Surface Second Order Optical Nonlinearity of Titanium Dioxide Sized in Nanometer Range

De-gang Fu,* Yu Zhang, Xin Wang, Ju-zheng Liu, and Zu-hong Lu
Key Laboratory for Molecular and Biomolecular Electronics of Ministry of Education, Southeast University
Nanjing 210096, P.R. China

(Received January 5, 2001; CL-010011)

The nanoparticles of a centrosymmetric material titanium dioxide (TiO_2) have been synthesied and characterized by hyper-Rayleigh scattering (HRS) technique. The particles with mean diameter of 10 nm have large first order hyperpolarizability in solution, which arise from the surface layer of the particles.

There has been a dramatic increase of interest in both the preparation and properties of nanocrystalline materials over the past decade. However, there are only a few studies about second order nonlinear optical properties of nanoparticles due to the difficult in determination. It is just from past two years that the researches appear more than before because of the use of HRS technique. HRS is an incoherent methodology, which is not constrained by the orientation, size, and/or charge restrictions inherent to conventional interfacial second harmonic generation (SHG) or electric-field-induced SHG measurement.[1] Until now, the HRS mechanism of nanoparticles is still preliminary and incomplete. For example, in the HRS studies of nanoparticles such as SiO_2,[2] CdSe[3] and CdS,[4] a bulklike contribution to HRS signals were included. But it is not clear that what a contribution to HRS signals can give by surface layer. So it is particularly interesting for direct observation of surface SHG from nanoparticles. This observation can give us definite evidences about role of surface, and such a observation will also show the possibility of applying second-harmonic spectroscopy (SHS) and sum-frequency spectroscopy (SFS) in the study of surface structure of nanoparticles. As we known, coherent SHS and SFS have become powerful tools for studying equilibrium and dynamic phenomena at interfaces.[5] But for very small particles such as nanoparticles, the size is far smaller than the wavelength of light. This suggests that there may be a cancellation of the surface contribution,[6] which will hinder the use of SHS and SFS in nanoparticles. The detectable surface second order optical nonlinearity from very small metallic particles has been theoretical expected.[7] In this letter we report the first observation of SHG on a centrosymmetric matter–titanium dioxide (TiO_2) with a diameter in 10 nm by HRS technique. Here HRS signals will mainly origin from interface of the material.

TiO_2 nanoparticles is a material with excellent merits in solar energy transferring and photo-catalysis of poison compounds in environment.[8] There have symmetric centers in its four forms of crystal structures: anatase, rutile, srilankite and brookite. We prepared the TiO_2 nanoparticles by adding 25 mL of Ti(O-*i*-Pr)$_4$ (tetraisopropoxide) into 4 mL of isopropyl alcohol. The mixture was added to 150 mL of distilled deionized water containing 2 mL of 70% nitric acid, and then kept stirring for 6 h at about 75°C. Approximately 150 mL of TiO_2 colloid solution, which was stable for several months at 4°C, was obtained after removing the organic layer. The pH value of the colloid solution was 0.9 and the initial concentration of TiO_2 molecular unit was 5.6×10^{-4} M. The crystal structure of the obtained nanoparticles was anatase with mean size of 10 nm from the analysis of transmission electron micrograph (TEM) (Figure 1).

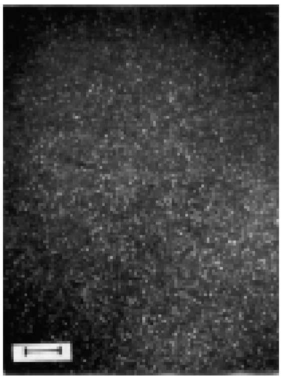

Figure 1. The transmission electron micrograph of TiO_2 nanoparticles record on JEOL 2000-EX with working voltage 120 kV (dark field). Scale is 200 nm.

