



Cadmium hydroxide and oxide nanoporous walls with high performance photocatalytic properties



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ABSTRACT

Cadmium hydroxide nanowalls were directly grown on glass substrate by a hydrothermal method. The concentration of hexamethylenetetramine plays a crucial role for controlling the thicknesses of cadmium hydroxide nanowalls. A part of the cadmium hydroxide nanowalls can be converted to cadmium oxide nanoporous walls by annealing cadmium hydroxide in air at 350 °C for 1 h. Cadmium hydroxide and oxide nanoporous walls exhibited very strong and broad emission properties in the cathodoluminescence spectrum. Furthermore, cadmium hydroxide and oxide nanoporous walls can also provide a higher surface-to-volume ratio to result their higher photocatalytic performance in degradation of methylene blue.

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1. Introduction

The unique physical properties of nanomaterials have stimulated the fabrication of complex and functional architectures, such as controlling the lateral placement of nanometer sized objects into specific arrangements, for use in optical, electrical, and magnetic properties [1,2]. Some optical properties, such as luminescence, photocatalytic, and sensing properties are strongly dependent on the particular exposed surface of the nanostructures [1,3–7]. The ability to systematically adjust these material parameters provides the opportunity to study and understand the relationship between chemical, structural, and quantum effects that occur uniquely at the nanoscale [8,9].

Recently, there has been great research interest in the synthesis of nanostructured transition metal hydroxide or oxide materials due to their important technological applications [10]. The nanostructured metal hydroxides including $\text{Ni}(\text{OH})_2$, $\text{In}(\text{OH})_3$, $\text{Cu}(\text{OH})_2$, and $\text{Cd}(\text{OH})_2$ have been synthesized as potential templates or precursors for the corresponding oxide materials [10–14]. Among them, $\text{Cd}(\text{OH})_2$ is an important precursor for the eventual synthesis of functional materials such as CdS and CdSe by reaction with appropriate compounds [15]. $\text{Cd}(\text{OH})_2$ is a wide band-gap, n-type semiconductor material with potential applications in solar cells, photodetectors, transparent electrodes, sensors, and cathode materials for battery applications [16–18]. Therefore, various

morphological $\text{Cd}(\text{OH})_2$ structures have been synthesized by different methods, such as hydrothermal [15], sonochemical [19], and liquid phase pulsed laser ablation methods [20]. The hydrothermal fabrication approach is the most successful fabrication method for growing nanowire bundles [21], hollow microspheres [15], nanodisks [22], nanoplates [19], nanostands [17], and nanorings [19]. However, there has no research focused on the formation of $\text{Cd}(\text{OH})_2$ nanowalls.

CdO is an important II–VI semiconductor and the preparation of CdO nanostructures has received much attention for various optoelectronic devices due to its high electrical conductivity (even without doping), high carrier concentration, and high optical transmittance in the visible region of the solar spectrum [21,23,24]. In addition, the materials can also be used in photodiodes, gas sensors, transparent electrodes, and catalytic properties [25–27]. CdO has a narrow direct band gap ranging from 2.2 to 2.5 eV and an indirect band gap of 1.98 eV [28]. The different band gap is attributed to cadmium and oxygen vacancies and strongly depends on the fabrication procedures [29]. CdO nanostructures have been fabricated by various techniques, such as pulsed-laser deposition [30], magnetron sputtering [31], sol–gel [32], metal–organic chemical vapor deposition [23], and hydrothermal methods [33]. Recently, a facile fabrication method can be used to convert the $\text{Cd}(\text{OH})_2$ nanostructures into CdO with similar morphology by thermal treatment [15,22]. Appropriate thermal treatment conditions can be beneficial to make $\text{Cd}(\text{OH})_2$ fully convert CdO . However, there are no reports published on the two mixture compounds of $\text{Cd}(\text{OH})_2$ and CdO nanoporous walls.

