JOURNAL OF SOLID STATE CHEMISTRY **139,** 124–127 (1998)
ARTICLE NO. SC987816

Electronic State Characterization of TiO_2 Ultrafine Particles by Luminescence Spectroscopy

Yingchun Zhu and Chuanxian Ding

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

and

Guohong Ma and Zuliang Du

Laboratory of Solid State Physics, Henan University, Kaifeng 475001, People's Republic of China

Received June 13, 1997; in revised form March 6, 1998; accepted March 13, 1998

The electronic states of TiO_2 ultrafine particles (UFP) are characterized by photoluminescence spectra and diffuse reflection spectra. The results obtained indicate that the surface structure, i.e., TiOH groups, $TiOC_2H_5$ groups, and the defect state, plays an important role in the electronic states of the TiO_2 UFP. Moreover, free exciton emission is observed at room temperature. This emission is attributed to the quantum confinement and the dielectric confinement effects on the TiO_2 UFP. © 1998 Academic Press

INTRODUCTION

Nanostructured titania as a semiconductor material has been extensively researched during recent years. It has found application in many fields, including photocatalysis, photoelectric conversion, dielectrics, and nonlinear optics (1–3). The electronic structure of titania has been studied theoretically and experimentally by many scientists. Daude *et al.* (4) calculated the electronic band structure by a combined tight-binding and pseudopotential method. Tsukada *et al.* (5) did similar work using discrete-variational (DV)–Xα calculations. De Haart *et al.* (6) studied the photoluminescence of many titanates and discussed the self-trapped exciton emission from titanates. Recently, Zou *et al.* (3, 7) reported that titania ultrafine particles coated with a surface dipole layer exhibited an absorption red shift, self-trapped states, and phonon localization. In this paper, we investigate the electronic states of TiO_2 UFP through luminescence spectra and report some new phenomena.

EXPERIMENTAL

Synthesis

TiO_2 UFP were synthesized through controlled hydrolysis of titanium butoxide. The obtained UFP powders were treated by three different processes: (a) direct precipitation followed by drying at 60°C under a pressure of 3×10^4 Pa; (b) direct precipitation followed by ethanol rinsing and drying at 70°C under a pressure of 3×10^4 Pa; (c) direct precipitation followed by ethanol rinsing and drying at 95°C under a pressure of 2×10^3 Pa. The powders obtained by the three processes are denoted sample a, sample b, and sample c, respectively. Detailed information on the synthesis of the TiO_2 UFP powders is given in ref 8.

Optical Spectroscopy

Luminescence spectra were obtained on Spex F212 fluorescence spectrophotometer. The diffuse reflection spectra were measured with a Cary 2390 UV–vis–near-IR spectrophotometer.

RESULTS AND DISCUSSION

The structure of the UFP powders of sample a is characterized by X-ray diffraction. A diffraction peak at 25.3° can be observed in Fig. 1, which corresponds to the (101) lattice plane of anatase (8). The particle size is estimated to be 4 nm from the X-ray diffractogram according to the Debye–Scherrer formula: $L = k\lambda/\beta \cos\theta$.

The diffuse reflection spectra of the TiO_2 UFP powders are presented in Fig. 2. From Fig. 2, it can be seen that the absorption band edges of the three samples are around 390 nm, obtained by extrapolating the steep slopes in the curves to the long-wavelength side. All three samples have slightly weak absorption in the range of visible wavelength. However, the absorption positions at long wavelength are different for the three samples and there is a tendency to longer wavelength in the sequence sample a → sample b → sample c. The same results are obtained from the excitation

0022-4596/98 $25.00
Copyright © 1998 by Academic Press
All rights of reproduction in any form reserved.

