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Current Applied Physics 6 (2006) 781–785
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

New synthetic method of semiconducting nanorods and nanowires CdE (E = S and Se) by γ-irradiation

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Received 17 June 2004; received in revised form 9 December 2004
Available online 3 June 2005

Abstract

Semiconducting nanorods and nanowires were synthesized by γ-irradiation at room temperature and the atmospheric pressure. The experiment was carried out in ethylenediamine and pyridine as solvents. Ethylenediamine and pyridine molecules were coordinated with metal ions and have an effect on the shape like nanorods and nanowires. Their crystallinity was determined with X-ray powder diffraction (XRD). Energy dispersive X-ray spectrometer (EDX) was used to characterize the elements. Transmission electron microscopy (TEM) images were used to determine the diameter and the length of them.

PACS: 68.47.Fd; 72.80.Ey; 78.40.Fy; 61.46.Tw; 81.07.−b

Keywords: Nanorods; Nanowires; γ-Irradiation; Ethylenediamine; Pyridine

1. Introduction

The special properties of nanomaterials have attracted much interest [1,2]. Unique structure, optical and electrical properties of one-dimensional (1D) semiconductors and metals make them the key structural blocks for a new generation electronics, sensors, and photonics materials [3–7]. Several synthetic methods of nanorod and nanowire production have been developed, but they all are based on point-initiated uniaxial growth of the crystal. The methods of nanorods and nanowires have been reported previously using several approaches including laser-assisted catalytic [3] and vapor-phase growth method [4], electrochemical method [5], and using template (as DNA [6]), block copolymer (as double-hydrophilic block copolymer [7]). The reaction sources used are usually toxic H_2S [8], CS_2 [9], and the noxious surfactants as TOP/TOPO [8]. In case of nanorods and nanowires, the heterogeneous reactants produced by laser ablation and difficulty in controlling nucleation in vapor-phase growth have limited the control of key properties with these methods. In colloidal reactions, the various templates are needed and removed from the synthesized materials.

A γ-irradiation method has been applied to prepare some ultrafine metal and oxide powders [10–12]. In general, the γ-irradiation method performed without toxic H_2S, CS_2, and TOP/TOPO, is a mild way to synthesize nanometer materials at the ambient conditions without high temperature and pressure. Due to the work at the atmospheric pressure and room temperature, this method can be used as a new method for the synthesis of inorganic nanoparticles via more simple process than

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1567-1739/$ - see front matter
doi:10.1016/j.cap.2005.04.039

one used in the past. When it is done by γ-irradiation, the solution system maintains a reducing atmosphere which reduces high valent metal ions to low valency. In this paper, we report a novel and easy-to-manipulate method to prepare the ordered semiconducting materials by γ-irradiation.

2. Experimental methods

2.1. Materials

All chemicals used were of analytical grade or of the highest purity available. Cadmium chloride hemipentahydrate ($CdCl_2 \cdot 5/2H_2O$, 99%) and selenium (Se, 200 mesh 99.5+%) were obtained from Aldrich Chemical Company Inc. Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 98+%) was obtained from Across Organics. Sodium oleate ($C_{17}H_{33}COONa$, 98%) and ethylenediamine (ed) were obtained from Junsei Chemical Company Co., Ltd. Sodium borohydride ($NaBH_4$, 98%) was obtained from Sigma Chemical Company Inc. Pyridine (py) was from Kanto Chemical Company Inc. All reagent-grade chemicals were used as received, and house-distilled water was passed through a four-cartridge Barnstead Nanopure II purification train consisting of Macropure pretreatment, organic free, and a 0.2 μm hollow-fiber final filter for removing particles. Its resistivity was determined as 18.4 MΩ and used throughout.

2.2. Preparation of CdE (E = S and CdSe) nanorods and nanowires

Sodium oleate (10 mmol) was dissolved in 40 mL of pure water. Cadmium chloride hemipentahydrate (5 mmol) was dissolved in 1 mL of water and mixed with the prepared sodium oleate solution and stirred for 2 h. The mixture was filtered and dried at room temperature.

