Journal of Colloid and Interface Science 430 (2014) 116–120

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

# Cactus-like and honeycomb-like Zinc Selenide microspheres on graphene oxide sheets with excellent optical properties

Junwei Han [a], Shaolin Xue [a,*], Weikang Zhou [a], Shuxian Wu [a], Pei Xie [a], Rujia Zou [a,b]

[a] College of Science, Donghua University, Shanghai 201620, China
[b] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

ARTICLE INFO

*Article history:*
Received 3 April 2014
Accepted 20 May 2014
Available online 29 May 2014

*Keywords:*
ZnSe
Microspheres
Graphene oxide
Hydrothermal method
Optical properties

ABSTRACT

Novel cactus-like and honeycomb-like ZnSe microspheres have been successfully grown on graphene oxide sheets by hydrothermal method at 190 °C for 24 h. The morphologies, structures, chemical compositions and optical properties of the as-grown ZnSe microspheres were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), X-ray energy dispersive spectrometer (EDS) and Raman spectra. It was found that the concentration of EDTA was important for the formation of morphologies of ZnSe microspheres. The cactus-like ZnSe microspheres were formed when the concentration of EDTA was 0.3 M. With increasing the concentration of EDTA to 0.45 M, honeycomb-like ZnSe microspheres were formed. The results of XRD revealed that the as-grown ZnSe microspheres have cubic zinc blende structure. Room temperature photoluminescence (PL) showed that the samples emit blue-green light under ultraviolet light. The results of Raman spectra, XRD and SEM showed that the ZnSe microspheres were grown on graphene oxide sheets. The formation mechanism of ZnSe microspheres grown on graphene oxide sheets was also discussed.



## 1. Introduction

During the past decade, nanostructured materials have attracted significant interest due to their novel characteristics in optics, electronics and photonics [1]. Among these nanomaterials, the high-density microspheres grown on a specific conducting substrate such as graphene can improve their physical properties to great extent. Hence, the well-regulated microspheres grown on given substrate provide widely potential applications in ultra-high-density advanced devices [2], such as light-emitting diodes, and energy harvesting devices [3–5].

In the II–VI group semiconductor materials, zinc selenide (ZnSe) is one of the most important materials. Zinc selenide has a bulk band gap of 2.67 eV (1 eV = $1.609 \times 10^{-19}$ J) and a high exciton binding energy (21 meV) at room temperature [6]. ZnSe-based nanostructures have attracted great interest in the optoelectronic devices such as photodetectors [7], blue laser diodes [8], light-emitting diodes (LEDs) [9], electroluminescence [10], white illuminant [11], photovoltaics [12], sensors [13], catalyst supports and so on. ZnSe nanostructures have been synthesized by a variety of methods such as hydrothermal method [6], solvothermal method [14], laser assisted catalytic method and metal organic chemical vapour deposition [15–17]. Guo et al. [18] have prepared a novel 3D ZnSe structure by chemical vapour deposition method. Ren et al. [19] have reported that well-dispersed ZnSe microspheres have been synthesized by a simple solvothermal method. Cao et al. [20] have reported that ZnSe microspheres have been synthesized by a solvothermal route and their photocatalytic activity has been investigated. Zhang et al. [21] have reported that ZnSe microspheres with the diameters of about 2 μm can improve emission performance and photocatalytic activity by an Ostwald ripening process. Therefore, the size and shape of ZnSe microspheres are important in order to obtain unique optical and electronic properties [22].

Graphene, a two-dimensional (2D) sheet consisting of $sp^2$-hybridized carbon atoms [23], has attracted tremendous attention from both academic and commercial communities since its first exfoliation from graphite in 2004 [24]. Graphene has unique mechanical and electrical properties such as high transparent and good soft [25,26], high electrical conductivity [24], far carrier mobility [27], high thermal conductivity [28], high chemical stability [29] and high aspect ratio [30], making it as an attractive material for optoelectronic and photonic devices [28], especially as a source of field emission. At present, the preparation methods of graphene have micromechanical cleavage [31], chemical

* Corresponding author. Fax: +86 21 67792089.
*E-mail addresses:* hjw0323@sina.com (J. Han), slxue@dhu.edu.cn (S. Xue), dhuzwk@sina.com (W. Zhou), boll.coach@163.com (S. Wu), peipeixie@sina.com (P. Xie), rujiazou@dhu.edu.cn (R. Zou).

http://dx.doi.org/10.1016/j.jcis.2014.05.038
0021-9797/

exfoliation [32], SiC epitaxial growth method [33], chemical vapour deposition (CVD) [34] and so on. CVD is the main method to prepare high-quality graphene and it has prepared large area of single-layer graphene. Single-layer graphene has good transparent quality, electrical conductivity and good soft, so it has been used as flexible light emitting devices [35]. Recently, graphene-based hybrid nanostructures with crystal materials have attracted great attention since the integrated nanomaterials bring additional functionality to the graphene sheets [21]. Yoon et al. [36] have reported that epitaxial $Co_5Ge_7$ nanowire and nanobelt arrays on a thin graphene sheet can improve field emission. Zou et al. [37] have reported that vertical, aligned and dense ZnO nanorods on graphene sheets can strengthen field emission, gas sensor and photocatalytic properties. However, the growth of ZnSe microspheres on graphene sheets has rarely been reported.

In the present work, we grow large-scale cactus-like and honeycomb-like ZnSe microspheres on the surface of graphene oxide sheets by hydrothermal method. Ethylene diamine tetraacetic acid (EDTA) acts as complexing agent and it can control the size and morphology of ZnSe microspheres. Besides, the reaction mechanism has been discussed. Optical properties of graphene oxide/ZnSe microspheres hybrid structure have also been investigated.

