

## Apparent Two-Dimensional Behavior of TiO<sub>2</sub> Nanotubes Revealed by Light Absorption and Luminescence

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Optical absorption and photoluminescence (PL) properties of colloidal TiO<sub>2</sub> nanotubes, produced by the alkali hydrothermal method, were studied at room temperature in the range 300–700 nm. Nanotubes having an internal diameter in the range 2.5–5 nm have very similar optical properties, in contrast to the expected behavior for quasi-1-D systems. This is explained by the complete thermal smearing of all 1-D effects, due to the large effective mass of charge carriers in TiO<sub>2</sub>, resulting in an apparent 2-D behavior of TiO<sub>2</sub> nanotubes.

Dimensionality has a profound effect on the behavior of solids. An additional quantisation of electronic states accompanying a reduction of dimensionality from 3-D to 2-D or from 2-D to 1-D results in dramatic changes to the electronic structure of the material. The best known systems<sup>1</sup> where such transformations have been studied are carbon-based materials, including schwarzite<sup>2</sup> (3-D), graphite (2-D), nanotubes (quasi 1-D), and fullerene (0-D). A reduction of dimensionality results in a qualitative change in physical-chemical properties, e.g., appearance of new optical bands and crystal structure change. For small particles within the same dimension, variation in particle size usually results in quantitative change of properties, e.g., melting temperature,<sup>3</sup> solubility,<sup>4</sup> band gap, etc. Since the discovery of quantum size effects in 1986,<sup>5</sup> many successful attempts have been made to experimentally observe size dependent electronic structure properties of diverse nanosized 3-D materials.<sup>6</sup> Such materials attract attention because of their possible application in many aspects of nanotechnology. A better understanding of their electronic properties could also significantly improve our theoretical knowledge in nanosized solid-state physics.

Titanium dioxide is one of the most studied materials and has been used in several applications,<sup>7</sup> including photocatalysis, photovoltaic cells, sensors, and electronic devices, etc. Titanium dioxide nanoparticles show a relatively small apparent band gap blue shift<sup>8,9</sup> (<0.1–0.2 eV) caused by quantum size effects for spherical particles sizes down to 2 nm. Such small effects are mainly due to the relatively high effective mass of carriers in TiO<sub>2</sub> and an exciton radius in the approximate range 0.75–1.90 nm,<sup>10</sup> such that only very small particles could possess an

increased band gap. Serpone et al.<sup>11</sup> have suggested that such a small blue shift of the band gap is due to the appearance of direct electronic transitions for small particles rather than to quantum confinement effects. The absence or weakness of quantum size effect has also been reported for other materials.<sup>12</sup>

Recently,<sup>13</sup> a new form of TiO<sub>2</sub> exhibiting a two-dimensional structure, lepidocrocite TiO<sub>2</sub> flat nanosheets, was produced by exfoliation of layered protonic titanates.<sup>14</sup> The revealed<sup>15</sup> electronic band structure of these nanosheets was compared with the calculated<sup>16</sup> one. It was shown that the band gap of nanosheets is strongly blue shifted relative to the band gap of bulk TiO<sub>2</sub>, due to lower dimensionality, i.e., a 3-D to 2-D transition. Also, it was demonstrated that similar TiO<sub>2</sub> nanosheets could be transformed to TiO<sub>2</sub> nanotubes in the presence of sodium ions,<sup>17</sup> resulting in additional loss of dimensionality, i.e., a 2-D to 1-D transformation. The true 1-D titania structure of TiO<sub>6</sub> octahedrons incorporated into the ETS-10 zeolites was also reported recently.<sup>18</sup> The problem of reduced dimensionality and its effect on the physical, and especially the optical parameters, of TiO<sub>2</sub> is important as this material is widely used in optoelectronic devices. Although the optical and PL spectra of 3-D and 2-D forms of TiO<sub>2</sub> have been studied, little is known about the optical properties of TiO<sub>2</sub> nanotubes.

In this paper, we present systematic studies of the effect of particle diameter of nanotubular TiO<sub>2</sub> on their optical properties. The average internal diameter of nanotubes in this work varies from 2.5 to 5 nm. The results obtained are compared with calculated changes of electronic band structure for multilayered concentric wall quasi 1-D nanotubes and for 2-D nanosheets.

