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Synthesis and photoelectric properties of cadmium hydroxide and cadmium hydroxide/cadmium sulphide ultrafine nanowires

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ABSTRACT

$Cd(OH)_2$ ultrafine nanowires with a high aspect ratio were fabricated by the hydrothermal method and were subsequently used as a sacrificial template to generate $Cd(OH)_2$/CdS nanowires. The transmission electron microscopy results show that the length of the nanowires reached several micrometres, and the diameter of the nanowires was approximately 10–20.0 nm. The charge transport properties of the $Cd(OH)_2$ and $Cd(OH)_2$/CdS nanowires assembled on comb Au electrodes was also investigated. The *I-V* results showed that the current intensity of the $Cd(OH)_2$/CdS nanowires was increased by four orders of magnitude compared with the $Cd(OH)_2$ nanowires, achieving 10^{-10} A.

1. Introduction

One-dimensional (1D) nanostructures, including nanorods, nanowires, and nanotubes, have attracted increasing interest because of their so-called size- and morphology-dependent physicochemical properties and technological applications compared with their bulk-phase counterparts [1–5]. In the last decade, remarkable advances have been made in the synthesis and characterization of such materials, which are expected to open the way for, for instance, nanoelectronics, ultrasmall optoelectronic devices,and biosensors [3,6,7]. Among these 1D materials, *II–VI* group semiconductors have been studied indepth and applied widely. They play an important role in optoelectronic devices such as laser light-emitting diodes and solar cells [8–10]. In recent years, CdS and $Cd(OH)_2$ have been synthesized by different methods such as template-guided synthesis and the hydrothermal method [11–13]. For example, Ichinose et al. have synthesized cadmium hydroxide nanostrands with an extremely narrow diameter of 1.9 nm that are formed by just raising the pH of a dilute $Cd(NO_3)_2$ solution [11]. Shinde et al. have synthesized ultralong $Cd(OH)_2$ nanowires on different substrates [12]. $Cd(OH)_2$ is a wide band-gap semiconductor and is widely applied to devices including solar cells, phototransistors and photodiodes, transparent electrodes, sensors, and cathode materials of batteries. Furthermore, $Cd(OH)_2$ is an important precursor that can be converted into cadmium sulphide (CdS) or into other functional materials such as cadmium oxide (CdO) and cadmium selenide (CdSe) by reactions with the appropriate compounds. The new materials can be used as electrode additives to increase the discharge capacity of Cd-Ni batteries [14–16].

Although $Cd(OH)_2$ and CdO nanowires from various synthetic methods have been reported, usually, their diameters are larger than 20.0 nm, and their electrical properties have not been intensively reported. In this work, $Cd(OH)_2$ nanowires were obtained with a diameter of 10–20.0 nm by the hydrothermal method. The synthesized $Cd(OH)_2$ nanowires were then used as sacrificial templates to generate $Cd(OH)_2$/CdS nanowires. The electron transport properties of two kinds of nanowires on an electrode were tested, and the current intensity of the $Cd(OH)_2$/CdS nanowires increased by four orders of magnitude compared with the $Cd(OH)_2$ nanowires.

2. Experimental section

2.1. $Cd(OH)_2$ and $Cd(OH)_2$/CdS nanowire preparation and assembly

$Cd(NO_3)_2{\cdot}4H_2O$ (154.2 mg, analytical reagent, Tianjin Kermel Chemical Reagent Co., Ltd) and 105 mg hexamethylenetetramine ($C_6H_{12}N_4$, analytical reagent, Tianjin Fu Chen Chemical Reagent Factory) were dissolved in 50 mL deionized water and stirred for 10 min. Next, the reaction solution was put into a 50 mL Teflon-lined stainless steel autoclave up to 80% of the total volume. The autoclaves were sealed and moved to a laboratory oven at 105 °C for 18 h. Then, the autoclaves were taken out of the oven and air-cooled to room temperature. The resulting white solid product was centrifuged, washed with deionized water and ethanol to remove ions possibly remaining in the final product, and dried at 60 °C. By this way, we obtained sample A.

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The pre-patterned Au electrodes were defined on Si/SiO_2 (a 300 nm thick SiO_2 layer on a highly doped p-type Si substrate) by using a conventional photolithography process. Sample A was assembled onto comb electrodes by dropping the sample dispersed in ethanol. This assembly was sample B after the ethanol evaporated. Sample C was obtained after sample B was put into a 100 ppm H_2S gas atmosphere for 40 h. Then, two kinds of nanowires were deposited on the electrode.

