Bright Visible Photoluminescence from Nanotube Titania Grown by Soft Chemical Process

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Bright visible photoluminescence was observed from nanotube titania (or dehydrated nanotube titanic acid) prepared by a soft chemical process. Its photoluminescence comes from the Ti−OH complex within the tubular structure. With the improvement of the crystalline structure and the desorption of physically adsorbed water on the inner and outer surfaces of the nanotube titania by annealing below 662 K, the photoluminescence intensity is enhanced. However, the intensity decreases dramatically if the tubular structure is destroyed at higher annealing temperature, and simultaneously Ti−OH bonds within the nanotube titania are broken. Therefore, the one-dimensional tubular structure is a very important factor for nanotube titania to obtain strong photoluminescence.

I. Introduction

Since the discovery of carbon nanotubes by Iijima in 1991, many other materials have been synthesized with a nanoscale tubular structure.[1−3] The unique electronic and optical properties of one-dimensional semiconductor nanotubes have great significance in both fundamental research and potential applications. For example, nanotube titainia has attracted extensive research for its potential applications in organic light-emitting diodes, photocatalysts, gas sensors, and high-effect solar cells,[4−6] among others.

Visible-light-emitting materials have long been of great interest for semiconductor full-color displays, but they are difficult to synthesize. Recently, strong photoluminescence (PL) has been obtained from one-dimensional materials such as nanotube silica, naotube BN, and nanowire zinc oxide. Such materials might have potential applications in future integrated optical devices. The photoluminescent properties of titania have also been an important subject of research for a long time, as it is known that, compared to bulk titania, nanoparticle titania exhibits stronger photoluminescence, which was attributed to quantum confinement effects or surface states.[7−8] In this article, we report the observation of a very strong visible emission from nanotube titania that is 40 times as great as that of nanoparticle titania, and we believe it is attributable to the one-dimensional tubular structure.

II. Experimental Details

In our experiments, the nanotube titania was synthesized by a simple "soft chemical process".[9] This so-called soft chemical process is a process by which the two-dimensional layer structure of titanate alkali is transformed into the one-dimensional nanotube structure of titania by proton exchange and dehydration at relatively low temperatures. A 120-mL portion of aqueous NaOH solution (40 wt %) was added to a PTFE bottle equipped with a reflux condenser. Then, the bottle was placed in an oil bath, where the solution was heated to 383 K. Two grams of TiO_2 (Degussa P-25, anatase/rutile = 4:1 by weight) was added, and the mixture was refluxed with magnetic stirring for 20 h. After the reaction completed, the mixture was cooled to room temperature, treated with distilled water, and then centrifuged to separate the powder from the solution. This procedure was repeated until the conductivity of the supernatant reached 10 mS/cm (sample A) and 70 μS/cm (sample B). Subsequently, sample B was neutralized with 0.1 M HCl solution to pH ~5; then it was filtered and washed with distilled water until it was free of Cl^-. Thereafter, when the electrical conductivity of the supernatant reached to 800 and 5 μS/cm, the powder samples were collected and denoted as sample C and sample D (nanotube titania), respectively. Transmission electron microscopic (TEM) images were recorded on a JEM-2010 electron microscope. Both PL spectra and Raman spectra were measured with a U-1000 laser Raman spectrometer using the 488 nm line of an Ar^+ laser as the excitation beam. The step lengths were 20 and 2 cm^{-1} for PL and Raman measurements, respectively. Because the amplification of ocular attachment on the Raman spectrometer was 50, the incident power can be established as ~5 mW. A Shimadzu IR-460 spectrometer was used for the infrared (IR) determination of samples in KBr pellets in an in situ IR cell that can be evacuated. Thermogravimetric analysis (TGA) and dif-

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ferential thermogravimetry (DTG) were used to examine weight loss behavior, and the energetics of structural transformations was measured by differential scanning calorimetry (DSC). All of these experiments were performed with an EXSTAR 6000 instrument (Seiko Instruments Inc.) at a heating rate of 10 K/min.

