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Research paper

ZnS/ZnO heterostructure semiconductor: A promising ionic liquid media approach without calcination

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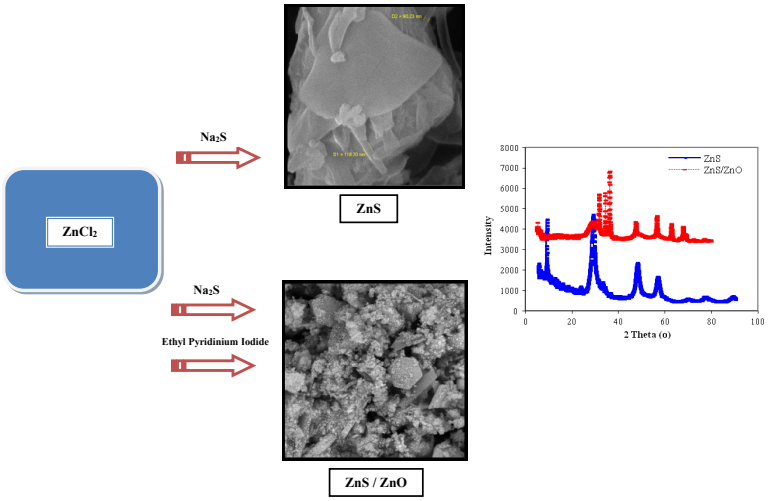
HIGHLIGHTS

- The band gap narrowing of ZnS/ZnO was due to the formation of a heterostructure.
- The hexagonal morphology of ZnS/ZnO had a thickness of about 90 nm.
- The XRD peaks were assigned to ZnS blende and ZnO zincite structures.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnS is a wide band gap semiconductor with excellent optical and electrical properties whose electronic structure can be modified with other semiconductors. In this study, ZnS and ZnS/ZnO heterostructure semiconductors were fabricated using the reaction between $ZnCl_2$ and Na_2S in the presence and absence of ethyl pyridinium iodide ionic liquid media via a reflux route without calcination. The as-prepared samples were characterized by XRD, FE-SEM, EDS, and DRS techniques. The main observations were the effects of ethyl pyridinium iodide on structural features, morphology, and band gap. The XRD patterns of ZnS represented peaks at 2θ = 8.8, 28.6, 32.9, 47.6, 56.4, 69.7, 76.9º of the blende structure. The crystalline nature of ZnS/ZnO at 29.05, 34.43, 47.51, 56.57, 69.06º and 31.80, 36.26, 47.51, 56.57, 62.85, 66.38, 67.90º is compatible with the standard pattern of ZnS blende and ZnO Zincite phases, respectively. The ZnS/ZnO heterostructure showed that the crystal truncated hexagonal had a thickness of about 90 nm. The rough hexagonal contained several layers, and the averaged elemental enrichment of Zn : S : O was 1 : 0.29 : 0.67. The synergistic effects of ZnS and ZnO promoted band-gap narrowing compared to the ZnS blende particles. So, in the ZnS and ZnS/ZnO cases, the band gap energy was 4.17, and 2.82 eV, respectively. The proposed ZnS/ZnO heterostructure composite has potential applications in semiconductors. The findings of this study opened new aspects of ZnO/ZnS heterostructure in terms of preparation, morphology, and band gap value.

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1. Introduction

Zinc sulfide (ZnS) has two types of crystal structures containing zinc blende, Sphalerite (β-ZnS, stable at low temperature) and Wurtzite (α-ZnS, stable at high temperature). This inorganic compound is a group of wide band gap semiconductor materials. The band gap value of these semiconductors can be narrowed to the visible regions. Recently, various methods have been studied to change the band gap value, such as changing morphology, altering the electronic properties, and forming heterostructures with other semiconductors [1-3]. Schrier *et al.* reported a narrowing band gap for ZnO/ZnS bulk heterostructures consisting of zinc-blende ZnO and ZnS [4]. They predicted a 2.31 and 2.07 eV band gap for ZnO/ZnS bulk and ZnO/ZnS core/shell heterostructured nanowires. Hart *et al.* [5] predicted that the band gap of ZnS can be reduced by forming layered ZnS/GaP structures. In another research, Saha *et al.* studied the electronic structure of ZnO/ZnS core/shell [6,7]. Based on their finding, the band gap of the hetero system decreases as the ZnS shell thickness increases. The synthesis methods widely used in the preparation of such hybrid semiconductors include wet-chemical [1,8,9], co-precipitation [10], thermal, and hydrothermal methods [11-13], and sulfurization of ZnO with noxious H_2S gas at high temperatures is also practiced [14-16]. Frequently used approaches apply toxic reactants, which can restrict their production. Therefore, developing environment-friendly and inexpensive processes to prepare heterostructured semiconductors is essential for semiconductor devices.

