Thin Solid Films 551 (2014) 79–85

Contents lists available at ScienceDirect

Thin Solid Films

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

Preparation, characterization and application of polyelectrolytes/TiO_2/CdSe self-assembled films

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ARTICLE INFO

Article history:
Received 5 July 2013
Received in revised form 28 November 2013
Accepted 29 November 2013
Available online 5 December 2013

Keywords:
Layer-by-layer technique
Self-assembled films
Polyelectrolytes
Inorganic semiconductors

ABSTRACT

The aim of this work was to prepare self-assembled films (SAF) via a layer-by-layer technique and to characterize the films by applying several instrumental techniques. The cationic system was composed of the organic polyelectrolyte poly(diallyldimethylammonium chloride) and the inorganic semiconductor cadmium selenide (CdSe), whereas the anionic system was composed of poly(acrylic acid) and nanoparticles of the photoactive semiconductor titanium dioxide (TiO_2). Through measurements of the diffuse reflectance spectrum, absorption bands were observed in the near ultraviolet region for TiO_2 and in the visible region for CdSe. The thicknesses of the SAF were determined through profilometry and scanning electron microscopy techniques, and the obtained values were on the order of microns. Finally, the SAF were irradiated with a Xe/Hg lamp, and the results indicated their potential for solar hydrogen production.

1. Introduction

The replacement of fossil fuels by systems that harness renewable energies has been considered one of the main challenges of the contemporary world. In this scenario, the use of solar energy emerges as one of the most promising energy alternatives for the production of a non-polluting fuel—hydrogen [1,2].

Studies reporting the production of hydrogen fuel through solar photocatalysis were published by Fujishima and Honda [2] in 1972. Since then, scientific and engineering interest in semiconductor photocatalysis has grown significantly, and storing solar energy by splitting water into hydrogen and oxygen has been considered a promising idea [3].

Hydrogen production occurs by a photocatalytic process when semiconductor materials absorb light at a wavelength that matches the characteristic absorption band of the material. In this process, the semiconductor material is excited by photons with energy equal to or greater than the bandgap energy (Eg) such that electrons can migrate from the valence band to the conduction band. Nanostructured systems have improved efficiency for this process because of their increased surface area [2,4].

In heterogeneous photocatalysis, a general concern is the synthesis of photocatalysts with high surface areas and large absorption of light to form electron-hole pairs with sufficient potential for water splitting [5–8]. However, in a recent work published by Dal'Acqua et al. [9], it was observed that thin films prepared using a layer-by-layer (LbL) self-assembly method and composed of photoactive TiO_2 semiconductor and gold nanoparticles produced hydrogen mainly in the bulk of the system. This class of materials enables a technological move towards the effective use of these innovative energy sources.

Assembly through the LbL technique typically involves the repeated, sequential adsorption of oppositely charged polyelectrolytes onto a substrate until the desired film thickness is achieved [10,11]. LbL is one of the most efficient methods for constructing nanostructured thin films, and this technique demonstrates many advantages, including simplicity of the process, the possibility of deposition at room temperature and careful control of the film thickness at the nanometer scale [10,11]. Additionally, multilayer thin films formed by incorporating nanoparticles have been applied in fuel cell membrane electrodes [12], fast energy transfer nanocrystal bilayers [13–16], photodetectors [17], photovoltaics [18–20] and water treatment [4,21–23].

Because of its low cost, good chemical stability, corrosion resistance and photocatalytic activity, TiO_2 is a natural semiconductor candidate for energy conversion applications. However, the absorption band of TiO_2 limits its photocatalytic properties to the ultraviolet region [2,24]. To extend the absorption band into the visible region, semiconductors with lower Eg have been combined with TiO_2 and used in conversion devices. Compared to other materials, binary compounds within the chalcogenide group, such as cadmium sulfide or selenide quantum

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0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.11.116

dots (CdS and CdSe QDs, respectively), exhibit better performance in terms of their photocatalytic properties in applications, such as ion exchangers in sensors, devices and luminescent solar cells [4,25].

