MPA in ACN	1.1	12 h	25

2. Experimental

2.1. Preparation of CdSe QDs

CdSe QDs were prepared by a solvothermal method as reported by Wang et al. [9]. Briefly, selenium reacted with cadmium myristate in toluene in the presence of oleic acid and trioctylphosphine (TOP). The reaction took place at 180 °C in an autoclave for 15 h. Finally, the obtained CdSe QDs solutions were purified by precipitation in ethanol, isolation by centrifugation and decantation for three times.

2.2. Preparation of CdSe QDs sensitized TiO₂ electrodes

Dyesol DSL 18NR-AO TiO₂ paste (20–400 nm particle size) has been spread onto bare SnO₂: F(FTO) glass substrates previously coated with a compact TiO₂ layer in the thickness of about 100 nm by spray pyrolysis. After being heated at 120 °C for 15 min, the TiO₂ electrodes were sintered at 450 °C for 30 min. The thickness of the TiO₂ films was approximately 10 μm as measured by a Dektak Profilometer from Veeco. After heating, the TiO₂ electrodes were immersed into the cysteine solution. Two different solvents were tested (water and toluene) as shown in Table 1. Subsequently, the substrates were rinsed with the correspondent solvent. As a reference, MPA in acetonitrile solution was also studied. Finally, the modified electrodes were dipped into the CdSe toluene solutions for at least 24 h.

2.3. Fabrication of CdSe QDs sensitized solar cells

The CdSe QDSSCs were prepared by assembling a QDs sensitized TiO₂ electrode with a Pt counter electrode by using a thermoplastic frame (Dupont™ Surlyn® 1702, thickness 25 μm). The Na₂S_x redox electrolyte consisted of 1 M Na₂S, 1 M S, and 0.1 M NaOH in Milli-Q ultrapure water.

2.4. Optical and electrochemical measurements

The UV–vis reflectance spectra of the samples have been carried out with a Shimadzu UV-2401 UV–vis spectrophotometer. The Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectra of the surface of the TiO₂ films have been obtained by a Nicolet/Nexus 670 FT-IR spectrophotometer. The TiO₂ films (10 μm in thickness) coated with cysteine or CdSe QDs were put onto the ZnSe prism to collect the ray reflected from the surface of the films. The ATR-FTIR spectra were obtained in air for dry films. Photocurrent-potential, open-circuit voltage decay and cyclic voltammetry curves were obtained with a FRA equipped Autolab PGSTAT-30 electrochemical work station. A solar simulator equipped with a 1000 W ozone-free xenon lamp and an AM 1.5 G filter (Oriel) has been used for illumination. The light intensity was adjusted with an NREL calibrated Si solar cell with a KG-5 filter to 1 sunlight intensity (100 mW cm⁻²).

3. Results and discussion

The solubility of cysteine in toluene is very low (less than 0.022 mol l⁻¹) as it has been experimentally checked. In order to increase the amount of adsorbed cysteine and consequently that of CdSe QDs onto the TiO₂ surface, a 0.4 mol l⁻¹ aqueous cysteine solution was investigated. Fig. 1 shows the UV–vis reflectance spectra of the CdSe QDs sensitized TiO₂ electrodes for different linker solutions accordingly to Table 1. For cysteine in toluene, in our experiments a dipping time from 12 h to 7 days has been investigated (at room temperature). We have checked that in this time range, the dipping time has not any influence on the adsorption of CdSe quantum dots. However, for the ATR-IR measurement, the sample with the dipping time of 7 days has been used. For the cysteine in water, in order to enhance the diffusion of cysteine into the pores of the TiO₂ electrodes, and to decrease the dipping time of the TiO₂ electrode in water which may has some extra influences to the TiO₂ films, a temperature of 70 °C and the dipping

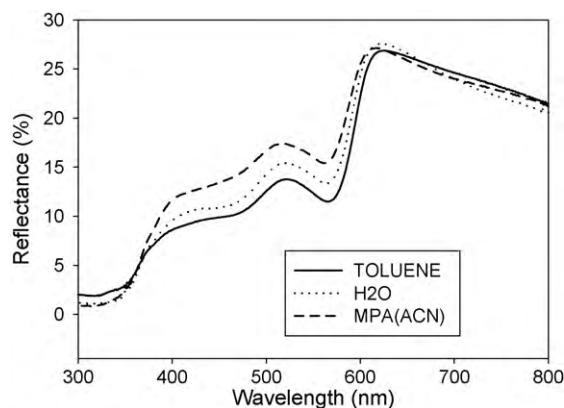


Fig. 1. The UV–vis reflectance spectra of CdSe sensitized TiO₂ electrodes for the different linker solutions.

time of 1 h has been used. The absorption peak around 564 nm is due to the first excitonic absorption of 2.8 nm CdSe QDs [8]. The absorbance of the QDs sensitized TiO₂ electrode at 564 nm became slightly weaker when the aqueous cysteine solutions were adopted, indicating a lower amount of adsorbed CdSe QDs. This is believed to be caused by an excess of adsorbed cysteine on the surface of the TiO₂ nanoparticles leading to a partial blocking of the nanopores. In comparison with MPA, the absorbance of the QDs sensitized TiO₂ electrode at 564 nm became higher when the cysteine solutions were used, as it has been recently reported [8].