Compared with the many studies on heterostructure semiconductors, there is little knowledge about this type of mild conditions. In this study, a ZnS/ZnO heterostructure semiconductor was prepared from the reaction between $ZnCl_2$ and Na_2S in ethyl pyridinium iodide ionic liquid media. This reaction was carried out under mild conditions in one step via the reflux route without calcination.

2. Experimental

2.1. Preparation of ZnS structure

To prepare ZnS, the reaction between $ZnCl_2$ (Merck, 99.9%) and $Na_2S.9H_2O$ (Merck, 60-62%) was carried out in a 1:2 molar ratio, respectively. $Na_2S.9H_2O$ (2.27 g in 10 ml water) was added to a solution of $ZnCl_2$ (2 g in 10 ml water), and the mixture was refluxed for 1.5 h. After the reaction was completed, the white precipitate was filtered and washed repeatedly with distilled water.

2.2. Preparation of ZnS/ZnO heterostructure

Three other products were fabricated in the ethyl pyridinium iodide (EI) ionic liquid with different molar ratios 1:4:2, 1:4:4, and 1:4:8 of $ZnCl_2$:Na_2S:EI. $Na_2S.9H_2O$ (4 mmol, 0.66 g) was added to the solution of $ZnCl_2$ (1 mmol, 0.28 g). Then, ethyl pyridinium iodide ionic liquid was used in various molar ratios (1, 2, and 4 g). The resulting mixture was refluxed for 4 h. After filtration, the precipitate was washed with distilled water and ethanol and finally dried.

2.3. Apparatus

As-prepared products were characterized with field emission scanning electron microscopy (FE-SEM, TESCAN, MIRA III, made in the Czech Republic), X-ray diffractometer (PHILIPS, PW1730, Netherlands and PHILIPS, PW1800 at room temperature with Co Kα radiation), energy-dispersive X-ray spectrometer (EDS), and diffuse reflectance spectroscopy (DRS, S-4100 SCINCO) techniques.

3. Results and discussion

SEM images of fabricated ZnS without ethyl pyridinium iodide were illustrated in Fig. 1(a), which indicates that sheets were agglomerated and irregular sheets were formed. The SEM images of the sample at higher magnification (Fig. 1(b)) suggested that the thickness of each sheet is about 90-140 nm. The SEM images of ZnS/ZnO fabricated through an ionic liquid approach showed that the structure is a truncated hexagonal with a thickness of about 90 nm (Figs. 1(c),(d)). The EDS element analysis confirmed that the averaged atomic ratios of Zn:S:O were 1:0.29:0.67. The results revealed that the ionic liquid media changed the samples' morphology and chemical composition.

The as-prepared products were further characterized using XRD analysis (Fig. 2). The XRD patterns of ZnS represented the characteristic peaks at 2θ = 8.8, 28.6, 32.9, 47.6, 56.4, 69.7, 76.9º of blende structure (JCPDS 98-006-1492). Then, the XRD pattern of the prepared

