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Optical limiting properties of CdS nanowires

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ABSTRACT

Intensity-dependent nonlinear optical transmission studies of cadmium sulfide (CdS) nanowires (~50–100 nm diameter) suspended in dimethylformamide have been carried out in the visible region using the Z-scan technique with 7 ns pulses from the second harmonic of an Nd:YAG laser. The optical limiting threshold of CdS nanowires suspension was determined to be 1.3 J cm^{-2}, with normalized transmittance of 0.47, which is relatively lower when compared with those of many popular metal nanowire suspensions reported in the literature. Based on an effective three-photon absorption model, nonlinear absorption and nonlinear scattering were identified as the dominant processes for the measured reduced transmittance.

1. Introduction

Optical limiting materials are those which attenuate intense and potentially dangerous laser beams to a safer, predetermined low level. They readily exhibit larger nonlinear extinction response at higher intensities, while permitting higher transmittance at lower intensities [1–3]. This fundamental ability of optical limiters thus plays a crucial role in protecting eyes and other imaging devices from any hazardous intense laser radiations. Numerous organic and inorganic materials like phthalocyanines, porphyrins, dyes and nanomaterials like fullerenes, carbon nanotubes, core–shell nanoparticles, inorganic nanowires, polymer grafted nanocomposites, etc., have been investigated for optical limiting application [4–10]. Mechanistically, nonlinear optical processes like multi-photon absorption, nonlinear scattering, reverse saturable absorption and free carrier absorption were identified as the key underlying processes resulting in optical limiting response of these materials [11–13]. Immense efforts were made in terms of functionalization and derivatization of these nanomaterials in order to synthesize an effective optical limiter. An effective optical limiting device needs to satisfy the following criteria (*i*) *lower limiting threshold*, (*ii*) *large dynamic range*, (*iii*) *high optical damage threshold*, (*iv*) *sensitive broadband response to long and short range*, (*v*) *faster response time*, (*vi*) *chemical and environmental stability and* (*vii*) *higher linear transmittance throughout the sensor bandwidth* [14]. To date, no single material which satisfies all the above mentioned criteria has been found, and hence many research groups around the world continue to look for novel materials and thereby optimize their optical limiting performance.

In recent years, nanostructured semiconducting materials have gained wide interest due to their inherently novel optical and electronic properties [4–6]. They are useful in hetero-junction light emitting diodes, solar cells, piezoelectric nanogenerators, photocatalytic reactors, field emitters, logic gates, and photoconducting devices [7–9]. Nanostructured sulfides and selenides (e.g. CdSe, ZnSe, CdS and ZnS) have been extensively studied with a view to establish a relationship between structure, size and optical properties [10,11]. Among these, the II–VI semiconductor cadmium sulfide (CdS) has shown strong optical nonlinearities in the band gap region. Studies hitherto on CdS nanoparticles have been reported to show notable nonlinear optical response due to strong quantum confinement effects [12–18]. Furthermore, (i) CdS multi-branched and individual nanorods have been found to exhibit enhanced two-photon absorption and higher nonlinear optical susceptibility in comparison to their bulk under picosecond and femtosecond laser pulse excitations [16,19–24] (ii) Ag_2S-coated CdS nanocomposites (core–shell) showed enhanced optical limiting performance in picosecond regime [21,25] (iii) Venkatram et al. have reported better optical limiting performance of thioglycerol capped CdS nanoparticle in both nanosecond and femtosecond regimes [27], (iv) CdO nanowires suspensions have also shown better optical performance than conventional two-photon absorber like C_{60} [28]. One or more nonlinear optical processes like free carrier absorption, multi-photon absorption and nonlinear scattering

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were identified as the origin of their optical limiting performance [3]. Here, we present a detailed investigation of the intensity-dependent nonlinear optical transmission studies on CdS nanowires with nanosecond pulses and evaluate its optical limiting performance.

Reliable methods for determining the nonlinear optical properties of materials have been developed for a wide range of applications such as optical limiting, multi-photon polymerization and optical switching. Of these methods, the "Z-scan" technique, introduced in 1985 and later developed by Eric Van Stryland is the most widely used technique [17]. In the Z-scan technique, the sample is translated through the beam waist of a focused laser beam and the transmitted power through the sample is measured. Z-scan has many possible configurations like EZ-Scan, white light Z-scan, two color Z-scan, etc. [25,30]. In its simplest configuration, it can be viewed as a single beam nonlinear transmission experiment. The two measurable quantities connected with the Z-scan technique are nonlinear absorption (NLA) and nonlinear refraction (NLR) which are usually determined using the open and closed aperture Z-scan configurations, respectively. These parameters are associated with the imaginary and real part of the nonlinear susceptibility, and provide important information about the properties of the material. Subsequently, through theoretical modeling one can deduce the magnitude and order of the relevant nonlinear processes. The loss in the transmittance due to various nonlinear processes can be easily correlated to the magnitude of optical limiting performance of the material being studied. We have employed an open aperture z-scan technique to measure the nonlinear absorption of CdS nanowire suspension.

