Absorption redshift in TiO2 ultrafine particles with surfacial dipole layer

Bingsuo Zhou, Liangzhi Xiao, Tie Jin Li, Jialong Zhao, Zhuyou Lai et al.

Citation: Appl. Phys. Lett. **59**, 1826 (1991); doi: 10.1063/1.106211
View online: http://dx.doi.org/10.1063/1.106211
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v59/i15
Published by the American Institute of Physics.

Absorption red shift in TiO_2 ultrafine particles with surfacial dipole layer

Bingsuo Zou, Liangzhi Xiao, and Tiejin Li
Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

Jialong Zhao
Changchun Institute of Physics Academia Sinica, Changchun 130023, People's Republic of China

Zhuyou Lai
Department of Applied Physics and Institute of Condensed Matter Physics, Shanghai JiaoTong University, Shanghai 200030, People's Republic of China

Shiwei Gu
Department of Applied Physics and Institute of Condensed Matter Physics, Shanghai Jiao Tong University Shanghai 200030, People's Republic of China, CCAST (World Lab), Beijing 100080, and ICMP, Academica Sinica, Shengyang 110015, People's Republic of China

(Received 2 January 1991; accepted for publication 9 August 1991)

It is found that the TiO_2 ultrafine particles (UFP) coated with a layer of stearic acid radicals has a significant red shift of optical absorption band edge and clear photoluminescence at room temperature (RT), which are in contrast with that of bulk TiO_2 and naked TiO_2 UFP. It was concluded that these results are related to the self-trapped exciton absorption due to the interfacial dipole layer of stearic acid radicals on the TiO_2 UFP surface.

The application of optical nonlinearities of semiconductors has been considered to be very important, and attracted wide attention of scientists in the world.[1] Until now various theoretical models for the nonlinear optical phenomena of semiconductors have been presented that widened the knowledge of the interaction of light and matter. In recent years, many artificial microstructures have been fabricated with some experimental techniques, and exhibit various new properties different from the natural bulk materials and molecular and atomic systems due to the pronounced spatial confinements.[2–5] The optical linear and nonlinear properties in the structure of quantum wells, quantum wires, and quantum dots have become the hot point of recent scientific work in this field.[2,6,7]

Semiconductor ultrafine particles (UFP), known as quantum dots (QD), exhibited stronger optical nonlinear response due to the confinement in all three dimensions, which were found in considerable value once applied to the device of optical switching and data processing. Their property varies with the size distribution, the primitive bulk substance properties, and the fabrication techniques to an unpredictable extent until some natural changes occurred. Most of the work has focused on semiconductor UFP in the past,[6,8] so more work is needed to understand the complete profile of UFP of various kinds. In the present letter the optical spectroscopic properties of TiO_2 UFP coated with a layer of stearic acid radicals are reported. There are some new phenomena, such as the red shift of the absorption band edge and the photoluminescence at room temperature (RT), related to self-trapped excitonic processes occurring in this system, which have not been reported in former publications. TiO_2 is a transition metal oxide (d^0) semiconductor with a direct band gap but dipole forbidden transitions.[9] For both the bulk and the UFP state TiO_2 has attracted wide attention out of theoretical and application interest, but it is the first time reporting the spectroscopic nature of TiO_2 UFP coated with stearic acid.

The TiO_2 UFP coated with St (stearic acid) could be obtained through the following reaction:

$$TiCl_4 + 2nH_2O \xrightarrow[\Delta]{C_{17}H_{35}COOH} (TiO_2)_n + 4nHcl\uparrow .$$

Here St's play a role in protecting the TiO_2 UFP from being condensed into larger powders, and spontaneously become chemically bounded to surfacial Ti^{4+} on UFP verified by the infrared spectra. The diameter of TiO_2 UFP is less than 50 Å obtained through the small angle x-ray scattering measurements on the Rigaku D/Max-Ra x-ray diffraction meter.

TiO_2 UFP would be readily dispersed into some organic solvents due to its surface modification. The absorption spectra of its toluene sol is obtained with the Shimadzu UV-365 spectrophotometer (Fig. 1), from which one may conclude that there is a strong band edge absorption in the spectrum region of $\geqslant$400 nm in wavelength, in contrast with bulk TiO_2, and the absorption coefficients obeying Urbach's rule[10] (see Fig. 2) in this region.