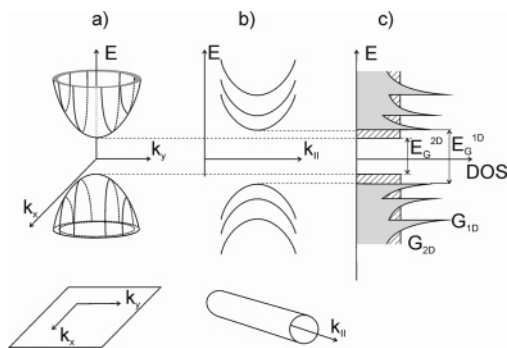
The method of preparation of the TiO<sub>2</sub> nanotubes was based on alkali hydrothermal transformation.<sup>19</sup> The diameter of TiO<sub>2</sub> nanotubes was adjusted by choosing the mass of initial TiO<sub>2</sub> powder or temperature during preparation.<sup>20</sup> Titanium dioxide (anatase) was added to 10 M NaOH solution and heated for 22 h at 140 °C. The white, powdery TiO<sub>2</sub> was thoroughly

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**Figure 1.** Schematic presentation of the transformation of the electron band structure of the nanosheet semiconductor accompanying the formation of nanotubes: (a) band diagram of 2-dimensional nanosheet, (b) band diagram of quasi-1-dimensional nanotubes, (c) energy density of states for nanosheets ( $G_{2D}$ ) and nanotubes ( $G_{1D}$ ).  $E_G^{1D}$  and  $E_G^{2D}$  are band gaps of 1-D and 2-D structures, correspondingly (see eq 5).  $k_x$  and  $k_y$  are the wave vectors.

washed with water then with 0.05 M  $H_2SO_4$ , followed by vacuum-drying at 80 °C. For the determination of nanotube diameter, the correlation<sup>20</sup> between average diameter determined from TEM histogram and average pore size determined from nitrogen adsorption data was used. The BJH pore size distribution of the  $TiO_2$  nanotubes was measured, using a Micromeritics ASAP 2010 instrument. Colloidal  $TiO_2$  was prepared by taking 0.1 g of powder suspended in 20 mL of distilled water at room temperature for 30 min using an ultrasonic bath. The precipitate was separated from the colloidal solution by decanting. The colloidal dispersion contains less than 1% of unfolded nanosheets and imperfect tubes.<sup>20</sup> Photoluminescence spectra of colloidal  $TiO_2$  were measured using a Perkin-Elmer Luminescence Spectrometer LS 50B to an accuracy of  $\pm 0.5$  nm. Samples of  $TiO_2$  colloids were diluted with distilled water to achieve an absorption of 0.5 at the excitation wavelength. Absorption spectra were measured using a Shimadzu UV-1601 spectrophotometer.

The mechanism of formation of  $TiO_2$  nanotubes and their exact structure are currently disputed.<sup>20,21</sup> There are at least three possible structures of nanotubes distinguished by the structure of nanotube walls: “spiral” (which can be produced by scrolling of a single layered nanosheet), “onion” (which can be realized by the curving of nanosheets to form a seam), and “concentric” (which can be produced by curving of conjoined nanosheets (see Figure 1 in ref 20 for details). We present electronic band structure calculations for nanotubes with a concentric structure of multilayered walls. Similar calculations for “spiral” and “onion” structures will result in similar formulas for the zone structure; only the scale of the effects will be smaller. It was found previously that the majority of tubes have an ideal concentric structure.

It is natural to expect that a reduction of dimensionality accompanying the formation of nanotubes from a 2-D material would result in a dramatic change of the energy spectrum, which, in turn, should result in a drastic modification of many of the electronic properties. Indeed, when a 2-D sheet is rolled up to form a nanotube the wave vector along the circumferential ( $k_{\perp}$ ) direction becomes quantized, such that

$$k_{\perp} = \frac{2\pi n}{d} \quad (1)$$

where  $d$  is the nanotube diameter and  $n$  is an integer. At the same time, the wave vector along the tube axis ( $k_{\parallel}$ ) remains continuous. Due to this quantization, the energy bands that are

produced by the surfaces in the  $k$ -space in a 2-D case, are reduced to a set of sub bands. This is illustrated in Figure 1a, where the valence and conduction bands of a 2-D semiconductor are schematically represented by two paraboloids. The energy spectrum of nanotubes in this case is a set of parabolas (Figure 1b), which are cross-sections of the 2-D bands by a set of parallel planes, each of which corresponds to a different value of the quantized vector  $k_{\perp}$  and is oriented perpendicular to the  $k_{\perp}$  vector. The separation of the subbands along both the  $k_{\perp}$  and energy axes depends on the nanotube diameter, increasing when  $d$  decreases.

