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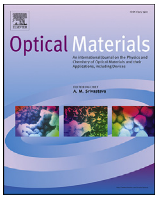

Growth, morphological and optical characteristics of ZnSSe nanorods

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Zinc seledide sulfide (ZnS_xSe_{1-x}) nanorods with wurtzite structure were synthesized by a low temperature solvothermal pathway. In a typical condition of solvothermal at 180 °C for 8 h, the ZnS_xSe_{1-x} was composed of nanorods 10–15 nm in diameter and 50–75 nm length. These results indicate that the nanoscale of ZnSSe nanocrystals may contribute to the solvothermal process and exhibit a tunable photoluminescence (PL) and band gap that depends on the variation of reaction conditions. The work suggests a promising route to single-mode “mirror-less” amplified spontaneous emission (ASE) from inorganic nanomaterials with the Cholesteric liquid crystals (CLC) providing additional potential functionality. The obtained products are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), UV–visible spectroscopy, and X-ray photoelectron spectroscopy (XPS). This approach for solvothermal growth can also be used with primary ZnSSe nanorods to achieve tunable optical properties and can likely be extended to nanomaterials of different shapes and other optical devices.

1. Introduction

Semiconductor nanocrystals with dimensions below the bulk exciton radius exhibit size-related optoelectronic properties [1,2]. It is well known that the performance of II- VI group depends strongly on its crystallite phase, dimension, and morphology, since they give a definitive affect on the chemical and physical properties. These phenomena are also of interest owing to the ability to tune the optical properties with adjusting sulfur or selenium element. Sulfides or selenides, as wide-band gap II-VI semiconductor materials, have been studied extensively in the fields of light-emitting devices, solar cells, sensors, and optical recording materials [3–6], because of their high photostability and their potential for high luminescence quantum yields.

Achieving well-defined size and shape distribution control in one dimensional synthesis and the natural strategy of the physical and chemical properties of the II- VI group forming the nanomaterials is challenging, since their final shape and their properties are sensitively interrelated. Crystalline ZnS or ZnSe nanostructures were usually synthesized using costly vacuum process [7–9]. The II-VI semiconductors system can be synthesized by a variety of ways such as thermal evaporation techniques [10], chemical bath deposition (CBD) route [11], and chemical vapor deposition (CVD) [12,13]. However, the widespread utilization of II-VI based nanostructures requires the use of high-cost vacuum deposition techniques. In order to achieve desired optical properties for specific applications, altering crystalline structure is by far the efficient general approach [14]. Solvothermal synthesis, a low temperature technology for materials evolution, was broadly applied to prepare various materials due to high reactivity of reactants, easy control of solution, less air pollution, and low energy consumption under vacuum or high temperature conditions [15–17]. Cholesteric liquid crystals (CLCs) can be regarded as one-dimensional photonic crystals (1D PCs) because of their periodic distribution of refractive index with a large modulation, in which rod-like molecules can rotate periodically along the so-called helical axis by interaction with the chiral dopants [18]. Because of this gap feature, CLCs can be used as mirrorless distributed feedback resonators. By doping active materials in the CLCs, the spontaneously emitted fluorescence will be suppressed within the gaps and instead enhanced at band edges. Principally, the multi-reflection of fluorescence at band edges can lead to a very small group velocity and very large density of photonic state (DOS) [19]. With the distributed feedback effect of the active multilayer of the resonator in the multireflection process, the rates of spontaneous and stimulated emissions for the fluorescence at band edges can both be amplified so that a high gain exceeding loss can be obtained to induce an amplified spontaneous emission (ASE) [20].

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2. Experimental section

Synthesis was carried out using a mixture of mixture of $ZnCl_2$ (4 mmol), ethanol (30 mL), hydrochloric acid (1 mg), and Diethylenetriamine (DIEN) were heated with stirring at 80 °C, while purging continuously with nitrogen for 1 h. S and Se precursors were made separately by dissolving S and Se powder in Trioctylphosphine oxide (TOPO) under a nitrogen atmosphere, forming TOPOS and TOPOSe, respectively. The S to Se molar ratios used for the TOPOSSe was 0.3:0.7, 0.5:0.5, and 0.7:0.3. The reagents were loaded into a 50 mL Teflon lined autoclave, which was then filled with anhydrous DIEN up to 80% of the total volume. The autoclave was sealed and was maintained at 180 °C for 8 h, and then allowed to cool to room temperature naturally. After the reaction, the solution was filtrated, washed by distilled water and absolute ethanol, respectively, and dried in a vacuum at 80 °C for 3 h and collected for its characterization. The cholesteric liquid crystal (CLC) mixture used includes a 65.3-wt% nematics (from Merck, MDA3970) and a 34.7-wt% chiral dopant with a left-handness (from Merck, S811). Afterwards, 1 wt% ZnSSe nanorods with an average diameter of ~50 nm is doped uniformly in the CLC mixture. A planar empty cell is made by piling up two ITO glass substrates, separated by Mylar spacers of 50-µm-thickness.

