Optik 125 (2014) 6558–6561

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Third-order nonlinear optical properties of multiwalled carbon nanotubes modified by CdS nanoparticles

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ARTICLE INFO

Article history:
Received 21 November 2013
Accepted 20 June 2014

Keywords:
Third-order optical nonlinearity
Z-scan
CdS nanocrystals
MWCNTs

ABSTRACT

CdS nanoparticles were coated on the side wall of multiwalled carbon nanotubes (MWCNTs) by a wet chemical synthesis approach via noncovalent functionalization of MWCNTs with poly(diallyldimethylammonium chloride) (PDDA). The as-prepared material was characterized by X-ray diffraction (XRD), UV–vis absorption, fluorescence and transmission electron microscopy (TEM). The results indicated that CdS nanoparticles were uniformly coated on the surface of MWCNTs. Third-order optical nonlinearity of the as-prepared material was studied with the Z-scan technique with picosecond laser pulses at 532 nm. The Z-scan curve revealed that CdS nanoparticle-modified MWCNTs exhibited negative nonlinear refraction index and positive absorption coefficient. The real part and imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}$ were calculated to be -4.9×10^{-12} and 6.8×10^{-13} esu, respectively.

1. Introduction

The third-order nonlinear optical phenomenon is fundamental to optical device applications such as optical limiting devices, all optical switching and computing, optical correlators and phase conjugators [1,2]. Since discovered by Ijima in 1991, carbon nanotubes (CNTs) have been widely and deeply investigated because of their one-dimensional π-electron conjugation and their unique physical and chemical properties [3–5]. The sp^2 hybridization of the carbon atoms leads to the greatly delocalized π-electron cloud along the axis of carbon nanotube. Therefore, CNTs exhibit large third-order nonlinear susceptibilities with ultrafast response time [6]. Recently, special interest has been devoted to study the potential of CNTs as a nonlinear optical material. A number of theories have predicted that the nonlinear optical properties of CNTs are determined by the structure [7–9]. In particular, Zhang et al. [8] have studied the third harmonic generation of CNTs by using the density matrix theory with effective-mass approximation and concluded that the third harmonic generation increase with an increase in the tube radius. In addition to the theory, a series of experiments were carried out to measure the third-optical nonlinearities in the nanosecond, picosecond and femtosecond regimes. For example, Liu et al. measured the third-order nonlinearity of CNTs using the picosecond and nanosecond degenerated four-wave mixing (DFWM) technique, and Gupta et al. reported the third-order nonlinearity of CNTs functionalized with water-soluble porphyrin by Z-scan technique with femtosecond laser pulse at 780 nm [10,11].

Nowadays, a great deal of research efforts have been devoted to explore novel strategies that can alter the physical properties of CNTs by surface modification with organic and inorganic species. These functional CNT-based composites show eminent prospects and opportunities for new applications in a wide variety of areas [12–14]. Among them, linking semiconductor nanoparticles to CNTs have emerged as an active field. Semiconductor nanoparticles can be grown on the surface of CNTs by noncovalent interaction, which utilize π-stacking, Vander Waals interaction, electrostatic interaction, etc., and it enables functionalization of CNTs while maintaining the electronic and structural properties of carbon framework [15]. Of the various types of semiconductors, CdS, a kind of II–VI semiconductor with a bandgap of 2.42 eV, has been used widely in displays devices, light-emitting diodes (LEDS) and biological applications. Besides, CdS nanoparticles exhibit third-order optical nonlinearity [16,17]. Many efforts have been tried to modify CNTs with CdS nanoparticles [18–20], however, researches on the third-order nonlinear optical properties of CdS nanoparticle-modified MCNTs are rare.

In the present work, MWCNTs modified by CdS nanoparticles were prepared by a facile wet chemical synthesis approach. The

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http://dx.doi.org/10.1016/j.ijleo.2014.06.166
0030-4026/

third-order nonlinear properties were measured by the Z-scan technique.

2. Experimental

The acid-treated MWCNTs with diameter of 10–20 nm were kindly provided by Chengdou Organic Chemical Co. For synthesis of CdS nanoparticle-modified MWCNTs, 30 mg of MWCNTs were introduced into 2 wt% methanol solution of PDDA, followed by further sonication for 30 min. The solution was stirred at room temperature for 20 h to ensure the full adsorption of PDDA on the surface of MWCNTs. Excess PDDA was removed by centrifugation/redispersion cycles, redispersing in methanol by stirring, and brief sonication. Following this procedure, a stable colloid of PDDA-wrapped MWCNTs in 30 ml of methanol was obtained. Afterwards, 30 ml of 0.01 mol L^{-1} $Cd(AC)_2$ methanol solution was added to the as-prepared MWCNTs/PDDA methanol suspension, and then sonicated for 30 min in order to drive the coordination reaction to completion. Then 30 ml of 0.01 mol L^{-1} Na_2S methanol solution was added dropwise into the above mixture, followed by vigorous stirring for 3 h.

The XRD patterns were obtained using Fangyuan DX-2700 X-ray diffractometer with Cu Kα radiation, operating at 40 kV and 30 mA. TEM was performed on a Hitachi H-600 electron microscope with an acceleration voltage of 75 kV. UV–vis absorption spectra were measured with the use of a Shimadzu UV-2550 UV–vis spectrophotometer. Fluorescence measurements were performed using a Shimadzu RF-5301 spectrofluorometer with excitation wavelength at 352 nm.