## 2. Experimental

### 2.1. Materials

All chemical reagents were of analytical grade and used as received without further purification. Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) ($\geqslant$99.0%) (Sinopharm Chemical Reagent Ltd., China), ethylene diamine tetraacetic acid (EDTA) ($\geqslant$99.0%) (Sinopharm Chemical Reagent Ltd., China), sodium hydroxide (NaOH) ($\geqslant$97.0%) (Pinghu Chemical Reagent Ltd., China), Se powder (Se) ($\geqslant$99.7%) (Sinopharm Chemical Reagent Ltd., China), ethanol ($C_2H_5OH$) ($\geqslant$99.7%) (Beijing Chemical Reagent Ltd., China). All aqueous solutions were prepared using with deionized water.

### 2.2. Synthesis

Graphene oxide sheets were synthesized from natural graphite by modified Hummers method [37]. The graphite powders were ultrasonically dispersed in ethanol and stirring to form a uniform suspension. The uniform suspension was spin-coated on Si substrates, and thermally reduced at 650 °C for 30 min under a 100 sccm $H_2$ gas flow [38].

A typical hydrothermal synthesis procedure is described as follows: First, 2.4 g NaOH was dissolved in 30 mL deionized water with magnetic stirring about 10 min. At the same time, 2.2 g $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.79 g Se powder were added into the solution and stirred about 60 min. Then, EDTA was added into the solution and stirred sufficiently. After stirring, the mixture solution and graphene oxide sheets were put into a 50 mL autoclave and were hydrothermally processed at 190 °C for 24 h. After the solution was cooled down to room temperature, the graphene oxide sheets were taken out from the solution and washed several times with ethanol and deionized water. The final samples were dried under vacuum at 60 °C for 6 h. Different samples can be obtained by changing the concentration of EDTA for the solution in the autoclave. Besides, the PL spectra of the cactus-like ZnSe microspheres (sample 3) have been measured by different excitation wavelength. The experimental conditions are shown in Table 1.

**Table 1**
The experimental condition of all the samples.

| Sample | EDTA, M | Excitation wavelength, nm | T, °C |
|---|---|---|---|
| 1 | 0.00 | | 190 |
| 2 | 0.15 | | 190 |
| 3 | 0.30 | 225/220/215/210 | 190 |
| 4 | 0.45 | | 190 |

### 2.3. Characterizations

The crystal structure of the as-grown samples were characterized by an X-ray diffractometer (XRD; Rigaku-Dmax 2550, Japan) with Cu K$\alpha$ radiation at 40 kV and 200 mA in a $2\theta$ range of 20–80°. The surface morphologies and component analysis of the samples were characterized using a field-emission scanning electron microscope (SEM; JEOL JSM-5600LV) and an X-ray energy dispersive spectroscope (EDS; Oxford IE 300 X). The optical absorbance of the samples was measured by an ultraviolet–visible spectrophotometer (UV–vis; PerkinElmer Lambda 35). The photoluminescence (PL) excitation and emission spectra were obtained by a luminescence spectrometer (PL; Edinburgh FLS920). The Raman spectra were measured using a dispersive Raman spectrometer (Jobin Yvon XploRA) ranging from 0 to 2000 $cm^{-1}$. All of the measurements were carried out at room temperature.

## 3. Results and discussion

### 3.1. Phase structure and component analysis

ZnSe microspheres were successfully grown on graphene oxide sheets by hydrothermal method at 190 °C for 24 h. The phase structure of the microspheres is investigated by an X-ray diffractometer. Fig. 1 shows typical X-ray diffraction (XRD) of the ZnSe microspheres at different concentration of EDTA. All diffraction peaks can be indexed as cubic zinc blende ZnSe phases ($a$ = 5.699 Å), which matches well with the reported for ZnSe of JCPDS File No. 80-2346. With increasing the concentration of EDTA, all the XRD patterns are similar, and the diffraction intensity varies almost homogeneous, as shown in Fig. 1(a–d). The five peaks at $2\theta$ = 27.3°, 45.4°, 53.7°, 66.0° and 72.6° are observed from Fig. 1. The very sharp and narrow diffraction peaks imply high crystalline of the as-grown ZnSe microspheres. Besides, the weak peaks at $2\theta$ = 21.2°, 24.5° and 25.0° are detected from Fig. 1 and are in agreement with the diffraction peaks of graphene oxide. The results prove that ZnSe microspheres are grown on the graphene oxide sheets. Above all, no other impurity peaks are detected, which indicates that the ZnSe samples are in high purity.

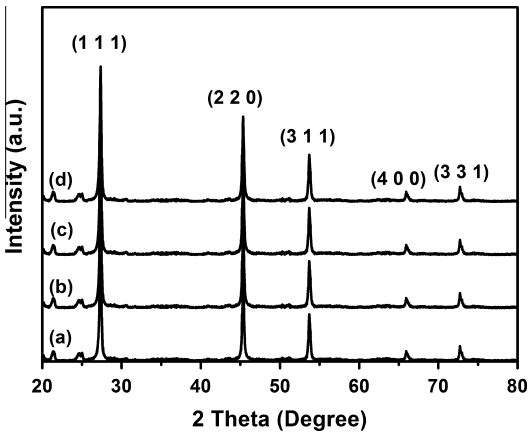


**Fig. 1.** The XRD patterns of the samples grown at 190 °C for 24 h using different concentration of EDTA: (a) 0 M, (b) 0.15 M, (c) 0.30 M, and (d) 0.45 M.