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Investigation on the Surface State of TiO_2 Ultrafine Particles by Luminescence

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The surface states of TiO_2 ultrafine particles (UFP) are characterized by luminescence spectra and UV-absorption spectra. In order to confirm whether the emission at 475 nm originates from the surface state, the as-prepared TiO_2 UFP are plasma-treated. The results indicate that surface states related to the TiOH and $TiOC_2H_5$ groups play an important role in the emission and UV-absorption of TiO_2UFP. Both quantum confinement and dielectric confinement effects have been used for discussing the emission and UV-absorption properties of TiO_2 UFP. © 1999 Academic Press

INTRODUCTION

Optical nonlinearities of semiconductor nanocrystals are of both fundamental and applicational interest and have attracted the wide attention of researchers (1–3). Semiconductor nanocrystals, also called quantum dots (DOS), exhibit novel properties different from those of their corresponding bulk materials (4–6). Various theoretical models have been presented to explain these novel optical phenomena (3, 7–9).

Semiconductive titanates are the popular materials whose electronic structure and luminescence properties have been deeply studied (7, 10–14). The electronic structure and luminescence of nanostructured titania have recently been actively researched (2, 4, 15–17). Luminescence at room temperature, which is impossible for bulk titania, was found for nanostructured titania, and the novel phenomenon was thought to result from spatial confinement and dielectric confinement. In a previous report (16), the luminescence of TiO_2 ultrafine particles, especially free exciton emission, was discussed. In this work, the luminescence of the surface state of TiO_2 UFP is discussed. In order to probe the origin of the luminescence of nanostructured titania, nanostructured titania is treated with a plasma beam and characterized by transmittance electron microscopy (TEM), infrared absorption spectroscopy (IR), and UV–vis absorption spectroscopy. It is found that the luminescence and UV–vis absorption spectra of TiO_2 ultrafine particles change dramatically after plasma treatment. The relationship between the structure and the luminescence properties is discussed.

EXPERIMENTAL

Synthesis

TiO_2 ultrafine particles were synthesized through controlled hydrolysis of titanium butoxide. Titanium butoxide solution diluted with anhydrous ethanol was dropped into deionized water under vigorous stirring and an opalescent sol was obtained, precipitate was rinsed with anhydrous ethanol and dried in a vacuum desiccator at 70°C under 3×10^4 Pa. Detailed information on the synthesis of the TiO_2 UFP powders is related in Ref. (18).

Plasma Treatment

An A-2000 vacuum plasma spraying equipment made by Sulzer Metco AG (Switzerland) was used to treat nano-TiO_2 particles. The plasma spraying process was carried out in argon atmosphere under pressure of 40 mbar with a power of 16 kW. A quartz glass plate was used as a substrate to collect the plasma-sprayed nano-TiO_2 particles.

Characterization

Luminescence spectra were obtained at room temperature on a Spex F212 Fluorescence Spectrophotometer. The UV-absorption spectrum was measured with a Cary 2390 UV–vis–NIR spectrophotometer. IR absorption spectrum was performed with a Nie-7199 infrared spectrometer.

RESULTS

TEM micrographs of plasma-treated TiO_2 UFP are shown in Fig. 1. Figures 1a and 1b are taken from different regions of plasma-treated TiO_2 UFP. It can be seen that the plasma-treated TiO_2 UFP have a wide size distribution of