III. Results and Discussion

Figure 1 shows the TEM (transmission electron microscopic) images of sample A, sample D, and nanotube titania after annealing in air at 673 K for 1 h, as well as that of the raw material (P-25). The raw material consisted of granular crystals approximately 20 nm in diameter. The structure of sample A, which was obtained immediately after the alkali treatment, was ribbonlike with a width of about 30−60 nm. In the HCl-treated tubular product, the formation of a tubular structure with an inner diameter of ∼5−7 nm and an outer diameter of ∼7−11 nm was clearly observed. The numbers of walls counted from the two sides of the tube were not identical to that with 2−5 layers. The distance between adjacent layers was about 0.8 nm. The width of a ribbonlike specimen approximately equals the perimeter of the nanotubes. This provides evidence that nanotube titania is rolled up by an alkali-treated specimen with a sheet shape.[5] The tubular structure remained unchanged in air until annealing temperatures reached 673 K.

The nanotube titania can emit high-brightness visible light at room temperature. Figure 2a shows photoluminescence (PL) spectra from nanotube titania and the raw material (P-25). The PL peak from nanotube titania is at ∼2.11 eV with a full width at half-maximum (FWHM) of ∼0.53 eV. The PL intensity from nanotube titania is about 40 times that from nanoparticle titania (P-25), but their PL peaks are in the same position. This implies that the origins of both instances of PL are identical, but the difference between the crystal structures of the two samples made caused variations in the PL efficiency and the number of luminescent centers. The inset of Figure 2a shows the relative PL intensity for different samples in the preparation process. The PL intensity gradually increased with the formation of nanotube titania. The PL spectra of nanotube titania annealed at different temperatures are shown in Figure 2b. The PL peak is blue-shifted to 2.13 eV with a FWHM of ∼0.54 eV as the annealing temperature is increased. This slight shift of the PL peak might be caused by the difference in the crystalline structure as well as the density and the number of emission centers. The PL intensity of nanotube titania increased with annealing temperature below 673 K (in air) and then decreased dramatically as soon as the annealing temperature exceeded 673 K.

