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# Hyper-Rayleigh Scattering of CdS Nanoparticles Capped with Hexametaphosphate

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Hyper-Rayleigh scattering (HRS) technique, an incoherent methodology, was used to measure the first-order hyperpolarizability (β) of CdS nanoparticles capped with hexametaphosphate (HMP). The results show that the "per particle" β value is $1.33\times10^{-26}$ esu. Two possible contributions to the large β value, bulklike contribution and the one from particle aggregates, are negligible. Contribution from nanoparticle surface emerges as the main HRS mechanism due to the large surface-to-volume ratio and the high density of surface defects.

*Keywords:* CdS nanoparticles; Surface; Hyper-Rayleigh scattering (HRS)

## INTRODUCTION

The third-order nonlinear optical (NLO) properties of nanoparticles have been extensively studied. However, for a long time the investigation of the second-order NLO properties for nanoparticles was neglected, because of the orientational, size, and/or charge restrictions for conventional NLO techniques such as coherent second harmonic generation (SHG) and electric-field-induced SHG (EFISHG) techniques. The incoherent HRS technique, developed at the beginning of the nineties, is an effective tool for determining the first-order hyperpolarizability β value of molecular chromophores in solution. In recent years HRS technique, which overcomes the restrictions above, has also been used to study the second-order NLO response of nanoscale particles. Several research groups

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reported the HRS studies for nanoscale $SiO_2$ and colloidal gold,[1–3] where it was demonstrated that the HRS technique is a new sensitive NLO method for probing the surface structure and aggregation state of nanoparticles. Here, we report the HRS studies of semiconductor CdS nanoparticles capped with HMP. Due to the surface capping, the HRS signal become not sensitive to particle aggregation, and the contribution from nanoparticle surface become the main HRS mechanism.



## EXPERIMENTAL

CdS aqueous colloid was prepared by adding the stoichiometric amount of $Na_2S$ solution to a solution of $Cd(NO_3)_2$ and HMP (molar ratio of 1:1) under vigorous stiring. The Concentration of the obtained CdS colloid was $5\times10^{-4}$ mol/l, calculated in terms of the formula unit CdS.

The HRS experimental setup we used is similar to the literature [4]. The Q-switched Nd-YAG laser pulse (10 Hz, 8–10 ns pulse width) at 1064 nm was focused into an 8 cm length glass cell in which a liquid sample was measured.

## RESULTS AND DISCUSSION

UV-vis absorption spectrum shows that the CdS nanoparticles have negligible absorption at frequency-doubling wavelength of 532 nm. TEM results show the mean particle diameter to be about 5 nm. Electronic diffraction pattern indicates that the CdS nanoparticles are the cubic zinc blende structure.

Figure 1 shows the power dependence of the HRS intensity $I_{2w}$ on the incident intensity $I_w$. Good agreement to a quadratic fit is observed, as expected for the second-order scattering process. The $\beta$ value of the CdS nanoparticles is determined by the internal reference method (IRM).[1] As predicted by IRM, the linear dependence of the HRS intensity on the CdS particle number density is obtained (Figure 2). The calculations show that the "per particle" $\beta$ value is $1.33\times10^{-26}$ esu and "per CdS formula unit" $\beta$ value is $3.58\times10^{-28}$ esu. For comparison, the $\beta$ value per CdS formula unit for bulk CdS is roughly estimated to fall on the order of $10^{-30}$ esu or less, when considering the local field correction and according to the $\chi^{(2)}$ value of bulk CdS reported in the literature.[5] It can be seen that there is an enhancement by at least two orders of magnitude in $\beta$ value when the size of CdS particles is smaller than the Bohr diameter (6 nm) of bulk CdS. In addition, the $\beta$ values of the CdS nanoparticles are larger than that of the

best molecular chromophores reported ($5.0\times10^{-27}$ esu per molecule and ($0.5–1.0$) $\times10^{-28}$ esu per atom).[6]

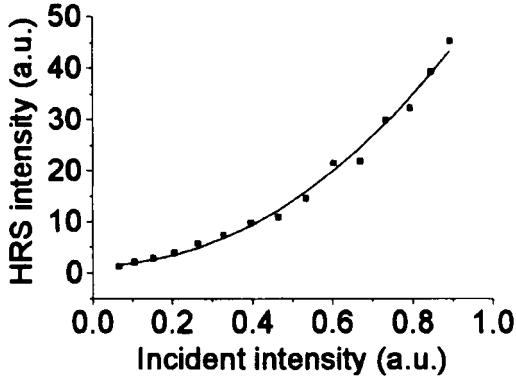


FIGURE 1 The quadratic dependence of the HRS intensity on the incident intensity for the CdS colloid

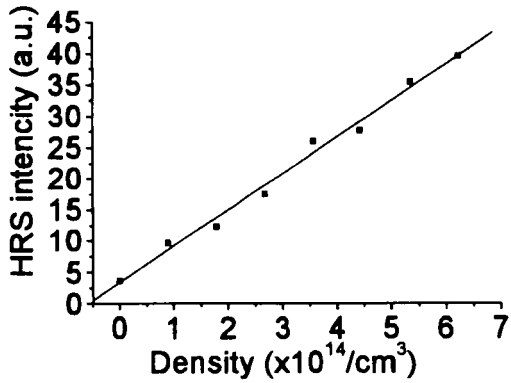


FIGURE 2 The concentration-dependence of the HRS intensity on the particle number density for the CdS colloid

Several contributions, involving bulklike contribution, surface contribution and the one from particle aggregates in colloidal solution, have been discussed in the previous reports.[1–3,7] The bulklike contribution from the noncentrosymmetric nanocrystal core has been demonstrated to be substantially trivial.[7] As to the contribution of particle aggregates, it was considered as arising from low symmetry of irreversible particle aggregates such as the colloidal gold particle aggregates induced via addition of aqueous NaCl, and resulted in the large change in

HRS signal.[2] In our experiments, however, it was found that the HRS intensity of the CdS nanoparticles remained almost unchanged with increasing $NaNO_3$ concentration (from $2.3\times10^{-4}$ mol/l to $9.09\times10^{-2}$ mol/l) in solution. For the sample containing $9.09\times10^{-2}$ mol/l $NaNO_3$, visible opalescence occurred but no floccules appeared. It implied that the CdS nanoparticles in solution aggregated gradually with increasing $NaNO_3$, which was also shown by long scattering tails in their UV-vis absorption spectra. We infer the fact that the HRS signal did not vary with particle aggregation is due to the capping layer (HMP) around the CdS particles which prevents the efficient contact between particles. The evidence was that the sample with opalescence became transparent again when diluted with water and then treated by ultrasonic wave. It is thus clear that, for the HMP-capped CdS nanoparticles, we may not consider the influence of the particle aggregation.

The foregoing analysis leaves us with the surface contribution as the main contribution mechanism for the observed large $\beta$ value. For nanoparticles, surface termination of the crystalline lattice creates a condition of non-centrosymmetry (surface and internal inhomogeneities comprised of only a few atoms).[8] And important features are the large surface-to-volume ratio and the high density of defects on particle surfaces such as dislocations, vacancies, surface chemical species and so on. As a result, the electron distribution around surface atoms is inherently highly noncentrosymmetric and highly polarizable,[7] which may contribute substantially to the HRS signal.

### Acknowledgements

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