Hyper-Rayleigh Scattering of CdS Nanoparticles with Different Surfaces

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The first-order hyperpolarizability β values of two kinds of CdS nanoparticles with different surfaces were experimentally determined in solution via an incoherent hyper-Rayleigh scattering (HRS) technique. It is found that the β value of CdS nanoparticles capped with 2,2'-bipyridine is 4.27×10^{-27} esu which is about a factor of 3 smaller than the β value (1.30×10^{-26} esu) of bare CdS nanoparticles whose surface is not modified by organic groups. This difference is interpreted in terms of a two-level model approximation derived from molecular chromophores, when considering the contribution of molecule-like scatterers at the particle surfaces.

The nonlinear optical properties of semiconductor nanoparticles are very sensitive to the surface chemical structure and the environment around particles, because of surface effects and dielectric confinement effects. The influence of surface chemical modification on the third-order nonlinear optical properties of semiconductor nanoparticles has been studied extensively.[1,2] However, there are only few studies about second-order nonlinear optical properties, because it is usually believed that the centrosymmetry or near-centrosymmetry of the spherical nanoparticles reduces their first-order hyperpolarizability (β) to zero or near zero. Recently, using an incoherent methodology, hyper-Rayleigh scattering (HRS) technique, insulator nanoparticle SiO_2, colloidal gold particles, and semiconductor CdSe nanocrystals in solution were studied and exhibit large β values, where an important contribution, surface contribution, was considered in the interpretation of the observed experiment results involving pH-dependence and size-dependence of the HRS response.[3–6] It has been demonstrated that the HRS technique is sensitive tool for studying the chemical composition of nanoparticle/solution interfaces. However, so far the studies on HRS mechanism of nanoparticles are still preliminary and incomplete. It seems that the direct change of surface chemical structure with the method of surface-modification is significant for exploring the HRS mechanism of nanoparticles. From this view, we studied two kinds of semiconductor CdS nanoparticles with different surfaces via the HRS technique. The HRS experiments were performed using a setup similar to the literature.[7] 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.

Two kinds of CdS colloids with different surfaces were used for the HRS experiments. 2,2'-Bipyridine-capped CdS nanoparticles (named as CdS/2,2'-bpy) in DMF were prepared by the method similar to the literature.[8] Another sample, which is called bare CdS colloid, was made using the reaction between aqueous solutions of $Cd(NO_3)_2$ and Na_2S at 4 °C and under strenuous stirring, where no stabilizer was added. From synthetic methods and our previous work,[8–10] it has been demonstrated that the surfaces of the two kinds of CdS nanoparticles are Cd^{2+}-rich.

The absorption spectra of CdS/2,2'-bpy in DMF and bare CdS colloid show that the two kinds of CdS nanoparticles studied have nearly the same size and size distribution, and have negligible absorption at the frequency-doubling wavelength of 532 nm. From the absorption edge, the diameter of the CdS nanoparticles was evaluated to be about 5 nm on the basis of the effective mass approximation,[11] which is in agreement with TEM results. The electronic diffraction pattern indicates that the two kinds of CdS nanoparticles are the cubic zinc blende structure.

Figure 1 shows the X-ray photoelectron spectroscopy (XPS) spectrum of the CdS/2,2'-bpy nanoparticle powder. Measurements were performed using a Britain VG ESCALAB MK-II electron spectrometer with Al Kα X-ray source of 300 W at pressures lower than 4×10^{-8} mbar. Considering the influence of charge up for semiconductor materials, all spectra were calibrated using the position of the C 1s peaks present in all spectra as a standard. The peaks at 405.2 eV and 161.75 eV in Figure 1 belong to the cadmium element and sulfur element, respectively, and are the same as those of the bare CdS nanoparticles under the same experimental conditions. The peak at 400.3 eV refers to the nitrogen atom of 2,2'-bipyridine on the particle surface. It is noteworthy that the binding energy of the nitrogen element in the sample produces a larger chemical displacement as compared with the nitrogen atom in pure 2,2'-bipyridine (about 398 eV), due to σ donation from 2,2'-bipyridine at 2-position to the Cd^{2+}-rich surface of the CdS nanoparticles.[9] The σ donation was also characterized by the FT-Raman spectroscopy in the previous work.[10]

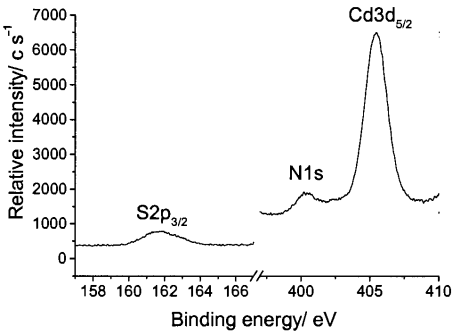

Figure 1. The spectrum of XPS for the CdS/2,2′-bpy nanoparticle powder ($S2p_{3/2}$: 161.75 eV, $Cd3d_{5/2}$: 405.2 eV, N1s: 400.3 eV).

