Journal of Photochemistry and Photobiology A: Chemistry 356 (2018) 489–501

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photoelectrochemical properties of ZnS- and CdS-TiO_2 nanostructured photocatalysts: Aqueous sulfidation as a smart route to improve catalyst stability

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ARTICLE INFO

Article history:
Received 21 August 2017
Received in revised form 1 January 2018
Accepted 23 January 2018
Available online xxx

Keywords:
TiO_2 nanofibers
Quantum dots
Hetero-nanostructures
Photoelectrochemical properties
X-ray photoelectron spectroscopy

ABSTRACT

ZnS- and CdS-TiO_2 hetero-nanostructures were synthesized by impregnation of polyol-made ZnS, CdS quantum dots (QDs) on the surface of TiO_2 nanofibers that were grown on Ti sheets by controlled corrosion. Due to their finite size, the grafted QDs were partly oxidized, when air exposed, reducing their ability to sensitize TiO_2 toward photoelectrochemical (PEC) water splitting application. We showed that a subsequent aqueous sulfidation allowed recovering the initial chemical composition of the produced catalysts improving their chemical stability and consequently their PEC properties.

1. Introduction

Great attention has been paid on photoelectrocatalytic (PEC) water splitting for Hydrogen generation. It is nowadays considered as a serious way to produce abundant and renewable energy and to reduce the word energy dependency on fossil resources. There are many reports on the production and the improvement of photoanodes for such a purpose, with a special emphasis on the increase of the conversion rate of solar light into hydrogen. They mainly concern the i) the extension from UV to visible light of the absorption spectra of the semiconducting photoanodes, ii) the limitation of their exciton recombination, iii) the increase of their life time in standard operating conditions (pH = 7, room temperature, passive electrolyte) and iv) the development of easy-to-achieve, reproducible and scalable material processing for their mass production and manufacturing [1].

Obviously, to build solar hydrogen cells with commercial and technological efficiency, it is important to develop and use cheap and easily prepared functional materials, exhibiting stable performance and high efficiency towards water redox reactions. Soft chemistry made wide band-gap TiO_2 anatase polycrystals [2] combined to narrow band-gap quantum dots (QDs) [3], are viewed as one of the most promising non-silicon polycrystalline combination to answer to the previously listed requirements [4], if their stability toward water or air exposition can be improved. Indeed, if TiO_2 exhibits good resistance to corrosion, QDs, like II–VI transition metal chalcogenide semiconductors, do not. Due to their finite size, they are often submitted to oxidative degeneration just by O_2 exposition [5]. ZnS and CdS QDs, for instance, look like core@shell $ZnS@ZnSO_4$ [6] or $CdS@CdSO_4$ [7] particles instead of pure ZnS or CdS crystals, when air exposed, making them less valuable for titania photosensitization and then less efficient toward PEC application. The formed sulfate shell is directly in contact with TiO_2 surface, in the built TiO_2-ZnS or TiO_2-CdS composite photoanodes and directly in contact with water and sunlight in standard PEC cells, affecting all the involved photoelectron generation and charge transfer processes.

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https://doi.org/10.1016/j.jphotochem.2018.01.038
1010-6030/

To avoid such a phenomenon, or at least to limit it, smart issues must be proposed to chemically post-transform the ZnS@$ZnSO_4$-TiO_2 or CdS@$CdSO_4$-TiO_2 catalysts into ZnS-TiO_2 or CdS-TiO_2 ones.

A rapid overview of the relevant literature shows that it is possible to easily produce a sulfide layer on an oxide surface by ionic exchange reaction. In practice, a metal oxide surface is exposed to S^{2-} ions in an aqueous solution [8]. The transformation may proceed by a progressive replacement of O^{2-} lattice anions by solvated S^{2-} ones through a double ion-diffusion pathway or it may proceed by a surface metal oxide dissolution followed by a metal sulfide precipitation. In the first scheme, O^{2-} anions move from the solid to the solution and reversely S^{2-} from the solution to the solid, transforming the metal surface oxide into a metal sulfide one, while in the second one, the dissolved metal cations react with S^{2-} in solution and form metal sulfide nanocrystals at the modified metal oxide surface.

In this context, we propose to apply such a treatment to transform ZnS@$ZnSO_4$ and CdS@$CdSO_4$ nanoparticles into pure ZnS and CdS ones and we evaluate its capability to improve the PEC properties of the related titania-based hetero-nanostructures. In practice, we prepared TiO_2 nanofibers (NFs) by Ti sheet hydrothermal corrosion [9] and we decorated them by polyol-made ZnS or CdS QDs by simple impregnation of TiO_2/Ti samples in a QD alcoholic solution [7b]. We checked the surface oxidation of QDs by X-ray photoelectron spectroscopy [7b] and we measured the photocurrent of the built ZnS@$ZnSO_4$–TiO_2/Ti and CdS@$CdSO_4$–TiO_2/Ti anodes under Xenon lamp illumination, using a Platinum wire counter-electrode and a Na_2SO_4 electrolyte solution. We repeated the same operations using this time S^{2-} treated QDs and then we compared the performances of the treated working electrodes with those of the non-treated ones. Our main results are presented in this work highlighting the efficiency of such a simple material processing method to significantly improve the PEC properties of QD sensitized titania nanostructures.