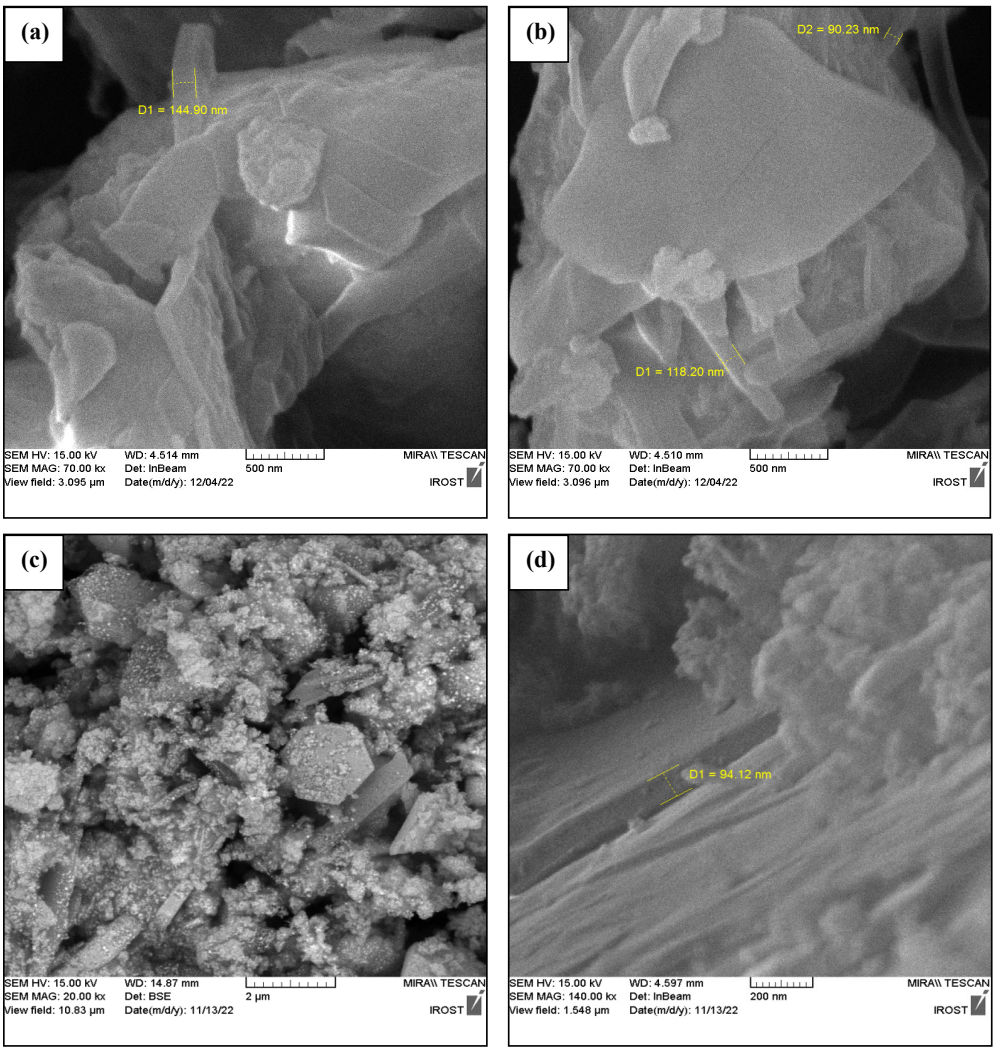

Fig. 1. SEM images of ZnS (a)-(b) and ZnS/ZnO (c)-(d).

sample in the 1:4:2 molar ratio of $ZnCl_2$:Na_2S:EI was investigated. The peaks indexed at 2θ = 32.07, 34.43, 36.74, 57.58, 64.03, 66.31, 67.89, 69.02, 73.78, 76.86º and 2θ = 13.28, 17.54, 22.03, 26.66, 31.32, 31.77, 33.44, 36.25, 37.99, 39.33, 40.45, 44.36, 45.96, 47.51, 51.51, 54.31, 54.84, 55.26, 56.16, 56.56, 59.28, 61.48, 62.81, 65.27, 67.01, 67.34, 69.80, 71.09, 72.50, 72.97, 75.37º were assigned to ZnO and $H_3NaZn_3S_2O_9$ crystalline phases, respectively (JCPDS 98-008-1268, and 98-012-2966). Next, the XRD technique was used to characterize the structural features of $ZnCl_2$:Na_2S:EI in a 1:4:4 molar ratio. In this pattern, the crystalline nature of ZnS and ZnO can be seen at 2θ = 29.05, 34.43, 49.04, 56.57, 69.06º, and 2θ = 31.80, 36.26, 47.51, 56.57 62.85, 66.38, 67.90, 72.56, 76.93º, respectively. All peaks are in good agreement with ZnS (JCPDS 98-006-1492), and ZnO (JCPDS 98-008-1268), respectively, and no other impurities were detected. The as-prepared sample of $ZnCl_2$:Na_2S:EI in a 1:4:8 molar ratio was incompatible with the ZnS structure. Therefore, one of the effective parameters in the preparation of ZnS/ZnO heterostructure is the molar ratio of ethyl pyridinium iodide ionic liquid. Changes in the molar ratio of ionic liquid have led to a change in the crystalline phase.

The band gap measurements of ZnS and ZnS/ZnO heterostructure were investigated by ultraviolet differential reflectance spectroscopy (UV-DRS) method (Fig. 3). The band gap was calculated by plotting the square product of the Kubelka-Munk function and the energy. The band gap value was found to be 4.17 and 2.82 eV in the ZnS and ZnS/ZnO heterostructure, respectively. These results show that band gap narrowing was obtained due to changes in the morphology and forming heterostructure with other semiconductors. Therefore, an increase in the ionic liquid is not only influential in the preparation of ZnS/ZnO, but as the ionic liquid increases, the amount of agglomeration and band gap value also decreases.