Cadmium oleate mixture (5 mmol) was dissolved in 40 mL of ed. $Na_2S \cdot 9H_2O$ (5 mmol) was added into the dissolved solution of cadmium oleate and then stirred for 2 h. The reactants were irradiated by γ-irradiation in the field of a ^{60}Co γ-ray source. The product was washed with absolute ethanol, diluted HCl solution (0.1 M) and absolute ethanol, filtered and then dried at room temperature. In case of nanowires, the solvent was changed from ed to py. Nanorods and nanowires of CdSe was synthesized with the same method.

2.3. Apparatus

The samples were characterized by X-ray powder diffraction (XRD) patterns to investigate the crystal structure. X-ray powder diffraction (XRD) spectra were collected using a Philips, X'Pert-MPD system. Transmission electron microscopy (TEM) was used to study on the morphology and particle sizes. Transmission electron microscopy (TEM) image was obtained using a Hitachi model S-2400. Samples for TEM were prepared on 300 mesh copper grids coated with carbon. A drop of material solutions was carefully placed on the copper grid surface and dried. Energy dispersive X-ray (EDX) spectra were obtained using a HITACHI model, H-7500.

3. Results and discussion

The whole process can be expressed as follows [13,14]:

$$Cd(en)_3^{2+} + S^{2-} \rightarrow CdS(en)_m \leftrightarrow CdS(en)_{m-n} + n(en)$$
$$(en = ethylenediamine)$$

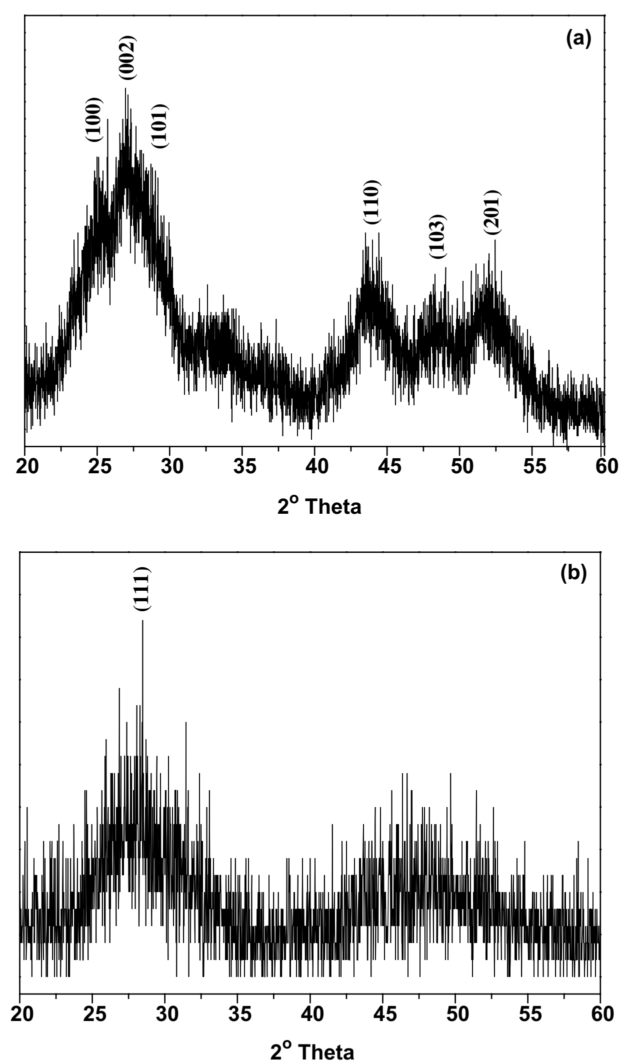

Fig. 1. XRD patterns of CdS nanorods (a) and nanowires (b) synthesized by γ-irradiation with a dose of 90,000 Gy.