Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/0S54-05
Chinese Physics
© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF TITANIUM DIOXIDE NANOPARTICLES AND NANOPARTICLES-DYE COMPOSITES

Wang Xin(汪 昕)[a)†], Zhang Yü(张 宇)[a)], Deng Hui-hua(邓慧华),[a)]
Shen Yao-chun(沈耀春)[a)], Lu Zu-hong(陆祖宏)[a)], and Cui Yi-ping(崔一平)[b)]
[a)] *National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing* 210096, *China*
[b)] *Laboratory of Optoelectronic Technology, Southeast University, Nanjing* 210096, *China*

(Received 1 January 2001)

Hyper-Rayleigh Scattering (HRS) technique was used to study the second-order nonlinear optical (NLO) responses of aqueous titanium dioxide (TiO_2) nanoparticles of 10nm in size, and two nanoparticles-dye composites prepared by adding rhodamine B (Rh610) or the organic tosylate salt of dimethylaminostilbazolium (DAST). Results showed that the "per particle" first hyperpolarizability β for TiO_2 nanoparticles is very large, in the range of 10^{-26} esu. With adding Rh610 and DAST, the HRS signals of the composites were further enhanced. And in TiO_2/Rh610 composite the enhancement was obviously greater than that of TiO_2/DAST composite. It has proved that non-centrosymmetry of the nanocrystal/solution interface contributes mainly to its large "per particle" β, overwhelming the nanocrystal core. So the interactions between nanoparticles surfaces and adsorbed dyes were very important for their second-order NLO responses. HRS technique provides a useful new NLO method to characterize the surface structures and microenvironment of nanoscale materials.

Keywords: nanoparticle, nanoparticle-dye composites, hyper-Rayleigh scattering (HRS), first hyperpolarizability (β), nonlinear optics
PACC: 6146, 4265, 6820

I. INTRODUCTION

The area of Nonlinear Optics and Optoelectronics has observed great progress during the past 30 years, many new nonlinear optical (NLO) phenomena were found and investigated successfully, and more attempts were made to find or synthesize high-quality NLO materials and to fabricate new optoelectronic devices. They are playing a very important role in the applications to such as optical computing, optical communication, optical information storage and signal processing. Investigations were initially focused on inorganic crystals, and then expanded to organic and semiconductor materials. In comparison with inorganic materials, organic materials have many advantages such as larger nonlinearities, faster response time, higher damage threshold and more flexible processability.[1] With the development of modern integrated microelectronics and opto-electronic techniques, functional components become smaller and smaller, thus nanoscale NLO materials now attract more and more attention.[2] Semiconductor or metal nanoparticles exhibit interesting optical properties due to the confinement of the electronic wavefunctions, the drastically changed surface-to-volume ratio, and their surface conditions. The optical properties include linear absorption, fluorescence and electroluminescence as well as NLO properties such as bleaching, electro-optic Stark effect, nonlinear absorption, and multiphoton fluorescence. Recently, many new composite material systems also appear and show very bright futures in application, such as organometallic compounds[3] and inorganic-organic host-guest systems.[4] For nanoparticle-organic composites, it is believed to show good NLO properties because it may combine the advantages of organic materials with the nanoscale materials. And it needs more thorough studies to clarify their NLO mechanisms, to design and control their physical properties, and to characterize their microstructures.

Up to now, most studies published about the NLO properties of nanoscale crystals were concentrated on the third-order nonlinearity $\chi(3)$ or γ. It is usually believed that the centrosymmetry or near-centrosymmetry structure (spherical model) of the ultra small particle eliminates its second-order nonlinearity $\chi(2)$ or first hyperpolarizability β to zero or near zero. And for a long time it remains a problem to directly study the second-order NLO properties of such small nanoscale particles by conventional NLO

† Corresponding author, E-mail:wxzr@seu.edu.cn; Fax: (+86-25) 3619983; Tel: (+86-25) 3792245.