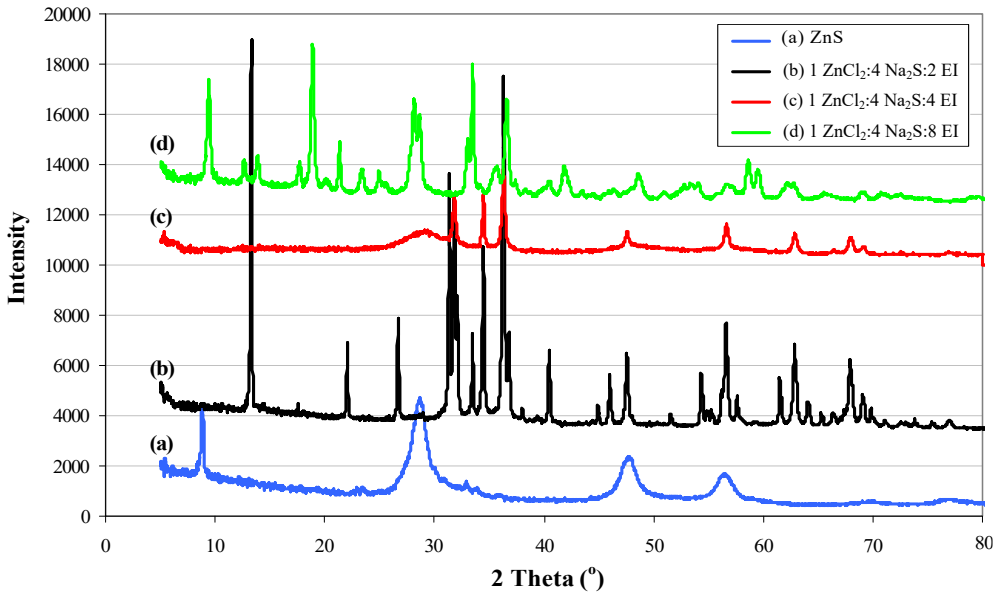

Fig. 2. XRD patterns of (a) ZnS, (b) 1:4:2 molar ratio of $ZnCl_2$:Na_2S:EI, (c) 1:4:4 molar ratio of $ZnCl_2$:Na_2S:EI, and (d) 1:4:8 molar ratio of $ZnCl_2$:Na_2S:EI.

4. Conclusions

In this research, a ZnS composite was prepared with different molar ratios of $ZnCl_2$, Na_2S, and ethyl pyridinium iodide ionic liquid. A ZnS/ZnO heterostructure was designed in a 1:4:4 molar ratio of $ZnCl_2$: Na_2S : EI via a one-step reflux process. The morphology and band gap values indicated crystal truncated hexagonal with a 2.82 eV value. In XRD patterns, the peaks indexed at 29.05, 34.43, 49.04, 56.57, 69.06°, and 31.80, 36.26, 47.51, 56.57 62.85, 66.38, 67.90, 72.56, 76.93° were assigned to ZnS blende and ZnO zincite structures, respectively.

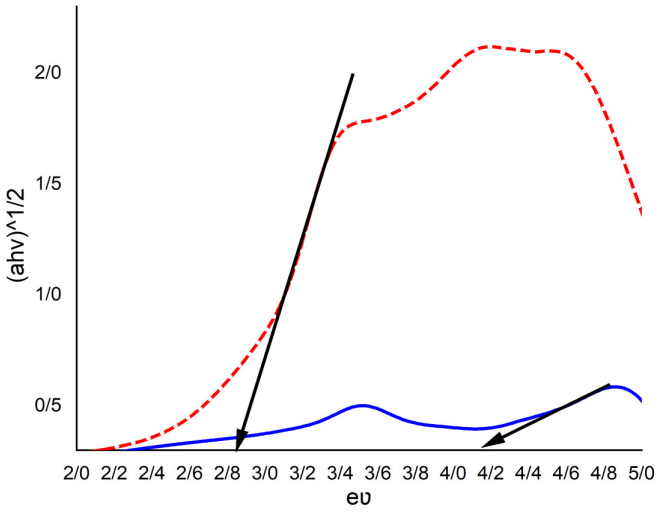

Fig. 3. Direct band gap values of ZnS (solid line) and ZnS/ZnO (dashed line).

Disclosure statement

No potential conflict of interest was reported by the authors.

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Additional information

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