Effect of the electrolyte composition on the response of a TiO$_2$|CDS-Based Photoanode

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ABSTRACT

Sulfide solutions are the most widely selected electrolyte for the photoelectrochemical characterization of metal chalcogenide (like CdS and CdSe) based solar cells because its good hole scavenging properties and improved stabilization of the semiconductor sensitizer. However, the photocurrent values of CdS sensitized TiO$_2$ photoanodes depend on the sodium sulfide analytical concentration and pH values in the electrolyte solution. In this report, we show that the mass transport of the sulfide hole scavenger is the main limiting process and if its concentration is lower than the HO$^-$ concentration there is a competition for adsorption sites onto TiO$_2$ surface, decreasing the photocurrent value. A careful optimization of these two variables it is necessary in order to attaining high overall photoelectrochemical cell efficiency.

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1. Introduction

Nanostructured semiconductor films have been successfully employed as photoanodes in photoelectrochemical cells [1]. The photoinduced charge separation achieved using the band gap excitation of the semiconductor films is crucial in maximizing the photocurrent generation efficiency. One approach to maximize the charge separation in such films involves coupling two different semiconductor materials. Sequential deposition of metal oxides like TiO$_2$ and metal chalcogenide films like CdS on an optically transparent electrode promotes charge separation by accumulating electrons and holes in two different semiconductor layers. The electrons are then expected to be transported to the collecting surface with minimal charge recombination [2].

In these cells the electrolyte which separates the anode and cathode regenerates the photoactive component facilitating the interfacial electron transfer. Dissolved in the electrolyte are redox couples which are used to react at the surfaces of the counter and working electrodes. The maximum photovoltage one would expect after the excitation of the semiconductor/electrolyte interface is the difference between conduction band and the redox potential of the electrolyte. This voltage can be manipulated by varying the redox potential of the couple. In consequence, this value and how

the components of the solutions interact with both electrodes are of great importance and play a crucial role in the performance of these cells [3].

The photo-conversion efficiency depends not only on the efficiency of light harvesting by the sensitizer but also on the efficiencies of transport of photogenerated electrons and holes in the cell [4]. In turn the efficiency of transport of the photo-formed electrons depends on the efficiency of electron injection from the sensitizer, efficiency of electron transport in nanostructured TiO$_2$ phase and efficiency of electron collection at the transparent electrode. In a similar way the efficiency of transport of the photo-generated holes can be related with efficiency of hole injection into the electrolyte, transport in the electrolyte phase, and efficiency of hole collection at the counter electrode. In sum, it is evident that the efficiency of the transport of electrons and holes through the whole circuit are strongly influenced by the nature of the redox electrolyte.

In a TiO$_2$ based liquid junction system, not all redox couples are compatible with all sensitizers. In the case of cells sensitized by chalcogenides like CdS- and CdSe- sulfide/polysulfide redox couple is so far the most effective not only in scavenging the photogenerated holes but also in avoiding the effects of photocorrosion [5,6]. It was reported that the S^{2-}/S$_n^{2-}$ redox couple also produces a significant shift in the conduction band energies of many chalcogenides toward negative potentials This effect arises from the surface interaction with sulfide (electron donor) as the metal chalcogenide surface becomes negatively charged [7]. Anodic corrosion in most

of the chalcogenides sensitizers is thermodynamically feasible because the photogenerated holes can participate in surface oxidation. The presence of sulfide, however, brings in stability because it scavenges the holes with a competitive kinetics.

Recombination of photogenerated charge carriers in chalcogenide nanocrystals is also an undesired process as it competes with the electron injection into TiO_2 [6,8]. On the other hand, the electron injection to TiO_2 can be facilitated by optimizing the energy difference between the conduction bands of sensitizer and TiO_2. One possibility is to shift the conduction band edge of TiO_2 by inducing the protonation of surface groups [9,10]. Regarding this last aspect, an increased rate constants with decreasing pH was found, supporting the idea that conduction band alignment is important to attain an efficient charge injection process, and hence higher photoconversion [8].

Acid base properties of TiO_2 may also influence the role of pH in the photoconversion process [10]. Charged surface species like TiO^{2-} or $TiOH^-$ at alkaline pH values have been reported in relation to photocatalytic activity of TiO_2; it was argued that electrostatic interaction due to the increase of charged particles on the surface affect positively or negatively the photodegradation of dyes and organic sulfides by TiO_2 [11,12].