The HRS experimental setup we used is similar to the literature.[9] 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 in which a liquid sample was measured. The equipment was well calibrated by para-nitroaniline (*p*-NA).[10] Here it should be noted that the TiO_2 nanoparticles we used have no absorption of incident light (1064 nm) and frequency-doubled light (532 nm). At such a situation, the relationship between observed intensity of frequency-doubled light ($I_{2\omega}$) and incident intensity (I_ω) can be described by eq (1) [1] for a two-component system with low solute concentration as:

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

where β is the first hyperpolarizability, N is the number density of each component, subscriptions 1 and 2 denote solvent and solute respectively, and the brackets indicate the orientational averaging. G is the constant parameter for low solute concentration that encompasses collection efficiencies as well as local field correction factors. At our case, water is the solvent with β_1 value as 0.56×10^{-30} esu.[2] N_1 is the number density of water. In whole experiment, good agreement to a quadratic fit of HRS intensity $I_{2\omega}$ on the incident intensity I_ω has been observed, as expected for the second-order scattering process. Figure 2 show the experiment results and the fitting curves. The β values "per particle" can be estimated to be 4.3×10^{-26} esu with the number density of the nanoparticles calculated from initial concentration of TiO_2 molecular unit and mean

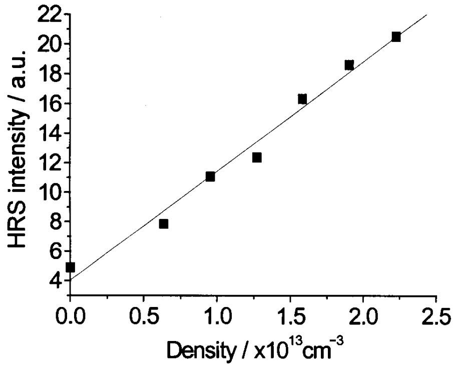

Figure 2. The linear dependence of the HRS intensity on the particle number density of the TiO_2 colloid with fixing incident intensity. β_2 was calculated from $(N_1B/A)^{1/2}\cdot\beta_1$, where A is intercept and B is slope.

diameter of the particles (10 nm). This value is in the largest values reported for solution species. For comparison, β values for the best molecular chromophores are on the order of 5.0×10^{-27} esu.[11]

It is believed that SHG is inherently absent for centrosymmetric structures in the electric dipole approximation.[12] However at an interface, the inversion symmetry intrinsically breaks. As a result, the surface originated SHG can be observed even in centrosymmetric materials.[13] For example, SHG spectrum has been used to probe the interactions between defects and small molecules on bulk TiO_2 surface.[14] Mostly, observed SHG mainly originated from the molecular chromophores absorbed on the surface. In our particles, there are no special molecular chromophores on the surface but the solvent water molecules. The solvent molecules can affect observed HRS signals in three ways. First, the first hyperpolarizability of water molecules β_1 is not equal to zero so that solvent will contribute to HRS signal (equation 2: $\beta_1\cdot EE$). This contribution was used as a reference and has been considered in equation 1. Second, the solvent will introduce an additional effective field F which is zero on the average, but with low frequency instantaneous fluctuations.[15] This addition field F can interact with two photons to contribute HRS signal involving the second hyperpolarizability of the TiO_2 nanoparticles γ_2 (equation 2: $\gamma_2\cdot EEF$). Third, under the pH condition (0.9), the surface of TiO_2 nanoparticles are positive charged,[16] so that a surface static electric field E(s) is product and extends to interfacial region.[17] With field E(s), the third nonlinear process concerning the second hyperpolarizability of interfacial water molecules γ_1 can also product HRS signal (equation 2: $\gamma_1\cdot EEE(s)$). The two of third order nonlinear process ($\gamma_2\cdot EEF$ and $\gamma_1\cdot EEE(s)$) will vary with total ion concentration of the solution, because the field F and E(s) are all depending on the ionic strength.[18] We adjusted the ionic strength of TiO_2 colloid solution by $NaNO_3$ and then determined the HRS intensity. We found that at same number density of TiO_2 particle, HRS intensity varied no more than ±5% which was within the systemic errors of the setup (10%). This means that the contributions from third order nonlinear processes are not important in this case. In fact, the contribution from third order nonlinear process to first hyperpolarizability was also found to be not important in charged SiO_2 nanoparticles.[2] In summary, the induced polarization P of TiO_2 colloids can be expressed as:

$$P=\alpha\cdot E+\beta_1\cdot EE+\beta_2\cdot EE+\gamma_2\cdot EEF+\gamma_1\cdot EEE(s) \qquad (2)$$