Fig. 2 shows the ATR-FTIR spectra of the TiO₂ films, the cysteine functionalized TiO₂ films using both solutions and the CdSe sensitized TiO₂ films (cysteine in toluene solution was used). The vibration band assignments of the spectra are shown in Table 2 [10]. Comparing the TiO₂ films functionalized with both cysteine solutions, the characteristic vibration modes of the IR curves are almost identical. However, the intensities of the adsorption peaks were stronger for the aqueous solution. Additionally, the –SH and –COOH groups could be observed only for the aqueous solution. This means that the amount of adsorbed cysteine on TiO₂ is larger for aqueous solutions since the solubility of cysteine in water is much higher compared to that in toluene. For the CdSe sensitized TiO₂ films, the absorption band around 1589 cm⁻¹ due to the COO–Ti groups as shown in curve (b) and curve (d) was overlapped with the absorption band around 1620 cm⁻¹ which can be attributed to H₂O. On the other hand, the absorption bands around 2925 cm⁻¹ and 2857 cm⁻¹ were attributed to the vibration mode of –CH₃ groups of fatty acids (oleic acids and myristic acids coming from the QD preparation and

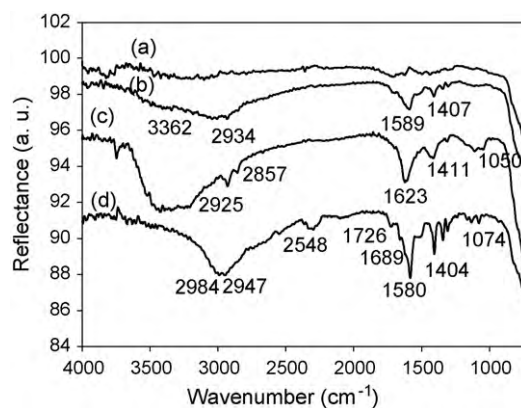


Fig. 2. The ATR-FTIR spectra of (a) the TiO₂ films, (b) the cysteine coated TiO₂ films for the toluene solution, (c) the CdSe sensitized TiO₂ films (cysteine in toluene solution was used), and (d) the cysteine coated TiO₂ films for the aqueous solution.

Table 2

The vibration band assignments of the ATR-IR spectra for the TiO₂ films coated with cysteine and CdSe QDs.

		TiO ₂ /Cys. toluene	TiO ₂ /Cys./ QDs	TiO ₂ /Cys. water
-NH ₂	ν_s N-H/cm ⁻¹	3362, 2934	/	2947
	δ_{as} NH ₃ ⁺ /cm ⁻¹	1695	/	1689
	δ_s NH ₃ ⁺ /cm ⁻¹	1532	/	1520
-CH ₃	ν_{as} CH ₃ /cm ⁻¹	/	2925	/
	ν_s CH ₃ /cm ⁻¹	/	2857	/
-SH	ν S-H/cm ⁻¹	/	/	2548
-COOM	ν_s O=C=O/cm ⁻¹	1589	1590, 1620	1580
	ν_{as} O=C=O/cm ⁻¹	1407	1411	1404
-COOH	ν C=O/cm ⁻¹	/	/	1726
	ν O-H/cm ⁻¹	/	/	2984
C-NH ₂	ν C-N/cm ⁻¹	1080	1050	1074

Table 3

Photovoltaic parameters of the QDSSCs for both cysteine solutions.

Solvent	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	η (%)
Toluene	0.49	3.8	0.22	0.41
H ₂ O	0.50	3.0	0.35	0.53

attached to the QD surface) and TOP which was coated on the surface of CdSe QDs. All these phenomena suggested that most of the surface of the CdSe QDs was still covered with fatty acids and TOP, and just few of these molecules have been exchanged by cysteine. The adsorption band around 1695 cm⁻¹ and 2934 cm⁻¹ attributed to the NH₃⁺ groups and the N-H groups have disappeared, which suggested that the amina group in cysteine can interact with the slightly acidic surface of TiO₂. This interaction can push closer QDs to TiO₂ surface explaining the better results for QDSSCs obtained using cysteine as linker molecule in comparison with MPA and TGA [8].

