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Nonlinear absorption and scattering properties of copper sulfide nanocrystals

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ABSTRACT

We investigate the nonlinear optical properties of Cu_9S_5 nanocrystals using the open aperture Z-scan method with 20 ps and 4 ns laser pulses at 532 nm. We found that optical nonlinearity arises from free carrier absorption in the former case, whereas in the latter it occurs mostly due to nonlinear scattering. Parameters characterizing free carrier absorption and nonlinear scattering were determined. The dynamics of the nonlinear processes was confirmed by pump-probe measurements with 20 ps pulses. Observation of optical limiting at both excitation time regimes indicates the potential of Cu_9S_5 nanocrystals in laser safety devices.

1. Introduction

Semiconductor nanocrystals (NC) and quantum dots (QD) have attracted considerable attention from both science and technology communities due to their potential applications in photovoltaics, optoelectronic and photonic devices, biomaterials, etc [1–5]. Owing to the strong confinement of excitons in low-dimensional structures, NCs also exhibit a wide variety of nonlinear optical (NLO) behaviors which are promising for NLO applications [6–10]. It is known that the band structure of NC can be tuned via defect doping. As a result, the NLO response of various doped semiconductor NCs and QDs, such as CdS [11], silicon [12], ZnO [13–15], ZnSe [16,18,19] and CdTe [17], have been reported. However, the structure–property relationship of impurities in NC is still far from fully understood. Recently, copper sulfide has been recognized as a promising candidate material for solar cell, solid state battery, optical limiter, biomaterials, etc [20–25]. One unique feature of the copper chalcogenides NC is that the pristine undoped CuS and Cu_2S can be transformed into various non-stoichiometric $Cu_{2-x}S$ phase without any impurities doping, which triggers considerable research interest [26–29]. Despite extensive studies of electronic and optical properties of doped copper sulfide NC, the nonlinear optical response of $Cu_{2-x}S$ NC is less explored in literature [30]. Therefore, it would be interesting to investigate the NLO properties and mechanism of $Cu_{2-x}S$ NC both from the viewpoint of fundamental research and for device applications.

In this paper, we investigate the NLO properties of non-stoichiometric Cu_9S_5 NCs dispersed in toluene. The open aperture Z-scan technique is used for the measurements, employing 20 ps and 4 ns laser pulses at 532 nm wavelength. We demonstrate that the optical nonlinearity arises from free carrier absorption and nonlinear scattering in the picosecond and nanosecond excitation regimes, respectively. Our results shed new light on the photophysical mechanism and kinetics of doped copper sulfide NCs, which could be helpful for the optimization of NLO nanomaterials.

2. Experimental

Cu_9S_5 NCs were synthesized via a modified thermal decomposition process with the procedure described elsewhere [31]. The crystalline structure and morphology of the NCs were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. XRD was measured using a Siemens Kristalloflex 810 D-500 X-ray diffractometer (Karslruhe, Germany) under an operating mode of 40 kV and 30 mA, with $\lambda = 1.5406$ Å radiation. The TEM images of the nanoparticles were obtained with a JEOL JEM-1011 electron microscope (Tokyo, Japan) with accelerating voltage of 100 kV. The linear absorption spectra were recorded using a Shimadzu UV-2450 UV-vis spectrophotometer (Kyoto, Japan) with a 1 cm optical path sample cuvettes. The NLO properties of the Cu_9S_5 NCs dispersed in toluene were investigated by open aperture Z-scan method. The 20 ps and 4 ns (FWHM) laser pulses were generated by a mode-locked Nd:YAG laser (EKSPLA,

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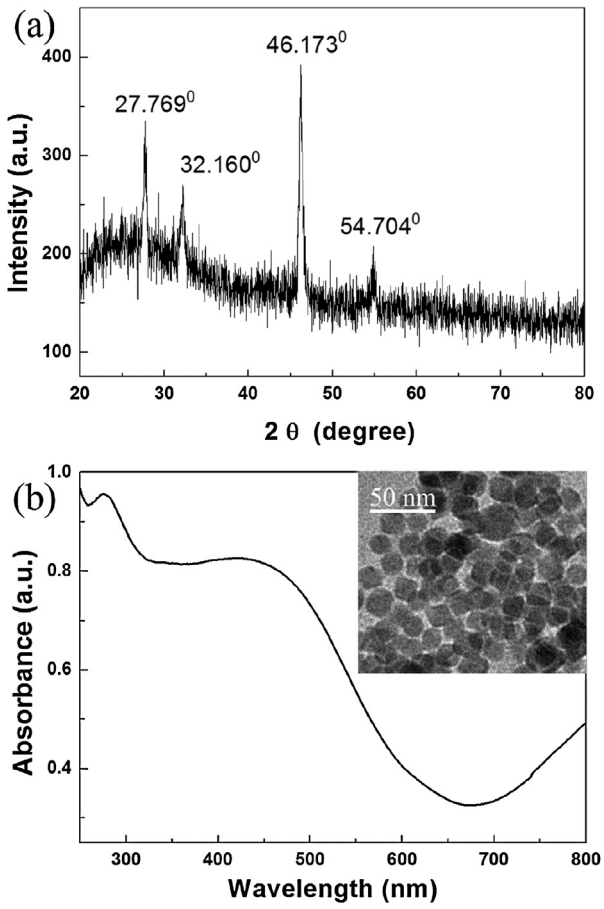

Figure 1. (a) XRD patterns of the as-synthesized Cu_9S_5 nanocrystals. The peaks are marked from JCPDS card (no. 47-1748). (b) UV–vis absorption spectra of Cu_9S_5 nanocrystals in toluene. The inset shows TEM image of Cu_9S_5 nanocrystals.

