



Short communication

Synthesis and solar light catalytic properties of titania–cadmium sulfide hybrid nanostructures



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ABSTRACT

A new approach for the synthesis of hybrid nanostructured titania–cadmium sulfide photocatalysts has been suggested. Photocatalysts TiO₂ on CdS and CdS on TiO₂ were characterized by various techniques including transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The photocatalysts have shown high activity in the partial oxidation of ethanol to acetaldehyde under the action of solar light ($\lambda > 420$ nm). The improved activity of the catalysts was attributed to the presence of heterojunctions between CdS and TiO₂ nanoparticles that results in a more efficient charge separation as compared with pure CdS or TiO₂. A better stability of the catalyst TiO₂/CdS was likely due to the formation of a TiO₂ protective coating on CdS nanoparticles.

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1. Introduction

Although the first works on selective oxidation occurring on metal oxide semiconductors under the action of solar light appeared more than 30 years ago [1,2], considerable advancement in this field took place only in the recent decade. At present, methods for selective oxidation of different organic substances, for example, cyclohexane [3], ethanol [4,5], or glycerine [6] are being actively developed. Along with the oxidation methods, methods for selective reduction, for example, for the reduction of carbon dioxide to cyclohexanol [7], are being worked out with the use of practically the same photocatalysts. Besides, the effect of different factors on selective oxidation is studied, for example, the presence of water in the reaction zone or humidity [3], and modification of semiconductors by alloying them with metals [8,9] and non-metals [9].

Photocatalytic processes under the action of solar light attract particular attention because of their potential not only in organic synthesis, but also for environmental restoration and inexpensive hydrogen production [10]. Among the possible applications, the partial oxidation of alcohols to aldehydes or ketones holds a special position. The effective

implementation of this process is of much interest, in particular for the pharmaceutical industry [11,12].

The photooxidation of alcohols to aldehydes or ketones has been widely studied on titania (TiO₂) [12]. High chemical stability and appropriate positions of the flat band potentials required for conducting the desired redox reactions on its surface [13] are the main advantages of TiO₂. The main disadvantages of TiO₂ are low selectivity toward partial oxidation under aerobic conditions [14] and low absorption of solar light. Both drawbacks can be solved by the use of the well-known photocatalytically active semiconductor, cadmium sulfide (CdS), which has a band gap of about 2.4 eV and correspondingly can be excited with solar radiation [15]. Additionally, CdS is capable of catalyzing partial oxidation with a high selectivity [5]. To improve the stability of CdS and simultaneously to increase the response of titania to the solar light, a coupling of TiO₂ with CdS is proposed. Controlled synthesis of hybrid semiconductor nanostructures for green chemistry has become of special significance. It was shown that the formation of CdS–TiO₂ core–shell structures allows one to obtain good photocatalysts with visible light absorption [16,17].

Therefore, in the present work, new methods for the synthesis of hybrid oxide–sulfide nanostructured photocatalysts, were proposed. The catalytic activity of two different types of catalysts is analyzed in the test reaction of the gas phase photooxidation of ethanol to acetaldehyde under visible light. Ethanol is a model of biomass-derived fuels and for this reason it is a common material for laboratory research [18].

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Moreover, acetaldehyde is an important intermediate in organic syntheses for the production of acetic acid, acetic anhydride and many other products [19,20]. Usually, CdS–TiO₂ nanostructures are used for photocatalytic hydrogen production [21] and liquid phase photooxidation of benzyl alcohols [22–24]. The selective gas phase photooxidation of ethanol to acetaldehyde was carried out under UV-light only [18,20]. Thus, our research gives new information about CdS–TiO₂ hybrid photocatalyst synthesis and ethanol photoconversion to acetaldehyde.

2. Experimental

2.1. Synthesis

Photocatalysts TiO₂/CdS (samples A–C) were prepared as follows. To prepare the initial suspension of CdS nanoparticles 25 ml of the aqueous solution of CdCl₂ (50 mM) was poured into 25 ml of Na₂EDTA (50 mM), then the resulting solution of Cd(EDTA)²⁻ complex salt was mixed with 50 ml of Na₂S (25 mM) while vigorously stirring.

The as-prepared suspension contained about 10¹⁶ CdS nanoparticles with an average size of 3 nm in 1 ml of the solution. Thereafter, 1 mmol (A) or 2 mmol (B and C) of Ti(OBu)₄ (99+%, Alfa Aesar) was added into the conical flask equipped with a magnetic stirrer, water condenser and dropping funnel. While vigorously stirring 10 ml of the CdS suspension was added drop wise in time intervals ranging from 10 to 15 min. The reaction mass was maintained at reflux for 1 h (A and B) or 3 h (C), centrifuged, the liquid portion was decanted and the TiO₂/CdS compacted precipitate was dried in air at ambient temperature for 2 days.

Photocatalyst D was prepared by the deposition of CdS on titania (Degussa P25) in accordance with a method described elsewhere [5].

