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A LOW TEMPERATURE, SIMPLE, SURFACTANT-FREE AND ONE POT SOLUTION CHEMISTRY ROUTE FOR SYNTHESIS OF ZnS NANOFLOWERS

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A low temperature, simple, surfactant-free and one pot solution chemistry route was employed to synthesize diverse Zinc sulfide (ZnS) nanostructured assemblies at 70 °C by varying the solvent (water or ethylene glycol, or their mixture in the ratio of 1:1). In 1:1 water-EG solvent ratio, ZnS nanoflowers morphology was obtained. Morphology, structure, and composition of the obtained products were characterized by X-ray diffraction, energy dispersive X-ray analysis, scanning electron microscope and photoluminescence spectroscopy.

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1. Introduction

Nanostructured semiconductors have attracted extensive attention not only in academia but also in industries, since the physical and chemical properties of semiconductors depend on their structures, phases, shapes and sizes [1]. Chalcogenides such as PbS, ZnS, CdS, CuS and Bi_2S_3 are semiconductor materials that have been drawing attention of researchers for their unique properties and potential applications [2-6]. Among these materials, Zinc sulfide (ZnS) is one of the most widely studied IIB-VI group semiconductor compounds with wide band gap energy of 3.7 eV [7], they find applications in many fields such as flat-panel displays [8], sensors [9], superconductivity [10],photocatalysis [11], lasers [12], electroluminescent materials [13], field effect transistors [14] and solar cells [15]. In recent years, much effort has been made to control the size, morphology, and crystallinity of ZnS nanocrystals with a view to tuning their physical properties [16]. Over the past few years, various nanoforms of ZnS such as nanorods [17], nanowires [18], nanospheres [19] and nanotubes [20] have been synthesized through the metal-organic chemical vapor deposition method (MOCVD) [21], ultrasound-assisted method [22] and sol-gel hydrothermal method [23]. In the past, ZnS nanostructures were mostly synthesized in the presence of templates using solution chemistry routes [24]. The use of a template requires multiple steps, which is time consuming and expensive. It is also difficult to completely remove the template material, which, therefore, affects the purity of the final product.

In this paper, for the first time, we report the preparation of ZnS nanoflowers using a simple, template-free and one pot solution chemistry route by varying the reaction medium at low temperature (70 °C). The main advantages of the present process of synthesizing ZnS nanoflowers self-assemblies are simpler reagents, lower temperature and shorter duration than that of previous reports [25, 26].

2. Materials and methods

Chemicals with analytical grade were as-received, without further purification. Typically, in a 50 mL round bottom flask, 20 mL of solvent (100% water or 100% ethylene glycol (EG) or their mixture in the ratio of 1:1) and 1 mmol zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and 1

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mmol sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) was taken. Then the solution was stirred to mix the precursors until a homogeneous solution was obtained. Then the flask containing solution was held at 70 °C and heated for 2 h with constant stirring. After 2 h, the flask was cooled down to room temperature. The precipitated product was filtered and washed with ethanol and water several times and dried at room temperature to characterization.

X-ray powder diffraction pattern (XRD) was performed on a SIEFERT XRD 3003 PTS diffractometer using Cu Kα irradiation (λ¼1.5418 Å). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were taken with a Hitachi S-4160 microscope with attached camera operating at 30 kV to determine the morphology, particle size and high purity of the prepared synthesized salt. Photoluminescence (PL) spectrum was performed with a HITACHI 850-type visible-ultraviolet spectrophotometer with a Xe lamp as the excitation light source. All the measurements were done at room temperature.