It is well known that small particles with direct band gap E_g have a characteristic relation:[11]

$$[\alpha\hbar\omega]^{1/2} = B[\hbar\omega - E_g],$$

in which $\hbar\omega$ is the photon energy, E_g is the apparent optical band gap, B is the characteristic constant of the substance, and α is the absorption coefficient. Therefore, the E_g of TiO_2 UFP can be obtained by the extrapolation of the above relation to be 2.25 eV (see Fig. 3), which is significantly less than that of the bulk TiO_2. This fact was in disagreement with the theoretical and experimental results on the optical properties of semiconductor UFP reported in the former literature,[3,12] which indicate that the optical absorption band edge of UFP shifted to the short-wave-

 0003-6951/91/401826-03$02.00

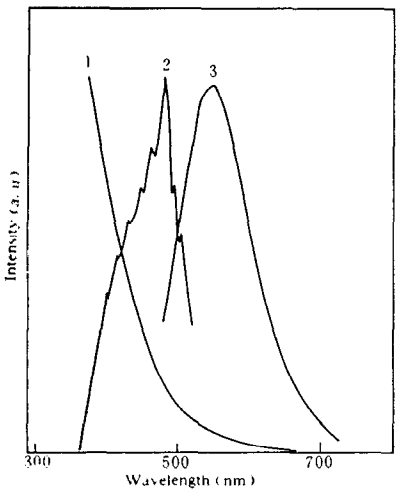

FIG. 1. The absorption (1), excitation (2), and photoluminescence spectra (3) of coated TiO_2 UFP.

length spectrum region as the size of UFP was reduced. It is worthy to point out that this difference would arise from the coated layer. In the photoluminescence experiment for TiO_2 UFP toluene sol with the HITACHI F-4000 fluorescence spectrophotometer, the 540 nm fluorescence wideband could be observed under the excitation of 380–500 nm light (in Fig. 1) at RT, but for bulk TiO_2 no photoluminescence could be observed at the same condition. However, at 77 K there was a wide fluorescence band near 500 nm, induced by the light of less than 400 nm in wavelength, which was attributed to the emission of self-trapped exciton in TiO_2.[13] The discussion about the results mentioned above were as follows. As for the band edge shift of optical absorption of semiconductor UFP, Brus[14] had taken it to result from the UFP's E_g changes along with their size reduction.

He described the electron wave function of UFP with

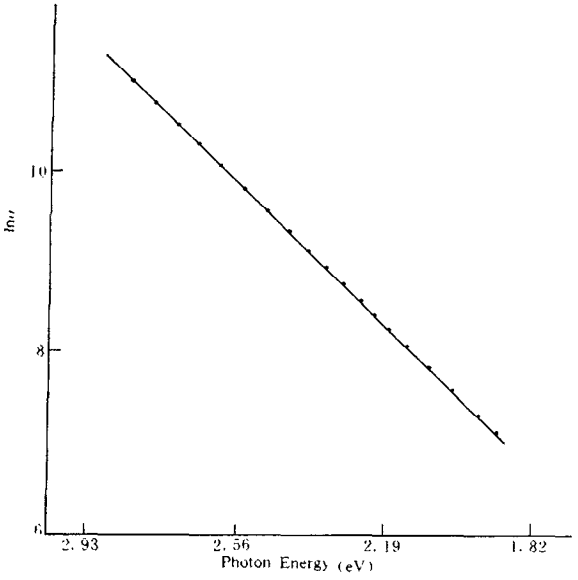

FIG. 2. The relation of absorption coefficient α and photo energy $\hbar\omega$ for coated TiO_2 UFP.

