



Photocatalysis and photoelectrocatalysis using (CdS-ZnS)/TiO₂ combined photocatalysts

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ABSTRACT

Powdered composite CdS-ZnS photocatalysts of variable composition have been synthesized by a co-precipitation method and were used as photocatalysts to produce hydrogen and as photoelectrocatalysts to produce electricity. Results of catalyst characterization show that composite sulphide photocatalysts form solid solutions and that their band gap energy can be tuned between that of ZnS (3.5 eV) and that of CdS (2.3 eV) by varying Cd (or Zn) content. The composite materials can photocatalytically produce substantial quantities of molecular hydrogen in the presence of sulphide–sulfite ions as sacrificial electron donors. Photocatalytic performance is significantly improved when small amounts of Pt crystallites are deposited on the photocatalyst surface. The rate of hydrogen production over the Pt-free CdS-ZnS powders depends on Cd (or Zn) content and is generally much higher for the composite materials than for pure CdS or ZnS. Pure semiconductors were found to be very poor photocatalysts under the present experimental conditions. Furthermore, two specific photocatalyst compositions, i.e., 67% and 25% CdS, gave maximum hydrogen production rates. An analogous behavior was observed when the same powders were used to make photoanode electrodes since both the rate of hydrogen ion reduction and the current flow are proportional to the number of photogenerated electrons. Composite CdS-ZnS photocatalysts were also applied by successive ionic layer absorption and reaction on TiO₂ films deposited on FTO electrodes. The obtained materials were used as photoanodes in a two-compartment photoelectrocatalysis cell filled with a basic electrolyte and with ethanol as sacrificial electron donor (fuel). The (CdS-ZnS)/TiO₂ photoanodes demonstrated a qualitatively similar behavior as CdS-ZnS photocatalysts. Thus 75%CdS–25%ZnS over TiO₂ was a better electrocatalyst than 100%CdS over TiO₂. When CdS-ZnS photocatalysts were combined with titania, they mainly functioned as visible-light-photosensitizers of this large band-gap semiconductor.

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1. Introduction

In view of the increasing awareness on environmental issues, the increasing interest in the employment of renewable energy sources and the need of recycling of waste materials, metal sulfides combined with large band-gap semiconductors have been studied as efficient photocatalysts for hydrogen production by water splitting or by consumption of waste materials [1–11]. It has been found that the combined photocatalyst by itself is not efficient enough unless it is associated with a co-catalyst like nanoparticulate Pt or other noble metals. The promoting effect of dispersed metal crystallites is usually attributed to their ability to act as traps of photogenerated electrons [12–17]. An essential requirement is

that the work function of the metal is higher than that of the semiconductor. When this condition is fulfilled, a Schottky barrier is developed at the metal–semiconductor interface, which leads to an efficient charge separation and, therefore, to a decrease of the rate of electron–hole recombination and other back reactions that limit system efficiency [12–17]. Dispersed metal crystallites may also function as classical thermal catalysts by enhancing the rate of “dark” catalytic reactions and/or selectivity to reaction products. For example, deposition of metal (e.g., Pt) and/or metal oxide (e.g., RuO₂) particles on TiO₂ has been reported to improve kinetics of the water-splitting reaction by decreasing the overpotentials of hydrogen and oxygen evolution, respectively [14,15]. Even though, the binary Pt/CdS catalyst has been shown to be very successful in several occasions [18–20], the ternary Pt-CdS-TiO₂ catalyst does not seem to be efficient at random combination [1,4,5]. In particular, it has been shown that CdS and Pt should in some cases be spatially separated. Thus in Ref. [1], Pt nanocrystallites were first deposited on titania nanoparticles and CdS nanoparticles were last deposited

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in order to occupy separate sites on TiO₂. It has been also found that, in order to make the ternary catalyst work, CdS/TiO₂ and Pt had to lie on a conductive electrode and be spatially separated [4]. This behavior can be explained by considering that spatial separation is necessary in order to achieve vectorial electron transfer in the direction CdS → TiO₂ → Pt (cf. SI in [5]) and avoid multi-vectorial transfer, which acts against efficiency [1].

The favorable electron transfer from photoexcited CdS to Pt through TiO₂ is not only demonstrated by the nanoparticulate ternary catalyst but is also realized in photoelectrocatalyst (photoelectrochemical) cells. In that case, TiO₂ is deposited on the anode electrode followed by deposition of CdS on the TiO₂ films. Deposition of CdS can be easily achieved by employing the so-called SILAR (Successive Ionic Layer Absorption and Reaction) method [21]. For this, the electrode bearing the titania film is successively immersed in a solution of a Cd²⁺-containing salt, then in a solution of a S²⁻ salt and so on. Both ions are absorbed and react giving small CdS nanoparticles (quantum dots) accommodated within titania mesoporous structure. When the so formed CdS nanoparticles are excited by visible light, the photogenerated electrons are transferred onto the lower-lying conduction band of titania [1,2,11,22]. Subsequently, photogenerated electrons move from the anode to the cathode electrode, which may carry Pt or other noble metal electrocatalyst, through an external circuit. Electrons arriving at the cathode may then participate in reductive reactions, including molecular hydrogen production from hydrogen ions. Indeed, as shown in previous publications, hydrogen and/or electricity can be photoelectrocatalytically produced by using CdS/TiO₂ photoanodes [2,6–8].