techniques. The $\chi(2)$ or β represents the lowest order asymmetric response. Up to the present time, the technique of electric-field-induced second harmonic generation (EFISHG) has been most widely used for measuring the β value of a NLO chromophore.[5] In this method, one requires the knowledge about ground state dipole moment μ, local field factors at fundamental frequency ω, at second harmonic frequency 2ω, and at zero frequency. Since an external electric field is applied to the sample, the third-order nonlinearity γ also contributes to the EFISHG intensity. More importantly, it relies on the existence of a permanent (or ground state) dipole moment to orient the NLO chromophore so as to remove the macroscopic centrosymmetry of the chromophore solution. Hence it cannot be used for molecules or systems that do not have permanent dipole moment. And it cannot be used for conducting solutions, i.e. ionic species. In as much as a reasonable electric field can be established for a conducting solution, the field will cause migration of the ionic species rather than dipolar orientation. Therefore EFISHG technique cannot be used to study the second-order NLO properties of organic salts and some nanoparticles, which usually carry excess charges on their surfaces. Another conventional NLO technique is called second harmonic generation (SHG).[6] However, because of the corresponding coherence length for the required incident radiation, practical sample size limitation (lower limit, about an order of magnitude less than the wavelength of the incident light) exists and it cannot be applied to the microscopic domain of a nanoscale particle.

Recently, some workers have made use of the newly developed Hyper-Rayleigh Scattering (HRS), i.e. the incoherent harmonic light scattering technique to study the second-order NLO properties of organic salts[7] and nanoparticles.[8,9] For normal molecules, the HRS signal arises from the random fluctuations of the chromophore density or chromophore orientation, which instantaneously break the centrosymmetry of the isotropic media in the microscopic area of the incident laser beam.[10] Thus HRS technique is not constrained by the orientation, charge or size restrictions as mentioned above. For nanoparticles the mechanism is similar. In nanoparticle colloids the random density fluctuations and orientation fluctuations still exist, and one new mechanism named surface fluctuations is also very important. Surface fluctuations can be explained in terms of the dynamic ion exchanging, molecular adsorption and desorption processes between the surface and solution, which can also instantaneously break the centrosymmetry of the isotropic media. Here we make use of HRS technique to study the second-order NLO responses of aqueous titanium dioxide (TiO_2) nanoparticles, and two nanoparticle-dye composites prepared by adding rhodamine B (Rh610) or the organic tosylate salt of dimethylaminostilbazolium (DAST). TiO_2 nanocrystal has been well investigated as a photoelectric conversion material for solar cells or photocatalytic agents, which is cheap, safe and usually stable. Rh610 and DAST are both excellent NLO organic materials with very large NLO responses. It is then interesting to study the compound TiO_2/Rh610 or TiO_2/DAST composites.

II. EXPERIMENTS

A. Preparation and characterization of samples

TiO_2 aqueous colloid solution was prepared by hydrolysis of tetrabutyl titanate.[11] The size of the colloidal particles was about 10nm, which was determined by the transmission electron microscope (TEM). Its UV-visible absorption spectrum was also measured, showing the absorption threshold at about 330nm.

The TiO_2/Rh610 or TiO_2/DAST composites were prepared by simply mixing TiO_2 solution with aqueous Rh610 or DAST solutions. The chemical structures of the two dyes are shown in Fig.1.

The pH value of the TiO_2 colloid solution is about 0.90, thus both the dye solutions were adjusted to the pH of 0.90 when mixing with TiO_2 colloid solution. The UV-visible absorption spectra of the two dyes were measured at pH=0.9. The absorption peak λ_{max} for Rh610 is 557nm, for DAST is 329nm. It should be pointed out that the λ_{max} for DAST has a great blue shift as compared to its λ_{max} (about 480nm) in organic solvents, for example, methanol. Here the solvent effect is remarkable, which can change the molecular structure and aggregation due to the interactions between DAST and water, and the H^+ in the acid solution may also have some influences on its structure.

After the mixing of the TiO_2 colloid solution and dye solutions, the TiO_2 nanoparticles did not aggregate and their size was not changed much (still about 10 nm). The UV-visible absorption thresholds for TiO_2 nanoparticle and their TEM images could confirm this.

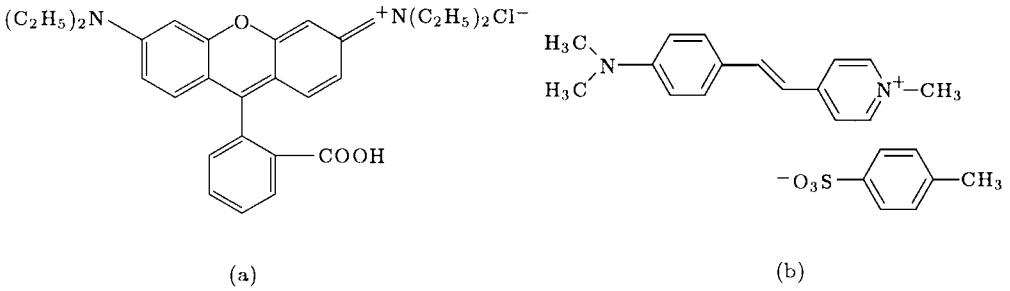


Fig.1. Chemical structures of (a) Rh610 and (b) DAST.

