Materials Research Bulletin 61 (2015) 400–403

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Short communication

Preparation of mesoporous CdS-containing TiO_2 film and enhanced visible light photocatalytic property

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ARTICLE INFO

Article history:
Received 21 March 2014
Received in revised form 13 September 2014
Accepted 20 September 2014
Available online 29 October 2014

Keywords:
Mesoporous structure
CdS nanoparticles
Photocatalyst
SILAR
Solvothermal method

ABSTRACT

Mesoporous TiO_2 films containing CdS nanocrystals were successfully fabricated by a two-step process of successive ionic layer adsorption and reaction (SILAR) technique and a solvothermal method followed by annealing. The distribution of CdS nanoparticles in the inner structures of the TiO_2 mesoporous films is confirmed by field emission scanning electron microscope. The CdS modification of the mesoporous films results in an increase in the visible light adsorption, and exhibits more excellent photocatalytic degradation of methyl orange (MO) under visible light irradiation.

1. Introduction

Since the discovery of water splitting on TiO_2 surfaces by photoirradiation [1], TiO_2 has been shown to be an excellent photocatalyst to decompose hazardous dyes, which has attracted extensive interest [2,3]. Comparing to TiO_2 nanopowders, TiO_2 mesoporous structure has larger surface area, better adsorption capacity and higher photocatalytic activity [4,5]. Therefore, TiO_2 mesoporous film has been widely studied as a model system for a range of photocatalytic processes. However, the large band gap of TiO_2 limits its photoactivity to the UV region of the solar spectrum [6–8].

The coupling of TiO_2 mesoporous film to semiconductors has been proved to be an efficient method to enhance its photoresponse under visible light irradiation [9,10]. In particular, the band-gap of CdS (Eg = 2.4 eV) and its relatively high absorption coefficient in the visible region make it highly desirable for use as photocatalyst in comparison with other semiconductors [11]. To date, CdS nanoparticles can be fixed onto the TiO_2 mesoporous film by various methods, including layer-by-layer deposition [12], sequential chemical bath deposition [13], high-pressure deposition [14], self-assembly [15], etc. For example, Tamiolakis et al. prepared TiO_2 mesoporous film sensitized by CdS nanoparticles by ion-exchange method, and the photocatalyst showed superior activity and stability in visible-light-driven oxidation of 1-phenylethanol [16]. However, these reported CdS nanoparticles were only deposited on the surface of the TiO_2 mesoporous films, which limited the photocatalytic efficiency. The present major challenge in photocatalysis is to develop highly visible-light-active TiO_2 mesoporous film containing uniformly CdS nanoparticle in the whole structures. To the best of our knowledge, few studies, so far, attempted to prepare TiO_2 mesoporous film that has a uniform distribution of CdS nanoparticles in the mesoporous structures [17].

On the basis of above considerations, we have been intent to develop a simple synthetic strategy to fabricate TiO_2 mesoporous film containing uniformly CdS nanoparticles. In the present paper, we report a novel loading of CdS nanoparticles into a TiO_2 mesoporous film prepared by using solvothermal method. The results indicate that the prepared mesoporous CdS-containing TiO_2 heterojunction film is able to significantly enhance the photo absorption abilities and photocatalytic activities as compared to those of TiO_2 mesoporous film alone under the same conditions.

2. Experimental

2.1. Preparation of TiO_2/CdS mesoporous film

CdS nanoparticles sensitized TiO_2 nanotube arrays were prepared using the SILAR method for 5 cycles, which was similar to our previous report [18]. The as-prepared samples were immersed into 1 M ethanol solution of ammonia held in a Teflon autoclave, which was subsequently transferred to a baking oven for solvothermal treatment at 180 °C for 12 h. After the autoclave

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http://dx.doi.org/10.1016/j.materresbull.2014.09.056
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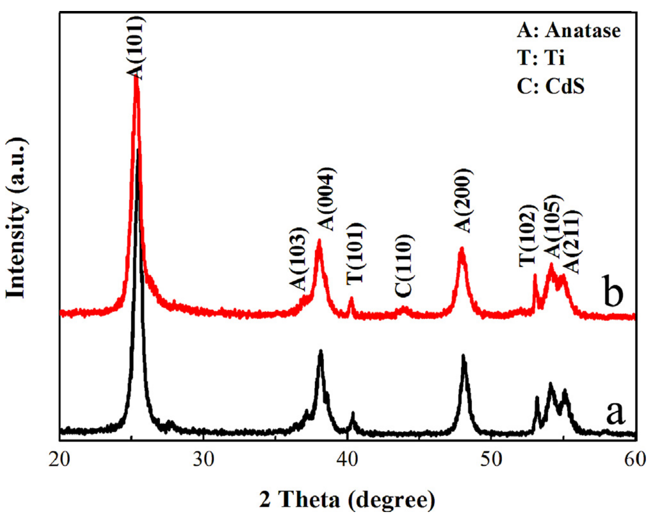

Fig. 1. XRD patterns of the MTF (a) and CdS–MTF (b).

cooled down naturally, the sample (denoted as CdS–MTF) was taken out and ultrasonically cleaned with acetone and deionized water. For comparison, the TiO_2 nanotube arrays without CdS nanoparticles sensitization were solvothermal treated under the same condition, which was denoted as MTF. Finally, the films were annealed at 300 °C for 1 h.