In the present work, we deal with two interrelated matters. The first one concerns a previously studied effect [23–26] of combining a large band gap semiconductor (ZnS) with a relatively small band gap semiconductor (CdS), a combination, which allows band gap tuning within a substantial range of the visible part of the spectrum. This combination is reviewed in terms of either photocatalysis for hydrogen production or photoelectrocatalysis for electricity generation. The second matter concerns the employment of the composite semiconductor as photosensitizer of titania. Results show that combination of these two metal sulfides and further combination with titania offers an advantage with respect to simple CdS or CdS/TiO₂ systems. The challenge is not only to develop efficient solar photocatalytic systems that can produce hydrogen from water, but also systems characterized by long term stability under irradiation. This is particularly important for CdS-based photocatalysts, which are known to be susceptible to photocorrosion and, therefore, can operate efficiently only in the presence of sacrificial electron donors. Ideally, the latter should be low- or zero-cost waste materials. In this respect, results presented here were obtained with the use of either sulphide/sulfite ions or ethanol in solution. The former reagent is an undesirable waste product in fossil fuel technology (e.g., oil refineries) whereas the second is an example of a biomass-derived compound that may be present in wastes of biomass processing industries. Even though, certain aspects of the behavior of the presently used combined photocatalysts have been previously treated, the new techniques of materials synthesis and deposition and the new dimensions and range of their application justifies the renewed [1–9] interest in these systems.

2. Experimental

2.1. Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. The nanocrystalline titania

was commercial Degussa P25 (specific surface area 50 m² g⁻¹). Millipore water was used in all experiments. SnO₂:F transparent conductive electrodes (FTO, Resistance 8 Ω/□) were purchased from Pilkington, USA, Carbon Cloth, 20% wet proofing and Pt/Carbon Black electrocatalyst (30% on Vulcan XC72) from BASF Fuel Cell, Inc., USA and Carbon Black, Vulcan XC72R, was a gift from CABOT Corporation.

2.2. Construction of CdS-ZnS/TiO₂ photoanode electrodes

FTO electrodes were cleaned by first washing in soap, rinsed with water and then sonicated in isopropanol, acetone and ethanol. Titania films were prepared by depositing on clean FTO electrodes a home-made paste based on pure titania Degussa P25, prepared according to the recipe given in Ref. [27]. Two layers were screen printed (90 mesh) giving a uniform film, which, after calcination in air at 550 °C, was about 8–10 μm thick [28]. The geometrical area of each film was 3 × 4 = 12 cm². Electric contact was made by using an adhesive copper ribbon and a copper wire soldered on it. A picture of such an electrode can be seen in Ref. [29]. CdS-ZnS composite catalysts at various proportions were deposited on the titania electrode by the SILAR method [21]. For this purpose, we used two aqueous solutions, one containing Cd(NO₃)₂·4H₂O or Zn(NO₃)₂·6H₂O or mixtures of both, and the second containing Na₂S·9H₂O. When metal salt mixtures were used, the total concentration of metal ions and the corresponding concentration of sulfur ions were 0.1 M. Other concentrations of salts have also been tried. The freshly prepared titania electrode was immersed for 5 min in the metal salt solution, then copiously washed with triple-distilled water, then immersed for 5 min in the Na₂S·9H₂O solution and finally washed again. This sequence corresponds to one SILAR cycle. 10 SILAR cycles were performed in all studied cases. Finally, the electrode with deposited (CdS-ZnS)/TiO₂ layer was dried, first in a N₂ stream and then it was put for a few minutes in an oven at 100 °C.

2.3. Synthesis of powdered photocatalysts

Composite CdS-ZnS photocatalysts of variable CdS content (0, 20, 25, 33, 40, 60, 67, 75, 100 wt.%) were prepared by a coprecipitation method [30,31]. For the synthesis of 5 g of CdS, an amount of 10.7 g of Cd(NO₃)₂·4H₂O was dissolved in 200 mL of water and heated at 70 °C under continuous stirring. A second solution was prepared by dissolving 8.31 g Na₂S·9H₂O in 200 mL of water and then mixed dropwise with the first. The resulting mixture was maintained under stirring at 70 °C for 30 min. After this, the precipitant was filtered, washed three times with triply distilled water and dried at 70 °C for 20 h. The resulting powder was crushed, sieved (*d_p* < 0.63 μm) and stored in the dark for subsequent use. Composite CdS-ZnS photocatalysts were prepared in a similar manner, with the use of appropriate amounts of Cd(NO₃)₂·4H₂O, Zn(NO₃)₂·6H₂O and Na₂S in order to obtain the desired composition in the final material.

A mixed (25%CdS–75%ZnS)/TiO₂ photocatalyst with a (CdS-ZnS):TiO₂ ratio of 1.0 (wt.% basis) was synthesized following the same above method, by addition of the corresponding amount of TiO₂ powder (Degussa P25) in the salt-containing solution prior to the addition of Na₂S.

Platinum-promoted photocatalysts were prepared by impregnation of the synthesized CdS-ZnS and (CdS-ZnS)/TiO₂ powders with an aqueous solution of (NH₃)₂Pt(NO₂)₂ (Alfa). The impregnated support was dried at 110 °C for 24 h, ground, sieved and finally reduced at 150 °C in H₂ flow for 2 h. The nominal metal loading of all materials thus prepared was 0.5 wt.% Pt.

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