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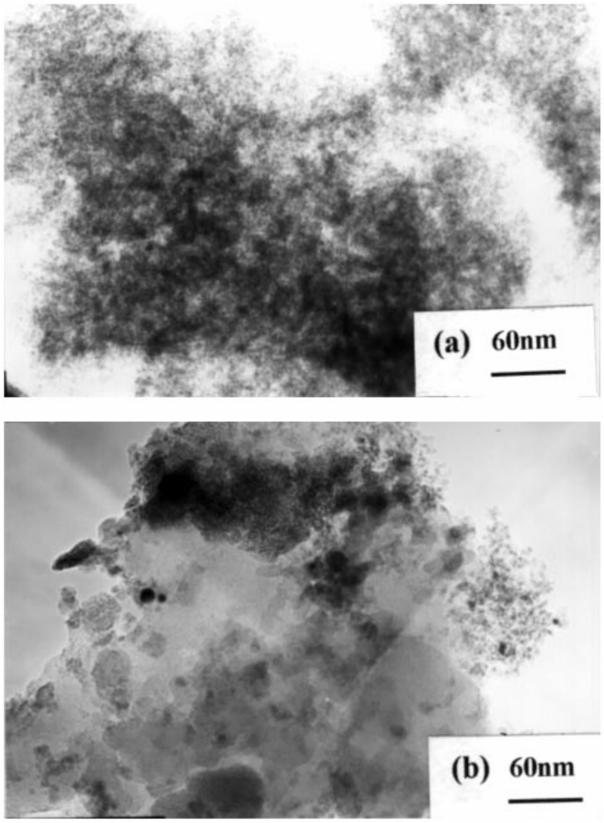

FIG. 1. TEM micrographs of plasma-treated TiO_2 UFP. (a) and (b) are taken from different regions.

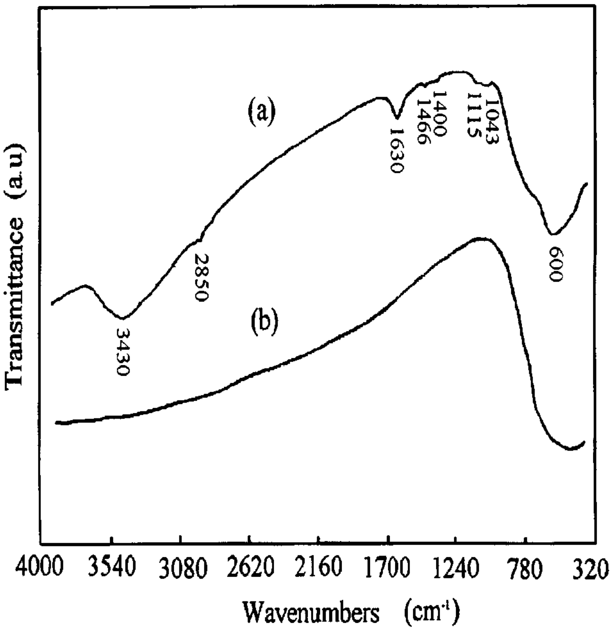

FIG. 2. IR absorption spectrum of TiO_2 UFP; (a) As-prepared TiO_2 UFP; (b) plasma-treated TiO_2 UFP.

about 2 to 50 nm in radius. The as-prepared TiO_2 ultrafine particles are about 2 nm in radius as determined by TEM (19). The IR spectra of the as-prepared and plasma-treated TiO_2 ultrafine particles are shown in Fig. 2. It can be found that the as-prepared TiO_2 UFP are coordinated with TiOH and $TiOC_2H_5$ groups on their surface as demonstrated in Ref 20 in detail, while the plasma-treated TiO_2 UFP contains no TiOH and $TiOC_2H_5$ groups, as shown in Fig. 2. The plasma-sprayed TiO_2 ultrafine particles are a mixture of anatase and rutile, and anatase is the main phase. Plasma spraying is a rapid process, the resident time of TiO_2 UFP in the plasma beam is less than 10^{-3} s, so TiO_2 UFP have little time to grow up. However, the temperature of the plasma beam is as high as 15,000°C (21); thus, the substance coordinated on the surface of TiO_2 UFP is evaporated during the plasma spray process.

