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Preparation and investigation on third-order nonlinear optical properties of ZnS/MWCNTs composite materials

Weifei Hu, Baohua Zhu, Yawan Cao, Shun Wang, Chong Wang, Zhengwei Zhang, Junhe Han, Peng Li, Shuxi Dai*, Yuzong Gu*

Institute of Microsystem, School of Physics and Electronics, Henan University, Kaifeng 475004, China

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ABSTRACT

ZnS/MWCNTs composite materials with different concentrations of ZnS were prepared and their third-order nonlinear optical properties were studied through experiments and theoretical analysis. Structure and morphology characterizations of the ZnS/MWCNTs composite materials showed that ZnS quantum dots (QDs) were uniformly attached on the surface of MWCNTs. Third-order nonlinear optical properties of all the MWCNTs samples, ZnS QDs and ZnS/MWCNTs composite materials were measured by using Z-scan technique with a picosecond pulse laser. Experimental results showed that the composite materials always presented saturated absorption properties of MWCNTs and a negative nonlinear refraction effect of ZnS.

1. Introduction

Carbon nanotubes (CNTs) have played a crucial role in many areas such as physics, chemistry, biology and material science due to their unique one-dimensional tubular structure and special physical and chemical properties [1,2]. CNTs have always been a hot topic [3–5] in the field of nonlinear optics. For example, their optical limiting behavior [6] makes them used in protecting sensitive optical sensor and human eyes, and their saturated absorption property [7] makes them used as saturable absorbers for passive mode locking in a Nd:glass laser since they can decrease the duration of light pulses to ultrashort pulses (3 ps). Zhu et al. [8] showed that large and ultrafast saturable absorption in ZnO-beaded MWCNTs could be used as saturable absorber devices. Zeng et al. [9] studied the nonlinear property of CdS/MWCNTs composite, they found the real part of its third-order nonlinear susceptibility was one order of magnitude bigger than the imaginary part, and its third-order nonlinear effect was caused by nonlinear refraction.

As an important wide-band gap II-VI semiconductor (3.7 eV), ZnS quantum dots (QDs) are found to be self-defocusing and two-photon absorption properties [10,11]. However, there are just few reports about the third-order nonlinear optical properties of ZnS/MWCNTs composite. In this paper, ZnS/MWCNTS composite materials with different concentration of zinc and sulfur source were synthesized. Structure and morphology characterizations of ZnS/MWCNTS composite materials were performed and their third-order nonlinear optical properties were also studied.

2. Experimental procedures

2.1. Syntheses of ZnS QDs

2.11 g of $Zn(CH_3COO)_2 \bullet 2H_2O$ and 1.13 g of thioacetamide was added into 30 mL of ethylene glycol respectively. The mixture was stirred for 20 min. Then the mixture was moved to a reactor and reacted at 140 °C for 14 h. The ivory slag ZnS was centrifuged from the mixture and rinsed with anhydrous ethanol and deionized water. Finally, solid ZnS was obtained after dried overnight in a vacuum oven at room temperature.

2.2. Syntheses of MWCNTs/ZnS composite materials

0.2 g of MWCNTs (untreated) was added into a mixed acid which was obtained by mixing concentrated sulfuric acid and concentrated nitric acid with the volume ratio of 3:1. The mixture was stirred for 30 min and sonicated for 3 h at 50 °C. After that, MWCNTs was rinsed until it was neutral. Filtered MWCNTs was added into 160 mL of ammonia, and processed with a similar procedure (stirring, sonicating and rinsing). After that, it was dried in a vacuum oven at 50 °C for 24 h. 0.15 g of dried CNTs was divided into five parts for use. Each part of the CNTs was added into 12 mL of zinc acetate solution with the concentration

* Corresponding authors.
E-mail addresses: shuxidai@henu.edu.cn (S. Dai), yzgu@henu.edu.cn (Y. Gu).