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The present study uses various concentration of HMTA and in conjunction with hydrothermal process to produce the different thicknesses of Cd(OH)₂ nanowalls. The mixture compounds of Cd(OH)₂ and CdO nanoporous walls can be easily fabricated by annealing Cd(OH)₂ nanowalls in air at 350 °C for 1 h. The Cd(OH)₂ and CdO nanoporous walls exhibited very strong and broad emission properties in the cathodoluminescence spectrum, which shall be beneficial in white light-emitting devices. Cd(OH)₂ and CdO nanoporous walls can also provide a higher surface-to-volume ratio to result their higher photocatalytic performance in UV and visible irradiation.

2. Experimental

2.1. Preparation of Cd(OH)₂ and CdO nanoporous walls

In a typical synthesis, 25 mM Cadmium acetate dihydrate (98%, Aldrich) and the different concentration of hexamethylenetetramine (99%, Aldrich) (HMTA) were dissolved in 40 mL of di-ionized water. Glass substrates were cleaned in a boiling piranha solution (H₂O₂:H₂SO₄, 3:7, v/v) for 10 min, and then rinsed with de-ionized water and ethanol. The cleaned glass substrates were placed at the bottom of sealed bottles containing the above solution. Then, the bottles were putted into an oven and maintained at 90 °C for 2 h. Finally, the Cd(OH)₂ nanowalls substrates were washed with deionized water several times, and dried under a N₂ purge. Cd(OH)₂ and CdO nanoporous walls were produced after annealing at 350 °C in air for 1 h.

2.2. Characterization

The morphology of nanostructures was examined with a field emission scanning electron microscope (FESEM) using a JEOL JSM-6500F SEM operating at 10 kV accelerating voltage. A JEOL-2010 transmission electron microscope (TEM) operating at 200 kV was used to examine the microstructures. Brunauer–Emmett–Teller (BET) specific surface areas of the samples were determined from the N₂ adsorption–desorption isotherms. The cathodoluminescence (CL) spectra were acquired with an electron probe microanalyzer (Shimadzu EPMA-1500) attached to a SEM. CL spectra were accumulated in a single shot mode within an exposure rate of 1 nm/s. All the CL spectra were taken at room temperature. The degradation of methylene blue aqueous solution was used to evaluate the photocatalytic activity of Cd(OH)₂ and CdO nanoporous walls. The methylene blue solutions were exposed to 10 W UV or visible lamp. For the photocatalytic activity evaluation, the concentration of photodegraded methylene blue was recorded by a Hitachi U-2900 UV–vis spectroscopy.

3. Results and discussion

3.1. Evaluation of Cd(OH)₂ and CdO nanoporous walls

Fig. 1 shows the top-view SEM images depicting the Cd(OH)₂ nanowalls grown from 25 mM cadmium acetate dihydrate and the different concentrations of HMTA by a hydrothermal method. The inset are cross-sectional SEM images exhibiting Cd(OH)₂ nanowalls. The concentrations of HMTA are 7.5, 12.5, 25, and 75 mM, respectively. The glass substrates were positioned at the bottom of the sealed bottles and heated at 90 °C for 2 h. The Cd(OH)₂ nanowalls are composed by many thin nanoplates. The average thicknesses of Cd(OH)₂ nanowalls are 1.28, 1.59, 1.94, and 3.24 μm, respectively. The average thicknesses of Cd(OH)₂ nanowalls were increased with the increase in the concentration of HMTA, as shown in Fig. 1e. The variation concentration of HMTA was found to affect the thicknesses of Cd(OH)₂ nanowalls. Furthermore, when the concentration of HMTA was increased, the Cd(OH)₂ nanowalls increased in sizes and almost bound together. On the other hand, the appropriate concentration of HMTA can be exploited to control the different sizes and thicknesses of Cd(OH)₂ nanowalls.

Fig. 2a shows a TEM image of a Cd(OH)₂ nanowall grown with 25 mM cadmium acetate dihydrate and 75 mM HMTA, which is composed by the different grains. The corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 2b, which indicates Cd(OH)₂ nanowall is polycrystalline. The concentric rings could be assigned as diffraction from [1 1 -1], [2 2 0], [2 4 0], [4 2 -1],

and [3 1 1] planes of monoclinic phase γ-Cd(OH)₂ (JCPDS Card No. 40-0760) from centermost ring, respectively. The high-resolution TEM (HRTEM) image taken from part of an individual Cd(OH)₂ nanowall is shown in Fig. 2c. From HRTEM image of the polycrystalline nanowalls exhibits two different lattice fringes with interplanar spacing of 0.496 nm and 0.365 nm, which are in good agreement with the d-spacing of the [1 1 0] and [1 -1 -1] planes, respectively. The chemical composition of the nanowalls was analyzed by energy-dispersive spectroscopy (EDS). As shown in Fig. 2d, the EDS spectrum reveals the composition of Cd(OH)₂ nanowalls with only cadmium and oxide component (Cu and C are from the TEM grid).

