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Size Dependence of First-order Hyperpolarizability of CdS Nanoparticles Studied by Hyper-Rayleigh Scattering

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Abstract: The second-order optical nonlinearity of CdS nanoparticles with different diameters of 28.0, 30.0, 31.5, 50.0, and 91.0 Å was studied by hyper-Rayleigh scattering technique. Results show that the first-order hyperpolarizability β value per CdS particle decreases as size is reduced to diameter of 31.5 Å; however, as CdS size further decreases, this trend is reversed and β value increases. Substantially, the normalized β value per CdS formula unit, β_0, exhibits systematic enhancement with decreasing size. This phenomenon is interpreted in terms of a so-called surface contribution mechanism.

Keywords: CdS nanoparticles, hyper-Rayleigh scattering, second-order optical nonlinearity, size dependence, surface contribution.

In the field of semiconductor physics, considerable activity is dedicated to the study of quantum-confinement effects in low dimensional systems. Especially interesting are the nonlinear optical properties of these structures which make them promising for various optical and electronic devices. In the past 20 years the third-order optical nonlinearities of semiconductor nanoparticles have been widely studied[1,2], having demonstrated that the nonlinearities are affected not only by particle size but also by their surface structure, since nanoparticles are characterized by large surface-to-volume ratios. In contrast, only few studies on the second-order optical nonlinearities of semiconductor nanoparticles have been performed during the recent years. It should be indicated that the second-order optical nonlinearity of nanoparticles can be studied owing to a powerful tool, incoherent hyper-Rayleigh scattering (HRS) technique, which is not constrained by the orientational, size, and/or charge restrictions compared with the conventional coherent second harmonic generation (SHG) and electric-field-induced SHG techniques. We previously studied the second-order nonlinearities of CdS/AOT-SO_3^-[3], CdS/HMP[4], CdS/2,2'-bipyridine[5], and CdS/$SC(NH_2)_2$[6] nanoparticles, including the HRS spectra, the quadratic power dependence of HRS intensity $I_{2\omega}$ on the incident intensity I_ω, the linear concentration relationship, the influence of the exchange of surface-modifying molecules

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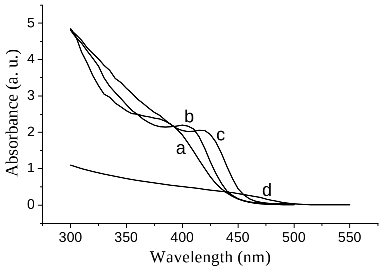
and the particle surface variation in aging process of aqueous colloid on HRS signal. It has been indicated that the first-order hyperpolariability of nanoparticles is sensitive to surface conditions and therefore the HRS technique is expected to develop into an effective tool for the characterization of nanoparticle surface. Here we mainly focus on the size-dependence of the first-hyperpolarizability of CdS nanoparticles.

Using the reverse micelle method[7,8], CdS nanoparticles modified by AOT-SO_3^-(anion of surfactant bis (2-ethylhexyl) sulfosuccinate, disodium salt) with 28.0, 30.0, and 31.5 Å mean diameters were prepared. These nanoparticles are named as CdS/AOT-SO_3^- with concentration of 1.67×10^{-3} mol/L calculated in terms of the CdS formula unit. CdS nanoparticles of 50 Å in mean diameter were prepared by the co-precipitation reaction between aqueous solutions of $Cd(NO_3)_2$ and Na_2S in the presence of hexametaphosphate (HMP) as stabilizer (named as CdS/HMP, 5×10^{-4} mol/L)[4]. For 91.0 Å CdS/HMP nanoparticles (cubic zinc blende structure), the size of which was determined from absorption spectrum and using the same calculation method as us, the first-order hyperpolarizability value is quoted from the reference[9]. And their synthetic method and HRS experimental conditions are similar to our experiments.

The HRS experiments were performed using a setup similar to the literature[10]. The Q-switched Nd-YAG laser pulse (10 Hz, 8-10 ns pulse width) at 1064 nm was focused into a 5 cm length glass cell with the pulse energy lower than 3 mJ.

Figure 1 shows the absorption spectra of the CdS/AOT-SO_3^- nanoparticles of three sizes and the 50 Å CdS/HMP nanoparticles. As shown, a typical blue shift of the absorption edges is clearly observed. From the absorption edges of 380, 405, 420, and 477 nm, the mean diameters of the four CdS nanoparticles were estimated to be 28.0, 30.0, 31.5, and 50.0 Å, respectively, according to a finite depth potential well model[11]. These results are in agreement with TEM observations. Electronic diffraction experiments show that the four CdS nanoparticles are cubic zinc blende structure. In addition, the absorption spectra also show that the four CdS nanoparticles have negligible absorption at the frequency-doubled light of 532 nm.

