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Starch-assisted synthesis and optical properties of ZnS nanoparticles

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ABSTRACT

ZnS nanoparticles are fabricated via starch-assisted method. The effects of different starch amounts on structure and properties of samples are investigated, and the forming mechanism of ZnS nanoparticles is discussed. By X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible (UV–vis) spectroscopy and fluorescence (FL) spectrometer, their phases, crystalline lattice structure, morphologies, chemical and optical properties are characterized. The results show that ZnS has polycrystalline spherical structure with the mean diameter of 130 nm. Sample without starch reveals irregular aggregates with particle size distribution of 0.5–2 μm. The band gap value of ZnS is 3.97 eV. The chemical interaction exists between starch molecules and ZnS nanoparticles by hydrogen bonds. The stronger FL emission peaks of ZnS synthesized with starch, indicate a larger content of sulfur vacancies or defects than ZnS synthesized without starch.

1. Introduction

Zinc sulfide (ZnS) is an important type II–VI semiconductor with sphalerite and wurtzite crystal structure, having direct wide band gap energies of 3.68 and 3.80 eV at room temperature, respectively [1]. ZnS has received more and more attentions due to its potentially applications in lasers [2], sensors [3], flat-panel displays [4], photocatalyses [5], electroluminescent materials [6], field effect transistors [7] and dye-sensitized solar cells (DSSCs) [8], etc. Many recent efforts have been devoted to the synthesis of ZnS nano/microstructures with various morphologies, such as microspheres [9], core–shell structures [10] and hollow microspheres [11]. Some of preparation techniques are disadvantageous because of special equipment or high temperature requirements, resulting in a high-cost and energy consuming process. Thus, simple, low-cost, and low-temperature techniques are necessary.

Among various synthesis approaches, green synthetic methods have been demonstrated to be appealing for preparing the morphology-controllable nano/microstructures with complexity and relevant fascinating functions. Fabrications of nano/microstructures using yeasts [12], starch [13], silk [14], albumen [15], DNA [16], wood [17], cyclodextrin [18], peptide [19], pollen grain [20], orange juice [21], rice [22] and egg-shell membrane [23] as bio-templates have been extensively investigated.

As known, microwave-assisted route which is one of the novel methods and a rapidly developing area of research, has been applied to prepare nano-structures [24]. Compared with the conventional methods, microwave-assisted synthesis requires very short reaction time, and is capable of producing many nanoparticles with uniform particle size, narrow distribution and high purity, attributed to fast homogeneous nucleation [25]. Starch is one of the most fascinating biotemplates that can be used for nanotechnology application. Starch is made up of granules consisting of two carbohydrate polymers, amylose and amylopectin. One of the remarkable features of starch is its gelling abilities in aqueous solution at 50–90 °C, which plays an important role in controlling morphology of materials. These peculiarities are representing the key structural elements for the synthesis of new functional nanomaterials [22]. In our study, starch is chosen as a soft biotemplate due to its eco-friendly attributes, namely very abundant, low-cost, non-toxic and renewable raw material. Up to now, facile synthesis and their photocatalytic activity of monodisperse porous ZnO spheres [26] by a soluble starch-assisted method has been investigated, and Cu_2O nano/microspheres [27] and silver nanoparticles [28] also have been obtained via starch-assisted synthesis process under microwave irradiation. However, to our best knowledge, no such study on synthesis of ZnS nanoparticles via a starch-assisted method under microwave irradiation is found in the open literature.

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In this paper, starch-assisted synthesis and possible formation mechanism of ZnS nanoparticles under microwave irradiation would be proposed. By using XRD, HRTEM, SAED, SEM, FTIR, UV–vis spectroscopy, and FL spectrometer, the phases, crystalline lattice structure, morphologies, chemical and optical properties could be investigated.

2. Materials and methods

2.1. Materials

In this work, zinc acetate dihydrate, $Zn(CH_3COO)_2{\cdot}2H_2O$, Hunan Xiangzhong Chemical Reagent Co., Ltd., China; thioacetamide, C_2H_5NS, Hunan Huihong Chemical Reagent Co., Ltd., China; soluble starch, $[(C_6H_{10}O_5)_n]$, Chendu Lichun Chemical Co., Ltd., China; $NH_3{\cdot}H_2O$ and C_2H_5OH, Hunan Huihong Chemical Reagent Co., Ltd., China. All reagents were of analytical reagent grade.

2.2. Preparation of ZnS nanoparticles

In a typical synthesis procedure, 2.19 g of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was dissolved in 50 mL the distilled water (solution A) and then 0.75 g of analytically pure thioacetamide (C_2H_5NS) was dissolved in 50 mL the distilled water (solution B). Adding different starch amounts (0 mL; 2 mL; 4 mL; 6 mL) of 0.1 mol/L starch solution to the solution A, and then the solution B was added to the above mixed solution drop by drop, adjusting the pH value to 7 with ammonia ($NH_3{\cdot}H_2O$). The mixture was moved into the microwave oven and heated at 80 °C for 6 min. The white precipitate was formed. The resulting deposition was recovered by centrifugation at a rotation speed of 4500 rpm, washed 3 times with distilled water and washed 2 times with ethanol so as to remove residual ions. The resultant product was dried at 80 °C for 12 h.