Within the effective mass model, the energy spectrum of 2-D  $TiO_2$  sheets can be described by<sup>22</sup>

$$E_{2D}^{\pm} = \pm \frac{E_G}{2} \pm \frac{\hbar^2 k^2}{2m_{e,h}} \quad (2)$$

where the “plus” and “minus” signs correspond to the conduction and valence bands respectively,  $E_G$  is the energy gap,  $\hbar$  is the Planck’s constant,  $m_e$  and  $m_h$  are effective masses of electrons and holes, respectively. The electronic band structure of a  $TiO_2$  nanotube, can be obtained from this relation by zone-folding and is given by a series of quasi 1-D sub bands with different indices  $n$  (Figure 1b):

$$E_{n,1D}^{\pm}(k) = \pm \frac{E_G}{2} \pm \frac{\hbar^2}{2m_{e,h}} \left[ k_{\parallel}^2 + \left( \frac{2\pi n}{d} \right)^2 \right] \quad (3)$$

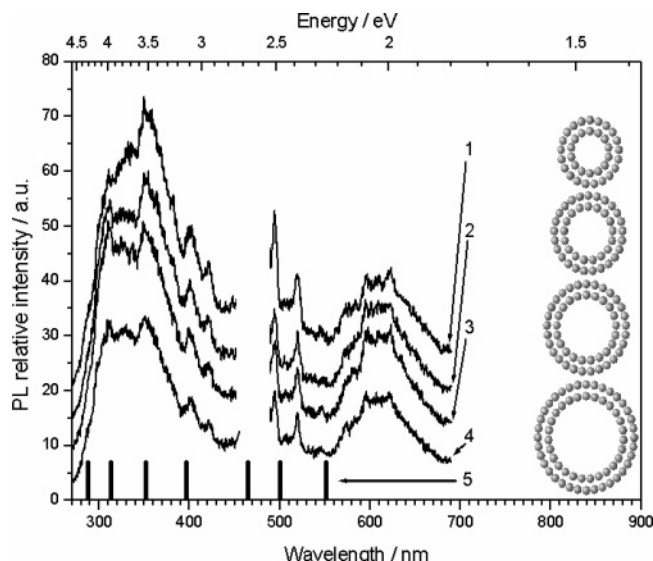
This transition from the 2-D to quasi 1-D energy spectrum has a dramatic effect on the energy density of states. In the 2-D case, the density of states,  $G_{2D} = m_{e,h}/\pi\hbar^2$ , has a constant value<sup>22,23</sup> for energies outside the energy gap (see Figure 1c). In the quasi 1-D case, however, the density of states of each sub-band

$$G_{n,1D}(E) = \pm \left\{ \frac{m_{e,h}}{2\pi^2\hbar^2 [E - E_n(0)]} \right\}^{1/2} \quad (4)$$

diverges at the band edge  $E_n(0)$  leading to van Hove singularities.<sup>22</sup> The resulting density of state is formed by a series of sharp peaks with long overlapping tails (Figure 1c). The energy gap between the valence and conductance bands in the quasi-1-D case is larger than that in the parental 2-D material and the difference increases with decreasing diameter of the nanotube.

All of these transformations in the energy spectrum that accompany a reduction in the dimensionality of a semiconductor from 2-D to quasi 1-D structure have been investigated in great detail for carbon nanotubes.<sup>24,25</sup> In such nanotubes the energy band gap increases as their diameter,  $d$ , decreases as  $E_G = 0.4d^{-1}$  [eV nm<sup>-1</sup>].<sup>1</sup> Van Hove singularities in the energy density of states of carbon nanotubes result in a strong modification of their optical properties in comparison with that of two-dimensional graphite. Optically induced transitions between peaks of the density of states are clearly seen as sharp peaks on absorption and photoluminescence spectra.<sup>26,27</sup> Photoluminescence was found to be a particularly useful tool for the identification of the diameter and chirality of nanotubes<sup>27</sup> because the positions of photoluminescence peaks are strongly dependent on these parameters.

