

Second-order nonlinear optical properties of centrosymmetric nanoparticles studied by hyper-Rayleigh scattering (HRS) technique

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Hyper-Rayleigh scattering (HRS) technique has been used to study second-order nonlinear optical (NLO) properties of some centrosymmetric metal and semiconductor nanoparticles. All the samples display big “per particle” first hyperpolarizabilities β_{par} . For centrosymmetric particles the contributions of multipolar radiations are very important to their second-order NLO responses. The metal nanoparticles show β_{par} two orders greater than that of the semiconductor ones, which can be explained by the enhancement of surface plasma resonance (SPR). It also reveals that the HRS signals are very sensitive to metal nanoparticles' aggregation.

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With the decrease of a solid's size or dimension, its electronic and optical properties will change remarkably due to “quantum size effects”. Metallic and semiconductor nanoparticles exhibit interesting optical properties due to the confinement of the electronic wavefunctions, the drastically increased surface-to-volume ratio, and the surface conditions. They are of great interest recently with wide applications in the areas of physics, chemistry, biology and electronics. It also shows potential applications in ultra fast telecommunication, optical information storage, optical computing and some optoelectronic devices. Metallic nanoparticles are interesting models of low-dimensional structures and can be obtained quite easily, which has fascinated scientists with their colorful colloidal solutions long before the semiconductor ones^[1]. The physical origin of the changing colors is their size and shape dependent collective oscillations of conduction band electrons excited by the incident light, which is well known as the surface plasma resonance (SPR). Semiconductor materials are of extreme importance in modern integrated microelectronic and optoelectronic techniques, and their nano-structures have also attracted intense interest. Most studies are concentrated on their linear optical properties such as absorption spectra, fluorescence, and electroluminescence; as well as third-order nonlinear optical (NLO) properties such as electro-optic Stark effect, nonlinear absorption, exciton bleaching, and two-photon fluorescence (TPF)^[2–4].

It is usually believed that nanoparticles with centrosymmetric structures will cause their second-order nonlinearities $\chi^{(2)}$ or “per particle” first hyperpolarizabilities β_{par} to vanish in the electric dipole approximation. Optical second harmonic generation (SHG) has been utilized to probe surfaces of metals or semiconductors with centrosymmetric lattices, as the bulk contributions are strongly suppressed due to the symmetry-broken at the interfaces^[5–7]. However, it is hard to make use of SHG to study the second-order NLO prop-

erties of such small a single particle, arising from the requirement of coherence length in the experiments, i.e., the practical sample size limitation of about the same order of magnitude as the incident wavelength. Hyper-Rayleigh Scattering (HRS) is a nonlinear incoherent light scattering process that has recently been employed to study the second-order NLO properties of molecules in solutions^[8]. It also emerges as a new tool to investigate the second-order NLO properties of nanoscale particles or interfaces^[9,10]. In this paper, second-order NLO properties of some centrosymmetric metal (Au and Ag) and semiconductor (TiO₂ and SnO₂) nanoparticles are studied via the HRS technique. Their “per particle” first hyperpolarizabilities β_{par} are experimentally measured and the differences between metals and semiconductors are clarified.

Four kinds of aqueous colloidal samples were synthesized by the traditional colloidal solution method and sol-gel method, two metals of Au and Ag (colloidal method) and two semiconductors of TiO₂ and SnO₂ (sol-gel method). Briefly, 4 ml of 1% (mass) sodium citrate was added to 100 ml of 0.01% (mass) boiling tetrachloroauric acid solution to get the Au nanoparticle suspension; 4 ml of 1% (mass) sodium citrate was added to 200 ml of 0.015% (mass) boiling AgNO₃ solution to get the Ag nanoparticle suspension; mixture of 25-ml tetrabutyl titanate and 4-ml 2-propanol was added to 120 ml of 0.92% (volume) nitric acid aqueous solution to get the TiO₂ nanoparticle suspension; and 1.7 ml of aquafor-tis was added to 100 ml of 7.4% (mass) SnCl₄ aqueous solution to get the SnO₂ nanoparticle suspension. All the samples' sizes were characterized by the transmission electron microscopy (TEM, Hitachi JEM-2000EX) and the UV-visible absorption spectra. It was found that their sizes will range from about 3 nm to about 20 nm in diameter according to different experimental conditions being controlled. In this paper we choose the four kinds of nanoparticles with sizes of all about 10 nm in diameter.