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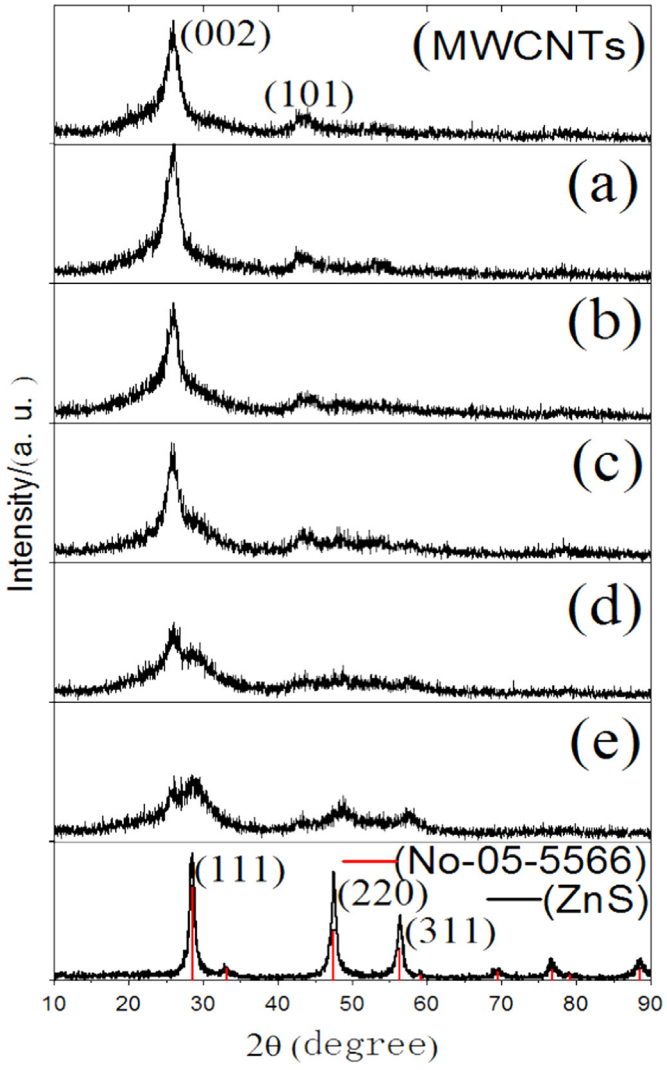

Fig. 1. XRD patterns of MWCNTs, sample a–e and ZnS.

of 3.125×10^{-3} mol/L, 6.25×10^{-3} mol/L, 12.5×10^{-3} mol/L, 25×10^{-3} mol/L, and 50×10^{-3} mol/L, respectively. Each mixture was sonicated for 30 min, and mixed with 12 mL of thioacetamide solution with a same concentration of zinc acetate. All mixtures were stirred for 30 min, sonicated and rinsed. Final products were dried in a vacuum oven overnight at 50 °C. These composite materials were marked as sample a–e separately.

X-ray diffraction (XRD) of samples was measured by X-ray diffractometer (DX-2500). Transmission electron micrograph (TEM) was measured by transmission electron microscopy (JEM-2100). Open and closed aperture curves were obtained by using a Z-scan detecting system [12] with a Nd:YAG mode-locked pulse laser (EKSPLA, PL2251) at 532 nm with 30 ps (FWHM) pulses and the repetition of 10 Hz. The beam waist at the centre of the sample is 10.6 μm by using a single lens of f=250 mm, and the aperture linear transmittance is 36.25%. Dimethyl formamide (DMF) was used as the solvent for samples during our experiment. The concentrations of MWCNTs and sample a–e are 10 mg/L, and the concentration of ZnS is 1 mg/L.