B. HRS and multi-photon fluorescence experiments

The measurements are performed by using a setup similar to that of Clays.[10] The incident beam of a Q-switched Nd:YAG laser (Continuum Surelite II) at 1064 nm operating at 5 Hz with 8–10ns pulse width is focused into a 5cm glass cell with the pulse energy lower than 1mJ. A 532nm (3nm bandwidth) interference filter is used at the entrance to the photomultiplier tube (PMT) to prevent any luminescence of the sample at other wavelength from reaching the detector. The signal from the PMT is analyzed with a microprocessor-based boxcar integrator (EG&G 4400, 4402) which is triggered by the Q-switch of the laser.

Because some samples have strong (in comparison with HRS signal) fluorescence emission due to multiphoton absorption of the incident photon, their multiphoton fluorescence (MPF) emission spectra were also measured. The MPF setup is the same as that of HRS but only the 532 nm interference filter is replaced by a series of interference filters (about 12nm bandwidth) at different wavelengths. In HRS experiments, the bandwidth for 532nm interference filter is only 3nm, which is already narrow enough to eliminate most of the MPF signals. But we still use another 532nm interference filter with 12nm bandwidth to obtain more information about the MPF in the neighborhood of HRS wavelength. And therefore we can obtain more accurate β values after cutting off the MPF from the HRS signals.

Hyper-Rayleigh scattering experiment allows for the direct assessment of sample first-order hyperpolarizability β (orientational average of the β tensors of the chromophores) in multi-component systems if β for other components has been previously established. It is called the internal reference method (IRM). If the incident intensity is I^{ω}, then the frequency-doubled light ($I^{2\omega}$) observed for a two-component system can be described by Eq.(1) for low solute concentration as follows:

$$I^{2\omega} = G(N_1 < \beta_1^2 > + N_2 < \beta_2^2 >)(I^{\omega})^2. \quad (1)$$

In Eq.(1), N is the number density of each component, G is a constant parameter for low solute concentration that encompasses a large number of factors including collection efficiencies and local-field correction factors, subscriptions 1 and 2 denote solvent and analyte respectively, and the brackets indicate the orientational averaging. N_1 is constant for low solute concentration and the plot of N_2 versus $I^{2\omega}/(I^{\omega})^2$ yields a straight line of slope $G < \beta_2^2 >$ and intercept $GN_1 < \beta_1^2 >$. As a result, β_2 can be obtained from the slope divided by the intercept when β_1 is known. To ascertain that our measurement gives a result consistent with the accepted data, we have calibrated our experiment procedure using para-nitroaniline (p-NA) dissolved in chloroform as the sample. And we obtained the β value of p-NA to be 37×10^{-30} esu in the density lower than 2mM, which is in satisfactory agreement with the literature value.[12]

Ⅲ. RESULTS AND DISCUSSION

A. Pure TiO_2 nanoparticle, Rh610 and DAST samples

Shown in Fig.2 is a plot of the concentration dependence of the HRS intensity from TiO_2 colloids at pH=0.9. As predicted by Eq.(1), the signals scaled linearly with the concentration of the colloids. From the linear fitting results, the value of β per TiO_2 formula unit was determined to be 3.49×10^{-28} esu by using water as an internal standard ($\beta_{\rm water}=0.56\times10^{-30}$ esu). This β value is very large in comparison with commonly studied organic chromophore. For example, it is larger than p-NA by about eight times. Figure 3 shows the MPF emission spectra of TiO_2 colloids in water at pH=0.9. Because the bandwidth of each

interference filter is about 12nm, the MPF emission spectra were grossly measured and could not provide delicate substructures of the spectra. From this we can see that the influence of MPF is negligible if we use the interference filter of 3nm bandwidth at 532nm wavelength.

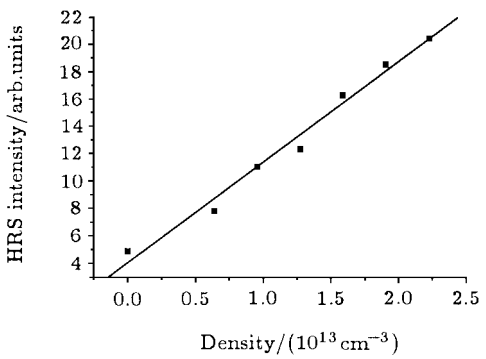


Fig.2. HRS intensities as function of molar densities for TiO_2 nanoparticles in water at pH=0.9.

