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# CdS for TiO<sub>2</sub>-based heterostructures as photoactive anodes in the photoelectrochemical cells



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## ABSTRACT

CdS nanoparticles (0D) were deposited using the SILAR method on the surface of titanium foil (2D), TiO<sub>2</sub> thin films (2D) and flower-like nanostructures (NF) of TiO<sub>2</sub> (3D). Flower-like TiO<sub>2</sub> was grown using chemical oxidation in a 30% H<sub>2</sub>O<sub>2</sub> solution. SEM analysis was performed to evaluate the influence of the SILAR deposition parameters and roughness of the substrate on the alignment and size of CdS. The analysis of XRD and Raman data revealed a mixture of anatase and rutile in different ratios for NF and a mixture of cubic and hexagonal polymorph for CdS. UV–vis–NIR spectrophotometry showed fundamental absorption edges originating from both TiO<sub>2</sub> (3.19–3.37 eV) and CdS (2.52–2.80 eV). The band gap energy of CdS was found to be blue-shifted. The values of photocurrent–voltage characteristics registered in a photoelectrochemical cell (PEC) were dependent by the parameters of SILAR deposition process. It was demonstrated that photoanodes based on TiO<sub>2</sub>/CdS heterostructures offer far better performance in PECs than those based on TiO<sub>2</sub>. Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Since the first publication by Fujishima and Honda [1] concerning the photoelectrochemical decomposition of water with the use of a TiO<sub>2</sub>-based photoanode, much effort was put into overcoming the inconvenience resulting from the high value of band gap energy, i.e. 3.2 eV. Such a wide band gap limits absorption only to the UV range of light ( $\lambda < 390$  nm) so extending this range to the visible spectrum is highly desirable. Literature that appeared in a last few years and concerns the photocatalytic decomposition of water allows to find a variety of semiconductors with properties interesting from the photoelectrochemistry point of view. Bismuth vanadate was found to work efficiently as photoanode [2,3].

Additionally, different ways of modification of BiVO<sub>4</sub>, such as: metallic dopants (Mo<sup>6+</sup>, W<sup>6+</sup>, and V<sup>5+</sup>), composites of BiVO<sub>4</sub> and WO<sub>3</sub>, deposition of co-catalyst (RhO<sub>2</sub>, Co–Pi, CoBi, FeOOH, and others) or TiO<sub>2</sub> passivation layer [2] improved BiVO<sub>4</sub> behavior in PECs and gave very promising results. Another example is iron (III) oxide: doped, undoped, and covered with a co-catalysts [2]. Also tungsten (VI) oxide photoanode can be used in the photoelectrochemical cell [4]. Satisfying amelioration was also obtained by formation of nanocomposite (WO<sub>3</sub>)<sub>1-x</sub>/(Fe<sub>2</sub>O<sub>3</sub>)<sub>x</sub> [5], deposition of passivation layer of HfO<sub>2</sub> on the surface of WO<sub>3</sub> [6], and formation of CuWO<sub>4</sub>/WO<sub>3</sub> heterojunction [7]. One can find very interesting results obtained for ZnO-based photoanodes including: ZnO/CdS gradient electrodes [8], ZnO/ZnSeO<sub>3</sub>/CuSeO<sub>3</sub> nanotubes [9], nanoarrays of ZnO sensitized with ZnIn<sub>2</sub>S<sub>4</sub> [10], and ZnO

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nanoarrays modified with quaternary Ag–Cu–Sb–S solid solution [11]. Finally, some reports about photoelectrochemical properties of ferrosinels  $\text{CoFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$  [12],  $\text{Ta}_3\text{N}_5$  covered with catalysts such as  $\text{IrO}_2$  or  $\text{Co}_3\text{O}_4$  [2],  $\text{Cu}_2\text{ZnSnS}_4/\text{CdS}$  or  $\text{TiO}_2$  heterojunctions [2], and  $\text{CuIn}_5\text{S}_8$  [13] can be found.

However, there is a consensus that titanium dioxide is a best semiconductor for photocatalytic applications. One of the most extensively studied way in which this can be accomplished is the creation of heterostructures composed of  $\text{TiO}_2$  and a narrow-band gap semiconductor, for example cadmium sulfide. With a band gap energy of 2.4 eV, CdS allows a considerable shift in absorption up to  $\lambda < 520$  nm. A major drawback of using CdS as a photocatalyst is its possible dissolution due to its photocorrosion [14]. Increase the photostability of CdS is, therefore, essential.