The typical spectrum of trapped state emission in 3-D spherical nanoparticles of  $TiO_2$  ( $d = 3$  nm) has wide bands at 445 nm and at 550 nm that do not show sharp peaks.<sup>28</sup> Photoluminescence spectra of quasi 1-D  $TiO_2$  nanotubes of controlled internal diameter are presented in Figure 2. The



**Figure 2.** Photoluminescence spectra of colloidal  $\text{TiO}_2$  nanotubes of different mean diameters: (1) 2.5 nm, (2) 3.1 nm, (3) 3.5 nm, (4) 5 nm. Room temperature, excitation wavelength 237 nm, slits width 5 nm. The range of wavelength 455–490 nm in the spectra is omitted due to the high signal of second harmonic from scattered excitation light. The curves are shifted vertically for clarity. Vertical lines (5) show position of peaks in PL spectrum of nanosheets<sup>13</sup>

spectra show several sharp bands in the wide range of wavelengths. The positions and relative intensity of all of these bands are practically identical and do not depend on the average internal diameter of nanotubular  $\text{TiO}_2$ . The shape and position of some peaks in the luminescence spectrum are similar to peaks in the luminescence spectrum of the colloidal solution of exfoliated  $\text{TiO}_2$  nanosheets<sup>13</sup> (see Table 1). The best match is for the peaks in a range of shorter wavelengths, 300–400 nm. In the longer wavelength range, 500–600 nm, luminescence peaks for  $\text{TiO}_2$  nanotubes differ from the long wavelength luminescence peaks of  $\text{TiO}_2$  nanosheets. This could be attributable to the nature of these low energy states as cations can be incorporated between two or more nanosheets<sup>29</sup> and the spectra consequently depend on the composition of surrounding media. Indeed,  $\text{TiO}_2$  nanotubes produced by hydrothermal alkali treatment contain residual amount of sodium ions<sup>30</sup> whereas  $\text{TiO}_2$  nanosheets produced by exfoliation of layered titanates can be contaminated with cesium and tetrabutylammonium ions.<sup>14</sup> Because luminescence from low energy states is very sensitive to the presence of cations in the solution, differences in the luminescence spectrum between nanotubes and nanosheets at longer wavelengths may be due to cation incorporation. A systematic comparison of PL spectra of  $\text{TiO}_2$  nanotubes with those of nanosheets and a study of the effect of addition of different ions or quenchers on the PL of  $\text{TiO}_2$  nanostructures is the subject of continuing studies.

It was also found that the PL excitation spectra of  $\text{TiO}_2$  nanotubes (see Figure 3b) do not depend on the diameter of nanotubes, indicating that not only the position of radiative states but also the position of absorption states remains the same for nanotubes of different diameter. In the PL excitation spectrum, several characteristic and relatively intensive sharp bands are seen at 5.22 eV (237 nm) and 4.84 eV (256 nm). These two bands are a good fit to those calculated by the DFT method<sup>16</sup> and the optical absorption spectrum of single layered  $\text{TiO}_2$  for polarization parallel to *b*-axis has two characteristic bands 240 and 260 nm. (see Table 1) This may indicate that rolling of nanosheets to form nanotubes occurs along the *b*-axis results in

a very high dichroism for nanotubes. Such a high dichroism has been observed for  $\text{TiO}_2$  nanosheets.<sup>31</sup>

The measured absorption spectra of  $\text{TiO}_2$  nanotubes are presented in Figure 3a. The absorption spectrum is very broad and has two features at 250 and 285 nm. The position of these two features does not change for nanotube samples of different internal diameter, indicating the absence of systematic size dependent changes. These absorption spectra are also similar to the spectra of  $\text{TiO}_2$  nanotubes suspended in absolute ethanol solution.<sup>32</sup>

According to Figure 4 the increase of average internal diameter of  $\text{TiO}_2$  nanotubes results in an increase of average thickness of multilayered walls in tubes, which is proportional to the number of layers in multilayered wall. Recently,<sup>15</sup> it has been observed that an increase in the number of layers in multilayered  $\text{TiO}_2$  films (produced by deposition of single layer nanosheets) does not change the electronic structure of this film, which is similar to the case of single layer nanosheets. The stacking several nanosheets does not effect the electronic properties of the solid, probably, due to the weak electronic interaction between layers. A similar situation probably exists in the case of  $\text{TiO}_2$  nanotubes.