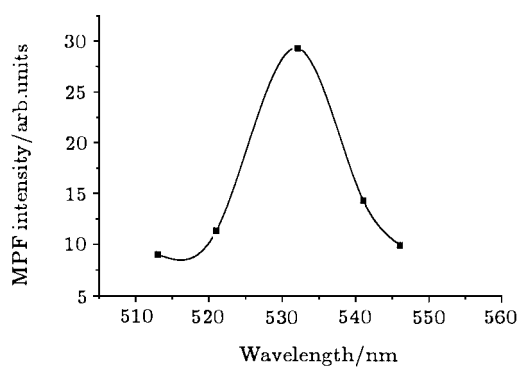


Fig.3. The MPF emission spectra of TiO_2 colloids in water at pH=0.9.

The foregoing analysis assumed that the HRS signal originating from the collective effects of the nanoscale particles, especially from the surface molecules with highly non-symmetry because of imperfection or defect of the surface crystal lattice. Hence a "per particle" β value is more suitable for assessment. Here we have estimated that one TiO_2 nanoparticle of 10 nm contains about 1.5×10^4 TiO_2 units. The "per particle" β value for TiO_2 nanoparticle was estimated to be 4.3×10^{-26} esu.

Similarly, we can gain the β values for Rh610 and DAST at pH=0.9 to be 1.55×10^{-27} esu and 1.47×10^{-28} esu respectively. The MPF measurements showed that Rh610 has very strong MPF signal even near 532 nm, but for DAST it is much weaker. Both β values for the two samples above have taken into consideration the influences of MPF and already cut them off.

B. TiO_2/Rh610 and TiO_2/DAST composites

Figure 4 shows the HRS signal of TiO_2/Rh610 composites by adding more and more TiO_2 nanoparticles to the Rh610 solution with the same concentration of 3.9×10^{-5}M. The "particle concentration" for TiO_2 varies from 5.3×10^{-9}M to 2.6×10^{-8}M. We can see that the HRS signal increases almost linearly with the addition of TiO_2, and we find that the signal is larger than the linear sum of signals from Rh610 and TiO_2. Figure 5 shows the change of UV-visible absorption spectra of Rh610 before and after the addition of TiO_2 nanoparticles. The λ_{max} almost remains unchanged but the absorbance decreases at λ_{max} and increases at side wavelengths. This gives us two hints: one is that there do exist some kinds of interactions between nanoparticle surface and Rh610, the other is that the interaction is not strong enough to change much of the electronic structure of Rh610 molecule. Thus the great enhancement of second order NLO responses for TiO_2/Rh610 composites is mainly due to

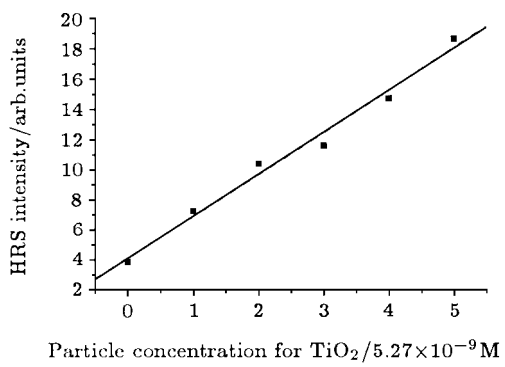


Fig.4. HRS signal of TiO_2/Rh610 composites with adding TiO_2 nanoparticles to 3.9×10^{-5}M Rh610 solution.

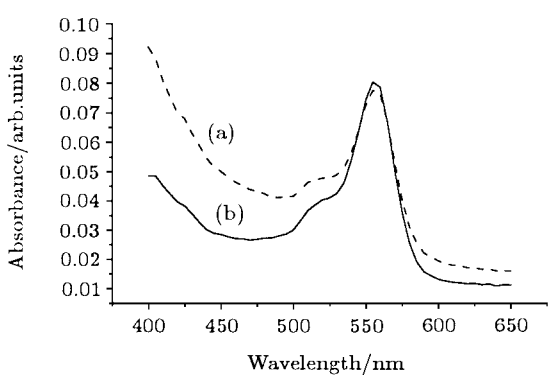


Fig.5. UV-visible absorption spectra of Rh610. (a) after, (b) before the adding of TiO_2 nanoparticles.

the interactions between nanoparticle surface and Rh610, and hence the change of surface conditions.