Research activities concerning  $\text{TiO}_2$ –CdS heterostructures focus mainly on the architecture of the elements of this system [15,16]. Several strategies towards achieving this arrangement of components have been proposed [17]. From a microstructural point of view, different types of elementary units can be used, such as nanoparticles (0D), fibers, nanotubes, corals (1D), plates, thin films (2D), or bulk materials (3D). The addition of CdS nanoparticles to  $\text{TiO}_2$  in one of the four above-mentioned forms (0D, 1D, 2D or 3D) provides light absorption in the visible range and ensures the effective separation of photoinduced electronic charge carriers, thus limiting the recombination process [16]. However, the incident radiation from the visible range of light may be screened out when the amount of CdS nanoparticles is too high. Such conditions are favorable for recombination processes involving photoinduced carriers. Thus, it is important to ensure a sufficiently large surface area of  $\text{TiO}_2$  which allows the appropriate number of active sites to be obtained. Shao et al. [18] demonstrated that the hierarchical structure of  $\text{TiO}_2$ – $\text{N}_x$  composed of different types of pores exhibits improved photocatalytic behavior in comparison with structure composed of one type of pores. The explanation given was that additional pores promote diffusion. Thus, it is crucial to design the architecture of heterostructures in such a way as to fully monitor both the microstructure of  $\text{TiO}_2$  and distribution of CdS nanoparticles on the surface of  $\text{TiO}_2$ . However, it is not less important to control the addition of CdS so as to obtain the optimal amount of nanoscale particles preventing agglomeration. Such an approach allows uniformly distributed nanoparticles which do not completely cover the surface of  $\text{TiO}_2$  to be obtained. In addition, it leads to a significant reduction in the photocorrosion of CdS as shown by Yang et al. during the cyclic degradation of Rhodamine B on  $\text{TiO}_2$ –CdS photocatalyst [16].

The aim of the present work was to study the influence of the substrate form on the size and morphology of cadmium sulfide nanoparticles. Systematic studies with the use of titanium foil (2D), titanium dioxide thin films (2D) and titanium dioxide in the form of flower-like nanostructures (3D) allowed us to make a conscious choice of the conditions for the deposition of CdS (0D) by means of the SILAR method. The usefulness of  $\text{TiO}_2$ –CdS heterostructures in the process of hydrogen production with the use of photoelectrochemical cells was also considered.

## Materials and methods

### Materials

The following materials and chemicals were used: acetone (POCH),  $\text{CH}_3\text{OH}$  (POCH, 99.8%),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (ACS reagent, ACROS),  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (analytically pure, POCH), titanium foil Ti (Sigma Aldrich, 99.7%, d-0.127 mm), isopropyl alcohol (POCH), 36% HCl (ACROS),  $\text{H}_2\text{O}_2$  (ACROS), argon (Air Liquide).

### Flower-like nanostructures formation

Flower-like titanium dioxide nanostructures (NF) were prepared from titanium foils according to the procedure described in our previous works [19,20]. After degreasing the Ti foil in an ultrasonic bath with acetone and isopropyl alcohol, the oxide layer was removed from the surface of titanium by means of etching in concentrated HCl which was followed by rinsing with distilled water. After drying in an argon atmosphere the prepared substrates were immersed in 30%  $\text{H}_2\text{O}_2$  at an elevated temperature prior to the synthesis of flower-like  $\text{TiO}_2$  nanostructures. The selected times of synthesis were 15, 45 and 120 min. After that time, the samples were rinsed with distilled water, and dried in air. The as-prepared materials were annealed in an argon atmosphere at 600 °C in order to form crystalline flower-like  $\text{TiO}_2$  nanostructures. A schematic representation of the structure of flower-like  $\text{TiO}_2$  and its morphology is shown in Fig. 1.

Changes in the microstructure of flower-like  $\text{TiO}_2$  nanostructures as a result of the increase of reaction time in  $\text{H}_2\text{O}_2$  were analyzed based on surface and cross-section SEM images presented in Fig. 2. Numerous effects of changes of reaction time may be distinguished according to Fig. 1. When the time of reaction in  $\text{H}_2\text{O}_2$  increases from 15 to 120 min: (1) the thickness of  $\text{TiO}_2$  nanostructures grows from 1.03 to 2.19  $\mu\text{m}$  together with (2) the thickness of the sponge-like  $\text{TiO}_2$  from 0.37 to 1.02  $\mu\text{m}$ ; (3) the ratio of the thickness of sponge-like  $\text{TiO}_2$ -to- $\text{TiO}_2$  layer increases; (4) amount of nanoflower  $\text{TiO}_2$ 's rises and (5) their shape becomes flatter; (6) due to stress some cracks appear.

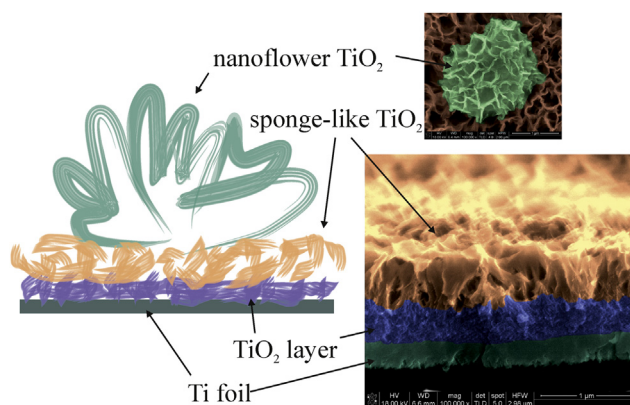


Fig. 1 – Structure of flower-like  $\text{TiO}_2$  nanostructures.

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