All of the above experimental results for  $\text{TiO}_2$  nanotubes, which show an apparent independence of optical absorption and PL spectra on the nanotube diameter, are in marked contrast with the behavior of carbon nanotubes. The theoretical treatment of a transition from a 2-D to a quasi 1-D semiconductor, as described above, is quite generic, requiring a certain similarity in the behavior of the both materials. This apparent contradiction between experimental and theoretical results arises because the magnitude of the effects is material dependent. For example, the change in the energy gaps after rolling of a nanosheet to a nanotube is

$$\Delta E_G = E_G^{\text{1D}} - E_G^{\text{2D}} = \frac{2\hbar^2}{d^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \quad (5)$$

In  $\text{TiO}_2$  the effective mass of charge carriers is large. According to different sources, the effective masses of electrons  $m_e$  can vary between  $5m_0$ <sup>33</sup> and  $30m_0$ <sup>34</sup> and mass of holes  $m_h$  is more than  $3m_0$ .<sup>11,35,36</sup> Taking  $m_e = 9m_0$  and  $m_h = 3m_0$ , we obtain 8 meV as the difference between energy gaps of nanotubes with diameters 2.5 and 5 nm. The energy difference between two first peaks in the density of states  $G_{\text{1D}}(E)$  (see Figure 1) is less than 24 meV for  $d = 2.5$  nm and 6 meV for  $d = 5$  nm. The obtained values are too small to be resolved in room-temperature experiments. Both the shift of band gaps and the  $G_{\text{1D}}(E)$  peaks should be completely smeared by thermal fluctuations that have an amplitude  $kT = 26$  meV. Quasi 1-D behavior could be recovered at low temperatures as soon as thermal fluctuations are suppressed and such cryogenic studies are the subject of further investigations. In contrast, the effective mass of charge carriers in semiconducting carbon nanotubes is much smaller than in  $\text{TiO}_2$  nanotubes ( $0.02 m_0$  for semiconducting zigzag nanotubes having a diameter of 2 nm<sup>37</sup>). This results in a strong manifestation of all 1-D properties for carbon nanotubes, one of which is a pronounced dependence of the photoluminescence peak positions on the nanotube diameter.

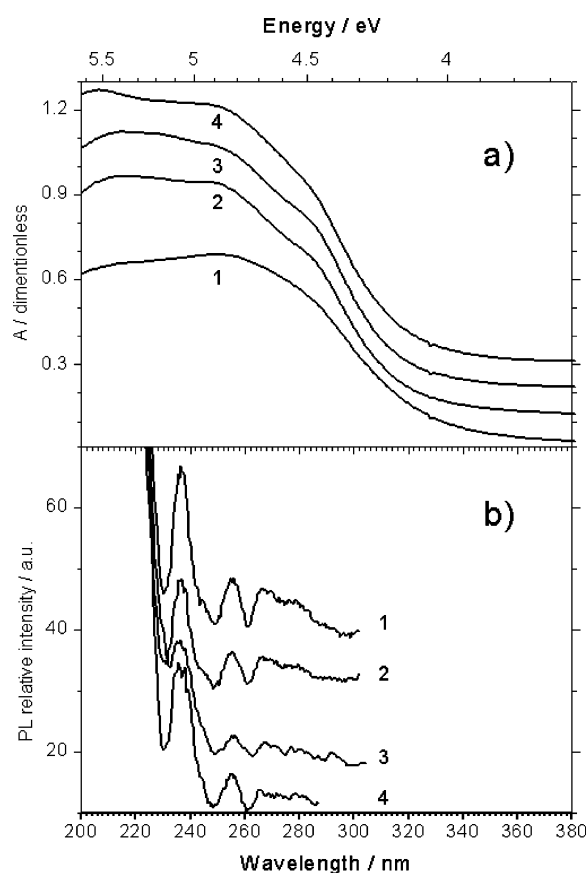
The large effective mass of charge carriers together with the size distribution of diameters in real  $\text{TiO}_2$  nanotubes samples should result not only in smearing out of all quasi 1-D features in nanotubes but also in making their behavior practically identical to that of 2-D sheets. Our experimental results show that  $\text{TiO}_2$  nanotubes have the same band gap (3.87 eV) as  $\text{TiO}_2$