As an example, the TEM image of TiO_2 nanoparticles is shown in Fig. 1(a). The size of metal nanoparticles was also measured on a submicro particle size analyzer (Beckman Coulter, N4 PLUS); size distribution for Ag nanoparticle is shown in Fig. 1(b) as an example.

The HRS experimental setup we used was similar to that in the literature^[8]. The Q -switched Nd:YAG laser pulse (Continuum Surelite II, 5-Hz, 8-10 ns pulse width) at 1064 nm was focused by a lens into a cylinder cell. The intensity of the fundamental beam could be adjusted by rotating a half-wave plate and was controlled under 0.1 mJ. An interference filter at 532 nm (3-nm bandwidth) was mounted at the entrance of the photomultiplier tube (PMT, Hamamatsu R105UH) to prevent luminescence at other wavelengths. The HRS signals were detected and averaged by a microprocessor-based boxcar integrator (EG&G 4400 and 4402). An internal reference method (IFM) is utilized for the colloids all in water. If we consider nanoparticles as “big molecules”, then for a two-component solution the HRS intensity $I_{2\omega}$ is given by^[8]

$$I_{2\omega} = G(N_1 \langle \beta_1^2 \rangle + N_2 \langle \beta_2^2 \rangle) \cdot (I_\omega)^2, \quad (1)$$

where I_ω is the incident intensity, and G is a parameter reflecting experimental conditions such as instrumental factor, collection efficiency and local field corrections. N is the number density and subscripts 1 and 2 refer to solvent (water) and solute (nanoparticle) respectively. The brackets indicate the spatial average of the nanoparticles within the focus area with spatial fluctuations.

As predicted by Eq (1), the experimental HRS signals scaled linearly with the concentration of the colloids for all the samples. Figure 2 shows concentration dependences of the HRS intensities for gold and TiO_2 colloids. Two-photon fluorescence (TPF) around 532 nm was also checked and it was found that TPF contributions could be neglected for TiO_2 and SnO_2 colloids, the measured TPF emission spectrum for TiO_2 colloids is shown in Fig. 3. For gold and silver colloids there were detectable TPF contributions due to the absorptions at 532 nm but the narrow bandwidth of the interference filter will minimize their influences, and we will not deduct the TPF parts from the results. The first hyperpolarizability of water is known to be 0.56×10^{-30} esu. From the linear fitting results, the β values per nanoparticle “ β_{par} ” are determined to be $\beta_{\text{par}}(\text{Au}) = 4.4 \times 10^{-25}$ esu, $\beta_{\text{par}}(\text{Ag}) = 2.2 \times 10^{-25}$ esu, $\beta_{\text{par}}(\text{TiO}_2) = 2.0 \times 10^{-27}$ esu and $\beta_{\text{par}}(\text{SnO}_2) = 2.4 \times 10^{-27}$ esu, for the samples with the same sizes of all about 10 nm.

We can see that all the samples display big “per particle” first hyperpolarizabilities. The β_{par} of the metals are extremely huge being about two orders greater than that of the semiconductors, which can be explained by the enhancement of collective oscillations of conduction band electrons i.e. the surface plasma resonance (SPR) under two-photon excitation. Gold nanoparticle presents stronger enhancement with SPR absorption peak (at about 520 nm) closer to the second harmonic wavelength (532 nm) than that of silver nanoparticle (at about 420 nm), and shows β_{par} twice bigger. While HRS responses of semiconductor TiO_2 and SnO_2 nanoparticles come mainly from their bounded valence electrons. All nanoparticles exhibit centrosymmetric crystal

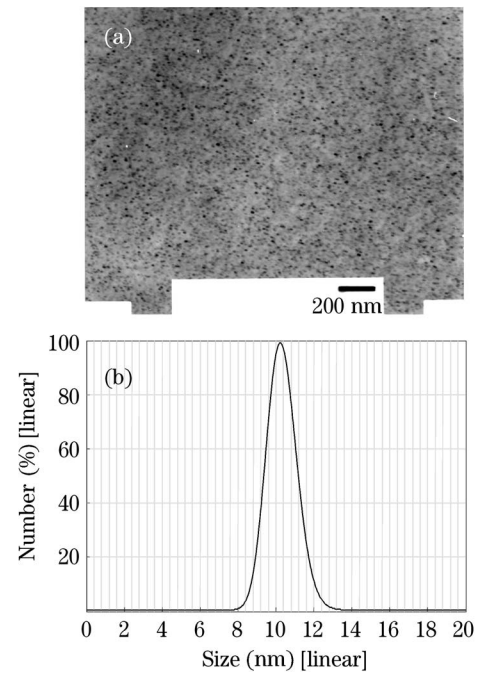


Fig. 1. (a) TEM image for TiO_2 nanoparticles of 10 nm in diameter, (b) size distribution for silver nanoparticles measured by submicro particle size analyzer.