2.3. Characterization

The crystal phase composition of the resultant samples was determined from XRD patterns recorded using a PANalytical X'Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm) in the 2θ range from 10° to 90° with 0.02° min^{-1}. Morphologies of samples were obtained by a SEM (Zeiss EVO LS-15, German) operating at 20 kV. UV–vis absorption spectrum was recorded on a Shimadzu UV-2501 ultraviolet–visible spectrophotometer. HRTEM and SAED (JEM-2100, Japan) pattern were employed to characterize the crystal lattice structure of the sample. FTIR was performed in the region 4000–400 cm^{-1} using Thermo-Nicolet AVATAR 360 FT-IR system by using a KBr wafer technique with a resolution of 4.00 cm^{-1}. The FL spectra were measured on Hitachi F-7000 fluorescence spectrometer. All measurements were performed at ambient temperature.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of obtained ZnS samples under different starch amounts (a: 0 mL; b: 2 mL; c: 4 mL; d: 6 mL). All the samples exhibit XRD peaks that correspond to the (1 1 1), (2 2 0) and (3 1 1) planes of a cubic sphalerite structure of ZnS as identified using the standard data JCPDS file no. 05-0566. The peak position of curves a–d have a right angle shift, indicating the crystal interplanar spacing shrinks. From the plane (111) of curve c, d_{111} = 0.3028 nm is got by Jade 5.0 software, while d_{111} = 0.3123 nm is calculated from the standard data JCPDS file no. 05-0566. In addition, no characteristic peaks of impurities are detected, shows

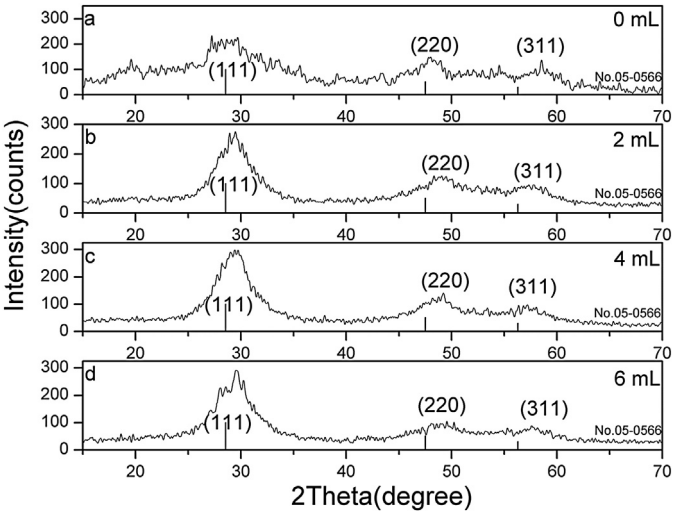

Fig. 1. XRD patterns of ZnS samples with different starch amounts (a: 0 mL; b: 2 mL; c: 4 mL; d: 6 mL).

that the obtained samples are the pure ZnS. The crystallite size can be calculated according to the Scherrer formula (Eq. (1)) [29]:

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where D_{hkl} is the mean crystallite size, λ is the wavelength of X-ray radiation (Cu Kα radiation, λ = 0.15418 nm), k is the shape factor and usually taken as 0.896, β_{hkl} is the full width at half maximum (FWHM), after subtraction of equipment broadening, and θ is the Bragg angle.

The crystallite size of samples at different starch amounts is different. From Fig. 1, the crystallite size of samples a, b, c and d is 1.3 nm, 2.7 nm, 2.9 nm and 2.2 nm, respectively. The crystallite sizes increase firstly and then decrease with the increase of starch amounts, revealing that starch plays an important role in crystal growth of ZnS nanoparticles.

3.2. HRTEM, SAED and SEM analysis

Fig. 2 shows HRTEM, SAED and SEM image of sample c (4 mL starch solution) and SEM image of sample a (without starch solution). Diffraction rings in SAED (in Fig. 2a_1) arise from sample c. The diffraction ring corresponding to the (111) plane with d_{111} = 0.2742 nm of sample c is observed, which reveals polycrystalline structure of sample c and the rest of the SAED rings are very obscure. From HRTEM image in Fig. 2a_2, the lattice fringes of sample c can be clearly observed. The fringes with a lattice spacing of 0.2738 nm correspond to the (111) plane of ZnS, which correspond to the result from SAED image in Fig. 2a_1 and also close to result from XRD pattern (d_{111} = 0.3028 nm from curve c). From Fig. 2b_1, it can be seen that the sample c has the spherical structure with the mean diameter of about 130 nm and wide particle size distribution between about 50 nm and 240 nm. SEM image in Fig. 2b_2 shows the morphology of sample a and irregular aggregates with particle size distribution with 0.5–2 μm arise.

3.3. FTIR spectroscopy

FTIR spectroscopy was used to investigate the effect of biotemplate (starch) on the resulting chemical properties of the ZnS nanoparticles. As shown in Fig. 3a, the FTIR spectra of the products involve characteristic peaks of starch, such as a broad