The UV-absorption spectrum of plasma-treated TiO_2 UFP is shown in Fig. 3. The absorption band edge of plasma-treated TiO_2 UFP can be estimated around 375nm (3.3 eV) by extrapolating the steep slopes in the curve to the long-wavelength side. Moreover, there is very weak absorption around 400 nm. It was found that the as-prepared TiO_2 UFP exhibited an absorption band edge at 390 nm (ca. 3.2 eV) and had weak absorption at 400–600 nm (16). By comparing the UV-absorption spectrum of plasma-treated TiO_2 ultrafine particles with that of as-prepared TiO_2 ultrafine particles, it can be found that the absorption of TiO_2 ultrafine particles shifts to shorter wavelength and the absorption at 400–600 nm nearly disappears after plasma treatment.

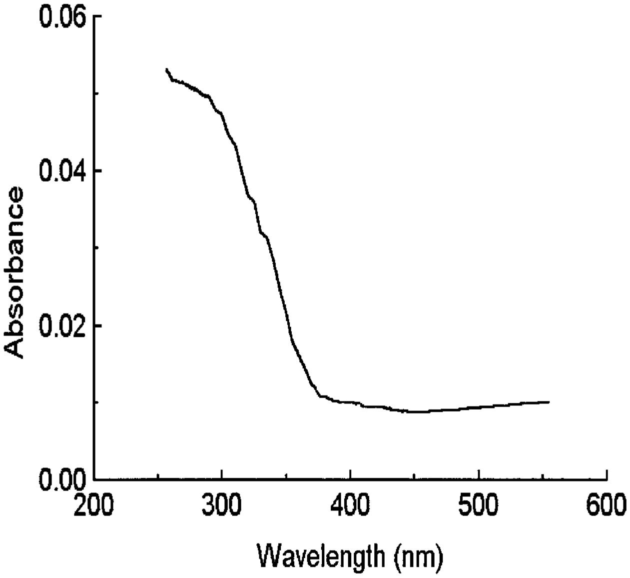

FIG. 3. UV-absorption spectrum of plasma-treated TiO_2 UFP.

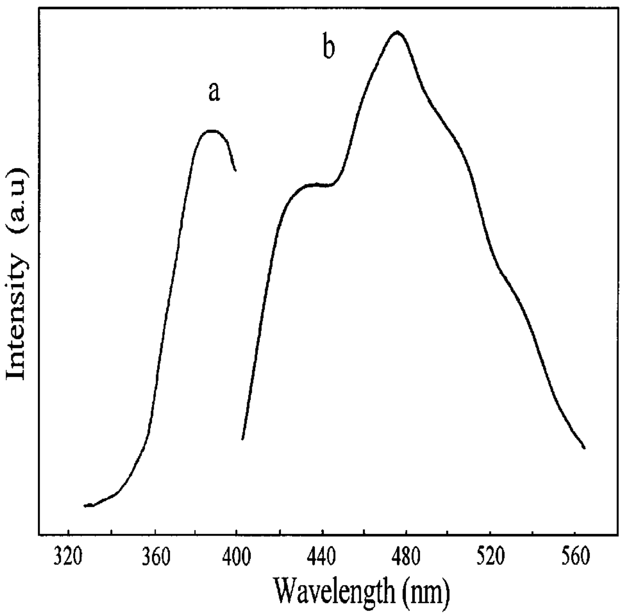

FIG. 4. Luminescence of as-prepared TiO$_2$ UFP. (a) The excitation spectrum of emission at 430 nm; (b) the emission spectrum of excitation at 370 nm.

Figure 4 is the luminescence spectrum of as-prepared TiO$_2$ ultrafine particles. The excitation spectrum of the emission at 430 nm exhibits a peak at 390 nm, which coincides well with the absorption band edge in the diffuse reflection spectra. The emission spectrum of the excitation at 370 nm gives two peaks at 425 and 475 nm. In order to confirm the origin of the 475 nm emission, plasma-treated TiO$_2$ ultrafine particles were also characterized by luminescence. The luminescence of TiO$_2$ ultrafine particles changes dramatically after plasma treatment as shown in Fig. 5. The excitation spectrum of the emission at 430 nm presents an excitation peak at 375 nm, which coincides well with the absorption band edge as shown in Fig. 3. The emission spectrum of excitation at 370 nm gives peaks around 425 nm. The emission band at 475 nm disappears, which is observed for as-prepared TiO$_2$ ultrafine particles in Fig. 4.