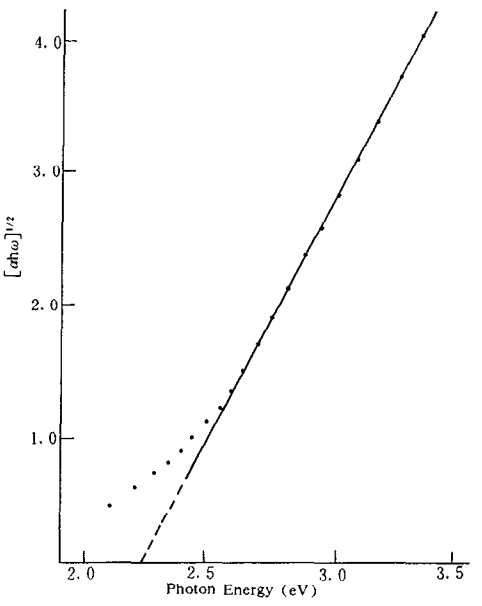

FIG. 3. The apparent energy gap (E_g') of coated TiO_2 UFP (from the extrapolation of equation $[\alpha\hbar\omega]^{1/2} = B(\hbar\omega - E_g')$.

the combination of Bloch wave functions, and approximately expressed the band-gap energy of the UFP system as

$$E_g = E_0 - \frac{1.8e^2}{\epsilon R} + \frac{\bar{h}\pi^2}{2R^2}\left(\frac{1}{M_e} + \frac{1}{m_h}\right) + \text{smaller terms},$$

in which the second term represents the red shift of optical band edge induced by the electron and hole Coulomb interactions, the third term represents the blue shift due to the quantum confinements of carriers, and the two were competing effects in UFP. Brus believed the band-gap change due to the size reduction was caused by the blue shift of the absorption band edge as the size was small enough (for example, CdS when less than 85 Å). Many experimental results supported his opinion,[12,15,16] but the results of our experiment about TiO_2 UFP coated with St (less than 50 Å) were in contrast with his conclusion, i.e., there existed a drastic red shift of the band edge in our system. This indicates that the variation of UFP's band edge absorption should relate to many factors. In reality, besides the factors considered by Brus, i.e., the size effect of UFP, the ambient media around UFP, the interfacial chemical condition, and so on, also can influence the band edge shift of UFP absorption when the diameter of the TiO_2 UFP was reduced to less than 50 Å, the number of the elementary cell was less than 15 in every dimension (the size of an elementary cell was about 3 Å), which is still in the region of the simple energy band theory if one does not consider the deformation effects. According to this approximation, because the wavevector k had $2\pi/k \ll R$ on the boundary of the Brillouin zone of the energy gap, so the modification of the energy band gap due to the quantum size effect was not remarkable. In another way, due to the lower symmetry and coordinate number on the UFP surface, the Ti^{4+} charge on the surface of naked UFP in hydrosol cannot be neutralized utterly in a short range,

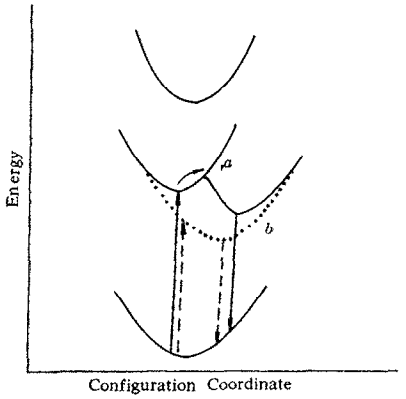

FIG. 4. The energy level diagram of bulk TiO_2 (a), naked UFP (a), and coated TiO_2 UFP (b).

whose dipole formed on UFP surface had a repulsion potential acting on the carriers inside UFP. This effect induced the blue shift of the UFP absorption band edge, which is enhanced as the size of the UFP was reduced. But once the TiO_2 UFP was coated with a layer of St, an important physicochemical process occurred, i.e., the negative hydrophilic radical of stearic acid would bind onto the surface of TiO_2 UFP, therefore, a dipole layer towards the inner TiO_2 UFP formed. It was this dipole layer that induced an attracting potential to electrons inside UFP, which contributed to the reduction of the band gap of TiO_2 UFP, i.e., this layer introduced a red-shift tendency of the absorption band edge. The band structures of TiO_2 were mainly dependent on the crystal field effect, from which no pronounced change of band structure could be introduced by the surfacial dipole layer. However, the influences of the dipole layer on the binding energy of the exciton, i.e., the Coulomb interaction of electron and hold in UFP, were considerable.[5,6] The dipole layer might become the trap center of the exciton, which could enhance the exciton binding energy more significantly, and induce the red shift of the absorption band edge of UFP. Furthermore the interface deformation potential might also become another kind of center of the self-trapped exciton, producing the red shift of the absorption band edge. The band edge absorption of this sort would obey Urbach's rule.[11,17]