**TABLE 1: Comparison of Energy Bands of TiO<sub>2</sub> Nanotubes with TiO<sub>2</sub> Nanosheets**

PL emission bands					energy bands					
nanotube		nanosheet <sup>13</sup>		match	nanotubes PL excitation		nanotubes absorption		nanosheets absorption	
nm	eV	nm	eV		nm	eV	nm	eV	nm	eV
310	3.99	288	4.29	yes	237	5.22	252	4.91	266 <sup>13</sup>	4.45
328	3.77	313	3.96		256	4.84	286	4.33	240 <sup>a</sup>	5.16
350	3.54	352	3.52		267	4.64			260 <sup>a</sup>	4.76
400	3.09	397	3.12	yes	279	4.44			305 <sup>a</sup>	4.06
421	2.94									
<i>b</i>		465	2.66	yes						
494	2.51	500	2.48							
520	2.38									
		551	2.25							
573	2.16									
595	2.08									
622	1.99									

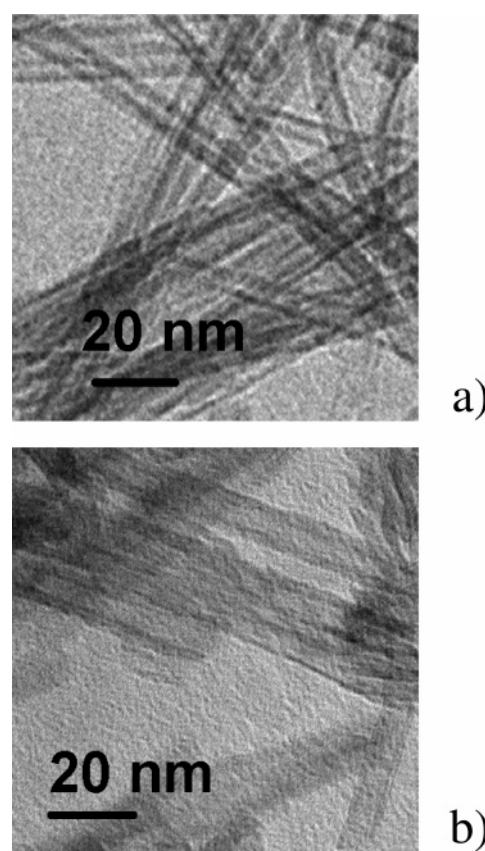
<sup>a</sup> Calculated in ref 16 for polarization parallel to *b* axis. <sup>b</sup> The range of wavelength 455–490 nm was removed due to the scattered light signal.



**Figure 3.** (a) Absorption spectrum and (b) luminescence excitation spectrum (wavelength of emission light is 400 nm) of colloidal TiO<sub>2</sub> nanotubes of different mean diameters: (1) 2.5 nm, (2) 3.1 nm, (3) 3.5 nm, (4) 5 nm. Path length: 1 cm. *T* = 295 ± 2 K. The curves are shifted vertically for clarity.

nanosheets (3.84 eV according to Sakai and colleagues<sup>15</sup>) and similar PL spectra (see Figure 2).

In conclusion, optical absorption and luminescence studies have shown that changing the internal diameter of TiO<sub>2</sub> nanotubes in the range 2.5–5 nm does not change the position of absorption and emission bands. The electronic structure of TiO<sub>2</sub> nanotubes is very close to that of TiO<sub>2</sub> nanosheets. Theoretical analysis of electronic band structure of the nanotubes shows that a decrease in the nanotube diameter from 5 to 2.5 nm results in a small increase in the energy gap (≤8 meV) making it impossible to detect the quantum size effect in TiO<sub>2</sub>



**Figure 4.** TEM images of TiO<sub>2</sub> nanotubes of mean diameters (a) 2.5 nm and (b) 5 nm.

nanotubes at room temperatures. Characteristic peaks in the quasi 1-D density of states cannot be resolved at room temperature due to thermal smearing. As a result, two-dimensional optical properties dominate in TiO<sub>2</sub> nanotubes.

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## References and Notes

- (1) Benedek, G.; Bernasconi, M. *Dekker Encyclopaedia of Nanoscience and Nanotechnology*; Marcel Dekker: New York, 2004; p 1235.
- (2) Barborini, E.; Piseri, P.; Milani, P.; Benedek, G.; Ducati, C.; Robertson J. *Appl. Phys. Lett.* **2002**, *81*, 3359