The nonlinear refractive index and nonlinear absorption coefficient of CdS nanoparticle-modified MWCNTs were determined by Z-scan technique [21]. A mode-locked Nd:YAG laser (continuum, PY61) was used as the light source with a repetition rate of 10 Hz and pulse width of 38 ps. A lens of 300 mm focal length was used to focus the laser pulse. The radius of beam waist (ω_0) was 24 μm at the focus. The sample solution was put in a quartz cell with 1 mm path length, which was moved in the direction of light incidence near the focal spot of the lens. The transmitted beam energy and reference energy were measured simultaneously by two energy detectors (J3-05, molectron). A typical peak power density of 1.4×10^{13} W/m^2 was maintained throughout our work. The light intensities transmitted across the sample were measured as a function of the sample position in the *Z*-direction with respect to the focal plane either through a small aperture (closed-aperture Z-scan) or without an aperture (open-aperture Z-scan). For the closed-aperture Z-scan, the linear transmittance of the far-field aperture, defined as the ratio of the pulse energy passing the aperture to the total energy was measured to be 0.3. The Z-san system was calibrated by using of CS_2 as a standard specimen.

3. Results and discussion

The XRD technique was used to characterize the crystalline structure of the sample. XRD patterns of the as-prepared CdS nanoparticle-modified MWCNTs are shown in Fig. 1. The diffraction peaks $2\theta = 28.6^\circ$ and 48.1° can be assigned to (111) and (220) planes of bulk cubic CdS, and we cannot observe the characteristic diffraction peak of MWCNTs located at $2\theta = 26^\circ$, for the following reasons: (1) the main peak of MWCNTs located at 26° is overlapped by that of CdS, and (2) there are too few MWCNTs in the sample. In addition, the diffraction peaks of nanocrystalline CdS are broad with intensity, indicating the small crystalline size.

The direct evidence for the formation of CdS nanoparticles on the surface of MWCNTs can be seen from the TEM micrograph shown in Fig. 2. The surface of MWCNTs was uniform covered

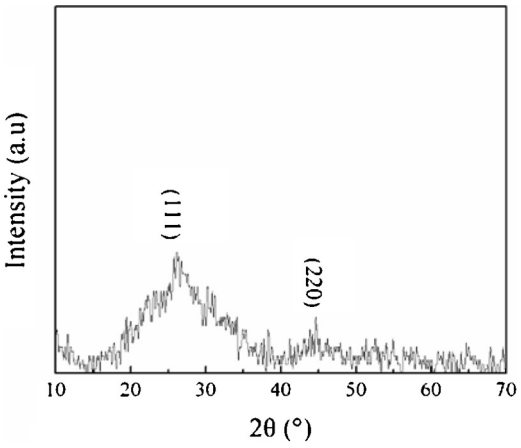

Fig. 1. XRD patterns of CdS nanoparticle-modified MWCNTs.

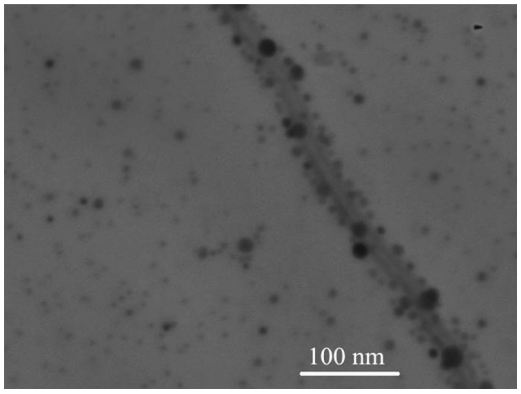

Fig. 2. TEM imagine of CdS nanoparticle-modified MWCNTs.

with a certain quantity of CdS nanoparticles, and the majority of assembled nanoparticles display a spatially isolated feature. The size distribution of CdS nanoparticles is broad, and the mean particle size lying in the range of about 8 nm.

Fig. 3 shows the UV–vis absorption of MWCNTs and CdS-modified MWCNTs. The MWCNT suspension exhibits broad and featureless spectra from 300 to 800 nm. When CdS nanoparticles were modified on MWCNTs, a shoulder peak appears at about 350 nm, which is the characteristic of CdS nanoparticles. The UV

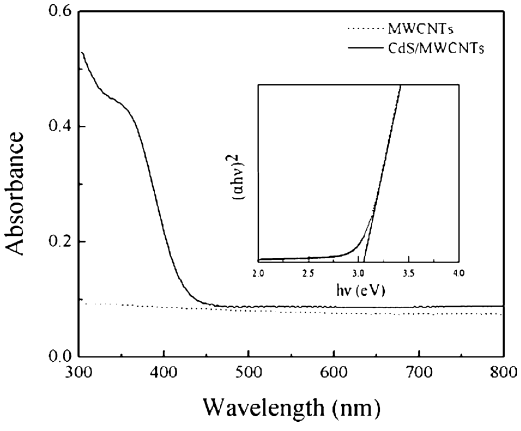

Fig. 3. UV–vis absorption spectra of MWCNTs and CdS nanoparticle-modified MWCNTs. The inset is a plot of $(h\nu\alpha)^2$ versus $h\nu$.