2. Experimental sections

2.1. Sample preparation

Micrometer in length sized TiO_2 NFs supported on Ti sheets were produced by a controlled hydrothermal corrosion of Ti sheets (0.5 mm thick, areal equal to $2 \times 1\ cm^2$) according to a well-described protocol in previous works [9].

QDs were synthesized using the polyol process [7b]. Typically, 132.4 mg of cadmium acetate dihydrated (respectively, 109.5 mg of zinc acetate dihydrated), 45.6 mg of thiourea and 193.2 mg of trioctylphosphine oxide (TOPO) were dissolved in 80 mL of diethyleneglycol (DEG). The reaction medium was heated up to 180 °C (6 °C min^{-1}) for 30 min before to be quickly cooled to room temperature. Light brown and yellow ZnS and CdS powders were recovered by centrifugation, washed with ethanol and then dried in air. A known mass was then dispersed in 4 mL of DEG by sonication (0.75 mg/mL) to form the so-called suspensions ZS1 (for ZnS) and CS1 (for CdS).

The same mass was dispersed in 4 mL of cyclohexane which is subsequently mixed with 4 mL of Na_2S aqueous solution (0.32 mol/L). The two-phase mixture was vigorously sonicated for 15 min, at least two times, until the constituting nanocrystals of the starting powder were transferred into the aqueous phase (Fig. 1). The organic phase was then discarded and the aqueous colloidal one (ca. 4.0 mL) was separated and denoted ZS2 (for ZnS) and CS2 (for CdS).

To prepare the desired photoanodes, the previously synthesized TiO_2/Ti sheets were immersed into both ZS1 and ZS2 (respectively CS1 and CS2) solutions, under vigorous sonication for 30 min. In all these solutions, QDs concentration is assumed to be about 0.125 M.

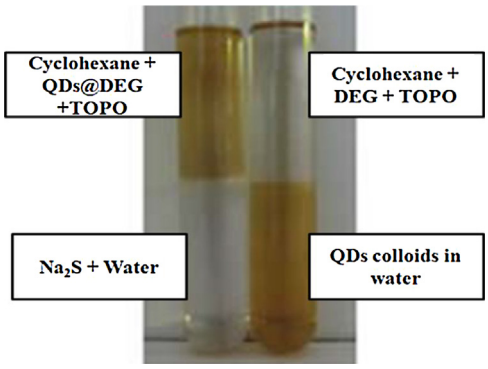

Fig. 1. Numerical image illustrating the QDs transfer from the cyclohexane phase to the aqueous one.

The sheets were then left in the impregnation solutions overnight. Finally, they were removed and washed in ethanol (for ZS1 and CS1) or distilled water (for ZS2 and CS2) under sonication before to be dried for 1 h at 80 °C. The resulting samples were denoted TZS1, TCS1 and TZS2, TCS2, respectively.

2.2. Sample characterization

2.2.1. Characterization of QD powders and colloids

First the structure of the recovered QD powders was checked by X-ray diffraction (XRD) using a Panalytical XpertPro diffractometer, equipped with a multichannel detector (Xcelerator) and a Cu Kα X-ray source (1.5418 Å). Measurements were carried out in the Bragg-Brentano θ–θ configuration. Their morphology was investigated by Transmission Electron Microscopy (TEM), using a JEOL JEM-100CX-II microscope operating at 100 kV. In practice a drop of the QDs polyol- or water-based colloids was deposited on a TEM carbon grid. After drying, the grids were introduced into the microscope and micrographs were recorded at different magnifications. SAISAM software (Microvision Instruments) was used to calculate the average surface diameter of the particles. At the end, optical absorption spectroscopy (OAS) was used to determine the energy band-gap value (Eg) of all the prepared QD colloids thanks to a CARY 56^E spectrophotometer working in a transmission scheme. In practice, $(\alpha h\upsilon)^2$ versus hυ curves were plotted (Tauc plots) and the intersection between the straight portion of these curves and the baseline was pointed out as Eg [10]. hυ and α correspond to the photon energy and the absorption coefficient, respectively.

2.2.2. Characterization of QDs-TiO_2/Ti sheets

The structure of TZS1, TCS1, TZS2 and TCS2 samples and their TiO_2/Ti parent was investigated using a Panalytical Empyrean diffractometer, equipped with a multichannel detector (PIXcel 3D) and a Cu Kα X-ray source (1.5418 Å). The diffractogramms were recorded in the w-2θ configuration using an incident grazing beam of w = 1°. Raman spectroscopy was also performed using a Bruker Senterra equipement. The spectra were recorded in the 50–2000 cm^{-1} energy range, employing a 20 mW 532 nm laser.

A Supra40 ZEISS field emission gun scanning electron microscope (FEG-SEM), operating at 2.5 kV, was then used to investigate the microstructure of the produced samples. Additionally, observations on a JEM 2100Plus transmission electron microscope (TEM), operating at 200 kV, were carried out on isolated NFs to confirm QDs grafting. The microscope was equipped with an Oxford AZtec EDX system with a detector SDD X-Max T for local compositional analysis. In practice, the produced sheets were placed in an ethanolic solution and vigorously sonicated for several minutes to remove titania fibers from their titanium sheets. A drop