The exciton trapping effects of the surface modification could increase not only the binding energy of the exciton but also the lifetime of the excitons which were related to the explanation of the peculiar photoluminescence of the surface coated TiO_2 UFP (see Fig. 1). For bulk TiO_2 even in monocrystal state it was difficult to observe photoluminescence phenomenon at RT, and for the photoluminescence band at 77 K observed, which was assigned to the emission of impurity bound excitons[18] or self-trapped excitons,[13] and the same for the naked TiO_2 UFP in hydrosol.[19] On the contrary, the photoluminescence of TiO_2 UFP coated with St could be observed at RT. As seen from Fig. 4, these differences were obvious to be handled. The self-trapped exciton could not form directly by optical absorption, and the efficiencies for self-trapped exciton generation[20,21] in bulk TiO_2 and naked UFP were small because there was a potential barrier to the self-trapped exciton from the free exciton, and the nonradiative electron-phonon coupling was strong, so the emission due to the self-trapped exciton was not seen at RT, but at 77 K, sufficient long-lived self-trapped excitons could form to emit. However, the St modification of TiO_2 UFP enhanced the interfacial dipole effects, which had the surface electronic structure on UFP altered, i.e., canceling the barrier for self-trapped exciton formation and hence greatly enhanced the self-trapped exciton absorption, i.e., the transitions to the level of self-trapped exciton were able to occur under this condition. Furthermore, along with the "giant oscillator strength effects" of localized exciton,[22] the sufficient long-lived self-trapped excitons were excited under light illumination to contribute to the photoluminescence at RT.

In conclusion, the optical properties of TiO_2 UFP coated with St are significantly different from that of bulk TiO_2 and naked UFP. The interfacial dipole layer due to surface modification of St was the main cause of these variances, i.e., this dipole layer assisted the long-lived self-trapped exciton formation and increased their binding energy.[18] The nonlinear optical properties of this system may be interesting for further study. The details of the quantitative theoretical calculation of the self-trapped exciton model in this system will be published elsewhere.

The authors would like to thank the National Natural Science Foundation of China for financial support and Professor Haosheng Fei for many instructions and discussions.

[1] H. Haug, Ed., *Optical Nonlinearities and Instabilities in Semiconductors* (Academic, London, 1988).
[2] S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).
[3] L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).
[4] A. Henglein, Chem. Rev. **89**, 1861 (1989).
[5] Y. Z. Hu, S. W. Koch, M. Lindberg, and N. Peyghambarian, Phys. Status Solidi (B) **159**, 249 (1990).
[6] S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, Phys. Rev. B **35**, 8113 (1987).
[7] M. Kumagai and T. Takagahara, Phys. Rev. B **40**, 12 359 (1989).
[8] T. Takagahara, Phys. Rev. B **39**, 10 206 (1989).
[9] N. Daude, C. Gout, and G. Jouanin, Phys. Rev. B **15**, 3229 (1977).
[10] F. Urbach, Phys. Rev. **92**, 1324 (1953).
[11] J. Tauc, in *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1970), p. 279.
[12] C. Kormann, D. W. Bahnemann, and M. R. Hoffmann, J. Phys. Chem. **92**, 5196 (1988).
[13] L. G. J. De Haart and G. Blasse, J. Solid State Chem. **61**, 135 (1986).
[14] L. E. Brus, J. Phys. Chem. **90**, 2555 (1986).
[15] Y. Wang and N. Herron, J. Phys. Chem. **91**, 5005 (1987).
[16] A. I. E. Kimov, Al. L. Efros, and A. A. Onushchenko, Solid State Commun. **56**, 921 (1985).
[17] H. Sumi and T. Toyozawa, J. Phys. Soc. Jpn. **31**, 342 (1971).
[18] L. G. J. De Haart and G. Blasse, J. Solid State Chem. **59**, 291 (1985).
[19] M. Anpo, T. Shima, and T. Kubokawa, Chem. Lett. **168**, 1799 (1985).
[20] Ch. Lushchik, I. Kuusmann, and V. Plekhanov, J. Lumin. **18/19**, 11 (1979).
[21] R. Leonelli and J. L. Brebner, J. Lumin. **31/32**, 96 (1984).
[22] T. Takagahara and E. Hanamura, Phys. Rev. Lett. **56**, 2533 (1986).