Although sulfide is currently the couple of choice as shown in the above considerations, there are so many processes that determine the overall efficiency of the cell that is difficult to find the optimal condition of the electrolytic solution in terms of pH and concentration. Additionally sulfide ion dissolved in aqueous solutions has shown to be a complex system with complicate acid-base and redox equilibria. Purbaix diagrams reported in the literature for this system indicate that is thermodynamically quite difficult to obtain free sulfide ion and polysulfide derivatives; and perhaps the existence of the last ones is mainly given by its slow redox kinetics towards the formation of oxoanions or other sulfide oxidation products [13]. As a consequence, there are numerous discrepancies and contradictions in the information reported in the literature. We present here a systematic study of the photocurrent response of CdS sensitized TiO_2 photoanodes at different sulfide concentration and pH values to evaluate the experimental conditions giving rise to higher photocurrent values.

2. Experimental

2.1. Materials

Sodium Sulfide (Tetrahedron), Cadmium Acetate (Anedra), Titanium(IV) tetraisopropoxide, Titanium(IV) oxide, anatase nanopowder (25 nm, Aldrich) and ethanol (Dorwil) were used as received to prepare CdS sensitizer and TiO_2|CdS films. Indium Tin Oxide coated glass cuvette slides (ITO glasses, Delta Technologies) were used as optically transparent electrode. Sodium hydroxide and hydrochloric acid (Cicarelli) were used to adjust the solution pH values. All solutions were prepared with ultrapure water (Mili Q-Mili RO system).

2.2. Preparation of TiO_2|CdS film photoanode

CdS was obtained by precipitation, mixing 0,1 M sodium sulfide and 0,1 M cadmium acetate solutions, filtering, washing with ultrapure water and drying. A mixture containing 90% w/w of TiO_2 nanopowder and 10% w/w of CdS (Ti:Cd atomic ratio = 13) was finely divided and homogenized in a mortar. A suspension of 0.25 g of TiO_2|CdS mixture in 1 mL of absolute ethanol was obtained after vigorous shake and sonication during 30 minutes. A volume of 150 μL of Titanium(IV) tetraisopropoxide was added to the previous suspension to obtain the final casting suspension.

This last dispersion was doctor bladed onto an ITO glass following the experimental details reported in [14]. After solvent evaporation, the deposited layer was sintered at 450 °C during 30 minutes to remove any organic residues and moisture as well as to obtain a mesoporous TiO_2|CdS layer.

2.3. Photoelectrochemical Measurements

All experiments were carried on a three electrode electrochemical cell adapted in a standard 1 cm path length spectrophotometric cuvette using a platinum wire as counter electrode and a Ag|AgCl|KCl$_{(sat)}$ as reference electrode. The photoanode was attached to one of the transparent faces of the cuvette with the conducting surface facing towards the solutions and back-face illuminated. Photoanodes were illuminated with a collimated, UV filtered light source (Kratos LH-150/l 150 W Xe). The illuminated area was 0.13 cm^2, with an irradiation intensity of 100 mW cm^{-2}. Photoelectrochemical measurements were conducted using an Autolab PGSTAT101 potentiostat/galvanostat. All measurements were performed at a potential corresponding to the dark open circuit potential (three-electrode configuration).

3. Results and Discussion

Sulfide solutions have been the preferred electrolyte for the photoelectrochemical characterization of photoanodes based on CdS semiconductor [5,15]. The main reason for this is the good hole scavenging properties of sulfide, from a kinetics and a thermodynamics point of view, and the improved resistance to corrosion of CdS in this electrolyte. Most reports of CdS sensitized photoanodes indicate that the use of sulfide solutions at high concentrations and extremely high pH values (pH∼ 13) are the best choice for a good photoelectrochemical performance [16]; however there are no clear evidences of the optimum analytical concentration and pH values necessary to obtain a reasonable good photoelectrochemical performance of CdS sensitized photoanodes. Some reports indicate that a high pH value is necessary to ensure the existence of the ion S^{2-} in the electrolyte [13]; however, it is very well known that S^{2-} is a strong base (Kb> 10) and its free concentration in an aqueous electrolyte is negligible. Due to this, we will consider that solutions prepared with sodium sulfide, with pH values ranging from 9 to 14, have HS^- as the main free sulfide derivative species.

In this report we evaluate the dependence of photocurrent values of CdS sensitized TiO_2 photoanodes at different analytical concentration of sodium sulfide and different pH values in the electrolyte solution.

Fig. 1 shows the photocurrent profile of a CdS|TiO_2 photoanode at different HS^- concentration when illuminated with white light. Clearly there is an optimum, intermediate concentration value that leads to a maximum photocurrent record. Lower HS^- concentration (1 mM, Fig. 1a) shows a steady photocurrent smaller than that developed at the beginning stage of illumination, while higher sulfide concentration leads to a decrease of the steady photocurrent value.