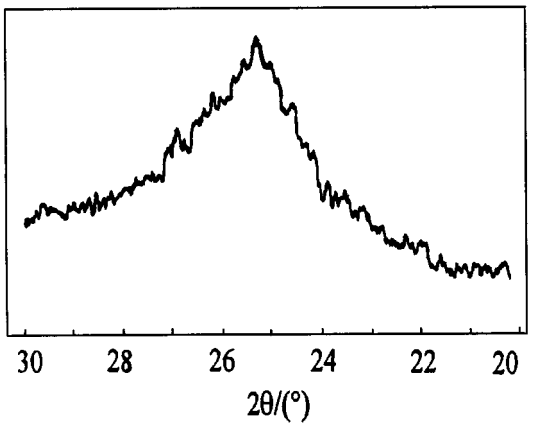

FIG. 1. X-ray diffractogram of the TiO_2 UFP of sample a.

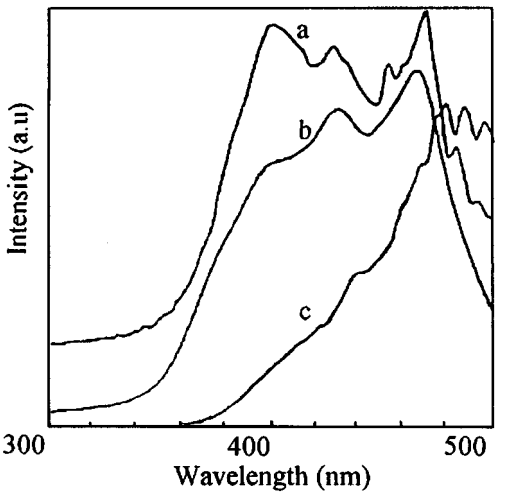

FIG. 3. Excitation spectra of the emission at 520 nm: (a) sample a; (b) sample b; (c) sample c.

spectra of the emission at 520 nm in Fig. 3. In curve a of Fig. 3, there are excitation peaks at 400, 427, and 470 nm, which have similar intensities. In curve b of Fig. 3, the intensity of the 400-nm excitation peak decreases compared with the peaks at 427 and 470 nm. In curve c of Fig. 3, the peaks at 400 and 427 nm almost disappear. There is a strong absorption around 480 nm and the absorption position moves toward longer wavelength. The discussion of the foregoing phenomenon is presented later. Absorption at long wavelength is often observed in titanates (6), which is assigned to the defect center of a titanium octahedron caused by oxygen vacancies (9). Absorption at long wavelength, which is called the absorption red shift, was also observed by Zou *et al.* with TiO_2 ultrafine particles coated with a surface dipole layer (3, 7). The authors attributed the absorption red shift to a dipole layer that induced an attracting potential to electrons inside the UFP and led to the reduction of the band gap of the UFP. According to the evidence we obtained, the absorption at long wavelength can be attributed to the structure, especially the surface structure, of the UFP, such as TiOH groups on the surface of the TiO_2 UFP. UFP powders prepared via process a contain many TiOH groups, which has been proven in ref 10. There are two kinds of chemisorbed OH groups as well as two kinds of chemisorbed water molecules in anatase powders (11). Moreover, there are $TiOC_2H_5$ groups on the surface of the TiO_2 UFP (8). These groups in the TiO_2 UFP could form intraband surface states (12), which can lead to the long wavelength absorption in the ultrafine particles. The excitation peak at 400 nm should be related to the TiOH groups and the peak at 427 nm to the $TiOC_2H_5$ groups in UFP. When sample a is rinsed with ethanol, some TiOH groups are removed in water form (8), so the peak at 400 nm decreases, but the peak at 427 nm does not change. When sample b is evacuated at higher temperature and under lower pressure, the TiOH groups as well as the $TiOC_2H_5$ groups further decrease, so the peaks at 400 and 427 nm almost disappear. The excitation peak around 470 nm should be attributed to the defect states. The transition energy from the defect level to the lowest empty Ti *d* bands is calculated to be about 2.6 eV (5), which coincides well with the excitation peak at 470 nm. The gray color of sample c supports the view that there are reduced species of titanium oxide (13). With the process of evacuation more and more vacancies of oxygen are formed in the TiO_2 UFP, so the peak gets stronger and moves toward longer wavelength.