2.2. $Cd(OH)_2$ and $Cd(OH)_2$/CdS nanowires structure and property characterization

Scanning electron microscopy (SEM, JSM5600 LV) and transmission electron microscopy (TEM, Jem 100CX-II) were used to investigate the $Cd(OH)_2$ nanowire size and morphology. The crystal structure was characterized by X-ray diffraction (XRD , Philips X'Pert Pro MPD), and the instrument was operated at 40 kV voltage and a 40 A current using Cu Ka radiation. X-ray photoelectron spectroscopy (XPS) was performed with an Axis Ultra-utility. The ultraviolet-visible (UV–vis) absorption of the $Cd(OH)_2$ and $Cd(OH)_2$/CdS nanowires were measured with a Heios (Unicam, Briain, PE-Lambda35), and the photoluminescence (PL) was obtained on a SPEX Fluorolog F212 (SPEX,USA). The probe station (Lake heating, CCR-VF) and the semiconductor characteristics tester (Keithley, 4200SCS) were used to obtain the electron transport properties of the two kinds of nanowires.

3. Results and discussion

Fig. 1 shows the XRD pattern of sample A prepared by the hydrothermal method from a $Cd(NO_3)_2{\cdot}4H_2O$ and $C_6H_{12}N_4$ aqueous solution at 105 °C for 18 h. All the peaks in this pattern can be readily indexed as the pure hexagonal phase of $Cd(OH)_2$ (space group,$P\bar{3}ml$) with lattice constants of a=3.494Åand c=4.710 Å(JCPDS31-0228). Fig. 2 shows the morphology of these as-prepared $Cd(OH)_2$ products as investigated by SEM and TEM. As shown in Fig. 2a and b, the sample consists of an abundance of nanowires, and the length of an individual $Cd(OH)_2$ nanowire is several micrometres. The higher magnification TEM image (Fig. 2c) reveals that the width of the nanowires is approximately 10–20.0 nm, and a small number of nanowires possess a diameter less than 10.0 nm. These ultrafine nanowires have a high aspect ratio. Their diameter is smaller than most reports; however, Ichinose et al. have reported cadmium hydroxide nanowires with an extremely narrow diameter of 1.9 nm. The high-resolution TEM (HRTEM) image in Fig. 2d suggests that the $Cd(OH)_2$ nanowires are polycrystalline, and the irregular grains have different sizes from ca.1.0 nm to ca.9.0 nm. Lattice images were successfully obtained from the corresponding circled areas in (d) and are shown in Fig. 2e and f. From these two lattice images, we can clearly observe spacings of 0.233 nm and 0.194 nm, corresponding to the (102) and (002) lattice planes of hexagonal $Cd(OH)_2$ shown as the two peaks in Fig. 1. It should be mentioned that these nanowires break into quantum dots under the electron beam, which is similar to the report by Georgi V. Stoychev et al. [17].

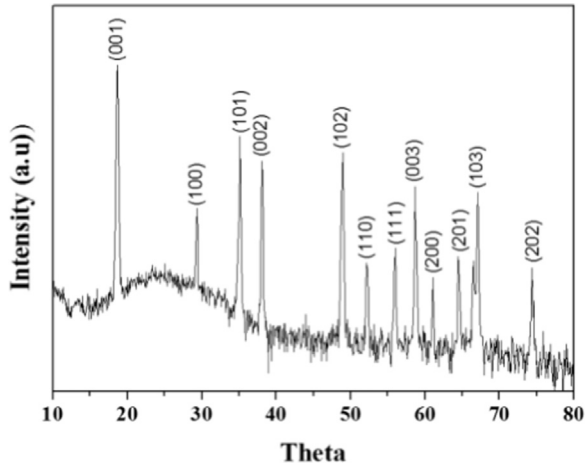

Fig. 1. XRD pattern of the $Cd(OH)_2$ ultrafine nanowires prepared by the hydrothermal method from a $Cd(NO_3)_2{\cdot}4H_2O$ and $C_6H_{12}N_4$ aqueous solution at 105 °C for 18 h.