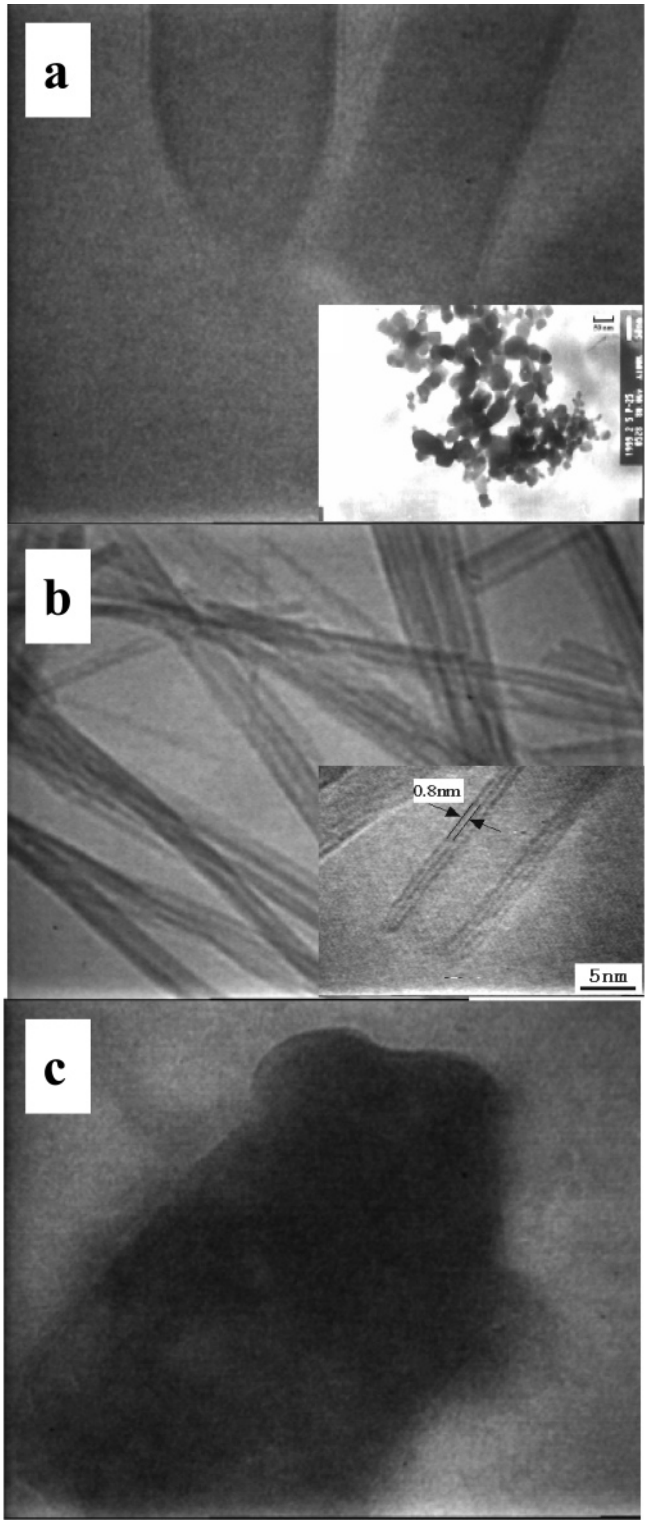

Figure 1. TEM images: (a) Sample A ($\times 4 \times 10^5$); (inset) P-25 ($\times 10^5$). (b) Sample D (nanotube titania) ($\times 2 \times 10^5$); (inset) four-layer nanotube wall with inner and outer diameters of 6.4 and 9.3 nm, respectively ($\times 2 \times 10^6$). (c) Nanotube titania after annealing in air at 673 K for 1 h ($\times 10^5$).

The emission of nanoparticle titania is attributable to the quantum confinement effect or surface states (i.e., Ti−OH). In the case of nanotube silica, the strong emission is also attributed to OH groups on the inner and outer surfaces.[10] To understand the details, further information about the nature of nanotube titania was obtained through infrared (IR) spectroscopy, differential thermogravimetry (DTG), and differential scanning calorimetry (DSC). Figure 3 shows IR spectra of samples of nanotube titania annealled at different temperatures. It can be seen that the deformation and stretching vibrations of the OH group of physisorbed water at 1618 and 3423 cm^{-1} are present in the IR spectrum of nanotube titania. Because of the strong interaction between Ti ions and OH groups within the tubular structure, a

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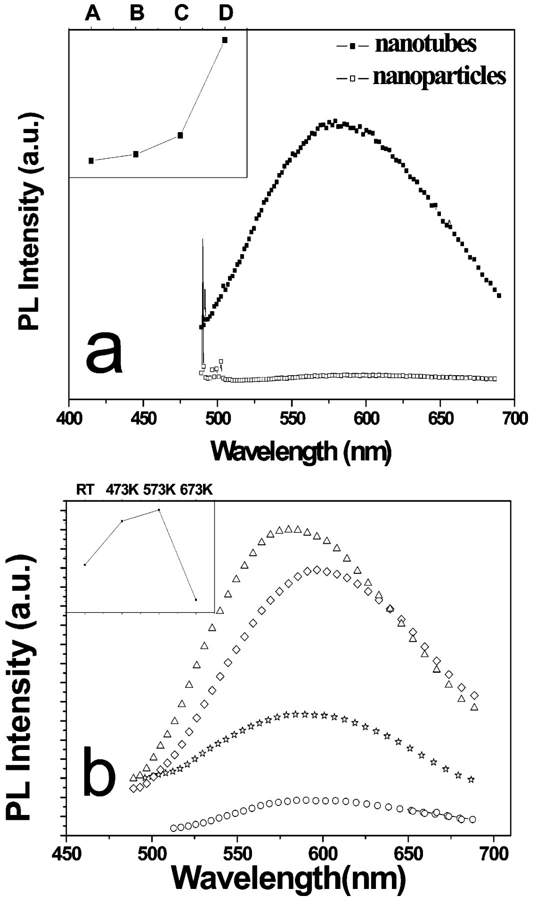

Figure 2. (a) PL spectra from nanotube titania and P-25; (inset) PL intensity of samples A, B, C, and D. (b) PL spectra of nanotube titania annealed at different temperatures (☆, as-prepared; ◇, annealed at 473 K; △, annealed at 573 K; ○, annealed at 673 K); (inset) PL intensity with increasing annealing temperature.

