

Second-order Nonlinearities of CdS Nanoparticles Studied by Hyper-Rayleigh Scattering Technique

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Abstract: A series of CdS nanoparticles with different surfaces were prepared by colloidal chemical method and reverse micelle method. Their second-order nonlinear optical (NLO) properties were experimentally studied in solution by newly developed hyper-Rayleigh scattering (HRS) technique. The results show that “per particle” first-order hyperpolarizability β values are sensitive to the synthetic method and the surface chemical modification.

Keywords: Second-order nonlinear optical properties, hyper-Rayleigh scattering (HRS), first-order hyperpolarizability, CdS nanoparticles, surface-modification.

Optical nonlinearities of semiconductor nanoparticles are of great interest recently. So far their third-order nonlinear optical (NLO) properties have been widely studied. However, there are only few studies on second-order NLO properties, because it is believed that the centrosymmetry or near-centrosymmetry of spherical nanoparticles eliminate their first-order hyperpolarizability β values to zero or near zero. And for a long time it remains a problem to directly study the second-order NLO properties of such nanoscale particles by conventional NLO technique such as interfacial second harmonic generation (SHG) and electric-field-induced SHG techniques which are constrained by the orientational, size, and/or charge restrictions¹. Fortunately, the newly developed hyper-Rayleigh scattering (HRS) technique overcomes the above restrictions, hence second-order NLO properties of nanoparticles can be studied. Recently, a few studies were reported about HRS for the colloidal gold and insulator nanoparticle SiO_2 ^{1,2}. Here the HRS technique is used to measure second-order NLO response of a series of semiconductor nanoparticles with different surfaces prepared by different methods.

The Cd^{2+} -rich CdS, S^{2-} -rich CdS, thiourea-stabilized Cd^{2+} -rich CdS and heteropolyanion-stabilized Cd^{2+} -rich CdS hydrosols are named as $\text{CdS}/\text{Cd}^{2+}$, CdS/S^{2-} , $\text{CdS}/\text{SC}(\text{NH}_2)_2$ and $\text{CdS}/\text{PW}_{12}\text{O}_{40}^{3-}$, prepared by rapidly mixing $\text{Cd}(\text{NO}_3)_2$ and Na_2S aqueous solutions under stirring. Using reverse micelle method³, the surface-modified CdS nanoparticles with Cd^{2+} -rich surface by AOT (bis (2-ethylhexyl) sulfosuccinate, disodium salt) or pyridine (Py) were synthesized (named as CdS/AOT and CdS/Py , respectively). The absorption spectra and TEM images show that the above CdS nanoparticles are about 5 nm in diameter with narrow size distribution and have

negligible absorption at the frequency-doubling light of 532 nm.

The HRS experiments use a similar setup to the literature⁴. The Q-switched Nd-YAG laser pulse (10 Hz and 8-10 ns pulse width) at 1064 nm is focused into a 5 cm length glass cell in which a liquid sample is measured. The β values of nanoparticles are determined in terms of the internal reference method (IRM)¹. The calculation shows that the β values of the CdS/Cd²⁺, CdS/S²⁻, CdS/SC(NH₂)₂, CdS/PW₁₂O₄₀³⁻ in water and CdS/AOT in heptane, CdS/Py in pyridine are 1.30×10^{-26} , 1.41×10^{-26} , 4.38×10^{-26} , 2.51×10^{-26} and 1.50×10^{-27} , 1.05×10^{-27} esu, respectively, which are among the largest values reported for solution species. It is found that the β values differ by one order of magnitude for the CdS nanoparticles prepared with the different methods. And the CdS nanoparticles with different surfaces also have different β values. As proved by Clays *et al.*⁵, surface termination of the crystalline lattice creates a condition of noncentrosymmetry which contributes to the large β values for nanoparticles with huge surface-to-volume ratio. It is apparent that synthetic methods and surface-modifications have strong influence on the surface structure of CdS nanoparticles. Therefore, β values of CdS nanoparticles can be controlled. This is significant for further detailed investigation of HRS mechanism of nanoparticles.

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