- (3) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
- (4) Vucenilovic, M. I.; Vukelic, N.; Rajh, T. *J. Photochem. Photobiol.* **1988**, *42*, 157.
- (5) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555.
- (6) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
- (7) Fujishima, A.; Hashimoto, K.; Watanabe, T. *TiO<sub>2</sub> Photocatalysis*; Bkc, Inc.: Tokyo, Japan, 1999.
- (8) Li, Y.; White, T. J.; Lim, S. H. *J. Solid State Chem.* **2004**, *177*, 1372.
- (9) Reddy, K. M.; Reddy, C. V. G.; Manorama, S. V. *J. Solid State Chem.* **2001**, *158*, 180.
- (10) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *J. Phys. Chem.* **1988**, *92*, 5196.
- (11) Serpone, N.; Lawless, D.; Khairutdinov, R. *J. Phys. Chem.* **1995**, *99*, 16646.
- (12) Masui, T.; Fujiwara, K.; Machida, K.; Adachi, G.; Sakata, T.; Mori, H. *Chem. Mater.* **1997**, *9*, 2197.
- (13) Sasaki, T.; Watanabe, M. *J. Phys. Chem. B* **1997**, *101*, 10159.
- (14) Sasaki, T. *Supramol. Sci.* **1998**, *5*, 367.
- (15) Sakai, N.; Ebina, Y.; Takada, K.; Sasaki, T. *J. Am. Chem. Soc.* **2004**, *126*, 5851.
- (16) Sato, H.; Ono, K.; Sasaki, T.; Yamagishi, A. *J. Phys. Chem. B* **2003**, *107*, 9824.
- (17) Ma, R.; Bando, Y.; Sasaki, T. *J. Phys. Chem. B* **2004**, *108*, 2115.
- (18) Uma, S.; Rodrigues, S.; Martyanov, I. N.; Klabunde, K. J. *Microporous Mesoporous Mater.* **2004**, *67*, 181.
- (19) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Adv. Mater.* **1999**, *11*, No. 15, 1307.
- (20) Bavykin, D. V.; Parmon, V. N.; Lapkin, A. A.; Walsh, F. C. *J. Mater. Chem.* **2004**, *14*, 3370.
- (21) Zhang, S.; Peng, L.-M.; Chen, Q.; Du, G. H.; Dawson, G.; Zhou, W. Z. *Phys. Rev. Lett.* **2003**, *91*, 25, 256103.
- (22) Kittel, C. *Introduction to Solid State Physics*, 8th ed.; Wiley: New York, 2005.
- (23) Hook, J. R.; Hall, H. E. *Solid State Physics*; Wiley: New York, 2003.
- (24) Hagen, A.; Hertel, T. *Nano Lett.* **2003**, *3*, 383.
- (25) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*; Eds.; Springer-Verlag: Berlin, 2001.
- (26) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. *Science* **2002**, *297*, 593.
- (27) Bachilo, S. M.; Strano, M. S.; Kittrell, C.; Hauge, R. H.; Smalley, R. E.; Weisman, R. B. *Science* **2002**, *298*, 236.
- (28) Ghosh, H. N.; Adhikari, S. *Langmuir* **2001**, *17*, 4129.
- (29) Xin, H.; Ma, R.; Wang, L.; Ebina, Y.; Takada, K.; Sasaki, T. *Appl. Phys. Lett.* **2004**, *85*, 4187.
- (30) Yang, J. J.; Jin, Z. S.; Wang, X. D.; Li, W.; Zhang, J. W.; Zhang, S. L.; Guo, X. Y.; Zhang, Z. J. *Dalton Trans.* **2003**, *20*, 3898.
- (31) Sato, H.; Hiroe, Y.; Sasaki, T.; Ono, K.; Yamagishi, A. *J. Phys. Chem. B* **2004**, *108*, 17306.
- (32) Hong, J.; Cao, J.; Sun, J.; Li, H.; Chen, H.; Wang, M. *Chem. Phys. Lett.* **2003**, *380*, 366.
- (33) Pascual, J.; Camassel, J.; Mathieu, H. *Phys. Rev. B: Condens. Matter* **1978**, *18*, 5606.
- (34) Boudreaux, D. S.; Williams, F.; Nozik, A. J. *J. Appl. Phys.* **1980**, *51*, 2158.
- (35) Kasinski, J. J.; Gomez-Jahn, L. A.; Faran, K. J.; Gracewski, S. M.; Miller, Dwyane, R. J. *J. Chem. Phys.* **1989**, *90*, 1253.
- (36) Real values of effective masses of carriers in nanotubes could be even larger due to a stronger localization in nanostructures.
- (37) Pedersen, T. G. *Phys. Rev. B* **2003**, *67*, 073401.