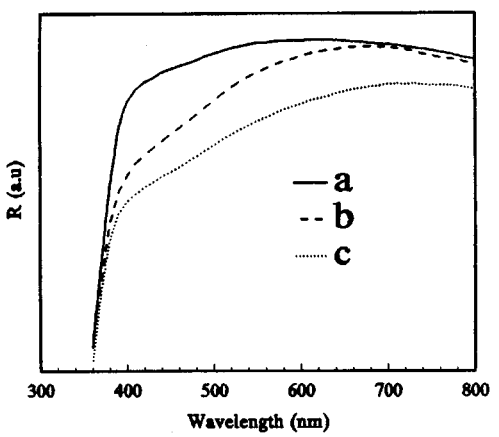

FIG. 2. Diffuse reflection spectra of the TiO_2 UFP powders: (a) sample a; (b) sample b; (c) sample c.

The luminescence spectra of the TiO_2 UFP of sample a are shown in Fig. 4. The excitation spectrum of the emission

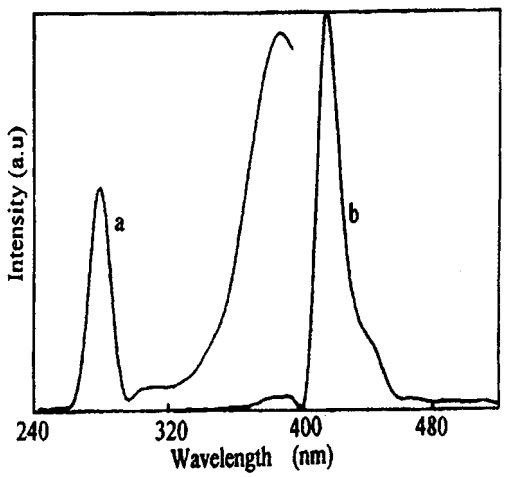

FIG. 4. Luminescence spectra of the TiO_2 UFP of sample a: (a) excitation spectrum of emission at 430 nm; (b) emission spectrum of the excitation at 280 nm.

at 430 nm presented in Fig. 4 exhibits peaks at 280 and 390 nm at room temperature. The excitation peak at 280 nm was found with titanate $SrZr_{0.98}Ti_{0.02}O_3$ at 77 K (6) and was ascribed to the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer transition within a regular titanate octahedron. An excitation peak at 350 nm was observed by Deb (14) with a polycrystalline TiO_2 sample at 77 K. Anpo (15) observed an excitation peak at about 310 nm with an anchored TiO_2 layer that had an amorphous structure. The excitation peak at 280 nm for anatase TiO_2 has not been reported as far as we know. We also attribute it to the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer transition. The emission spectrum of the excitation at 280 nm of sample a in Fig. 4 gives a strong sharp emission peak at 418 nm. Samples b and c give similar emission spectra and excitation spectra with an excitation peak at 280 nm and an emission peak at 418 nm. In this situation, the excitation peak at 280 nm should belong to the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer transition of a regular titanate octahedron. The 418-nm emission can be assigned to the Wannier–Mott free exciton emission. A similar emission at 412 nm was observed by Haart with rutile single crystals at 4.8 K, which disappeared with increasing temperature (16). It is impossible to detect the exciton emission with bulk TiO_2 at room temperature by ordinary fluorescence spectrophotometry due to its weak exciton binding energy and short radiative lifetime. However, according to the results of Takagahara and Takeda (17), the exciton binding energy and radiative lifetime are strongly size dependent. The spatial overlap of the envelope functions of an electron and a hole increases with the reduction of the size of the semiconductor quantum dots, and this leads to the increase of the exciton binding energy. Furthermore, the increased exciton binding energy prolongs the exciton radiative lifetime. At the same time, the dielectric confinement effect also enhances the exciton binding energy due to the penetration of the electric force lines between an electron and a hole into the surrounding medium (18). Moreover, the dielectric confinement effect becomes stronger in smaller quantum dots such as TiO_2 ultrafine particles, which have a large dielectric constant, because the small size introduces more opportunity for the electric force lines to penetrate into the surrounding medium with relatively smaller dielectric constant. According to the foregoing discussion, TiO_2 UFP should have a large exciton binding energy and thus a long exciton radiative lifetime, which leads to the photoluminescence of the Wannier–Mott free exciton, and the free exciton emission can be observed by ordinary fluorescence spectrophotometry at room temperature. Another excitation spectrum peak at 390 nm can also be observed in Fig. 4. This peak coincides well with the absorption band edge at 390 nm in the diffuse reflection spectra in Fig. 2. The excitation spectra at 390 nm may be assigned to the exciton absorption that corresponds with the exciton emission at 418 nm in Fig. 4.