DISCUSSION

According to the foregoing experimental results, we have the following facts. The as-prepared TiO$_2$ UFP has a UV–vis absorption edge at about 390 nm, with weak absorption from 400 to 600 nm, and exhibits an excitation peak at 390 nm as well as emission bands at about 425 and 475 nm, while the plasma-treated TiO$_2$ UFP shows a UV–vis absorption edge at about 375 nm, with very weak absorption around 400 nm which may be introduced by the minor rutile phase and larger particles, and exhibit an excitation peak at about 375 nm as well as emission bands at about 425 nm.

UV–vis absorption and excitation spectra confirm that the absorption edge of as-prepared TiO$_2$ UFP is 390 nm, while that of plasma-treated TiO$_2$ UFP is 375 nm. It can be seen that the absorption edge of plasma-treated TiO$_2$ UFP shifts 0.1 eV to shorter wavelength compared with as-prepared TiO$_2$ UFP. Taking the band gap of bulk anatase as 3.2 eV (22), the absorption band edge of plasma-treated TiO$_2$ UFP shifts 0.1 eV to shorter wavelength. Some plasma-treated TiO$_2$ ultrafine particles remain about 2 nm in radius as shown in Fig. 1, which is close to the exciton radius of TiO$_2$ (about 7.5 – 19 Å) (23). Therefore, it is reasonable for the TiO$_2$ ultrafine particles to exhibit a shift of the absorption band edge to shorter wavelength because of the quantum confinement effect (24). Why the as-prepared TiO$_2$ ultrafine particles with radius about 2 nm did not exhibit a shift of absorption band edge to shorter wavelength could be explained by surface groups, i.e., TiOH and TiOC$_2$H$_5$, which formed surface states and led to absorption of longer wavelength (16).

Surface state is introduced by surface structure; i.e., groups coordinated on the surfaces of materials could form electronic states (14). Surface components different from those of bulk component could form surface states (12). Surface state is a major factor influencing the emission of excitons. Bányai reported that with decreasing dot radius and confinement potential, the electron–hole-pair state shifted from a volume state to a surface trapped state, in which

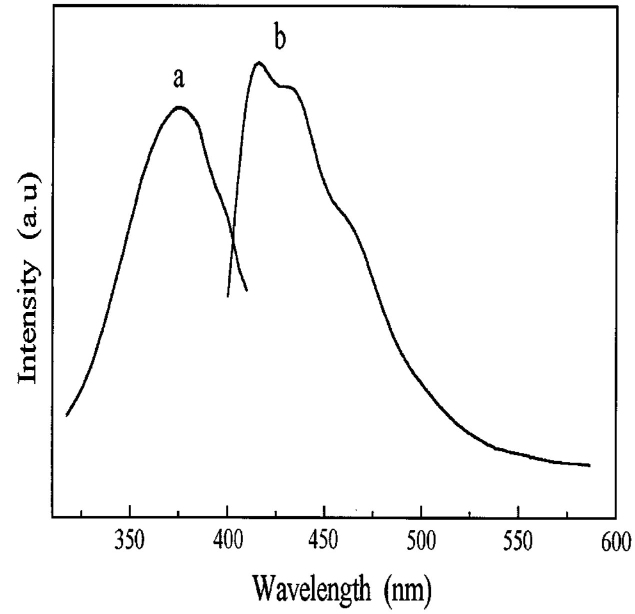

FIG. 5. Luminescence of plasma-treated TiO$_2$ UFP. (a) The excitation spectrum of emission at 430 nm; (b) the emission spectrum of excitation at 370 nm.

the surface polarization caused the carrier to be self-trapped at the surface of the quantum dot (25). Berger reported that compounds at the surface of QDS could weaken the surface potential and therefore change the energy of the surface state (3). Coating the surface of TiO_2 UFP with stearic acid led to emission at 540 nm (2). An intraband surface state assigned to partially coordinated surface titanium atoms could be promoted by chelation of the surface titanium atoms (23). Emission from the surface state relating to TiOH surface groups was also observed (26). Obviously, different surface structures could lead to various surface states.