Fig. 2 summarizes the dependence of steady state photocurrent values as a function of the HS^- concentration. Clearly, for the evaluated experimental conditions, there is an optimum HS^- concentration of 0.010 M, which gives the maximum photocurrent recorded.

Low HS^- concentration values give smaller photocurrent. It can be argued that a lower concentration decreases the rate of the hole scavenging reaction; however it seems the mass transport of HS^- is mainly responsible for the small photocurrent value at low HS^- concentration values. Fig. 3 compares the photocurrent profiles obtained at different HS^- concentration values for quiescent
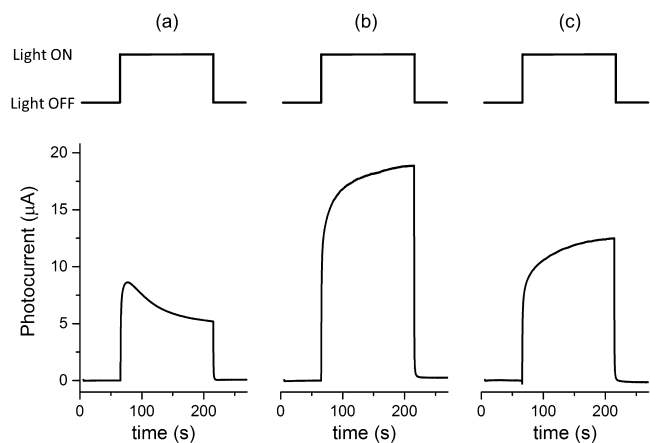
Fig. 1. Photocurrent measurements of TiO$_2$|CdS at different HS$^-$ concentration values: a) 1 mM (pH= 10.7), b) 10 mM (pH= 11.7), c) 100 mM (pH= 12.8).
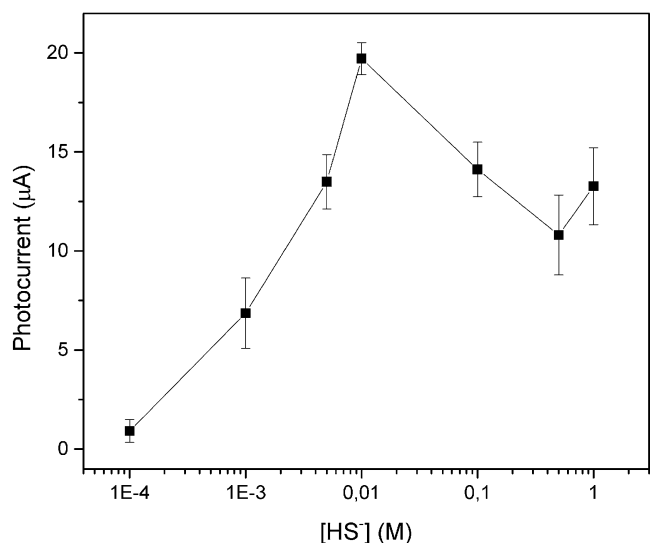

Fig. 2. Stationary photocurrent values of TiO$_2$|CdS at different HS$^-$ concentration values. The error bars are the range of six different measurements.

oxygen free electrolyte and convection forced by nitrogen bubbling. Clearly, convection of the electrolyte has an effect on the rate of the hole scavenging reaction and the photocurrent value reaches a constant of 20 μA at two different HS$^-$ concentrations (5 mM and
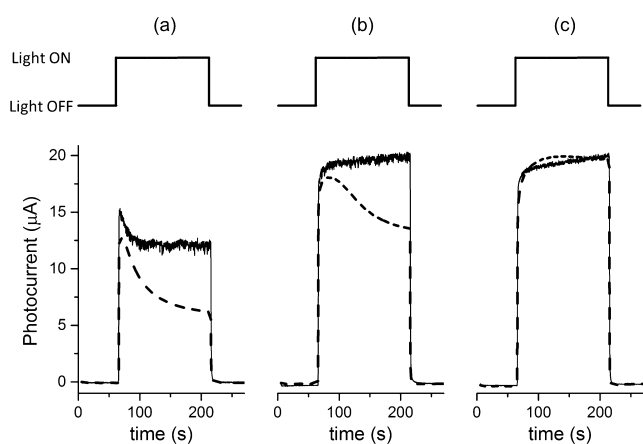

