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Surface-roughness-assisted formation of large-scale vertically aligned CdS nanorod arrays via solvothermal method

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ABSTRACT

Large-scale cadmium sulfide (CdS) nanorod arrays were successfully synthesized on several different substrates through solvothermal reaction. During the growth experiments, we observed that the adhesion strength of the CdS nanorod arrays to different substrates differed dramatically, causing some of the CdS coating being easily flushed away by deionized water (DI water). With doubts and suspicions, we seriously investigate the original morphology of all the substrates by using atomic force microscopy (AFM). The phase, morphology, crystal structure and photoelectric property of all the products were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and current–voltage (*I–V*) probe station. The growth mechanism of solvothermal reaction was proposed on the basis of all the characterizations. Our approach presents a universal method of liquid phase epitaxy of 1D material on a wide range of substrates of any shape.

1. Introduction

Low-dimensional nanostructured materials such as graphene, nanowires, carbon nanotubes and quantum dots have drawn significant interests in the science community for decades for their unique optical and mechanical properties. Among low-dimensional materials, one-dimensional (1D) materials have particular potential for device application ranging from broad-band light-emitting diodes (LEDs) and lasers [1] to biochemical sensors [2] due to their readily tunable optical, electrical and nanomechanical properties [3].

CdS, a direct bandgap material with Eg of 2.42 eV at room temperature, can be widely used for photoelectronic devices such as solar cells [4], LEDs [5], optical antennas [6], etc. Various methods for the preparation of 1D CdS have been developed as chemical vapor deposition [7], solvothermal reaction [8,9,20,22], electrochemical synthesis [10] and thermal evaporation [11]. The properties of the 1D CdS [4,7,11] as well as CdS incorporated composites [9,12–14] or heterostructures with other materials [10,15–18] have been well studied so far. But how the surface properties of the substrate affect the synthesis of 1D CdS has been little explored previously.

In this work, we investigate the growth mechanism of large-scale vertically aligned CdS nanorod arrays on different substrates via a facile solvothermal routine [8]. It turned out that the morphology of the selected substrate was quite critical for the adhesion intensity between the CdS seed layers and the substrate. We believe the adhesion difference originates from the key property of the substrate, that is, surface roughness. By this approach, we proposed a possible formation mechanism of the solvothermal synthesis of a wide range of 1D nanomaterials. Moreover, this work points out a very promising way to fabricate heterostructures readily.

2. Experimental

2.1. Synthesis of CdS nanorods

All the chemicals used were of analytical grade and purchased from Nanjing Wanqing Chemical Glassware Instrument Co. LTD. In a typical procedure, 1 mmol of cadmium nitrate $Cd(NO_3)_2{\cdot}4H_2O$, 3 mmol of thiourea and 0.6 mmol of glutathione were dissolved in a Teflon-lined stainless autoclave filled with 40 ml DI water. After placing a prepared substrate inside, the clave was sealed and maintained at 200 °C for 3.5 h and then cooled down to room

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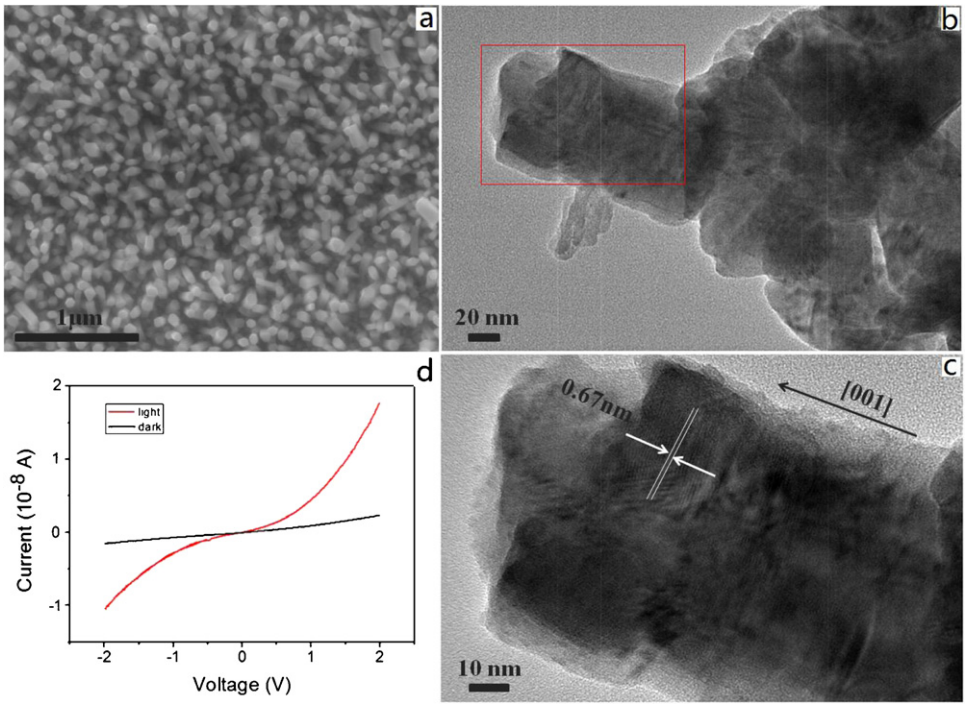