In 2007, Sung-Hwan Han et al. [26] reported the effect of CdSe nanoparticles on the optical absorption of TiO_2 porous films fabricated using a spin-coating method. These authors demonstrated that the combination of these elements is highly effective for the development of photoelectrochemical solar cells. In 2008, Nazeeruddin et al. [27] prepared solar cells using a screen printing technique with a combination of TiO_2 and CdSe QD semiconductors. Hydrogen production using a water splitting technique was reported by Chi et al. [24]. In that work, self-assembled films of TiO_2 sensitized with CdS/CdSe, which were obtained using a spin-coating technique, were heat treated. The authors observed that the hydrogen production rate decreased slightly with irradiation time due to photocorrosion of the electrodes, which is commonly observed in CdS/CdSe systems. Furthermore, the heat treatment improved the performance of the films in terms of hydrogen production but showed little effect on inhibiting photocorrosion.

Taking into consideration the potential applications of photocatalysis presented in the literature for TiO_2/CdSe semiconductors as well as the use of thin films in energy conversion systems [24,26,27], the aim of this work was to prepare and characterize thin films composed of[(poly(diallyldimethylammonium chloride) − PDDA + CdSe)/(poly(acrylic acid) − PAA + TiO_2] and to evaluate the use of these materials in a device to produce hydrogen fuel by solar irradiation.

2. Experimental section

2.1. Sample preparation

To perform this work, three different substrates were used as a support for the growth of the LbL-assembled films: glass (VWR, Cat # 48312-027), polystyrene (PS) coverslip (Fisher Scientific, Cat # 174977) and silicon (Ted Pella Inc., Cat # 16006). The substrates were cleaned in a neutral Extran solution (5% v/v) for 30 min at 60 °C and were then soaked in a solution of acetone:methanol (1:1 v/v) for 10 min. At the end of this procedure, the substrates were washed with deionized water (resistivity of <18.2 MΩ/cm) obtained from a Milli-Q system (Millipore) and were left to dry at room temperature.

The self-assembled films (SAF) were obtained by sequential dipping of the substrates into aqueous solutions of polyelectrolytes with rinsing between each deposition step. PDDA ($M_w = 180{,}000$ g/mol, 35 wt.% in water, Sigma-Aldrich) was used as the polycation, whereas PAA ($M_w = 90{,}000$ g/mol, 25 wt.% in water, Polysciences) was used as the polyanion. All polyelectrolytes were used as received without further purification and were prepared as 0.01 mol L^{-1} solutions (based on the repeat-unit molecular weight). The pH values of the polyelectrolyte solutions were adjusted to the desired pH (±0.01) with a 0.10 mol L^{-1} solution of HCl or NaOH.

2.2. Synthesis of the CdSe and TiO_2 nanoparticles

The TiO_2 colloidal solution was prepared from titanium dioxide powder (Degussa, P-25, $M_w = 80$ g/mol) dispersed in deionized water (pH = 5.0) to yield a 0.12 wt.% solution.

The CdSe colloidal solution was prepared using three distinct steps. The first step consisted of reducing selenium (powder) to selenide through high-frequency ultrasonic radiation for 5 min. In the second step, sodium borohydride was added to the selenide solution. This mixture was irradiated under the same conditions as in the first step, and a clear solution of sodium selenite (Na_2Se) was formed. The reduction process was conducted under an inert atmosphere of nitrogen gas. In the final step, 0.50 mol L^{-1} mercaptoacetic acid (AMA) was added to 0.02 mol L^{-1} cadmium perchlorate under constant stirring. The pH of the mixture was adjusted to 10.5 with a 0.10 mol L^{-1} solution of NaOH. Finally, the resulting Na_2Se solution was rapidly added to the Cd/AMA mixture. After manual stirring, a clear, yellow suspension of CdSe QDs was obtained. The final ratio of the system components was 4:1:2 (v:v:v) to Cd:Se:AMA [28].