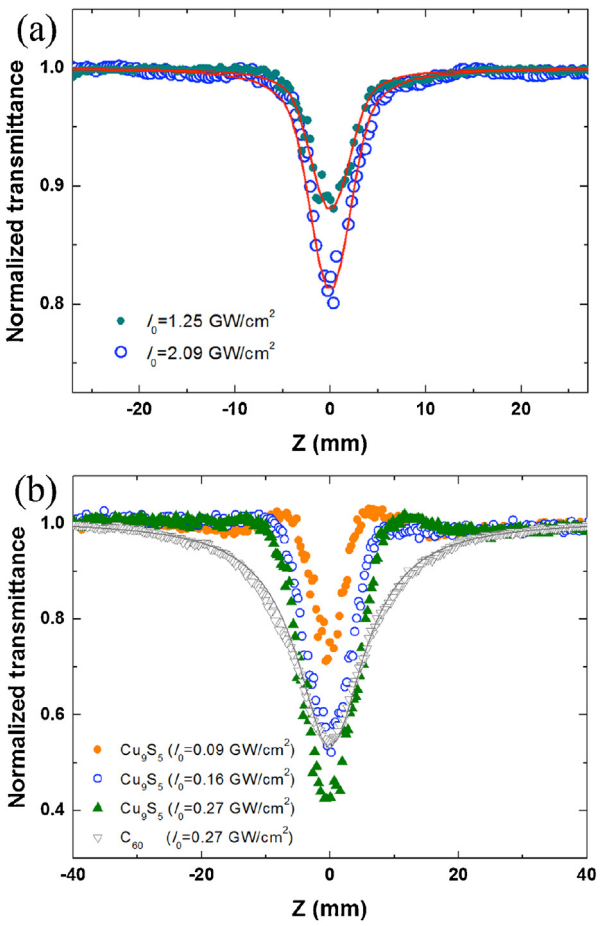

Figure 2. (a) Open aperture Z-scan curves of the Cu_9S_5 nanocrystals with 20 ps laser pulses. The solid lines are theoretical fitting. (b) Open aperture Z-scan curves of Cu_9S_5 nanocrystals and C_{60} with 4 ns laser pulses.

PL2143B) and a Q-switched Nd:YAG laser (Continuum, Surelite-II), respectively. The laser wavelength was 532 nm and the repetition rate was 10 Hz. The Z-scan configurations were similar to the pervious report [32,33]. The laser pulses were focused onto a 2 mm thick quartz cuvette which contained the Cu_9S_5 NCs, with a minimum beam waist of 27 μm and 25 μm for ps and ns Z-scan. The linear transmittance of the NC solutions was adjusted to 60% at 532 nm, corresponding to a number density of 8.9×10^{17} cm^{-3}. The pump-probe measurement was carried out using the same 20 ps laser pulses used in ps Z-scan. The setups of the pump-probe scheme have been described in detail previously [33]. The pump beam was focused on the 2 mm quartz cuvette with the diameter of 250 μm, and the probe beam with the diameter of 24 μm was overlapped with the pump beam. The polarizations of pump and probe beam were perpendicular to each other. A mechanical delay stage was used to vary the time delay between pump and probe pulses. To delineate the contribution of nonlinear scatting to nonlinear limiting effect, an angle-dependent optical limiting measurements were performed in ns excitation regime. The transmittance of laser beam after the 5 mm cuvette at an angle of 0° and 30° to the propagation direction was collected by two silicon detectors.

3. Results and discussion

A typical XRD pattern of the synthesized Cu_9S_5 NCs is shown in Figure 1a. All of the diffraction peaks can be indexed to the rhombohedral phase Cu_9S_5, which are in good agreement with the diffraction data Card No. 47-1748. Figure 1b presents the UV–vis absorption spectra of the NC solution. The spectra exhibit an absorption edge at ~660 nm, thus the band gap of Cu_9S_5 NC is evaluated to be 1.9 eV. This value agrees well with the previous reports [28,29]. The inset of Figure 1b shows the TEM image of the as-prepared Cu_9S_5 NCs. The image shows a relatively monodispersed nanoparticles with an average size of 16 ± 4 nm.

The open aperture Z-scan curves of Cu_9S_5 NCs solution in ps and ns excitation regime at different laser intensity are shown in Figure 2a and b, respectively. The solvent toluene was also measured under identical experimental conditions and found to have negligible NLO response. The results reveal that the Cu_9S_5 NCs have reverse saturable absorption (RSA) in ps excitation regime. It is known that the RSA effect can be induced by a variety of mechanisms such as multiple-photon absorption (MPA), free carrier absorption (FCA) and two-photon absorption induced free carrier/excited state absorption [7]. Since our excitation photon energy (2.33 eV) is greater than the band gap of Cu_9S_5 NCs (1.9 eV), one-photon absorption is speculated to be the dominant absorption process [9,11]. In this case, the instantaneous MPA nonlinearity and two-photon absorption induced free carrier/excited state absorption become negligible [34,35]. Therefore, we ascribed the RSA effect to FCA. To interpret the ps Z-scan results, we use the rate equation model [36]:

$$\frac{dI}{dz'} = -(\sigma_0 N_g + \sigma_1 N_e) I \tag{1}$$

where I is the beam intensity, z' is the penetration depth within the sample cell, σ_i and N_i are the absorption cross-sections and