Journal of Solid State Chemistry 214 (2014) 101–107

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Synthesis and characterization of Cr-doped ZnO nanorod-array photocatalysts with improved activity

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ARTICLE INFO

Available online 30 September 2013

Keywords:
Photocatalyst
Cr-doped
Zinc oxide
Photoelectrochemical effect
Scanning electrochemical microscopy

ABSTRACT

Immobilized photocatalysts with high catalytic activity under UV light were prepared by growing Cr-doped ZnO nanorods on glass substrates by a hydrothermal method. The effects of Cr dopant on the surface texture, crystallinity, surface chemistry, and photoinduced charge separation and their relation with the photocatalytic degradation of Cr-doped ZnO were investigated by scanning electron microscopy, diffuse reflectance spectra, photoelectrochemical scanning electrochemical microscopy, and X-ray photoemission spectroscopy. Adding the appropriate amount of Cr dopant is a powerful way to enhance the separation of charge carriers in ZnO photocatalyst. The photocatalytic activity was improved due to the increase in surface oxygen vacancies, the separation of charge carriers, modification of the band gap, and the large surface area of the doped ZnO nanorod photocatalyst.

1. Introduction

The use of semiconductive photocatalyst for photocatalytic photodegradation of organic pollutants in water caused by pesticides, dyes and heavy metals has attracted much attention [1,2]. Wide-bandgap semiconductor photocatalysts such as TiO_2 and ZnO can degrade various organic pollutants under UV irradiation, which offers great potential for the complete elimination of toxic chemicals. Various kinds of nanostructured ZnO can be used for applications such as transparent conducting layers [3,4], solar cells [5,6], gas sensors [7,8], light-emitting photonic devices [9], photocatalytic degradation of dye pollutants [10–12], and second-order nonlinear optical applications [13]. The potential for photo-dissolution is a major concern for zinc oxide (ZnO) photocatalysts. Lathasree et al. [14] investigated the reusability of ZnO photocatalysts. They found that a small extent (0.04%) of ZnO underwent photo-dissolution after 2 h of reaction. Yassitepe et al. [15] reported that the photocatalytic activity of ZnO plate gradually decreased, but if the photocatalysts are stored in the dark overnight, the activity of the photocatalyst can be recovered. Also, Zhu [16] reported that photocorrosion can be inhibited and photoactivity can be enhanced for zinc oxide via hybridization with monolayer polyaniline. ZnO photocatalysts suffer rapid dissolution under extreme pH levels (≤ 5 or ≥ 11). Adjusting the pH is an important procedure for almost all waste water treatment processes. The ZnO photocatalyst can be used for treatment of waste water if the photocatalytic decolorization procedure can be performed after the pH is adjusted. Therefore, a ZnO-based photocatalyst was studied in this research.

Recently, catalysts and photocatalysts have demonstrated promising performances in one-dimensional (1D) semiconductor nanostructures in the form of nanorods, nanowires, or nanotubes [17], triggering a wide range of subsequent research on the photocatalytic properties of 1D ZnO nanostructures [18,19]. In addition, the introduction of transition metal doping states will improve the photocatalytic activity due to the band-gap narrowing resulting from the creation of dopant energy levels below the conduction band [20,21]. Cr has an ionic radius parameter similar to that of Zn^{2+} [22–24], which indicates that Cr^{3+} can fill the Zn^{2+} position in the crystal lattice or penetrate into ZnO crystal [25]. The doping of Cr in ZnO is expected to modify the absorption, luminescence, photocatalytics, and other physical or chemical properties of ZnO. Wang et al. [26] and Guan [27] reported that aligned Cr-doped ZnO nanorods exhibited ferromagnetism.

The motivation in this work is to improve the photocatalytic property of ZnO nanorods by introducing the Cr dopant and to investigate the effects of Cr dopant on the structure, surface texture, morphology, surface chemistry, and the photoinduced charge separation rate, and their relation with the photocatalytic activity of Cr-doped ZnO prepared by a hydrothermal method. The photocatalytic performance has been investigated by employing the photocatalytic decolorization of dye solution used in the ink industry.

2. Material and methods

2.1. Materials

Zinc nitrate 6-hydrate was provided by J.T. Baker. Hexamethylenetetramine (HMTA) was bought from Riedel-de Haën. Chromium nitrate was provided by Sigma-Aldrich. Methyl orange was the product of Alfa Aesar. Direct Blue 86, Direct Violet 99, Direct Yellow

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0022-4596/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2013.09.039

132, and Food Black 2 were purchased from Bayer, and *n*-hexadecyltrimethylammonium hydroxide was obtained from TCI.

2.2. Preparation of seed solution

For the fabrication of the seed solution, 0.1 M zinc acetate was dissolved in ethanol at 60 °C and stirred for 2 h. After the solution was cooled to 0 °C, *n*-hexadecyltrimethylammonium hydroxide (HTAOH) was added (Zn^{2+}/HTAOH = 1/2) and the solution was stirred for 30 min. The resulting mixture was then agitated at 60 °C for 2 h to yield a homogeneous and stable colloid solution, which served as the seed solution. We dripped the seed solution on the glass slides and then dried and annealed the slides at 300 °C for 1 h to deposit a seed layer on the glass slides.

2.3. Growth Cr doped ZnO nanorods on glass slides

To synthesize the Cr-doped ZnO nanorod arrays, different amounts of Cr $(NO_3)_3 \cdot 9H_2O$ were added to an aqueous solution of 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1 M hexamethylenetetramine as a Cr source to fix their concentrations at 0.1, 0.5, 1.0, and 1.5 mM, respectively. The glass slides were placed face down in the solution and held at 95 °C for 4, 16, and 48 h to grow nanorods on the glass slides. After that, the substrate was removed and rinsed with distilled water several times before being stored at room temperature.

