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Quantum dot sensitized titania for photo-fuel-cell and for water splitting operation in the presence of sacrificial agents

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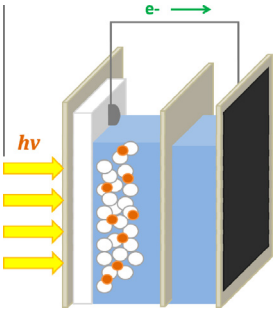
HIGHLIGHTS

- Photoelectrochemical cells producing hydrogen or electricity.
- Quantum dot sensitized photoanodes.
- Photo-fuel-cell operation for the production of electricity.
- Water-splitting operation for the production of hydrogen.
- Protocol of applicable quantum dot sensitizers.

GRAPHICAL ABSTRACT



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ABSTRACT

Photoelectrochemical cells have been constructed using quantum dot sensitized nanocrystalline titania photoanodes and were operated under photo-fuel-cell operation to produce electricity or water-splitting operation to produce hydrogen. In the first case, the cell functioned in the presence of an alkaline electrolyte using ethanol as fuel. The obtained data allowed to define the optimal thickness of the titania film, which was approximately 15 μm. Functional sensitizers were CdS or ZnSe combined with CdS. Small band gap quantum dot sensitizers like CdSe and PbS were not functional in photo-fuel-cells, owing to the limited oxidative power of their valence-band holes. For water-splitting operation, we mainly used a S^{2-}/SO_3^{2-} electrolyte. In that case, panchromatic sensitization is possible. Thus the photoanode, which gave the highest hydrogen production rate, was constructed by combining TiO_2/FTO with ZnS/CdSe/CdS quantum dots. Hydrogen was produced by applying an external bias of 0.5 V. In the absence of bias the quantity of hydrogen was very small. Hydrogen production rate was also very small in a purely alkaline environment with ethanol as fuel.

1. Introduction

Photoelectrochemical conversion of solar energy is a research subject that enjoys immense popularity. It has taken several forms and operates by several different procedures. Photoelectrochemical cells may function in the presence of sacrificial agents and may be used for production of hydrogen or for production of electricity. The underlying virtue of the employment of sacrificial agents is related with the consumption of waste material with the help of solar energy in order to produce usable forms of energy. In the case of electricity production, photoelectrochemical cells can be classified as photo-fuel-cells (PFCs) [1–7], since they photocatalytically consume a fuel to produce electricity. A common material that is used as photocatalyst on the photoanode electrode is nanocrystalline titania (nc-TiO_2), which may be

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sensitized in the Visible by quantum dot sensitizers [5], typically, metal sulfide semiconductors. Depending on the electrolyte filling the cell and mainly on the type of fuel (i.e. the photodegradable sacrificial agent), functional quantum dot sensitizers may be limited in number. Thus for cells operating in alkaline electrolytes in the presence of organic fuels, only medium band gap sensitizers may be used, since only they have enough oxidative power to photodegrade the fuel [5]. Examples of such materials will be treated in the present work. On the contrary, in the presence of sulfide–sulfite electrolytes, even small band gap sensitizers can be employed and are operable. Photoelectrochemical hydrogen production is obtained by reduction reactions at the cathode electrode in the absence of oxygen. The following reactions describe molecular hydrogen production at two pH extremes [2]:

$$\text{Low pH } (0.00\text{ V at pH} = 0) \quad 2H^+ + 2e^- \rightarrow H_2 \tag{1}$$

$$\text{High pH } (-0.83\text{ V at pH} = 14) \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

Of course, any intermediate pH situation may be envisaged with potential being modified according to the equation [8]:

$$\Delta V\ (\text{Volts}) = -0.059 \times \Delta\text{pH} \tag{3}$$

For most common oxide semiconductor photocatalysts, in particular, nanocrystalline titania, the conduction band (CB) level lies very close to the hydrogen generation level [9]. Therefore, the potential difference between anode and cathode is too small to provide sufficient drive to run a cell. In order then to produce hydrogen using a nc-TiO_2 photoanode it is necessary to apply an anodic bias. This is the reason that the cell of Fig. 1a is depicted with applied anodic bias. On the contrary, in the presence of oxygen, reduction reactions are carried out at positive potentials:

$$\text{Low pH } (+1.23\text{ V at pH} = 0) \quad 2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O \tag{4}$$

$$\text{High pH}(+0.40\text{ V at pH} = 14) \quad H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^- \tag{5}$$

thus providing sufficient potential difference from the nc-TiO_2 conduction band and sufficient drive for the cell without external bias. PFCs thus operate with an aerated cathode (cf. Fig. 1b). For this reason they run without bias and they generate high open circuit voltage, as it will be seen later. These brief electrochemical considerations will be taken into account in dealing with the cells of the present work.