shoulder at 3208 cm^{-1} from Ti−OH bonds was observed. It confirmed that there are a great number of OH groups on nanotube titania but in different states. In contrast, there are only weaker peaks at 1618 and 3423 cm^{-1} in the IR spectra of nanoparticles (not shown here). This means not only that few Ti−OH bonds exist within the tubular structure but also that some physisorbed water exists on the nanotube surface, whereas only physisorbed water existed on nanoparticles. When the annealing temperature is increased, physisorbed water desorbs first, which causes the intensity of the 3423 cm^{-1} peak to decrease as well as the location of the IR peak of OH group stretching vibrations to be shifted to low energy. However, when the annealing temperature exceeded 673 K, the stretching vibrations of the OH group shifted to 3423 cm^{-1} again. This suggests that the Ti−OH bonds within the nanotube titania had been broken. Because the annealed sample was kept in air, adsorbed water was inevitable, and the weak peak at 3423 cm^{-1} still existed. Moreover, the DTG results demonstrate that there are four weight loss peaks at 323, 448, 573, and 662 K, respectively (as shown in Figure 4a). Because no other elements are present except for Ti and O, as indicated by EDS measurements, it can be concluded that there exist different states of H_2O molecules, including dissociated H_2O molecules and physisorbed and chemisorbed H_2O molecules, which correspond to the weight loss peaks at 323, 448, and 573 K, respectively. Figure 4b shows DSC data for nanotube titania. Three endothermic peaks at 333, 445, and 573 K were caused by desorbed water in different adsorbed states, which is consistent with the IR and DTG results for nanotube titania at different annealing temperatures. In addition, one exothermic peak is located at 660 K. From the Raman spectrum, it can be seen that the tubular structure transformed to an anatase-type crystal after annealing at 673 K (as shown in Figure 4c). TEM imagines also showed that the tubular structure of nanotube titania was destroyed upon annealing temperatures over 673 K. Because there is a weight loss peak for the removal of water at 662 K, it can be deduced that Ti−OH bonds must exist within tubular structure. Moreover the Raman spectrum of nanotube titania is similar to that of TiO_2 prepared from $H_2Ti_3O_7$,[11] which confirms that the nanotube material is TiO_2 or dehydrated nanotube titanic acid rather than $H_2Ti_3O_7$.[12] Because two Ti−OH bonds can both shrink to form a Ti−O−Ti group and desorb one molecule of H_2O, exothermic phenomena occur with the phase transition from the tubular structure to anatase. As soon as the tubular structure has been destroyed with increasing annealing temperature, the Ti−OH bonds would be broken and dehydrated from the nanotube titania, causing the destruction of the tubular structure. The Ti−OH complexes within the nanotube titania can act as a luminescent center similar to that in nanoparticle titania, and the emission peaks at ∼2.11 eV. Because the number of Ti−OH complexes within nanotube titania is far

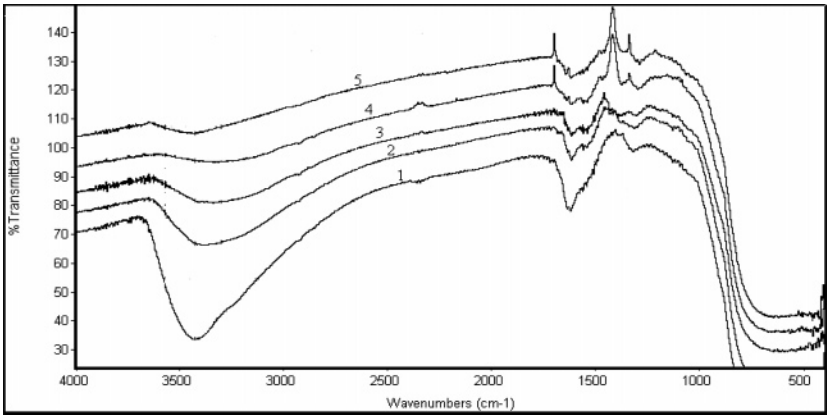

Figure 3. IR spectra of nanotube titania annealed at different temperatures (1, as-prepared; 2, annealed at 373 K; 3, annealed at 473 K; 4, annealed at 573 K; 5, annealed at 673 K).