2.4. Photocatalytic degradation

Cr-doped ZnO nanorod pore-array photocatalysts were added into a testing vessel with 10 mL aqueous dye solution. The dye solution was continuously stirred until the UV light or visible light irradiation started. About 3.5 mL DB86 aqueous solution was taken to monitor the absorbance spectra. The degradation procedure was monitored by a UV–Vis absorbance spectrometer measuring the absorbance of MO at the 465 nm wavelength. The UV light (or visible light) for the photocatalytic degradation test was shut off during the absorbance monitoring procedure.

Afterward, 3.5 mL dye aqueous solution was poured into the testing vessel. The light irradiation of the dye solution continued. The absorption spectra were recorded and the rate of decolorization was observed in terms of change in intensity at λ max of the dyes. The decolorization efficiency (%) can be calculated as

$$(Co - C)/Co \times 100(\%)$$

where Co is the initial concentration of dye and C is the dye concentration after UV light (or visible light) irradiation.

2.5. Characterizations

The morphology images were determined by multimode scanning probe microscope (AFM, Digital Instrument NS4/D3100CL/MultiMode). X-ray diffraction patterns were obtained on a Bruker D8 SSS multipurpose thin-film X-ray diffractometer (HRXRD) with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The field emission scanning electron microscope images were recorded on a HITACHI S-4800 field emission scanning electron microscope (FESEM). The energy dispersive X-ray (EDX) and high-resolution TEM (HRTEM) images were recorded on a transmission electron microscope (Philips Tecnai F20 G2 FEI-TEM). The photoluminescence spectra and absorbance of the dye solution of the catalyst film were measured by a PL 2006 multifunctional spectrometer (Labguide Co.). The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ULVAC-PHI, PHI 5000 VersaProbe. The photoinduced current of the photocatalyst was measured by scanning the photocatalyst pattern using PC-controlled PEC-SECM (photoelectrochemical scanning electrochemical microscopy, CHI model 900C, CHI Instruments), and PEC-SECM images were obtained by screening the undoped and Cr-doped ZnO nanorod arrays using SECM in 0.2 M NaOH solution under UV illumination with a scan rate of 500 μm/s.

3. Results and discussion

3.1. Morphology

Fig. 1 presents the top view and cross-sectional view FESEM images of Cr-doped ZnO nanorods with different rod-growth times. In this study, zinc oxide nanorods were prepared by using the HMTA template as capping molecules. The crystallization process confined in the HMTA capping molecules is responsible for the formation of rod-like ZnO nanostructures. Well-crystallized ZnO nanorods with hexagonal structures were synthesized because the surface defects were partly passivated by HMTA. Nucleation occurred on the active sites of the seeds, grew along the 1D direction, and recrystallized into hexagonal ZnO nanorods. The number of nanorods per unit area (number density) decreased when the nanorod growth time was extended, although the length of the nanorods increased. When the nanorod growth time reached 24 h, the number density of the nanorods decreased, although the aspect ratio of the longest nanorods continued to increase with increasing growth time. Some of the nanorods stopped growing. Similar phenomena were observed in our previous study [28]. Similar phenomena were also reported by Goh et al. [29,30]. They found that the orientation of the TiO_2 nanorods depends on the initial nucleation density. A larger proportion of elongated *c*-axis TiO_2 crystallites growing normally to the substrate were formed on the samples with higher initial nucleation density. The higher initial nucleation density meant that laterally growing nanorods would be obstructed much sooner, as the adjacent nanorods were much closer. In this study, the cross-sectional images revealed that not all the nanorods grew vertically; some grew at a tilted angle. During the growing process, a 'collision' between two adjacent ZnO nanorods would stop the growth of the tilted nanorod. Meanwhile, the nanorod that was hit on its side would continue to grow after the 'collision'. Therefore, the number density of nanorods decreased as the growth time was extended.

To compare the effect of growth time on the morphology of the nanorods, the concentration of precursor was kept unchanged (0.1 mM). The top view and cross section view of ZnO nanorods prepared with different rod growth times are shown in Fig. 1. The length and diameter of the nanorods increased with increasing rod growth time. With the growth time increased from 4 to 48 h, the diameter of nanorods increased from 73 to 111 nm. Meanwhile, the length increased from 1.0 to 2.6 μm.

3.2. HRTEM

The HRTEM and SAED were recorded to characterize the morphology and structure of the nanorods. Fig. 2a shows the HRTEM image and SAED of a pure ZnO nanorod. The lattice fringes can be clearly seen in the HRTEM images, indicating that the nanorods were highly crystalline. The lattice spacing of pure ZnO nanorods was 0.26 nm, matching the (0 0 2) planes of the wurtzite ZnO. Fig. 2b shows the HRTEM image and SAED of a Cr-doped ZnO nanorod. The lattice spacing of Cr-doped ZnO nanorods was 0.24 nm. No additional phase was observed in the HRTEM images of doped ZnO nanorods. For Cr-doped ZnO nanorods, the Cr, Zn, and O atomic contents were 0.14, 46.3, and 53.56%, respectively.

3.3. Diffuse reflectance spectra

Fig. 3 shows the UV–Vis diffuse reflectance spectra of Cr-doped ZnO (0.5 mM) and undoped ZnO. The doping with Cr changed the light absorption properties of the photocatalyst. As shown in Fig. 3, the Cr-doped ZnO photocatalyst had a red-shift of the absorption