Materials Letters 182 (2016) 138–142

Contents lists available at ScienceDirect

Materials Letters

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

Surface modification of ZnO tetrapods using sodium sulfide and their two-photon luminescence properties

Qun Luo, Yongfu Qiu *, Pingru Xu, Dan Zhu, Zhiyu Cheng *, Hongbo Fan

College of Chemistry and Environmental Engineering and Technology Research Center for Advanced Nanomaterials, Dongguan University of Technology, Guangdong 523808, PR China

ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form
4 June 2016
Accepted 24 June 2016
Available online 24 June 2016

Keywords:
Nanomaterials
Semiconductors
ZnS
Tetrapods
Luminescence

ABSTRACT

In this paper, the surfaces of ZnO tetrapods were modified by Na_2S to form composite ZnS/ZnO hollow tetrapods for the first time. Two-photon luminescence spectra with the excitation having double longer wavelength than the emission indicated that two-photon absorption was involved in the excitation processes, and the photon luminescence enhancement of ZnS/ZnO hollow tetrapods more than that of ZnO tetrapods was ascribed to the capping of ZnS, which could passivate the surface traps of ZnO. The time-resolved PL decay traces showed that the lifetime of ZnO/ZnS hollow tetrapods was much longer than that of ZnO tetrapods due to the capping of ZnS on the surface of ZnO causing the reducing surface defects and then significant effect on its surface states.

1. Introduction

The ability to design and control properties of materials directly at the nanoscale level is of topmost importance for lots of applications [1]. One-dimensional (1D) nanostructures, such as nanorods, nanowires (NWs), nanotubes and nanotetrapods have been widely investigated owing to their unique physicochemical characteristics and numerous applications [2,3]. ZnO and ZnS nanomaterials have been devoted great efforts to synthesize because of their interesting physical properties [4,5]. Accordingly, the composite ZnO/ZnS nanomaterials would be expected to have significant physical properties owning to the synergistic effect between ZnO and ZnS [6,7]. In this reports, The ZnO tetrapods were prepared by an oxidative-vapor-transport-deposition method; [8] Using ZnO tetrapods as templates and Na_2S as S sources, ZnS/ZnO hollow tetrapods were prepared for the first time and their two-photon luminescence (TPL) were studied.

2. Experimental

2.1. Synthesis of ZnS/ZnO hollow tetrapods

The ZnO tetrapods were prepared by an oxidative-vapor-transport-deposition method as our previous report [8]. In a typical synthesis of the ZnS/ZnO hollow tetrapods, ZnO tetrapods were used as template. Firstly, a solution with 0.1 g Na_2S and 25.0 mL deionized water was obtained and its pH value was adjusted to ~7 by using HCl solution (1 M). Next, 20 μg of ZnO tetrapods were added into above solution with stirring. Finally, the mixture solution was performed using ultrasonic agitation for 30 min and consequently placed at 40 °C for 24 h. After filtration, the product ZnS/ZnO hollow tetrapods were collected and washed three times with deionized water.

2.2. Characterization

The morphologies of as-prepared products were directly examined by SEM using JEOL 6701 F at an accelerating voltage of 10 kV. For TEM observations, the as-prepared products were ultrasonically dispersed in ethanol and then dropped onto carbon-coated copper grids. TEM observations were carried out on a JEOL 2010 F microscope that operated at 200 kV. The XRD analyses were performed on a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (wavelength λ=0.154 nm) at a scanning speed of 0.025°/s over the 2θ range of 20–70° at room temperature; XPS

* Corresponding authors.
E-mail addresses: qiuyf1979@foxmail.com (Y. Qiu), mszycheng@scut.edu.cn (Z. Cheng).

http://dx.doi.org/10.1016/j.matlet.2016.06.096
0167-577X/

spectra were obtained using a KRATOS AXIS ULTRA DLDXPS instrument equipped with a monochromatic Al K_a ($h\nu = 1486.6$ eV) X-ray source. All of the XPS spectra were collected at a takeoff angle of 90°, with the path energy of the photoelectron analyzer at 40 keV and a step size of 0.1 eV. For optical measurement, the two-photo luminescence (TPL) spectra were recorded by a spectrometer (Spectrapro 2500i, Acton) with a liquid nitrogen cooled CCD detector (SPEC-10, Princeton) and a mode-locked Ti: sapphire laser as excitation source (Mira 900, Coherent). The excitation source delivers ~3 ps pulses at a repetition rate of 76 MHz and its wavelength was fixed at 720 nm. The time-resolved PL (TRPL) decay traces were recorded by a time-correlated single photon counting system (PicoQuant GmbH).