3. Results and discussion

Fig. 1 shows the XRD results of MWCNTs, ZnS and ZnS-modified MWCNTs samples. Pure MWCNTs without any modification has typical diffraction peaks at $2\theta=25.99°$ and 43.21°, corresponding to (002) and (101) planes of MWCNTs. There are obvious diffraction peaks of ZnS in $2\theta=28.57°$, 47.26° and 56.26°, corresponding to (111), (220) and (311) planes of ZnS (JCPDS No-05-0566). XRD pattern indicates that the ZnS QDs is zinc blende structure. Crystal size of ZnS particles was calculated to be about 10 nm according to Scherrer equation: $D_{hkl}=k\lambda/\beta\cos\theta_{hkl}$ [13]. As shown in the XRD patterns of ZnS/MWCNTS sample a–e, the diffraction peaks of ZnS (111), (220) and (311) planes are enhanced gradually with increasing the content of ZnS, and there are nearly no shift for their positions by comparing with each others. From the scanning electron microscope (SEM) observations of MWCNTs and sample a–e (figures not given), we found that the size of ZnS QD in the composites enlarges, the density increases, and the thickness of it thickens with the increase of the ZnS concentrations.

Fig. 2 shows the TEM images of MWCNTs, ZnS/MWCNTS and ZnS QDs samples. Pure MWCNTs show smooth surface without any material attached. The surface of the MWCNTs (sample c) is attached uniformly with ZnS quantum (10 nm), and no excess particle is found around MWCNTs. It indicates that the ZnS QDs have been attached to the MWCNTs successfully. The particle size of pure ZnS QDs was measured to be about 10 nm, which is close to the crystal size calculated from XRD results.

Z-scan results show similar curves for all ZnS/MWCNTS sample a–e. Here, typical Z-scan curves of sample a with the lowest concentration of zinc and sulfur source are selected for analysis. Fig. 3 shows the Z-scan results of pure MWCNTs, sample a and ZnS. Solid squares represent the open-aperture data, and the hollow circles represent the closed-aperture data, solid and dashed lines are the

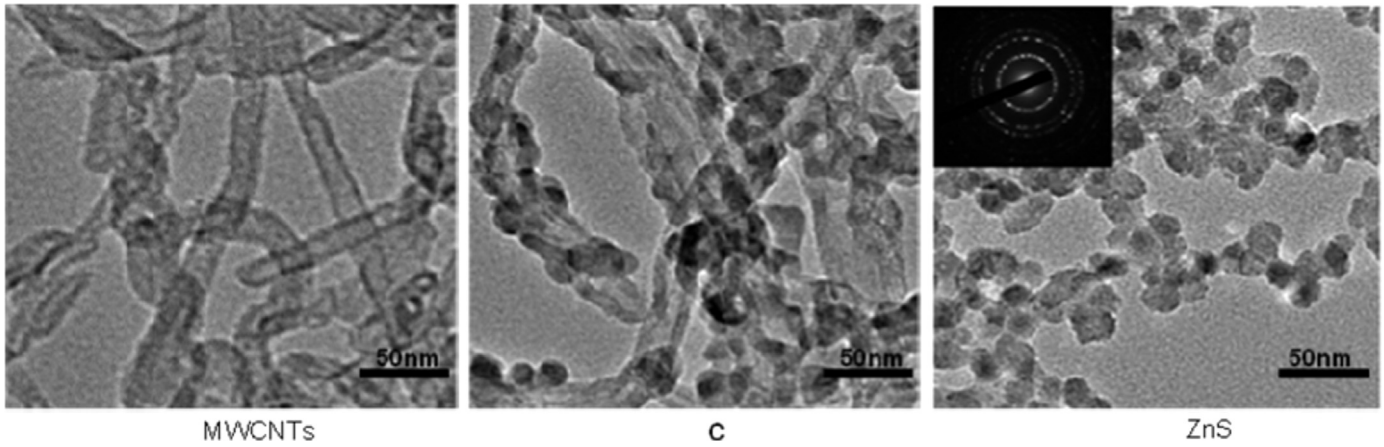

Fig. 2. TEM images of MWCNTs, sample c and ZnS QDs.