3. Results and discussion

The morphology of as-synthesized ZnS nanostructured materials was examined with SEM. Either aqueous (100% water) or alcohol (EG) or a mixture of these two solvents was taken to observe their effect on the formation of ZnS nanostructures while keeping all other parameters such as precursor molar, reaction temperature and reaction duration fixed. Fig. 1a-c shows the SEM images of ZnS nanostructures obtained in different solvent medium, i.e., (a) water, (b) 1:1 water-EG and (d) EG. In the aqueous medium, the as-synthesized ZnS product was found with a spherical morphology of diameter ~300-600 nm (Fig. 1a). These spheres are actually composed of agglomerated nanoparticles (30-50 nm). In 1:1 water-EG solvent ratio, the morphology of the product is found to be drastically different to 100% water. As the EG in the reaction medium is increased, the stabilizing effect of EG leads to formation of deformed spheres composed. Here we obtained a nanoflower morphology with ~400-600 nm diameter (Fig. 1b) of the product. These nanoflowers appear to grow in every direction from one central nucleation point. It is important to note that the nucleation and aggregation of nanoparticles are normally slower in a non-aqueous solvent than an aqueous solvent. This is because of fewer surface hydroxyl groups and a higher viscosity of non-aqueous solvent. This allows the self-assemblies to occur at different rates, forming different morphologies in different solvents [27]. With 100% EG, the morphology of the product (Fig. 1c) was a spherical type with a deformed shape. The higher viscosity of EG increases the steric hindrance in reaction system causing reduction of particle sizes of the product [28], which is obvious in the present case.

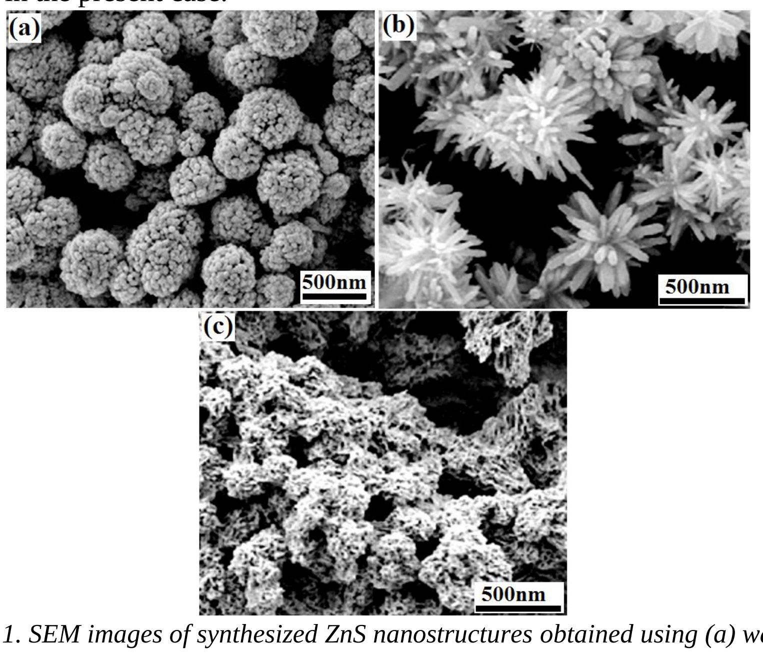

Fig. 1. SEM images of synthesized ZnS nanostructures obtained using (a) water, (b)1:1 water-EG and (f) EG, as solvent

Powder XRD pattern of the ZnS nanoflowers is showed in Fig. 2a. The broadening of peaks in the XRD pattern compared to those of bulk ZnS indicates the nanocrystalline nature of the samples. These diffraction features appearing at 28.5°, 47.5° and 56.3° correspond to the (111), (220), and (311) planes of the cubic zinc blended structure, which is very consistent with the values in the standard card (JCPDS No. 5-0566). Also no specific peaks due to any impurities were observed. The chemical purity of the ZnS nanoflowers as well as their stoichiometry was tested by EDX spectrum. Fig. 2b verified the existence of zinc and sulfide in the final product. This analysis showed a purity of 100% for the synthesized compound which is in good agreement with the XRD data.