We used the internal reference method (IRM) to determine the β values of the CdS nanoparticles. Namely, their β_2 values can be calculated by comparison with the HRS intensity of a solvent, whose β_1 value is known. The relationship between the HRS signal (frequency-doubled light of 532 nm) intensity $I_{2\omega}$ and the incident light intensity I_ω is expressed by eq 1:[3]

$$I_{2\omega} = G(N_1 \langle \beta^2_1 \rangle + N_2 \langle \beta^2_2 \rangle) (I_\omega)^2 \quad (1)$$

where N_1 is the solvent molecular number density (cm^{-3}), N_2

the particle number density (cm^{-3}), and G a parameter relating to collection efficiencies and local field corrections.

The HRS experiments show that the two kinds of CdS nanoparticles exhibited strong HRS signals. As predicted by eq 1, the linear relationship between $I_{2\omega}$ and the particle number density N_2 is obtained in Figure 2. The calculation results show that the "per particle" β value is 4.27×10^{-27} esu for the CdS/2,2'-bpy nanoparticles, which is 3 times smaller than the β value of the bare CdS nanoparticles (1.30×10^{-26} esu).

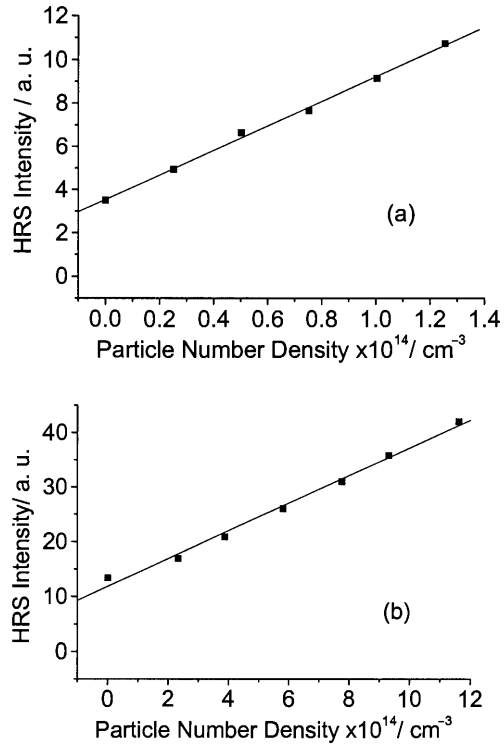

Figure 2. The relationship between the HRS intensity and particle number density for the CdS nanoparticles: (a) bare CdS in water; (b) CdS/2,2′-bpy in DMF.

Regarding the β value, a bulklike contribution from the noncentrosymmetric zinc blende CdS core should be considered. However, this bulklike contribution is substantially trivial, as shown in the previous report.[6] The large first-order hyperpolarizability of the nanoparticles is mainly due to the contribution of surface layer.[3,6] As previously indicated, the surface layer of media ranging from bulk to nanometer dimensions is a source of second-order nonlinearity due to the surface termination of the crystalline lattice.[12] Especially, the surface contribution is much important in nanoparticles because of large ratio of surface atoms to volume atoms and a great quantity of surface localized defects such as dislocations, vacancies, surface chemical species and so on. Surface defects break the homogeneity of surface and also can localize the electron distribution,[2] so that the nanoparticle surface is highly polarizable. As a approximation, the surface contribution can be described with surface-localized "molecule-like" scatterers.[3] Here we consider surface or defect localized sulfur-to-cadmium charge-transfer transition arising from the polarization of the Cd–S bonds at the particle surface. We use a two-level model, which has been extensively adopted for a molecular system such as in a solvatochromic experiment, to describe the second-order optical nonlinearity of the CdS nanoparticles in this letter. For the surface molecule-like scatterers, the expression of the two-level model is as follows:[13,14]

$$\beta = \frac{3\mu_{12}^2 \Delta\mu_{12} E_{op}^2}{2\left(E_{op}^2 - E_{inc}^2\right)\left(E_{op}^2 - 4E_{inc}^2\right)} \qquad (2)$$

where β is the first-order hyperpolarizability, E_{op} the surface or defect localized sulfur-to-cadmium charge-transfer transition energy, E_{inc} is the energy of incident radiation, $\Delta\mu_{12}$ the change in dipole moment, μ_{12} the transition dipole moment.

Note that E_{op} can be affected by the surface-modifying molecules.[3] More electron transfer from surface coordinating atom to cadmium atom, larger sulfur-to-cadmium charge transfer transition energy E_{op}. Comparing the nitrogen atoms of 2,2'-bipyridine with oxygen atom of water which are the coordinating atoms in the CdS/2,2'-bpy and bare CdS nanoparticles, respectively, oxygen atom has larger electronegativity, so that there are more electron transfer from nitrogen atom to cadmium atom than that from oxygen atom to cadmium atom. That is to say, there is larger sulfur to cadmium charge transfer transtion energy E_{op} in the CdS/2,2'-bpy nanoparticles due to the σ donation of nitrogen atom to cadmim atom. Relying on the two-level model (equation 2), the β value is approximately inversely proportional to E_{op}^2. Therefore, the β value of the CdS/2,2'-bpy is smaller that of the bare CdS nanoparticles as observed in experiment.

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