2.2. Characterization

The phase composition of the products was determined by a Rigaku D/Max 2400 X-ray diffractometer (XRD) equipped with graphite monochromatized Cu Kα radiation. The morphology and element composition of the products were directly observed by a JEOL JSM-5600LV scanning electron microscope (SEM) equipped with energy dispersive spectroscope (EDS). UV–vis diffuse reflectance spectra (DRS) of the samples were recorded on a UV-2550 UV–vis spectrophotometer with an integrating sphere attachment. $BaSO_4$ was used as a reflectance standard in the wavelength range of 200–800 nm.

2.3. Photocatalytic activity test

The photocatalytic activity of the prepared samples was evaluated by photocatalytic decomposition of MO in 15 mL dye aqueous solution and 2 mL 0.2 M Na_2S and Na_2SO_3 solution under 500 W Xe lamp irradiation. Before photodegradation, adsorption equilibrium of the dye on the sample with area of 2 cm^2 was established by mechanical stirring for 30 min in the dark environment. The change in MO concentration was monitored by determining the UV-visible adsorption of 3.0 mL sample taken from the solution every 1.5 h at 464 nm. After measurement, the sample was put back to the reaction solution to conduct the photo-degradation experiments with the same procedure as mentioned above.

3. Results and discussion

The typical powders XRD patterns of the MTF and CdS–MTF are shown in Fig. 1. The MTF sample demonstrates a distinct XRD pattern that confirms the formation of crystalline TiO_2 with anatase phase indexed to a standard JCPDS card (PDF no. 21-1272, labeled "A"). One can also observe the signals from the underlying Ti (PDF no. 44-1294, labeled "T"). This result indicates that the amorphous structure of TiO_2 nanotubes can be transformed to anatase TiO_2 after solvothermal treatment at 180 °C. Compared with curve (a), the XRD pattern of the CdS–MTF (Fig. 1b) exhibits a new diffraction peak at 43.8°, which is corresponding to (110) crystal planes of CdS phase (JCPDS no. 65-3414, labeled "C").

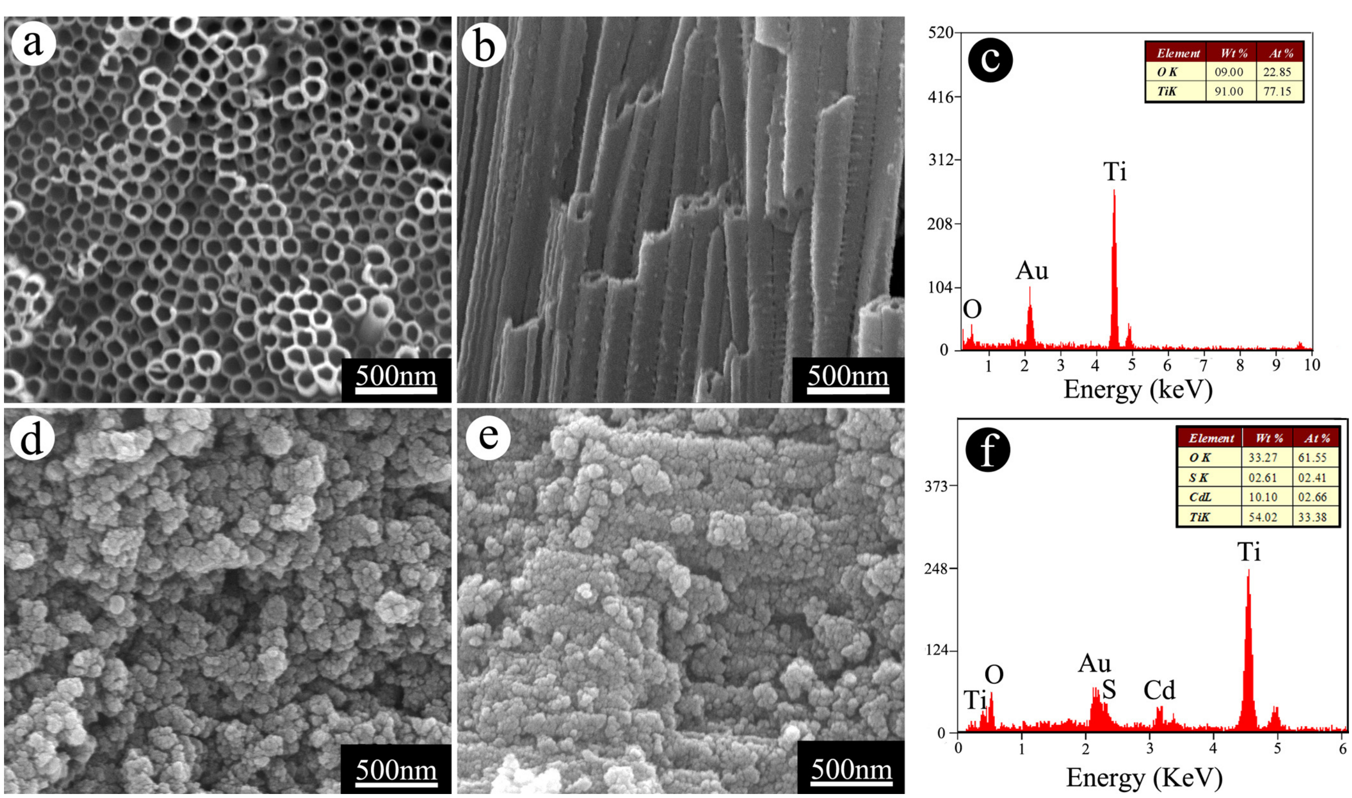

Fig. 2. SEM images of the TiO_2 nanotube arrays (up) and CdS–MTF (down): (a, d) Top-view, (b, e) Cross-sectional view and (c, f) EDS spectra.