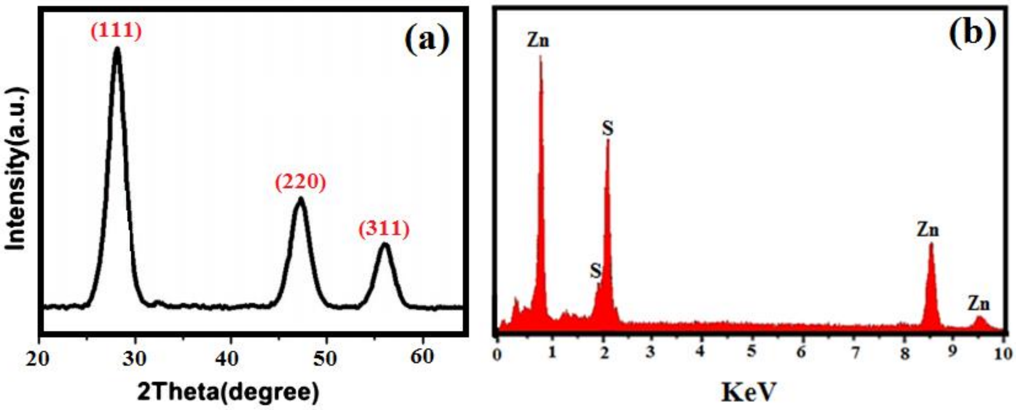

Fig. 2. (a) XRD and (b) EDX patterns of ZnS nanoflowers

Fig.3 displays the photoluminescence (PL) behavior of as-prepared ZnS nanoflowers dispersed in an ethanol solution. The excitation spectrum of ZnS nanoflowers, indicating a strong absorption peak centered at 375 nm, corresponding to the band gap of 3.3 eV. As compared to the band gap of bulk ZnS which is 3.7 eV, the absorption spectrum of as-prepared samples exhibits a blue-shift, perhaps due to the existence of defects [29]. As we know, photoluminescence spectroscopy is a useful tool for the investigation of recombination phenomena in semiconductors. By using photoluminescence spectra, band gap can be determined along with the relative energetic position of sub-band gap defect states [30]. The emission spectrum of the ZnS nanoflowers, displaying a stable and strong blue emission band centered at 480 nm under the excitation of 375 nm. The energy of emission is 0.7 eV less than the energy of absorption, which may be ascribed to the transitions involving vacancy states [31], defect levels of anion vacancies [32] and interstitial lattice defects [33] in ZnS nanocrystals.

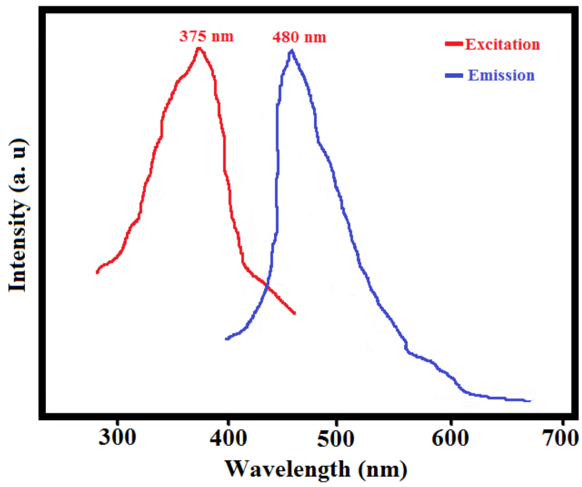

Fig. 3. PL spectrum of the as synthesized ZnS nanoflowers

4. Conclusions

In summary, sub-micrometer range ZnS nanostructures without any surfactant were synthesized using a simple solution chemistry route at low temperature (70 °C). The effect of solvent (water to EG) ratios on the shape, size and structures of products was studied into the details. In 1:1 water-EG solvent ratio, a nanoflower morphology with ~400-600 nm diameter was obtained. The photoluminescence results indicate that the ZnS nanocrystal has a band gap of 3.3 eV, while the strong blue emission centered at 480 nm demonstrates the existence of defect states. This simple and one pot method may also be used for synthesis of other nanostructured semiconductors with different shapes.

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