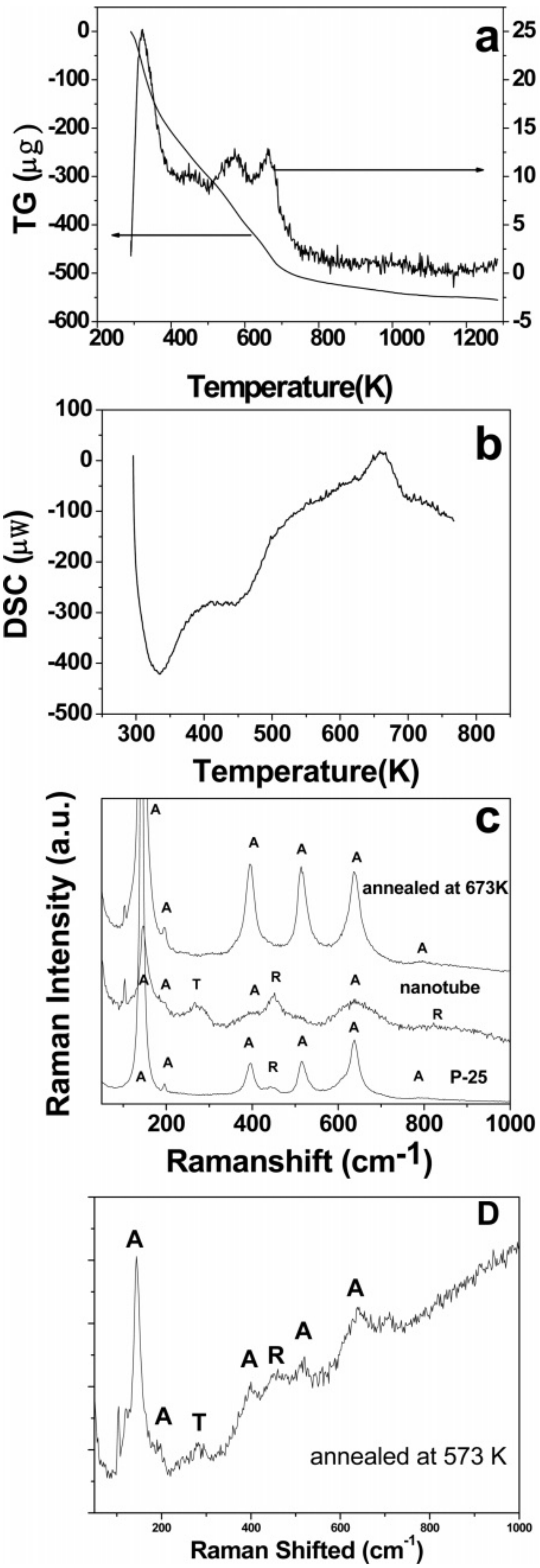

Figure 4. (a) TGA and DTG data for nanotube titania. (b) DSC curves of nanotube titania. (c) Raman spectra of the raw materials, nanotube titania, and nanotube titania annealed at 673 K (A, anatase; R, rutile; T, nanotubes). (d) Raman spectrum of nanotube titania annealed at 573 K.

greater than the number of Ti−OH bonds on the nanoparticle surface, the PL intensity is much stronger. With increasing annealing temperature, physisorbed water for quenching luminescence desorbed from the inner and outer surfaces of the nanotube titania.[13] The relative intensity of the OH group in the IR spectra decreased. Therefore, the PL intensity of nanotube titania increased with annealing temperature below 673 K. From the Raman spectrum of nanotube titania annealed at 573 K (Figure 4d), it can be seen that the Raman peak at 266 cm^{-1} of the nanotube structure still remains and also that the photoluminescence intensity in the background is very strong.[14] After annealing at 673 K, the IR intensity of the OH group changes slightly, but the PL intensity decreases dramatically. Therefore, there must be other factors that can affect the PL intensity.

The breaking and shrinking of Ti−OH bonds within the nanotubes desorbs H_2O and then causes the destruction of the tubular structure after annealing over 673 K. Therefore, the Ti−OH bonds within the tubular structure are very important for the formation and stability of nanotubes. Once these Ti−OH bonds have been broken, the tubular structure is damaged As the size and microstructure of materials are critical factors for the efficiency of PL, a one-dimensional tubular structure with specially curved crystal structures might enhance PL efficiency. With the formation of a tubular structure, the translational symmetry in the TiO_6 octahedron remains along the tube axis but no longer exists around its circumference, becoming a cyclic symmetry. The connecting form of the TiO_6 octahedron is different from nanotubes to nanoparticles. The electronic band structure must have changed so that highly efficient recombination occurred. Thereby, PL from the one-dimensional tubular structure of nanotube titania would be much stronger than that from zero-dimensional nanocrystal titania. When the tubular structure of titania was destroyed, the high PL efficiency originating from the one-dimensional tubular structure was absent; simultaneously, the luminescent center of Ti−OH complexes within tubular structure was reduced. As a result, the PL intensity decreased rapidly after annealing over 673 K.