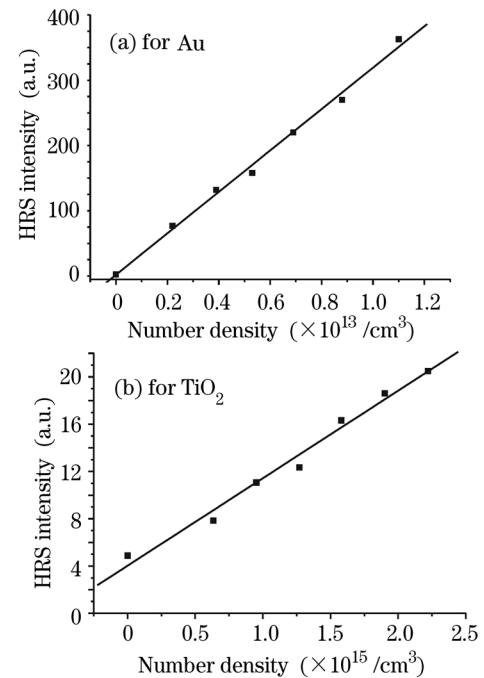


Fig. 2. HRS intensities as function of molar densities for colloids in water. Solid lines are linear fitting of the experimental data.

structures: face-centered cubic structure for Au and Ag; anatase structure for TiO_2 , and rutile structure for SnO_2 nanoparticle. So contributions of multipolar radiations are very important, for example, electric quadrupole effect and magnetic dipole effect^[5,6]. Electric dipolar contributions from the “dipoles” (surface defects or adsorbates) near the interfaces of a particle should be trivial

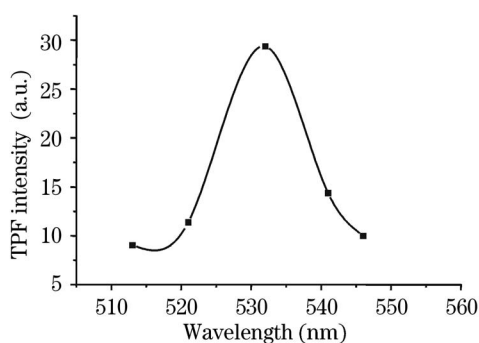


Fig. 3. The TPF emission spectrum of TiO_2 colloids in water.

because of the small first hyperpolarizabilities of these “dipoles” and the symmetry of the nanoparticle ensemble in the focus area.

Au and Ag nanoparticles’ aggregations induced by KNO_3 , pyridine or surface modifications were also studied by HRS and have been reported previously^[11,12]. Interaction between the nanoparticles will affect the collective excitation of SPR in the aggregates as revealed by their UV-visible absorption spectra. The dramatically enhanced HRS responses of the aggregates can be understood by the enhanced electromagnetic fields near the surfaces of metal nanoparticles as they approach. It again supports the model of multipolar radiation because no diminish of the HRS signals are found even for symmetrical aggregates, for example, dimers.

In summary, metal (Au and Ag) and semiconductor (TiO_2 and SnO_2) nanoparticles of 10 nm in size are synthesized and their second-order NLO properties are studied by HRS technique. All the nanoparticles display big “per particle” first hyperpolarizabilities β_{par} with centrosymmetric crystal structures. The metals show β_{par} two orders greater than that of the semiconductors, which can be explained by the enhancement of surface plasma resonance (SPR). The contributions of multipolar radiations are very important to their second-order NLO

responses. Studies on metal nanoparticles also reveal that the HRS signals are very sensitive to nanoparticles’ aggregations, and the dramatically enhanced signals can be understood by the enhanced electromagnetic fields near the surfaces of metal nanoparticles as they approach. HRS technique provides a useful new NLO method to understand the polarization mechanisms and to characterize the surface structures or microenvironment of nanoscale materials.

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