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Measurement of third order susceptibility by nonresonant nondegenerate four wave mixing in polymer embedded cadmium sulfide quantum dot systems

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Abstract

We report clear evidence of third order nonlinearity $\chi^{(3)}$ in polymer embedded cadmium sulfide quantum dot system as a result of nonresonant nondegenerate four frequency mixing. We notice thickness dependent enhancement of nonlinear absorption with increase in incident intensity of light. Two pump beams ($\lambda = 1064$ nm) were oppositely directed into the sample and to receive phase conjugated signal, a probe beam was focused at the point of intersection on the sample. In the conditions satisfying self diffraction phenomena, we have measured change in refractive index as a function of incident power. We have observed very high value of third order susceptibility ($\chi^{(3)} \sim 10^{-7}$ e.s.u.) and predict figure of merit as high as ~1.9 for the thinnest quantum dot sample (0.54 μm). Nonlinear susceptibility drops by nearly 10 times for the thickest sample (1.211 μm) due to considerable suppression in nonlinear absorption.

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1. Introduction

Low dimensional composites consisting of metallic or semiconducting materials embedded in dielectric hosts have unusual nonlinear optical properties of interest for both scientific and technological reasons. Measurements of nonlinear optical response, in both semiconductor and metal quantum dot composites, indicate complementary but favorable characteristics in terms of switching speed, magnitude of nonlinearity and switching energy. Indeed, there is enough scope for the possible deployment of these materials in photonic devices for optical switching and computing.

The nonlinear optical phenomena has been discussed in various general texts [1–3]. In the special case of designing devices, there exists a so-called 'figure of merit' to grade the optical nonlinearity for application. The concept which generally succeeds is the evaluation of the nonlinear optical properties in terms of nonlinear susceptibility $\chi^{(3)}$ of respective materials. The mechanism determining nonlinear susceptibility is actually different for various kinds of nanomaterials. In nanoscale devices one has no option to use optical resonators to enhance the nonlinear effects-a trick often exploited when the physical dimensions of a nonlinear device are larger than the wavelength of light. Therefore, one has to rely on the nonlinearity of the medium itself. In composite systems like CdS_xSe_{1-x} where the host matrix is either a glass or a polymer, exploiting the intensity dependent change in the refraction coefficient, determination of third order nonlinearity has been reported by many different processes. They include third harmonic generation (THG), interferometry (IF), pump probe spectroscopy (PP) and degenerate four wave mixing (DFWM) [4–9]. Measurement of third order susceptibility

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has been reported [10–13] and reviewed [14,15] by various workers using z-scan and FWM techniques. However, all these methods involve resonant excitation which is relatively slow (~ns) and there is adequate signal loss due to high value of absorption coefficient (~10^5/cm) where as nonresonant excitation is faster and involves low absorption coefficient value (~10^2/cm). In this report, we highlight contribution to the third order susceptibility by nonresonantly excited polymer embedded cadmium sulfide quantum dots based on nondegenerate four frequency mixing (NDFWM) phenomena. The measured optical nonlinearity involves the principle of self diffraction and an established formula which was verified by Cotter et al. for 3.5–6 nm CdSe–Te clusters dispersed in glass [16].

2. Theory

Semiconductor quantum dots represent unique class of quasi-zero dimensional material systems which reveal large optical nonlinearity and hence are potential candidates for optoelectronic and photonic devices. The nature of the nonlinear optical response to an incident light-field can be profoundly influenced by the dimensionality of the material. Nonlinear optical effects are generally strongest in geometries in which the optical intensity is high in the largest possible volume. The practical application of nonlinear optical effects requires field strength as high as ~10^6 V/m [17,18]. In order to explain nonlinear effects, it is normally assumed that the nuclei and associated electrons of the atoms in the solid form electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate which, by the classical laws of electromagnetism, results in the formation of dipoles which now act as sources of new electromagnetic radiation. If the amplitude of vibration is small, the dipoles emit radiation of frequency comparable to the incident radiation. While the intensity of the radiation increases, the relationship between intensity and amplitude of vibration becomes nonlinear resulting in the generation of harmonics of the frequency of the radiation emitted by oscillating dipoles.

Typically, a nonlinear refraction coefficient n_2 is defined by

$$n(\omega) = n_0(\omega) + \Delta n(\omega) = n_0(\omega) + n_2 I \tag{1}$$

where n_0 is the linear (normal) low intensity refractive index and I being intensity of the light beam. Considering the case due to Yoffe et al. [19]

$$n = n_0 + \frac{2\pi}{n_0}\chi^{(3)}E^2 \tag{2}$$

$$\Delta n_{\chi^{(3)}} = n - n_0$$

and

$$= \frac{2\pi\chi^{(3)}E^2}{n_0} \tag{3}$$

$$= \frac{2\pi\chi^{(3)}I}{n_0}$$

The result has been verified by Cotter et al. [16] for CdSe–Te nanoclusters dispersed in glass. Further, along with Eq. (1) for solid semiconductors, nonlinear refractive index can be written as [20]

$$n_2 = \frac{16\pi^2 Re\chi^{(3)}}{cn_0^2}\text{e.s.u.} \tag{4}$$

and

$$I = \left(\frac{cn_0}{8\pi}\right)E^2 \tag{5}$$

In the thin-grating approximation, $d \ll 2\Lambda^2/\lambda$ (d thickness of the grating, Λ the grating constant and λ the wavelength of the light) [21]. The efficiency of a thin-grating is correlated with the nonlinear change in the refractive index in the simple approximation

$$\eta = \frac{I_1}{I_T} \approx \left|\frac{\pi\Delta nd}{\lambda}\right|^2 \tag{6}$$

where I_1 is the intensity of the first order diffraction obtained by photon counts on the reverse side of the sample and away from principal beam corresponding to incident intensity (I_0), I_T is the transmitted intensity of the pump beam (zeroth order intensity), d the thickness of the grating and λ the wavelength of the probe-laser. Instead of incident intensity, use of the transmitted intensity allows one to take absorption losses into account. Both I_1 and I_T are measured corresponding to different incident intensities I_0.

In fact, there are two regimes concerned with the nonlinear response, the resonant and the nonresonant cases. The response time for the resonant regime is relatively slow, of the order of a nanosecond, but $\chi^{(3)}$ values can be enhanced by exciton effects to the order of 10^{-9} e.s.u. and even values as high as 10^{-6} e.s.u. has been reported for iron nanoparticles in amorphous $BaTiO_3$ [22]. Biexciton contribution to the third order nonlinearity was observed by Spocker et al. [23] in resonantly excited nondegenerate four wave mixing (NDFWM). The penalty for working in the resonant mode is the loss in the transmitted light due to the high α-values (10^5–10^6/cm) which limits possible practical applications. On the other hand, nonresonant response time is faster and ideally should be in the order of a picosecond. The additional advantage of concentrating on this regime is the damping factor due to low α-values, thus avoiding attenuation of the signal. Working in this regime therefore, involves only the real part of Δn, and since $\chi^{(3)}$ value is low, the signal is weaker than for the resonant case. Even then; nonresonant process is interesting due to safe passage of light without degrading quality of the specimen. The nonresonant case is simple to handle, since one is concerned with optical effects far removed from the optical absorption edge, i.e., when the photon energy of the incident light $\hbar\omega$ is less than the energy gap E_g of the quantum dot material. In other words, absorption coefficient is low, exciton effect and multiple-photon absorption are absent, and the major factors involved are the local field and the anharmonicity of the electronic structure. Reports based on nonresonant