Fig. 3 shows the photocurrent–voltage curves of the CdSe QDSSCs for both cysteine solutions. The photovoltaic parameters of the cells are shown in Table 3. The V_{oc} of both tested cells is almost identical. Conversely, J_{sc} was higher for the toluene solution in good

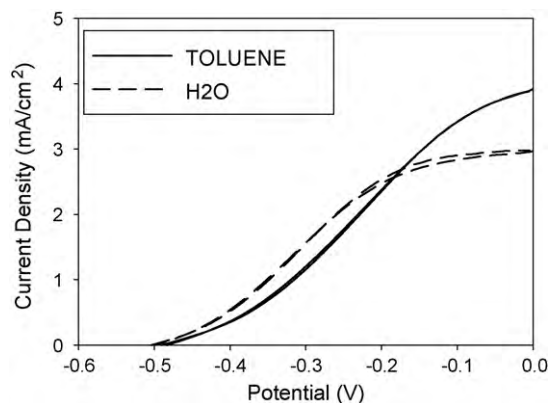


Fig. 3. The *j*-*V* curves of the CdSe QDSSCs for both cysteine solutions.

correspondence with the results showed in Fig. 1. However, the fill factor was much higher for the water solution. This suggests that the large amount of adsorbed cysteine on TiO₂ may reduce electron recombination at the interface between the TiO₂ electrodes and electrolyte, leading to higher recombination resistance and higher fill factor [11].

Fig. 4a shows the open-circuit voltage decay (OCVD) curves for the CdSe QDSSCs for the different cysteine solutions. The electron lifetime τ can be derived from the OCVD curves as follows [12,13]:

$$\tau = -\frac{kT}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (1)$$

where *k* is the Boltzmann constant and *T* is the absolute temperature. Fig. 4b shows the electron lifetime determined from OCVD. The electron lifetime was higher for the water solution, indicating that the interfacial charge transfer has been suppressed by the cysteine molecules adsorbed on the TiO₂ surface [14]. This perfectly agrees with the results showed in Fig. 3.

Fig. 5a shows the cyclic voltammetry (CV) curves of the CdSe QDSSCs for both cysteine solutions and Fig. 5b shows the total resis-

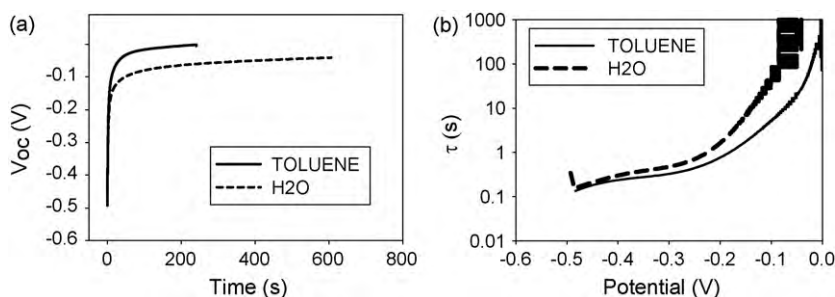


Fig. 4. The open-circuit voltage decay curves (a) of the CdSe QDSSCs and the electron lifetime (b) for the different cysteine solutions.

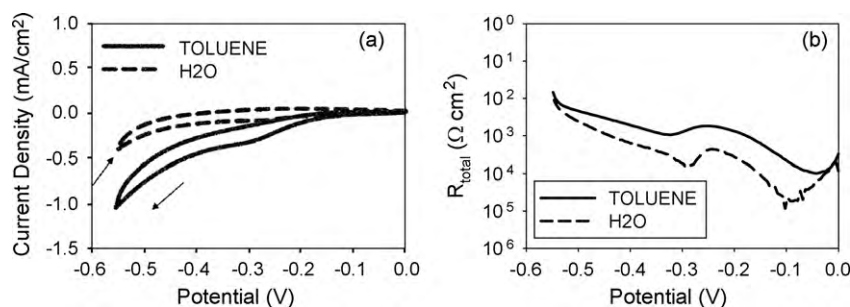


Fig. 5. The cyclic voltammetry curves (a) and the total resistance in dark (b) for the CdSe QDSSCs for both cysteine solutions.

tance of the cells calculated from CV, averaging anodic and cathodic currents, according to following formula [15,16]:

$$R_{\text{total}} = \frac{dV}{di} \quad (2)$$

The current in dark was smaller and the total resistance was larger for the water solution, indicating a lower electron recombination if the variation of the series resistance is ignored and assuming that the main contribution to the total resistance, R_{total} , is the recombination resistance [11]. This agrees with the results from OCVD (Fig. 4) and the j - V curve (Fig. 3). The small peak at -0.3 V was attributed to surface states as it has been previously pointed out [11].

4. Conclusions

From the obtained experimental results, it is clear that the higher solubility of cysteine in water (compared with toluene), leads to a higher amount of adsorbed molecules onto the TiO_2 substrates. The over-adsorption of cysteine on the surface of the TiO_2 electrodes when the water solution is used, leads to a partial inhibition for the adsorption of CdSe QDs. These QDs do not completely substitute their surfactant molecules by cysteine as illustrated by the ATR-FTIR measurements. The photoelectrochemical behavior of the tested electrodes suggests that a large amount of cysteine on the surface of the TiO_2 electrodes could reduce the electron recombination at the interface between the TiO_2 electrodes and electrolytes, pointing out the importance of surface treatments in QD sensitized cells. On the other hand the amina group can interact with the slightly acidic surface of TiO_2 , reducing the distance between QD and TiO_2 , increasing the performance of QDSSCs when this linker is used.

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