The composition of the as-synthesized nanowires in Fig. 2 was also characterized by XPS, the results of which are shown in Fig. 3. Fig. 3a shows a typical XPS survey spectrum of the as-prepared nanowires. The strong XPS peaks of Cd 3d, C 1s, and O 2p can be observed. Fig. 3b and c show the Cd 3d and O 2p high-resolution XPS spectra, respectively. In Fig. 3b, the binding energies for the Cd 3d3/2, Cd3d5/2 peaks are observed at 412.1 eV and 405.2 eV, respectively. They are both attributed to bivalent cadmium. The O 1s at 531.75 eV is positively attributed to hydroxyl groups based on our process of preparation and is shown in Fig. 3c. The measured composition is 23.85% (Cd), and 76.15% (O) for the $Cd(OH)_2$ nanowires. As is known, for the case of $Cd(OH)_2$ nanowires , the chemical formula usually exists as $Cd_n(OH)_m(H_2O)_{np\text{-}m}^{(2n\text{-}m)+}$ [11]. The stoichiometric ratio of Cd and O is approximately 0.3, which is less than 0.5. Therefore, the XPS data clearly confirm that the obtained nanostructures consisted of hydrates and cadmium, or $Cd(OH)_2$ rich with oxygen or water.

The growth mechanism of these $Cd(OH)_2$ nanowires can be explained as follows:

$$C_6H_{12}N_4+10H_2O\rightarrow 6CH_2O+4NH_3{\cdot}H_2O$$

$$NH_3{\cdot}H_2O \leftrightarrows NH_4^+ + OH^-$$

$$n[Cd(H_2O)_p]^{2+} + mOH^- \leftrightarrows [Cd_n(OH)_m(H_2O)_{np-m}]^{(2n-m)+} \rightarrow [Cd_n(OH)_{2n}](s) + (np - m)H^+$$

In the solutions, when the product of the Cd^{2+} and OH^- ions is greater than the K_{sp} of $Cd(OH)_2$ ($0.6–2\times10^{-14}$), the precipitation of $Cd(OH)_2$could be obtained. This process was named hydroxyl olation [11].

In this report, the $Cd(OH)_2$nanowires were also used as a sacrificial template to generate $Cd(OH)_2$/CdS nanowires for the latter's important application [18]. The as-prepared $Cd(OH)_2$ nanowires were assembled on an electrode (sample B) and then were put into an H_2S atmosphere for 40 h (sample C). First, the chemical composition of sample C after the $Cd(OH)_2$ nanowires reacted with the H_2S gas was characterized by XPS, and the results of which are shown in Fig. 4. Fig. 4a shows the presence of S,C,O and Cd in the sample. The peaks for Cd 3d at 412.2 eV and 405.4 eV are also observed, as shown in Fig. 4b. They are both attributed to bivalent cadmium. Fig. 4c shows the S 2p XPS spectrum, and the S 2p peak at 161.8 eV is attributed to bivalent sulphur. Fig. 4d shows the O 1s XPS spectrum, and the O 1s peak at 532.4 eV is attributed to bivalent O in the $Cd(OH)_2$ nanowires. It is believed that only a part of the $Cd(OH)_2$ nanowires reacts with H_2S, and the $Cd(OH)_2$/CdS ultrafine nanowires were obtained by this method. As is generally known, CdS could be formed when $Cd(OH)_2$ is exposed to H_2S without the accompanying O_2. In the current experiment, the precursory $Cd(OH)_2$ nanowires were introduced into an H_2S atmosphere at low pressure, and the $Cd(OH)_2$/CdS ultrafine nanowires were obtained in situ.

Fig. 5a shows UV absorption spectra of the same $Cd(OH)_2$ and $Cd(OH)_2$/CdS nanowires. As shown as a dark line, the initial absorption location is at 450 nm, and there is a bump near 385 nm marked with a dotted circle. Fig. 5b shows the PL spectrum of $Cd(OH)_2$/CdS, and there is a peak at 532 nm, which is the typical surface-state PL for CdS. Both of these results showed that CdS was formed from the $Cd(OH)_2$ nanowires by reaction with H_2S.

The morphology of sample C was also observed by TEM, as shown in Fig. 6a. The TEM image (Fig. 6a) shows that the product consists exclusively of 1D wire-like nanostructures with several micrometres in