Fig. 3. Photocurrent measurements of TiO$_2$|CdS with (continuous line) and without (dash line) N$_2$ bubbling, at different HS$^-$ concentration values: a) 1 mM, b) 5 mM, c) 10 mM.
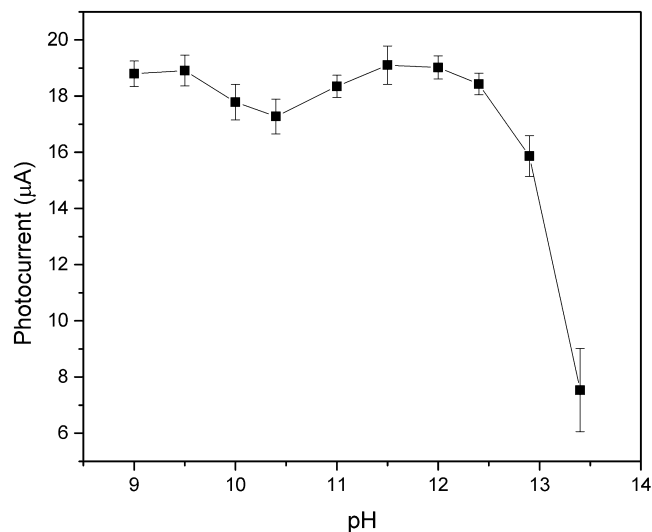

Fig. 4. Photocurrent of TiO$_2$|CdS in 10 mM HS$^-$ electrolyte, at different pH values. The error bars are the range of five different measurements.

10 mM; Fig. 3b and 3c respectively). This last observation evidences that even at low HS$^-$ concentration values (∼5 mM) the hole scavenging reaction is mainly dominated by HS$^-$ mass transport and that the reaction kinetics does not depend on the HS$^-$ concentration value. These previous results were recorded with the use of HS$^-$ solutions with different pH values, given by the basic nature of sodium sulfide. Then, the observed trend would be given by a change of the electrolyte pH value. Fig. 4 shows the dependence of the steady photocurrent as a function of the electrolyte pH value, at a constant HS$^-$ concentration (10 mM). It can be observed that the steady photocurrent is constant (considering the error bar overlapping) up to a pH= 12.5; beyond this pH value the photocurrent suddenly decreases. This decrease could not be associated with and acid-base equilibrium involving S^{2-} and HS$^-$, because the acid constant for the last is very small (pK$_{a2}$ > 15) [13,17–19]. It should be noted, from Fig. 4, that at pH > 12.5 the HO$^-$ concentration is considerable high, in fact, higher than the HS$^-$ concentration used in these experiments (10 mM). Then, a simpler explanation for this trend could arise from a competitive ionic exchange between HO$^-$ and HS$^-$ over the available adsorption sites on CdS. As HO$^-$ is not a good hole scavenger, when compared to HS$^-$, an increase of the HO$^-$ concentration hinders HS$^-$ to adsorb on CdS; this implies a decrease of photocurrent. Additional evidence for this fact is shown in Fig. 5, where two photocurrent profiles at different HS$^-$ concentration with the same pH value are shown. Higher HS$^-$ concentration, without changes in the HO$^-$ concentration, produces a photocurrent increase. It should be noted that this increase reaches a value of 15 μA, the same constant value obtained in the trend observed in Fig. 2 at high HS$^-$ concentration.
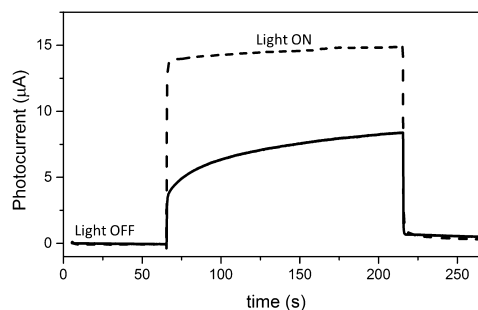

Fig. 5. Photocurrent measurement of TiO$_2$|CdS at pH= 13.3. HS$^-$ concentration: 10 mM (continuous line) and 100 mM (dash line).
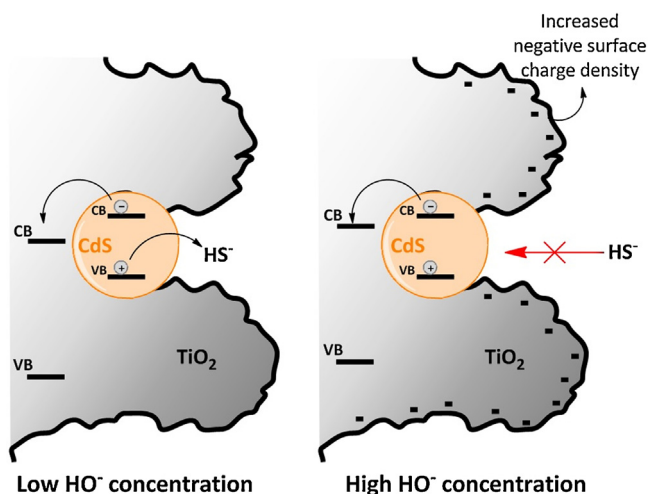
Fig. 6. Scheme showing the electrostatic hindrance of HS$^-$ over negatively charged TiO$_2$.