In previous work, the Cd(OH)₂ hollow microspheres can be easily converted to CdO semiconductors with similar morphology by calcining Cd(OH)₂ in air 350 °C for 4 h [15]. Herein, we used the same calcining temperature (350 °C) and short time (1 h) to make a part of Cd(OH)₂ nanowalls (75 mM HMTA) to convert CdO nanoporous walls, as shown in Fig. 3a and b. From the SEM image, the morphology of Cd(OH)₂ nanowalls were changed to Cd(OH)₂ and CdO nanoporous walls by a thermal treatment process. Fig. 3c shows a TEM image of a Cd(OH)₂ and CdO nanoporous wall, which is composed by the amount of grains. The SAED pattern indicates a Cd(OH)₂ and CdO nanoporous wall is polycrystalline, as shown in Fig. 3d. The concentric rings could be assigned as diffraction from [1 1 1], [2 2 0], [2 2 2], and [4 0 0] planes of cubic phase CdO (JCPDS Card No. 78-0653) from centermost ring, respectively. Furthermore, the concentric rings are still with the diffraction from [1 -1 -1], [2 2 0], [2 4 0], [4 2 -1], and [3 1 1] planes of monoclinic phase γ-Cd(OH)₂ (JCPDS Card No. 40-0760) from centermost ring, respectively. The results confirm that the nanoporous walls are constructed by Cd(OH)₂ and CdO. In addition, the HRTEM image taken at the interface clearly reveals two distinct sets of lattice fringes, as shown in Fig. 3e. An interlayer spacing of 0.497 nm was obtained in the nanoporous region, which is good agreement with d-spacing of [1 1 0] lattice planes of monoclinic phase γ-Cd(OH)₂ crystal. Another nanoporous region an interlayer spacing of 0.145 nm was obtained, which matches well to the lattice spacing of the [3 1 1] plane of the cubic phase CdO crystal. Fig. 3f indicated that the peaks are corresponded to monoclinic phase γ-Cd(OH)₂ and cubic phase CdO, respectively. No peaks of impurities were observed. This result can also confirm that the products are composed of Cd(OH)₂ and CdO.

3.2. Optical property of Cd(OH)₂ and CdO nanoporous walls

The cathodoluminescence (CL) spectrum of Cd(OH)₂ nanowalls obtained from 75 mM HMTA, which have two emission peaks centered at 432 nm (2.87 eV) and 450 nm (2.76 eV), as shown in Fig. 4a. Emission peaks observed at 2.87 eV and 2.76 eV may arise due to the electronic transitions from the bottom of the conduction band to the top of the valence band (corresponding to the band gap) and to the Cd²⁺ vacancy level/OH⁻ ion at interstitial positions (hole trap levels), respectively [20]. The two peaks are attributed to the quantum confinement effect from the different grain sizes of each wall. For the CL emission spectrum, the energy shift of nanorods with diameters far beyond the quantum confinement regime is ascribed to the surface effect due to the increased surface-to-volume ratio [34]. The peak intensity of 2.87 eV is a little higher than 2.76 eV. This result confirms that the amount of small grain sizes of Cd(OH)₂ is more than large grain sizes.

After annealing Cd(OH)₂ nanowalls in air 350 °C for 1 h, the CL spectrum exhibit the very strong and broad range emission, as shown in Fig. 4b. For Cd(OH)₂ and CdO nanoporous walls, there are still with two peaks of 432 nm (2.87 eV) and 452 nm (2.74 eV) from Cd(OH)₂. The little red shift is attributed to the quantum confinement effect arising from the increased grain sizes

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