Groups coordinated on the surface of titania UFP have great influence on the crystallinity of titania particles (20, 27). It was found that OC_2H_5 groups coordinated on the surface of titania UFP groups could lead to the distortion of the crystal structure of titania UFP, enhancing the IR-active modes and weakening the Raman-active modes of TiO_2 UFP (20). Certainly, the energy bands of UFP particles are associated with their crystallinity. The coordinated groups distorted the crystallinity of titania UFP, especially that of the surface component. The distorted surface component formed a surface state energy band, which could lead to absorption at longer wavelengths. When these groups were removed from TiO_2 UFP, these energy bands disappeared and the absorption edge shifted to shorter wavelengths.

The emission of titania varies violently. Deb observed emission at 510 nm with a polycrystalline TiO_2 sample under excitation within a band gap at 77 K (28). Titania with an amorphous phase anchored onto porous Vycor glass gives an emission at 440 nm and anatase powders give a weak emission at 460 nm at 77 K (29). An emission at 485 nm was observed by Haart *et al.* with rutile single crystals at 4.8 K, which was ascribed to bounded exciton emission due to trapping of free excitons by titanate groups near defects (7). The maximum emission bands of titanates ranged from 410 to 530 nm (10). However, it is difficult to observe emission from titania at room temperature.

The results showed that both the as-prepared TiO_2 UFP and the plasma-treated TiO_2 UFP exhibited emission at 425 nm. The emission bands around 425 nm should be assigned to free excitons of TiO_2 ultrafine particles. In previous report (16), an emission band at 418 nm was observed for titania UFP, which was assigned to free exciton emission. The emission band at 425 nm should be the same as the 418-nm emission band. The difference in emission wavelength could be caused by the particle size distribution (1). As in the foregoing discussion, both the as-prepared and the plasma-treated TiO_2 UFP should display a quantum confinement effect, and the quantum confinement effect and the dielectric confinement effect make these emissions possible (8, 9). Conversely, the emission bands around 425 nm confirmed the presence of a quantum-size effect. We also found that when the as-prepared TiO_2 UFP were 5 nm in radius after being sintered at 300°C, no luminescence from the TiO_2 UFP could be found. Since large titania particles did not emit, the emission bands around 425 nm should correspond to ultrafine particles which displayed quantum confinement effects.

The as-prepared TiO_2 UFP exhibited an emission band at about 475 nm, while plasma-treated TiO_2 UFP did not. The emission band at 475 nm is also related to the surface state. As in the forgoing discussion, the quantum confinement effect and the dielectric confinement effect favor the formation of self-trapped states via binding to surface defect states (25). Thus, we intend to assign the emission band at 475 nm to self-trapped states bound to defect states induced by coordinated surface groups. After plasma treatment, these groups are removed and the crystallinity of titania UFP is improved, which leads to loss of the emission center and disappearance of the emission band at 475 nm.

CONCLUSION

The results show that plasma-treated TiO_2 UFP have a wide distribution of about 2 to 50 nm in radius, and the surface groups, i.e., TiOH and $TiOC_2H_5$ groups, are removed. UV-absorption spectra show that the absorption edge of TiO_2 ultrafine particles shifts 0.1 eV to shorter wavelength and the absorption at 400–600 nm disappears after plasma treatment. Luminescence spectra show that as-prepared TiO_2 UFP exhibit two emission bands at 425 and 475 nm with excitation at 370 nm, while plasma-treated TiO_2 UFP only gives emission around 425 nm without emission at 475 nm. Surface states corresponding to TiOH or $TiOC_2H_5$ groups are related to the 475-nm emission and cause an absorption edge shift of as-prepared TiO_2 UFP to longer wavelength.

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