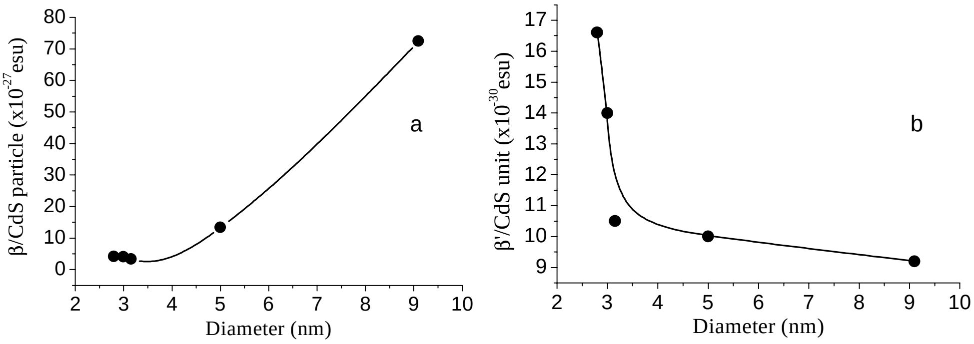
Figure 1 Absorption spectra of CdS colloids



a, b, c are the CdS/AOT-SO_3^- nanoparticles of 28.0, 30.0, 31.5 Å mean diameter, respectively, in haptane; d is the CdS/HMP nanoparticles of 50.0 Å mean diameter in water

We use the internal reference method (IRM) to determine the β value of nanoparticles[3,6]. **Figure 2**(a) shows the size dependence of the first-hyperpolarizability β value per CdS nanoparticle. It can be seen that the β value reduces with decreasing particle size. However, as size is decreased to 31.5 Å, this trend is reversed and the β value increases. In **Figure 2**, the β value (7.24×10^{-26} esu) of 91.0Å CdS/HMP nanoparticles is from the reference[9].

Figure 2 The size dependence of the first-order hyperpolarizability



a. per CdS nanoparticle; b. per CdS formula unit

Previously, we reported that the strong coordinating bond formation on CdS nanoparticle surface or the change in electronegativity of coordination atoms such as O and N atoms can modify the second-order optical nonlinearity of CdS nanoparticles[5]. However, due to nearly same electronegativity between SO_3^- and PO_3^- and similar electrostatic interaction between CdS and SO_3^- or PO_3^-, we may ignore the influence of surface modification on the β value of the CdS/AOT-SO_3^- and CdS/HMP nanoparticles. For the five CdS nanopaticles studied, the cubic zinc blende crystal structure, as indicated above, is noncentrosymmetric. From this, a bulk-like contribution resulting from the polarization of the individual cadmium sulfide bonds should be considered. Hence, the β value reduces with decreasing particle size for CdS nanoparticles of larger sizes in **Figure 2a**. However, for diameter < 31.5 Å CdS nanoparticles, the reverse change in β values implies that this bulk-like contribution become trivial for very small CdS nanoparticles. This may be due to enhanced surface contribution for very small particles with enhanced surface-to-volume ratio.

To directly reflect the size dependence of the second-order optical nonlinearity of CdS nanoparticles, the relationship between size and normalized first-hyperpolarizability value per CdS formula unit, β_0 (β/n, n is CdS formula unit number per CdS particle), is obtained, which reveals a substantial systematic enhancement with decreasing size (**Figure 2b**). This is easily understood when considering a surface contribution mechanism.

An important feature of nanoparticles is the enhancement of the ratio of surface atoms to volume atoms. For example, a 50 Å CdS nanoparticle has ~15% of the atoms on the surfaces[12]. The existence of this vast surface can have a profound effect on the physical and chemical properties of nanoparticles. Most of the nanoparticles synthesized so far have imperfect surfaces, which may act as the source of the incoherent second harmonic generation (HRS). And it has been shown that the second-order optical nonlinearity of CdS nanoparticles is strongly affected by surface structure change[3,5,6]. Recently, the HRS of TiO_2 nanoparticles (10 nm mean diameter) with centrosymmetric nanocrystal core have been studied. The study indicated that the second-order optical nonlinearity of TiO_2 nanoparticles originates mostly from surface contribution, because the centrosymmetric nanocrystal core does not contribute to the second-order optical nonlinearity in the dipole approximation[13]. In fact, surface termination of the crystalline lattice creates discontinuous surface structure due to surface dangling bonds, surface lattice constriction, and surface defects (dislocations, vacancies and so on) *etc*. These lead to that surface or defect-localized “molecule-like” scatterers (Cd-S polar bonds) are highly noncentrosymmetric and highly polarizable. In addition, these characters, especially surface defects which can localize electronic distribution on particle surface, also result in the surface inhomogeneities of whole CdS nanoparticle, implying that the HRS signals on opposite sites of spherical nanoparticle surface can not be cancelled out.

From above analysis, it can be seen that the contribution from nanoparticle surface becomes a main HRS mechanism. The surface atoms play an important role in contribution to HRS signal. With decreasing CdS nanoparticle size, the ratio of surface atoms to volume atoms increases, resulting in enhanced contribution to β_0 in small nanoparticles. In addition, it has been shown that the electronic distribution on nanoparticle surface is easier localized by surface defects in smaller nanoparticles[14], leading to the enhanced asymmetry of surface electronic distribution, which is helpful for increasing β_0. Hence, β_0 increases with decreasing CdS nanoparticle size. Previously, the β_0 value per CdS formula unit for bulk CdS was estimated to be 1.3×10^{-30}esu according to the known value of the bulk nonlinear coefficient[4]. This β_0 value is 7.1 times smaller than that of the 91.0 Å CdS nanaparticles and 12.8 times smaller than that of the 28.0 Å CdS nanoparticles. Obviously, these comparisons also provide evidences for above surface contribution mechanism.

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