The as-prepared samples morphologies were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). TEM characterization was conducted on a JEM-2000EX system using an acceleration voltage of 160 kV. X-ray diffraction (XRD) was carried out on a D/MAX-500 X-ray powder diffraction system with Cu K radiation (λ = 1.5418 Å). A scanning rate of 0.02 s^{-1} was applied to record the patterns in the 2 Theta range of 15–85°. The UV–visible absorption spectra of the nanomaterials in toluene were recorded at room temperature using a PerkinElmer, Lambda 750 UV/vis/near-IR spectrophotometer. X-ray photoelectron spectra (XPS) analyses were recorded using a VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatized Mg Ka X-rays as the excitation source. To optically excite the nanorods, two types of lasers were used: a Q-switch Nd:YAG laser (LAB-130, from Quanta-Ray, 7ns, 10 Hz) and a DPSS CW 325 nm laser.

3. Results and discussion

The phase identification was carried out by X-ray diffraction (XRD) as shown in Fig. 1a. These diffraction peaks became sharper and more intense with increasing reaction time. The complete evolution of the crystallization process showing the most intense reflection from the (100) plane and a few minor reflections from the (002), (101), (110), (103), (112), and (102) planes at longer reaction time. The characteristic peaks of wurtzite ZnSSe were markedly intensified, and those of impurity peaks were weakened and finally disappeared when the reaction time was extended to 8 h. The reflection peaks of the different products can be indexed as wurtzite rod-structured ZnS and ZnSe, which is in good agreement with the literature values (JCPDS 36–1450 and 80–0008) [21,22]. As shown in Fig. 1 b–d, the typical XPS survey spectra for both sets in the entire binding energy region indicate that Zn, S, and Se exist, which demonstrates the high purity of the as-synthesized ZnSSe nanocrystals. The distinct Zn 2p peaks appear at 1021.6 eV (2p1/2), thereby verifying the presence of Zn [23]. The peaks of S 2p located at 161.2 (3d3/2) eV confirm the S state [24]. The peaks of Se 3d3/2 located at 54.81 eV confirm the Se state [25]. Compositional analysis by XPS showed that the average composition of the nanocrystals in the sample has a molar Zn/S/Se ratio of 1: x: 1−x (x = 0.3, 0.5, and 0.7, respectively.) and the composition of individual particles measured by EDS were 1: x: 1−x with a variation from particle to particle less than the experimental error of ca. ±2 atom % (see Table 1).

Fig. 2a shows the TEM image of ZnSSe nanorods with an average lateral dimension of 10 nm. The HRTEM image in Fig. 2b indicates

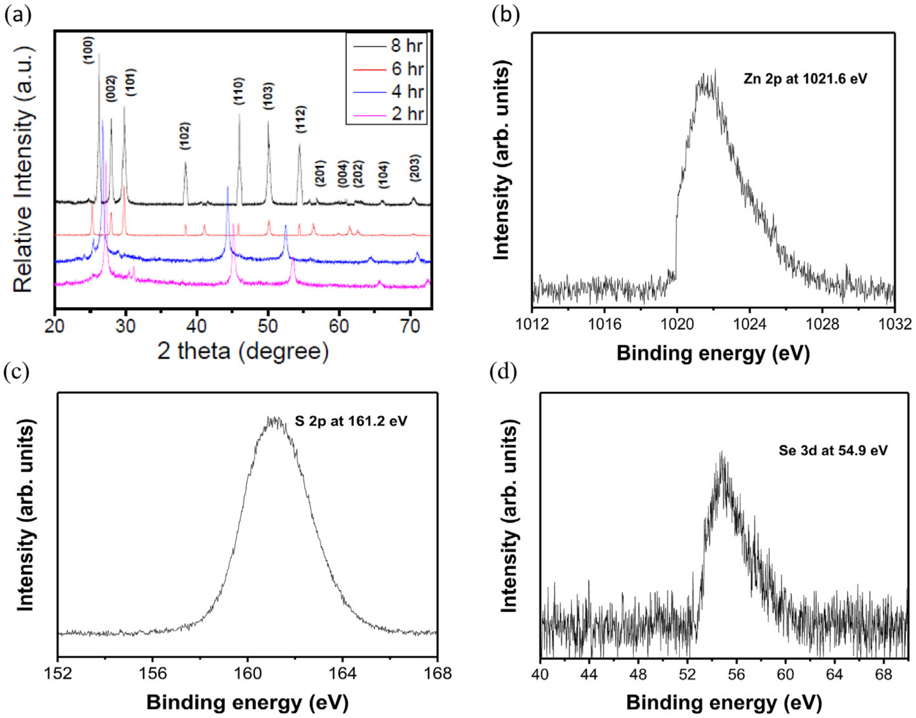

Fig. 1. (a) XRD patterns of ternary $ZnS_{0.5}Se_{0.5}$ nanocrystals synthesized by the solvothermal process for 2, 4, 6 and 8 h, respectively. Typical XPS spectra of the synthesized wurtzite ZnS_xSe_{1-x} nanofibers: (b) Se 3d, (c) S 2p, and (d) Zn 2p.