The XRD results for nanotube titania are shown in Figure 5, demonstrating that nanotube titania is an orthorhombic system with the lattice constants $a_0 = 19.26$ Å and $b_0 = 3.78$ Å, which implies that the tubular structure has a lower symmetry than the anatase and rutile structures. According to the XRD results, after annealing at above 673 K, along with the formation of the anatase phase, the nanotubes have been destroyed. The tubular structure was transformed to an anatase-type structure with a lower symmetry and more corner-sharing TiO_6 octahedra compared with rutile during the phase transition as the sample was annealed at 673 K. The dehydration of Ti−OH induced the change of crystalline form from the orthorhombic system to anatase; at the same time, the nanotube morphology was destroyed. Both of these changes result in the weakening of the nanotube titania's PL emission.

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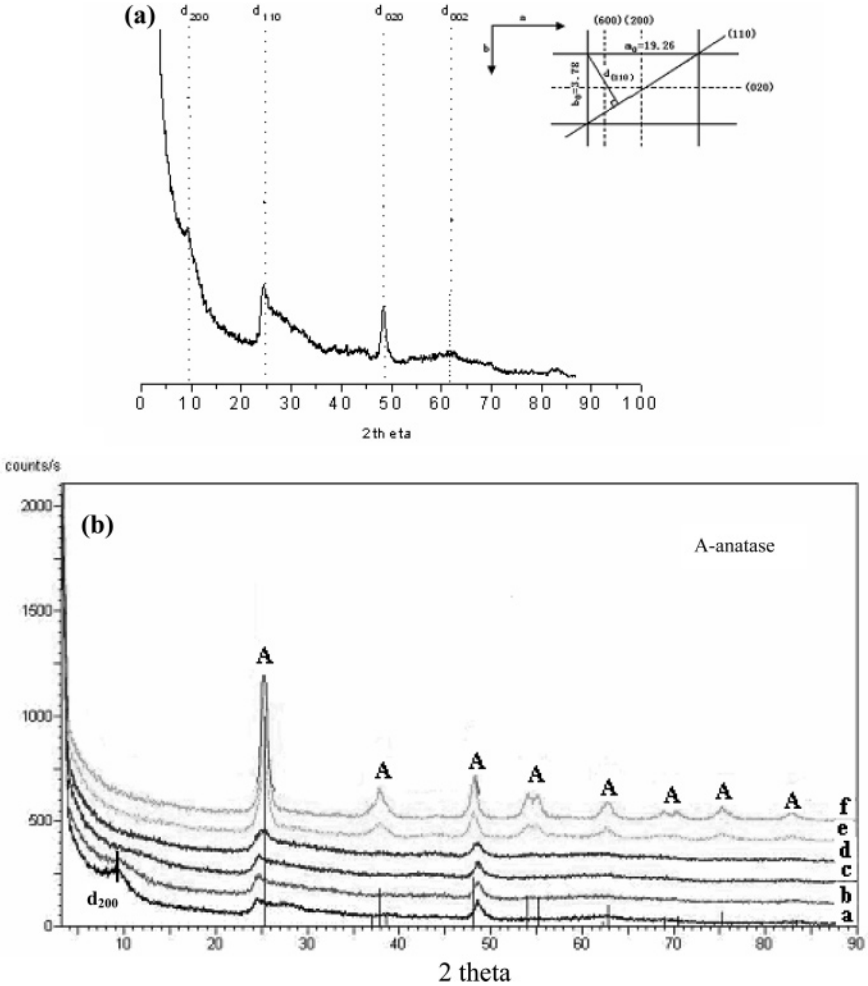

Figure 5. 5. (a) XRD spectra of nanotube titania; (inset) hypothetical schematic view of the orthorhombic system, $X-Y$ direction. (b) XRD spectra of nanotube titania annealed in air at different temperatures for 2 h (a, as-prepared; b, annealed at 373 K; c, annealed at 473 K; d, annealed at 573 K; e, annealed at 673 K; f, annealed at 773 K).

IV. Conclusion

In summary, very strong visible photoluminescence has been observed from nanotube titania with a peak at ∼2.11 eV, and we believe that it is attributable to the presence of Ti−OH complex within the tubular structure. These Ti−OH bonds are not only very important for the formation and stability of nanotube titania, which might improve PL efficiency, but also can act as luminescent centers. The enhanced PL intensity in one-dimensional nanomaterials implies a significant application for the microminiaturization of photoelectric devices.

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