2. Experimental

2.1. Sample preparation

Crystalline CdS nanowires were prepared using a pulsed laser vaporization technique without the use of a catalyst as described elsewhere [18]. In brief, a Nd:YAG laser (1064 nm excitation, 650 mJ/pulse, 10 Hz) was used to ablate a rotating target prepared from CdS powder. The rotating target was placed inside a quartz tube reactor, which is maintained at ~650 °C. A gentle flow of hydrogen causes the ablated material to flow downstream and collect on a water-cooled copper cold finger. The morphology and crystallinity of the nanowires were characterized using high-resolution transmission electron microscopy (HRTEM) [18]. The CdS nanowire suspensions were prepared by sonicating ~3 mg of the as-prepared material in 10 mL of dimethylformamide (DMF) and the UV–Visible absorption measurements were performed using a PerkinElmer Lambda 950 spectrophotometer.

2.2. Nonlinear spectroscopy

In our Z-scan experimental setup, 532 nm excitation wavelength with 7 ns pulse width from a Nd:YAG laser (*Quanta Ray*, *Spectra Physics*) was used as the light source. The laser beam was focused on to the sample using a converging lens of 18.5 cm focal length. The radius of the Gaussian-profile laser beam at the focal point was measured to be 18 ± 2 μm using the knife-edge method, and the change in the transmitted signal was recorded as a function of the sample position using a pyroelectric energy probe (*RJP 765*, *Laser Probe*). Data acquisition was accomplished using a fully automated computer interface and the pulse-to-pulse intensity fluctuations were normalized relative to a reference energy probe at every sample position. The CdS nanowire suspension was poured into a 1 mm thick fused silica cuvette and the linear transmittance was measured to be 70% at 532 nm. These suspensions were stable for more than an hour, and each Z-scan run lasted for only about 5 min each thus ensuring reliable data acquisition. The optical response of the solvent (DMF) was first recorded and no nonlinear transmission response was observed at 532 nm excitation wavelength.

3. Results and discussion

Fig. 1 depicts a representative UV–Visible absorption spectrum, SEM image of the as-prepared CdS nanowires, and a TEM image of an isolated CdS nanowire with a diameter of ~50 nm. The weak peak near 489 nm (2.53 eV) is indicative of the presence of excitons in nanostructured CdS and is absent in the corresponding spectrum recorded for the bulk. Since the average diameter of the CdS nanowires is ~50–100 nm (with an uncertainly of ±0.1 nm) [18], which is much larger than the exciton Bohr radius of ~3 nm for CdS [29], a strong quantum confinement effect is not expected in the present study. Such quantum confinement was also confirmed from photoacoustic spectroscopy [18] where we found very meager but distinguished signal from that of corresponding bulk.

The open aperture Z-scan curve (○) of CdS nanowires shows a clear symmetric valley indicating the presence of nonlinear absorption (Fig. 2). Depending on the absorption mechanism, one obtains either peak (valley) with a maximum (minimum) at the focal point ($z=0$) where the input intensity or the fluence is maximum [17]. The intensity variation along the beam propagation direction (z) in a medium with mutliphoton absorption can be described as in Eq. (1)

$$\frac{dI}{dz} = -\left(\alpha_0 + \gamma^{(n+1)} I^n\right) I. \tag{1}$$

Here α_0 is the linear absorption coefficient, $\gamma^{(n+1)}$ is the $(n+1)$ photon absorption coefficient and I is the intensity. Eq. (1) reduces to a two-photon absorption (2PA) process with $n=1$ while $n=2$ reduces it to a three-photon absorption (3PA) process, involving third and fifth order nonlinear optical processes, respectively. It should be noted that Eq. (1) does not distinguish between direct and cascaded absorption, and therefore in the context of this study, both processes are treated identical. The strength of these nonlinearities is evaluated by the magnitude of "γ" which in turn is estimated by numerically fitting the position dependent transmittance, T(z)

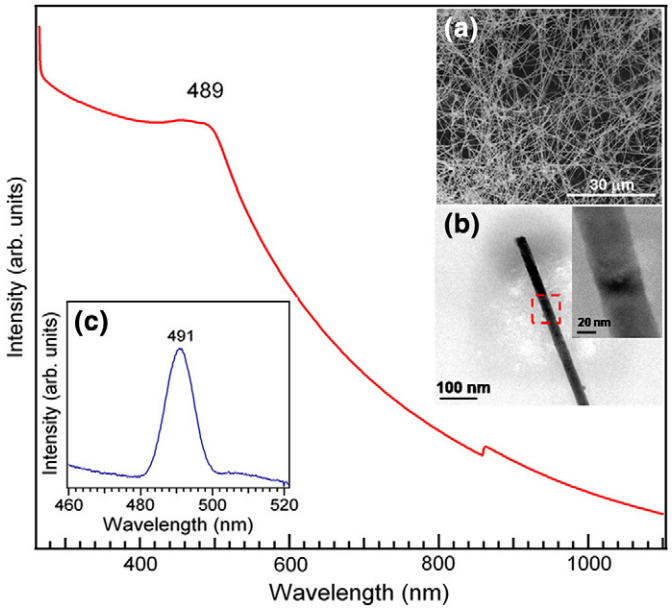

Fig. 1. UV–Visible absorption spectrum of CdS nanowires (~3 mg) suspended in 10 mL of DMF; insets: (a) SEM image of as-prepared CdS nanowires; (b) TEM image of isolated CdS nanowire with diameter ~50–100 nm; (c) photoluminescence spectrum of CdS nanowire with emission around bandgap edge ~491 nm.