3. Results and discussion

3.1. Structural characterization

The characteristic SEM morphologies of the ZnO and ZnS/ZnO hollow tetrapods are shown in Fig. 1. Overall, the ZnO tetrapods shown in Fig. 1A consist of four arms branching from the same center, and the angles between the arms are nearly analogous to the spatial geometry of a methane molecule. The growth mechanism of the tetrahedral ZnO particles can be explained by Iwanaga as a so-called octa-twin model (Fig. 1B) [9]. Fig. 1C is the SEM image of a ZnS/ZnO hollow tetrapod. Its surface was attached with some particles. Fig. 1D shows that one of its arms was broken, and the hollow structure of arm could be clearly seen. In order to further make characterization of the structures of ZnO and ZnS/ZnO hollow tetrapods, their TEM images are shown in Fig. 2A and B. Clearly, ZnS/ZnO tetrapods have the hollow structure in the arm compared with ZnO tetrapods. XRD pattern of ZnS/ZnO hollow tetrapods is shown in Fig. 2C, only ZnO crystal structure is found, which suggests that the size of particles of ZnS were too small to be detected. In order to verify this hypothesis, XPS was performed and the results in Fig. 2D clearly show that Zn, O and S are co-existence, which indicates that the tetrapods contained ZnS and ZnO and had the hollow structure. Zn 2p and S 2p core level XPS spectra and FTIR spectroscopy for ZnS/ZnO hollow tetrapods shown in Fig. 3 confirm the existence of ZnS and ZnO.

3.2. Two-photon luminescence (TPL) spectra and emission dynamics investigations

TPL spectra excited by the pulsed laser with the wavelength at 720 nm for the ZnO tetrapods and ZnS/ZnO hollow tetrapods are shown in Fig. 4A. There are three emission peaks in the TPL spectrum of the ZnO nanotetrapods, which are the second harmonic generation (SHG) around 360 nm, narrow UV emission at

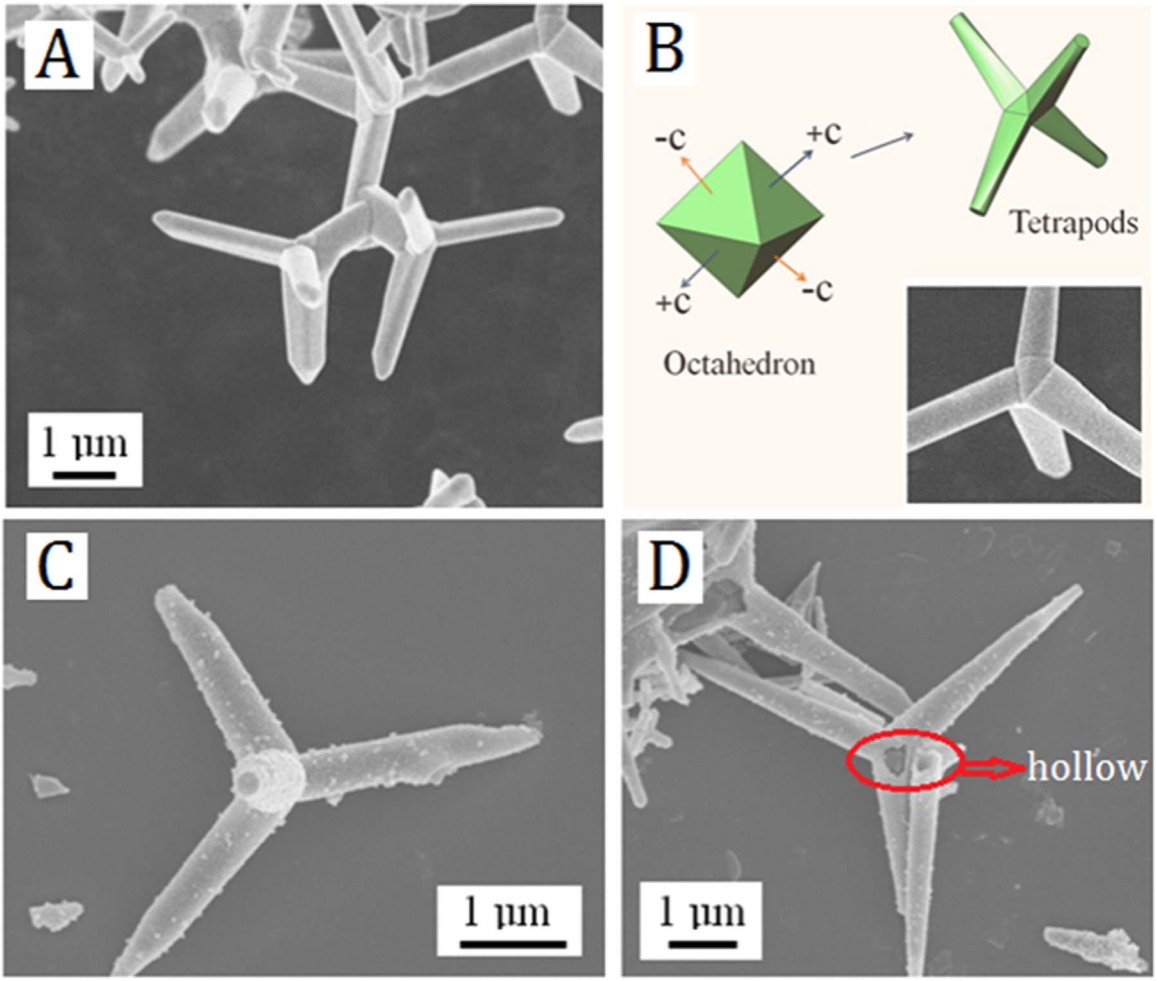

Fig. 1. SEM images of ZnO tetrapods (A) and ZnS/ZnO hollow tetrapods (C, D). (B) Formation mechanism of ZnO tetrapods; Inset in (B) is SEM image of ZnO tetrapod.