Optics Communications xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

Solution synthesis of stannous sulfide and stannic disulfide quantum dots for their optical and electronic properties

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ARTICLE INFO

Keywords:
SnS
SnS_2
Quantum dots
Ultrasonic method

ABSTRACT

Quantum dot devices have been viewed as one of solutions for the next step in the development of integrated circuit. Two-dimensional (2D) layered semiconductors such as tin sulfide (SnS) and tin disulfide (SnS_2) are promising materials for fabricating quantum dots (QDs) devices. However, the challenges in the synthesis of QDs with pure phases severely limit applications in such fields. In this work, uniform SnS and SnS_2 QDs were synthesized via a convenient and facile ultrasonic method. TEM and AFM images confirmed the morphology of the SnS and SnS_2 QDs. The optical characteristics of the QDs were obtained via UV–vis absorption and Raman spectroscopy. Finally, volt-current measurements of devices fabricated using the SnS and SnS_2 QDs were carried out. Our results demonstrate the potential of SnS and SnS_2 QDs for optical and electronic applications.

1. Introduction

2D materials, such as graphene [1], transition metal dichalcogenides (TMDCs) [2,3] and black phosphorus [4,5], have drawn a great deal of interest in sensors, optoelectronics and other applications, due to their attractive properties. The engineering of the size and dimensions of 2D materials may even endow them with novel properties and broaden their applications. Owing to edge effects and quantum confinement, QDs with lateral sizes of less than 10 nm usually exhibit different electrical/optical behaviors from those of nanosheets or bulk materials [6–10]. Electrical/optical devices based on QDs may also exhibit low power consumption and fast response.

Considering the feasibility of QDs devices, we sieved through different n-type and p-type semiconductor materials for a suitable material. Tin sulfide (SnS) is a p-type semiconductor with an indirect band gap of 1.1 eV and a direct band gap of 1.3 eV [11], while tin disulfide (SnS_2) is n-type semiconductor with an indirect band gap of 2.1 eV and a direct band gap of 2.8 eV [12,13]. SnS and SnS_2 are abundant in the earth and environmentally friendly, both of them having layered structures with strong Sn-S bonds in each layer and weak van der Waals interactions between different layers. Both SnS and SnS_2 have already been widely studied in lithium batteries, solar cells and other optical or electronic applications [11–16].

Apart from traditional mechanical exfoliation, colloidal methods and chemical precipitation methods can also be used to synthesize quantum dots [17,18]. Lately, MoS_2/WS_2 QDs and black phosphorus QDs prepared by ultrasonication method have been reported. The method is economical and feasible for the high-yield preparation of QDs in solution phase [19–21]. In this work, SnS and SnS_2 QDs were prepared through an ultrasonication method. Various characterizations confirmed the uniform morphology, optical and electrical properties of quantum dots. Our results demonstrate the potential of SnS and SnS_2 QDs for electrical/optical devices.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical grade and applied as-received without further purification. $SnCl_4{\cdot}5H_2O$, $SnCl_2{\cdot}2H_2O$, $Na_2S{\cdot}9H_2O$ and thiourea were purchased from Aladdin Industrial Corporation. N-monthylpyrrolidinone (1-methyl-2-pyrrolidinone) and PEG (Poly methyl ether amine) were purchased from Sigma-Aldrich.

2.2. Methods

Details of the SnS or SnS_2 powders are presented in the supplementary materials. In the Fig. S1, orthorhombic SnS nanobelts were

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http://dx.doi.org/10.1016/j.optcom.2016.11.060
Received 23 August 2016; Received in revised form 13 November 2016; Accepted 23 November 2016
Available online xxxx
0030-4018/