Fig. 1. SEM, TEM images, and *I–V* curves of CdS nanorods grown on self-prepared ITO-glass substrate (sample 1). (a) SEM image of CdS nanorods array with the magnification of 20 K. (b) TEM image of an individual CdS nanorod. (c) HRTEM image of the area marked a red rectangular in (b). (d) *I–V* curves with and without illumination. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

temperature. At last, the produced samples were rinsed with DI water and dried naturally.

2.2. Characterization

All the samples' phase compositions were examined by X-ray diffractometer D/max 2500VL/PC with Cu K_α radiation. SEM images were acquired on a SEM LEO 1550. Transmission electron microscopy (JEOL 2100) was applied to confirm the crystallinity and the growth orientation of the CdS nanorods. Raman spectrometer (JY T64000) was operated by a 50 mW and 514.5 wavelength Ar green laser to study the phonon vibration. AFM height images were taken on a Veeco Multimode8, showing the original morphology of all the substrates. *I–V* test was performed on an Aglient 4156C parameter analyzer.

3. Results and discussion

In this paper, we adopted five different substrates for the experiments: self-prepared indium tin oxide (ITO)-glass through electron beam evaporation (EBE), silicon wafer, purchased ITO-glass, Au-ITO-glass (purchased ITO-glass coated with thin Au film) and naked glass. After the synthesis process of CdS nanorod arrays, the final products were labeled as sample 1, 2, 3, 4 and 5, accordingly. Fig. 1 shows the SEM, TEM images and *I–V* test result of sample 1. It is clearly seen from Fig. 1a that the substrate is fully coated with high-ordered CdS nanorods, most of which are vertical to the substrate. High-resolution TEM (HRTEM) image (Fig. 1c) was taken of the red rectangular area in Fig. 1b. The lattice plane spaces were calculated to be 0.67 nm, corresponding to the lattice constants of *c*-axis of wurtzite CdS [19], which indicates clearly that the growth is along the [0 0 1] orientation. Basic *I–V* characterization was carried out on a probe station for testing the electrical and photoconductive properties of the CdS nanorod arrays. Each sample had a non-linear *I–V* characteristic for a −2 V to 2 V sweep. Fig. 1d is a representative graph of sample 1. Obviously, under white light illumination the output current of the nanorods increased at least by one order of magnitude compared to measurements in dark conditions, showing a strong potential in photovoltaic applications.

Fig. 2a–d are the SEM images of the CdS nanorod arrays synthesized on the other four substrates. We found that the parameters of the nanorods were nearly of the same size (about 100 nm) no matter what the substrate was. Moreover, all the CdS nanorods were vertically well-aligned except for sample 2 (Fig. 2a), which definitely have some connection with the surface condition of silicon wafer. Fig. 2e–f are the TEM images of the CdS nanorods scratched off from sample 4 (Fig. 2c). The HRTEM image (Fig. 2f) taken of the red rectangular area in Fig. 2e clearly reveals a set of fringes for (0 0 2) planes of wurtzite CdS with a lattice spacing of about 0.33 nm [20], in accordance with the conclusion above that the [0 0 1] direction is the preferential growth orientation.

X-ray diffraction (XRD) patterns of CdS nanorod arrays grown on all the substrates were collected in Fig. 3 with the diffraction angle 2θ ranging from 10° to 90°. All the diffraction peaks can be assigned to wurtzite CdS [21] with the exception of the high peak in sample 1 attributed to ITO film [22], some of the strong and sharp peaks in sample 2 attributed to silicon wafer and the peak in sample 4 attributed to Au film [23]. Beyond contemplation, the corresponded ITO diffraction peak of sample 3, 4 were much weaker than sample 1. We attribute that to the larger thickness (∼500 nm) and higher quality of the self-prepared ITO-glass by EBE. Furthermore, the CdS nanorod arrays exhibit much stronger reflection at [0 0 2] direction as revealed from the XRD patterns, which in another way suggest that the CdS nanorods grew preferentially oriented along the *c*-axis.

Although all the five substrates support the growth of CdS nanorod arrays, the stabilities of the final products differ