2.3. Preparation of the self-assembled films

The SAF were prepared with NanoStracto Sequence equipment. The substrates were initially immersed in the cationic system (PDDA + CdSe) for 15 min, dried under ambient conditions for 1 min, rinsed in deionized water for 30 s and finally dried under ambient conditions for 30 s, thus forming the first monolayer. Then, the substrates were immersed in the anionic system (PAA + TiO_2) for 15 min. This immersion was followed by rinsing in deionized water for 60, 30 and 30 s to form the second monolayer. This process was repeated until the desired number of layers was formed [29].

The volumetric proportions and the pH of the solutions used in the preparation of the SAF are summarized in Table 1.

2.4. Characterization of the semiconductors and self-assembled films

The optical properties of the SAF and colloidal solutions of TiO_2 and CdSe were measured with a VARIAN Cary 5000 ultraviolet–visible (UV–Vis) double beam spectrophotometer from 300 to 800 nm. The Eg of TiO_2 and CdSe were also determined with UV–Vis measurements.

Experiments to identify the crystalline phases of the CdSe and TiO_2 in the SAF were conducted using a SHIMADZU XRD-6000 diffractometer over a 2θ range of 15–55° with a step size of 0.05° and a $\lambda = 1.5406$ Å; the counting time per point was 10 s for TiO_2 and was 1 s for CdSe. The resulting diffraction patterns were analyzed by comparison with JPCDS file 78-2486 for TiO_2 and JPCDS file 88-2346 for CdSe in the ICSD database.

The crystal structure can be deduced from the positions of the peaks in the diffraction pattern [30]. All of the diffraction patterns were normalized to the peak with the highest intensity. The average sizes of the crystals can be estimated by crystallite size analysis using the (111) peak for CdSe and the (101), (110) and (200) peaks for TiO_2. The positions and the full width at half-maximum (FWHM) values of the fitted crystalline peaks were used to determine the *d* spacings (Bragg's law). The average crystallite sizes were determined from Scherrer's equation [31], which can be expressed as follows:

$$\varepsilon = \frac{K\lambda}{\beta\cos\theta}$$

where *K* is a constant (in general equal to 0.9), λ is the radiation wavelength, β is the FWHM of the peak, and θ is the diffraction angle of a given peak. Scherrer's equation was used in this study to estimate the crystal size because this equation has been widely used in many previous studies for this purpose. A detailed description of the method is available in the literature [32].

The morphologies and compositions of the TiO_2 and CdSe nanoparticles in the SAF were investigated using scanning electron microscopy (SEM) with an FEI Quanta 200 FEG microscope at an accelerating voltage of 20 kV that was equipped with an energy dispersive X-ray

Table 1
Volumetric proportions of the solutions used in the preparation of the SAF.

Films	$\{[PDDA_z + CdSe_z](x{:}y) + [PAA_z + (TiO_2)_z](x{:}y)\}_i$
(*a*)	$\{[PDDA_{7.0} + CdSe_{10.5}](4{:}1) + [PAA_{6.0} + (TiO_2)_{4.5}](1{:}1)\}_{80}$
(*b*)	$\{[PDDA_{7.0} + CdSe_{10.5}](4{:}1) + [PAA_{6.0} + (TiO_2)_{4.5}](1{:}1)\}_{160}$
(*c*)	$\{[PDDA_{7.0} + CdSe_{10.5}](3{:}1) + [PAA_{6.0} + (TiO_2)_{4.5}](3{:}1)\}_{80}$
(*d*)	$\{[PDDA_{7.0} + CdSe_{10.5}](3{:}1) + [PAA_{6.0} + (TiO_2)_{4.5}](3{:}1)\}_{160}$

x = volumetric proportion of the PDDA and PAA polyelectrolyte solutions;
y = volumetric proportion of the CdSe and TiO_2 inorganic solutions;
z = pH of the solutions;
i = number of layers.