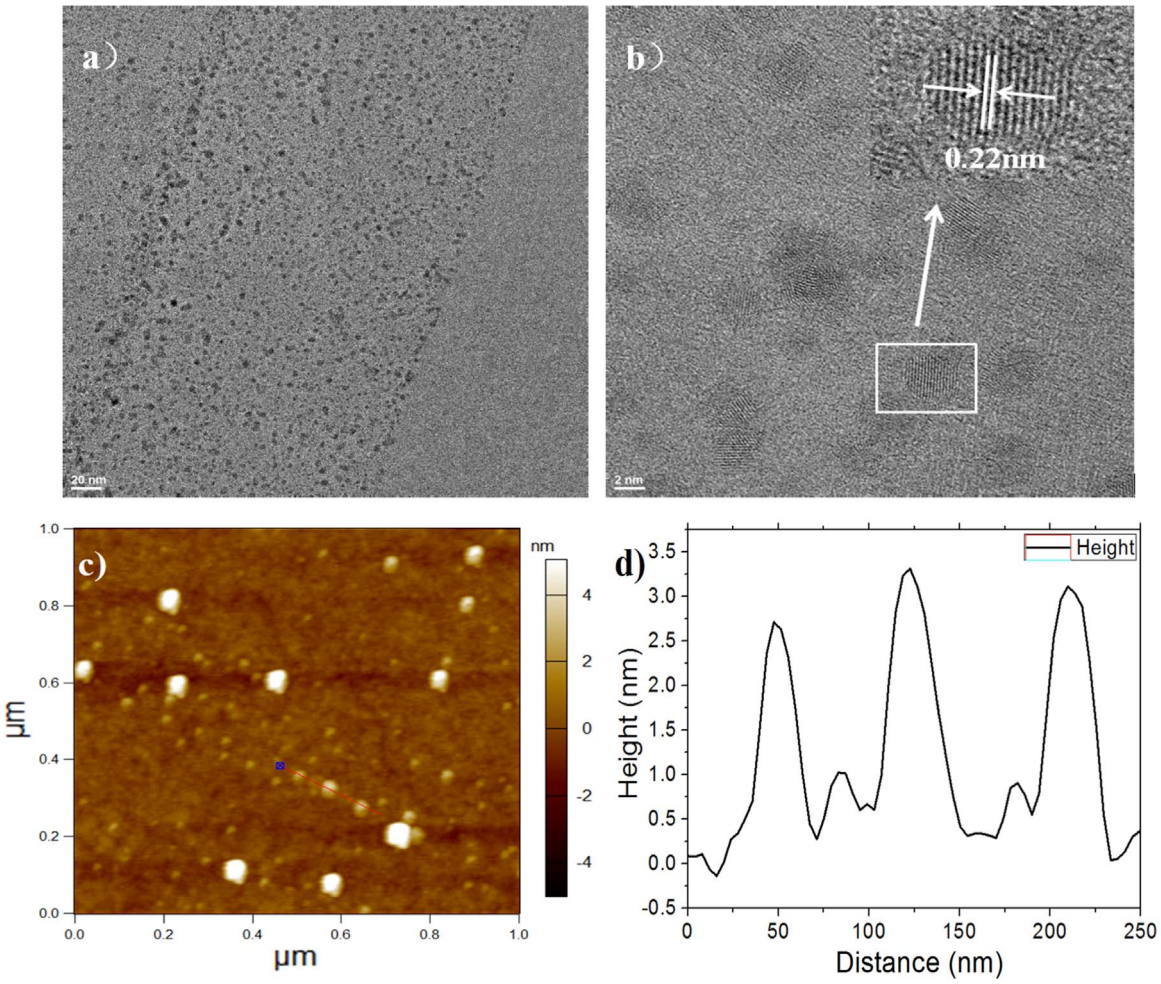

Fig. 1. Morphology characterization of SnS QDs. a) TEM image of SnS QDs. b) HRTEM image of SnS QD. c) AFM image of SnS QDs. d) Height profiles along the red line in (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

shown. Flower-like SnS_2 were shown in the Fig. S2. The XRD results of both powders (SnS and SnS_2) were also provided in the supplementary materials (Fig. S3 and Fig. S4).

2.2.1. *Synthesis of SnS/SnS_2 quantum dots*

10 mg SnS (SnS_2) powder and 20 ml NMP were put into a 20 ml bottle and sonicated for 6 h in an ice bath to exfoliate the SnS (SnS_2) powder using a sonicator (KQ-3200E) with an output power of 150 W. The suspensions were centrifuged for 20 min at 7000 rpm to separate the centrifugate and extract the supernatant. The respective batches of supernatant were then centrifuged for 40 min at 12000 rpm and the centrifugate further separated. The corresponding batches of precipitates were then extracted, washed and dissolved in ethanol.

2.2.2. *Fabrication of devices*

Taking reference from the fabrication of black phosphorus QDs devices [22], 30 μL PEG was pipetted into the as-prepared quantum dot samples to enhance the stability and improve the resistivity. After PEG conjugation, the samples were spin coated on the silicon oxide substrate at 1000 rpm for 10 s. Then, several 20 nm thick Au electrodes (1 mm length and 3 mm width) were deposited using thermal evaporation at 10^{-6} Torr using shadow masks.

2.3. *Characterizations and measurement*

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL model JEM2100 instrument at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) images were taken by Cypher S microscopy. UV–vis absorption behavior of samples was tested using a UV-3600 spectrophotometer. Raman spectra were obtained using a Raman spectrometer (LabRam HR800) excited by the 514.5 nm line of an Ar laser under 10 W. Volt-ampere measurements was carried out on Keysight B1500A probe station.

3. Results and discussion

As synthesized quantum dot samples collected in 1.5 ml centrifuge tubes were shown in the Supplementary materials. As shown in Fig. S5, the color of SnS quantum dots is dark brown while the color of SnS_2 quantum dots is almost transparent. TEM and AFM were used to measure the morphology of SnS quantum dots. Figs. 1a and b show TEM and HRTEM of SnS quantum dots respectively. The relatively uniform quantum dots, with a spacing distance of about 0.22 nm corresponding to the lattice plane (002) of SnS (JCPDs65-3812), have a diameter of ~5 nm. Three QDs with an average distance of ~80 nm were characterized by AFM, as shown in Figs. 1c and d. The heights of the QDs are almost 2.7–3.2 nm, corresponding to 2–3 single layers of SnS (1.118 nm, Crystallography Open Database ID: 1011253).

Similarly, the morphologies of SnS_2 QDs were obtained. From the TEM and HRTEM images shown in Figs. 2a and b, the size of SnS_2 QDs is smaller than that of SnS QDs, with a diameter of 2–5 nm. The distance of the lattice fringes spacing is 0.21 nm, corresponding to the (102) plane of SnS_2 (JCPDs23-0677). From Figs. 2c and d, the height