2.2. Catalyst characterization

Phase composition of the samples was analyzed by X-ray diffraction (XRD) on a D8 Advance diffractometer (Bruker, Germany) using CuK α radiation. The XRD patterns were recorded in the 2 θ range from 20 to 80° with a step of 0.05°. The XRD reflexes of CdS and TiO₂ were separated and average crystallite sizes were determined with the use of the TOPAS software (Bruker, Germany). The XRD patterns of a disordered CdS structure were simulated with the use of an application-specific software [25]. The samples were studied by high resolution transmission electron microscopy (HRTEM) using a JEM-2010 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a resolution of 0.14 nm. The local elemental composition was analyzed with an energy-dispersive (EDX) spectrometer equipped with a Si(Li) detector with an energy resolution of 130 eV. The diffuse reflectance spectra were recorded on a Lambda 35 UV/vis spectrometer (Perkin Elmer) with an RSA-PE-20 integrating sphere (Labsphere, USA) in a wavelength range from 200 to 700 nm.

XPS measurements were performed using a photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Germany) equipped with an XR-50M X-ray source, a FOCUS-500 ellipsoidal crystal monochromator, and a PHOIBOS-150 hemispherical electron energy analyzer. The core-level spectra were obtained using monochromatic AlK α radiation. The charge correction was performed by setting the C1s peak at 284.9 eV resulting from adventitious hydrocarbons.

2.3. Photocatalytic tests

Photocatalytic activities of prepared catalysts were characterized in the vapor oxidation of ethanol in a flow reactor under visible light irradiation. The only products of oxidation were acetaldehyde and water:



The samples were illuminated with a high pressure mercury lamp (DRSH-1000) with a cut off filter ($\lambda > 420$ nm). Catalysts were

uniformly deposited on a glass plate ($S = 7.5$ cm²) with a surface density of 1 mg/cm². The intensity of the irradiation was 30 mW/cm². The emission spectrum of the lamp is represented in Fig. 1SI. The initial concentration of ethanol was about 30 μM . The gas phase composition was analyzed by in-situ FTIR spectroscopy. The IR absorbance peaks of acetaldehyde overlap with the peaks of water and ethanol. Therefore, the peaks of ethanol were subtracted from the spectra of the reaction mixture and then a concentration of acetaldehyde was determined from the area of the band between 2500 and 3100 cm⁻¹. This technique is described in detail in the Supplementary data.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of samples A–C are shown in Fig. 1. As seen from the picture, all these samples consist of TiO₂ and CdS phases. TiO₂ has the anatase structure with average crystallite sizes of 4.0, 4.3, and 5.0 nm for samples A, B, and C, respectively. The XRD pattern of CdS contains only three or even two broad peaks. The first peak situated in the 2 θ range between 20 and 35° has an asymmetric shape. Two peaks located in the range between 40 and 60° have lower intensities and overlap each other. Such a pattern is typical of nanocrystalline CdS [25,26]. Simulation of the XRD patterns shows that CdS has neither the sphalerite (cubic) structure nor the wurtzite (hexagonal) one (Fig. 2SI). The most suitable structural model represents a completely random sequence of closely packed CdS layers. The average crystallite size of CdS with the disordered structure is about 2 nm. The XRD pattern of photocatalyst D contains peaks of both anatase and rutile TiO₂, and it is common to disordered CdS deposited on TiO₂ Degussa P25 (Fig. 3SI).

To analyze quantitatively the phase composition of photocatalysts A–C, we calculated the ratios of areas for the first peaks due to TiO₂ and CdS. They were 0.34, 0.50, and 1.90 for samples A, B, and C, respectively. If we accept that the CdS to TiO₂ molar ratio for sample C

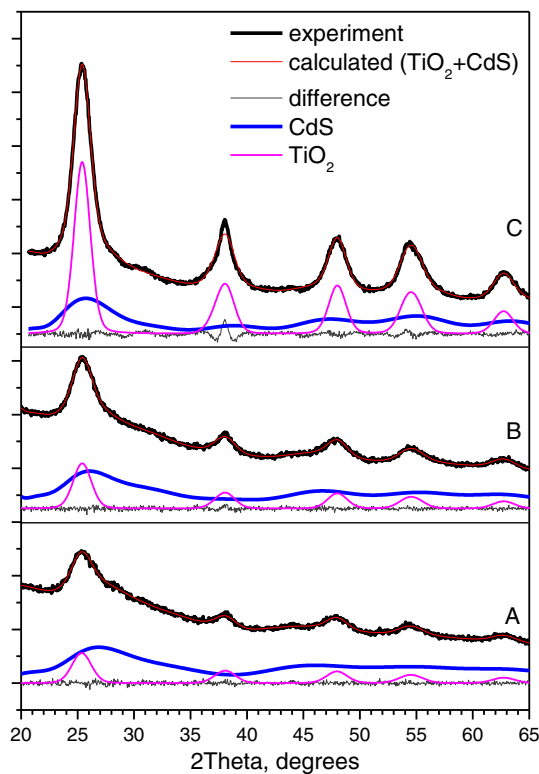


Fig. 1. Experimental XRD patterns of samples A, B, and C. Each XRD pattern was decomposed into individual XRD patterns of CdS and TiO₂ (anatase).

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