CONCLUSION

Investigation of the X-ray diffraction reveals that TiO_2 UFP powders have an anatase structure and 4-nm mean particle size. The electronic states of the TiO_2 UFP have been demonstrated by diffuse reflection spectra and photoluminescence spectra. It is found that the absorption band edge of the TiO_2 UFP is at 390 nm. The intraband absorption peaks at 400, 427, and 470 nm correspond to TiOH groups, $TiOC_2H_5$ groups, and the defect state, respectively. In particular, the excitation peak at 280 nm, corresponding to the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer transition, and the emission peak at 418 nm, corresponding to the free exciton emission, are observed at room temperature.

REFERENCES

1. V. Sukharev, A. Wold, Y. M. Gao, and K. Dwight, *J. Solid State Chem.* **119,** 339 (1995).
2. M. Gratzel, *Nature* **353,** 737 (1992).
3. B. S. Zou, J. G. Lin, L. Wang, J. R. Xu, and L. J. Zhao, *Acta Phys. Sin.* **45,** 1239 (1996).
4. N. Daude, C. Gout, and C. Jouanin, *Phys. Rev. B* **15,** 3229 (1977).
5. M. Tsukada, C. Satoko, and H. Adachi, *J. Phys. Soc. Jpn.* **47,** 1610 (1979).
6. L. G. J. De Haart, A. J. De Vries, and G. Blasse, *J. Solid State Chem.* **59,** 291 (1985).
7. B. S. Zou, L. Z. Xiao, T. J. Li, J. L. Zhao, Z. Y. Lai, and S. W. Gu, *Appl. Phys. Lett.* **59,** 1826 (1991).
8. J. H. Hang, L. Gao, J. Y. Chen, D. S. Yan, *J. Inorg. Mater.* **11,** 51 (1996).
9. H. Ihrig, J. H. T. Hengst, and M. Klerk, *Z. Phys. B* **40,** 301 (1981).

10. Y. C. Zhu, J. F. Zhou, C. P. Chen, Z. Q. Zhu, and Z. J. Zhang, *J. Henan Univ.* **24,** 39 (1994).
11. K. Tanaka and J. M. White, *J. Phys. Chem.* **86,** 4708 (1982).
12. P. Salvador and C. Gutierrez, *J. Phys. Chem.* **88,** 3696 (1995).
13. M. Shirkhanzadeh, *Nanostruct. Mater.* **5,** 33 (1995).
14. S. K. Deb, *Solid State Commun.* **11,** 713 (1972).
15. M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, and E. Giamello, *J. Phys. Chem.* **89,** 5017 (1985).
16. L. G. J. De Haart and G. Blasse, *J. Solid State Chem.* **61,** 135 (1986).
17. T. Takagahara and K. Takeda, *Phys. Rev. B* **46,** 15578 (1992).
18. T. Takagahara, *Phys. Rev. B* **47,** 4569 (1993).