The purpose of the present work is to experimentally briefly review and verify these aspects of photoelectrochemical cell operation and to design a protocol of applicable materials with emphasis on materials employed for the construction of photoanode and cathode electrodes.

2. Experimental

2.1. Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. Commercial nanocrystalline titania Degussa P25 was used in all cell constructions and Millipore water was used in all experiments. SnO_2:F transparent conductive electrodes (FTO, resistance 8 Ω/square) were purchased from Pilkington.

2.2. Summary of materials deposition and cell construction

Cell construction obeyed the following specifications. An outline is given in this subsection while details are presented in the following paragraphs. The photoanode carried nanocrystalline titania (nc-TiO_2), which was deposited on an FTO electrode in two layers, a bottom thin compact layer and a top open structure facilitating sensitizer and electrolyte penetration. The bottom layer was deposited by sol–gel and the top layer by screen printing using a paste made of commercial Degussa P25. Deposition of such a two-layer titania film is a common practice with the construction of titania photoanodes. The bottom compact layer ensures attachment of the top layer, provides higher conductivity, blocks short circuits and increases fill factor, while the top porous layer provides high active interface with electrolyte. Formation of nc-TiO_2 film was followed by deposition of quantum dot (QD) sensitizers. First, we deposited a layer of CdS by Successive Ionic Layer Adsorption and Reaction (SILAR method). When necessary, we added ZnSe, CdSe or mixtures of both by Chemical Bath Deposition (CBD) and on the top a passivation layer of ZnS. In another occasion, PbS was deposited by the SILAR method. The active area of the anode electrode was in some cases 1 cm × 1 cm = 1 cm^2 and in other cases 3 cm × 4 cm = 12 cm^2. As cathode electrode we used two different constructions: Pt nanoparticles mixed with carbon black and deposited on carbon cloth (Pt/CC), which provides an "air breathing" cathode (cf. Fig. 1b) or Cu_2S grown on a brass foil (Cu_2S/brass) by treatment in HCl and polysulfide solution. The first case applied to alkaline electrolytes and the second to sulfide–sulfite electrolytes. The active area of the cathode electrode was in all cases 3 cm × 4 cm = 12 cm^2. Aqueous alkaline electrolyte

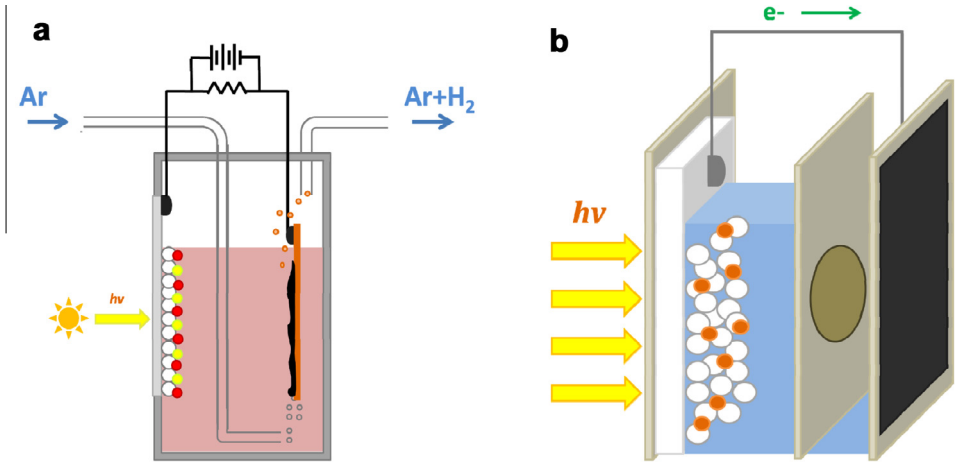

Fig. 1. Schematic representation of the cell used for water splitting and hydrogen production (a) and for photo-fuel-cell operation (b).