There are previous reports of band shifting of TiO$_2$ at increasing pH values that would in principle modify the band alignment with CdS and produce a slower electron injection from the sensitizer to TiO$_2$ conduction band [8]; however, the evidence shown in Fig. 5 cannot be explained just by a lack of band alignment. If this were the case, an increase of HS$^-$ concentration at a high pH value, would not improve the electron injection efficiency; rather an improvement of the hole scavenging process would be responsible of the observed increase of photocurrent. As photogenerated holes reside in the CdS valence band, is not expected that a shift of the TiO$_2$ valence and conduction bands due to an increase of HO$^-$ concentration would have any effect on the hole scavenging process (Fig. 6). Accordingly, an electrostatic hindrance of HS$^-$ to reach the TiO$_2$ membrane, now with more negative charge on its surface (HO$^-$ adsorption or TiO$^-$ surface sites), is a simpler explanation for the observed evidences (Fig. 6).

4. Conclusions

It has been shown that the mass transport of the hole scavenger (HS$^-$) is the main limiting process towards getting an optimum photocurrent value of the CdS|TiO$_2$ sensitized photoanode. Actual concentration of HS$^-$ has little effect on the hole scavenging reaction if its concentration is higher than the HO$^-$ concentration, which has a deleterious effect on the photocurrent when it begins to compete by adsorption sites. Additional research is going through to establish the relative surface excess of HO$^-$ and HS$^-$ over TiO$_2$ and CdS.

In summary, a careful optimization of the HS$^-$ concentration is needed on any particular thin layer cell configuration to ensure enough mass transport kinetics. On the other hand, the HO$^-$ concentration should always be smaller than the HS$^-$ concentration, independently on the cell configuration.

References

[1] B. O'Regan, M. Gratzel, Nature 353 (1991) 737.
[2] N. Chandrasekharan, P.V. Kamat, J. Phys. Chem. B 104 (2000) 10851.
[3] P.V. Kamat, K. Tvrdy, D.R. Baker, J.G. Radich, Chem. Rev. 110 (2010) 6664.
[4] S. Yanagida, T. Kitamura, Y. Wada, in: M. Iwamoto, K. Kaneto, S. Mashiko (Eds.), Nanotechnology and Nano-Interface Controlled Electronic Devices, Elsevier Science B.V. (2003) 83.
[5] V. Chakrapani, D.R. Baker, P.V. Kamat, J. Am. Chem. Soc. 113 (2011) 9607.
[6] J.H. Bang, P.V. Kamat, ACS Nano 3 (2009) 1467.
[7] A.B. Ellis, S.W. Kaiser, J.M. Bolts, M.K. Wrighton, J. Am. Chem. Soc. 99 (1977) 2839.
[8] V. Chakrapani, K. Tvrdy, P.V. Kamat, J. Am. Chem. Soc. 132 (2010) 1228.
[9] J.M. Bolts, M.S. Wrighton, J. Phys. Chem. 80 (1976) 2641.
[10] T. Watanabe, A. Fujishima, O. Tatsuoki, K. Honda, B. Chem. Soc. Jpn. 49 (1976) 86.
[11] I.K. Konstantinou, T.A. Albanis, Appl. Cat. B-Environ. 49 (2004) 1.
[12] M.H. Habibi, H. Vosooghian, J. Photoch. Photobio. A 174 (2005) 45.
[13] G.H. Kelsall, I. Thomson, J. Appl. Electrochem. 23 (1993) 279.
[14] D.S. Zhang, T. Yoshida, T. Oekermann, K. Furuta, H. Minoura, Adv. Functional Mater. 16 (2006) 1228.
[15] Y. Lee, C. Chang, J. Power Sources 185 (2008) 584.
[16] N. Guijarro, T. Lana-Villarreal, Q. Shen, T. Toyoda, R. Gómez, J. Phys. Chem. C. 114 (2010) 21928.
[17] W. Giggenbach, Inorg. Chem. 10 (1971) 1333.
[18] B. Meyer, K. Ward, K. Koshap, L. Peter, Inorg. Chem. 22 (1983) 2345.
[19] S. Licht, J. Manassen, J. Electrochem. Soc. 134 (1987) 918.