The reason of HRS signal enhancement can be roughly illustrated as follows. In an acid environment, the surface of TiO_2 nanoparticles is abundant with H atoms and Ti atoms, only a small part of O atoms is present. And the O atom of carbonyl part of Rh610 molecule can bond with the Ti atom of the surface. The interaction is something like that for organometallic compounds, and the metal-ligand charge transfer (MLCT) may enhance the oscillator strength and contribute to the great NLO responses. Here the ligand is the Rh610 molecule with large π-conjugation system and the metal ion is Ti atom.

For TiO_2/DAST composites we can have similar results. The HRS response was also enhanced but it is not so obvious as the former one. The differences between the two composites could be explained as follows: Firstly, the chromophore part (the part which carries positive charge) of DAST (see Fig.1) has no effective functional groups which can combine with the Ti atoms (because of steric hindrance). It may indirectly interact with TiO_2 nanoparticle through the tosylate part of its counterpart ion (the O atom of benzosulfonate can bond with Ti atom), therefore the interactions is not as strong as that of TiO_2/Rh610 composite. Secondly, Rh610 is a dish-like big molecule, while the tosylate part of DAST is a rod-like small group, consequently the latter is easier to interact with and passivate the surface and might eliminate the surface defects and some of the surface states. This would be a negative factor to the second order NLO responses because it is usually believed that defects on the surface can benefit the generation of HRS signal. Finally the absorption peak λ_{max} for Rh610 is very close to the HRS wavelength at 532nm, so the HRS signal of TiO_2/Rh610 composite will be resonantly enhanced. But for TiO_2/DAST composite the resonant enhancement is very weak because both TiO_2 and DAST have almost no absorption at 532nm. The classical two-level model can roughly interpret the resonance effect.

IV. CONCLUSION

We have synthesized aqueous titanium dioxide (TiO_2) nanoparticles of 10nm in size, and two nanoparticle-dye composites which can be denoted by TiO_2/Rh610 and TiO_2/DAST with adding rhodamine B (Rh610) and the organic tosylate salt of DAST respectively. Results obtained show that the "per particle" first hyperpolarizability β for TiO_2 nanoparticle is very large, being in the range of 10^{-26} esu. For TiO_2/Rh610 and TiO_2/DAST composites the HRS signals are further enhanced. And for TiO_2/Rh610 composite the enhancement is obviously greater than that of TiO_2/DAST composite. This shows that TiO_2 and TiO_2/Dye composites are good candidates for the applications in optoelectronic and NLO areas. The results reveal that non-centrosymmetry of the nanocrystal/solution interface contributes mainly to its large "per particle" β, overwhelming the nanocrystal core. And the interactions between nanoparticle surface and adsorbed dyes are very important for their second-order NLO responses. HRS signal is very sensitive to the structure of nanoscale interface and can give some useful information that cannot be obtained by normal physical, chemical or optical methods. Therefore HRS technique is a useful new NLO method to characterize the surface structures and microenvironment of nanoscale materials.

ACKNOWLEDGEMENT

We would like to thank Dr. Fu De-gang and Mr. Chen Ji-qi for helpful suggestions in experiments and discussions.

References

[1] Chemla D O and Zyss J 1987 *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic Press, Orlando) Vol. 1, Chap. 1 and Chap. 2, pp 54-79
[2] Brus L 1991 *Appl. Phys.* A **53** 465
[3] Long N J 1995 *Angew Chem. Int. Ed. Engl.* **34** 21
[4] Cox S D, Gier T E, Stucky G D and Bierlein J 1988 *J. Am. Chem. Soc.* **110** 2986
[5] Ledoux I and Zyss J 1982 *Chem. Phys.* **73** 203
[6] Shen Y R 1989 *Nature* **337** 519
[7] Wang X, Lu Z H, Cui Y P *et al* 1999 *Proc. SPIE* **3863** 162
[8] Vance F W, Lemon B I, Ekhoff J A *et al* 1998 *J. Phys. Chem.* B **102**(11) 1845
[9] Wang X, Zhang Y, Shen Y C *et al* 2000 *Proc. SPIE,* **3937** 123
[10] Clays K and Persoons A 1991 *Phys. Rev. Lett.* **66**(23) 2980, And references therein.
[11] Kormann C, Bahnemann D W *et al* 1988 *J. Phys. Chem.* **92** 5196
[12] Pauley M A, Guan H W, Wang C H *et al* 1996 *J. Chem. Phys.* **104**(20) 7821