Where β_1, β_2 are first hyperpolarizability of water molecule and TiO_2 nanoparticles, respectively. Only last three terms have a contribution to the determined β value of TiO_2 nanoparticles. As shown above, solvent and surface charge effects are not important and can not be used to explain observed large first hyperpolarizability of TiO_2 nanoparticles. The phenomena should be considered as an inherit property of the nanoparticles attributed to its surface atoms.

When considering surface molecule-like scatters, surface Ti–O bonding may be the origins of observed HRS signals in TiO_2 nanoparticles as Cd–S bonding in CdS nanoparticles and Si–O bonding in SiO_2 nanoparticles.[2, 4] But the detailed mechanism that why surface layer has so large second order nonlinearity are not clear at present. The result we report here reveal that surface layer can have important contribution to second order nonlinearity in nano-materials, and surface contribution may become the main source of SHG because the enhancement of ratio of surface atoms to volume atoms.

This work was finical supported by National Natural Science Foundation (29874008) and Ministry of Education of China.

References

1 K. Clays and A. Persoons, *Rev. Sci. Instrum.*, **63**, 3285 (1992).
2 F. W. Vance, B. I. Lemon, J. A. Ekhoff, and J. T. Hupp, *J. Phys. Chem.*, **102**, 1845 (1998).
3 M. Jacobsohn and U. Banin, *J. Phys. Chem. B*,**104**, 1 (2000).
4 B. S. Santos, G. A. L. Pereira, D. V. Petrov, and C. Donega, *Opt. Commun.*, **178**, 187 (2000); Y. Zhang, X. Wang, D-G. Fu, J-Z. Liu, Y-P. Chui, and Z-H. Lu, *Chem. Lett.*, **2001**, 46.
5 K. B. Eisenthal, *Chem. Rev.*, **96**, 1343 (1996).
6 A. Srivastava and K. B. Eisenthal, *Chem. Phys. Lett.*, **292**, 345 (1998).
7 J. I. Dadap, J. Shan, K. B. Eisenthal, and T. F. Heinz, *Phys. Rev. Lett.*, **83**, 4045 (1998).
8 B. O'Regan and M. Gratzel, *Nature*, **353**, 737 (1991); M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
9 D. G. Fu, M. Li, X. Wang, J. Q. Cheng, Y. Zhang, and Z. H. Lu, *Supramole. Sci.*, **5**, 495 (1998).
10 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977).
11 S. M. LeCours, H. W. Guan, and M. J. Therien, *J. Am. Chem. Soc.*, **118**, 1497 (1996).
12 R. W. Boyd, "Nonlinear Optics", Academic Press, San Diego (1992), p. 41.
13 P. Guyot and Y. R. Shen, *Phys. Rev. B*, **33**, 8254 (1986).
14 A. N. Shultz, W. M. Hetherington III, D. R. Baer, L-Q. Wang, and M. H. Engelhard, *Surf. Sci.*, **392**, 1 (1997); E. Kobayashi, K. Matsuda, G. Mizutani, and S. Ushioda, *Surf. Sci.*, **427**, 294 (1999).
15 S. N. Yaliraki and R. J. Silbey, *J. Chem. Phys.*, **111**, 1561 (1999).
16 G. T. Brown and J. R. Darwent, *J. Chem. Soc., Chem. Commun.*, **1985**, 98.
17 K. F. Haytes, G. Redden, W. Ela, and J. O. Leckie, *J. Colloid Interface Sci.*, **142**, 448 (1991).
18 S. Ong, X. Zhao, and K. B. Eisenthal, *Chem. Phys. Lett.*, **191**, 327 (1992).