Blue Light Emitting Nanosized TiO_2 Colloids

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Nanometer-scale materials have been intensively studied and have given rise to a new generation of various devices in recent years.[1−3] Particle size has a significant effect (the so-called quantum-size effect) on the electronic, magnetic, and optical properties of semiconducting solids when their size, in at least one dimension, becomes comparable with the exciton (Bohr) radius (1−10 nm).[4] A number of semiconductors such as CdS,[5] ZnS,[6] and ZnO[7] have been shown to exhibit spectral blue shifts in the absorption band edge as a consequence of exciton confinement with decreasing particle size. In general, the preparation of colloidal TiO_2 typically results in particles with diameters between approximately 5 and 20 nm exhibiting physical properties of the bulk.[4,8] Several recent accounts[3,7,9] have claimed quantum-size effects in very small TiO_2 colloid particles ($d < 3$ nm), while most of the emitted light from such colloidal TiO_2 extends into the near-infrared region (1.5−1.24 eV) far beyond the bandgap energy (3.2 eV).

In this report, we describe a method for the synthesis of very small ($d \approx 3$ nm) TiO_2 colloidal solutions with a yellow-green color. It will be demonstrated that the yellow-green color of the TiO_2 colloidal solution, in contrast to that of ordinary transparent or opaque solutions, results from the luminescence of the bandgap.

In a typical preparation of cationic TiO_2 complex, reagent grade $TiCl_4$ cooled to 1 °C was slowly added dropwise to a flask, kept in an ice bath, containing 6 M aqueous HCl under vigorous stirring to make the resulting solution 0.5 M in $TiCl_4$. The immediate formation of a transparent colloidal dispersion was observed. The solution was covered with several pieces of aluminia paper and aged at room temperature, and then at 80 °C in an oven, each for 4 h. The TiO_2 colloidal solution began to appear light green after aging at 80 °C for 1 h, and became a shiny green-yellow after aging overnight at 80 °C. The green-yellow TiO_2 colloidal solution was stable for at least seven months without any added stabilizers. The particle size ranges from 2 to 4 nm, and the average size in the dispersion was 3 nm as revealed by TEM micrographs.

UV−vis spectroscopy (Hitachi U-2001) was used to characterize the optical absorbance of the colloidal solution. The absorption and the corresponding bandgap energy of TiO_2 are $\lambda_{OS} = 385$ nm and $E_g = 3.2$ eV for anatase[10] and $\lambda_{OS} = 415$ nm and $E_g = 3.0$ eV for rutile.[11] Figure 1 shows the UV−vis absorption spectrum of the TiO_2 colloidal solution, where the onset of absorption appears at 370 nm or 3.35 eV. A blue shift of approximately 0.15 eV relative to bulk anatase TiO_2 is evident for the synthesized ultrasmall TiO_2 colloids. There is no optical absorption at $\lambda > 370$ nm, suggesting that the color may result from the luminescence of TiO_2 colloids.

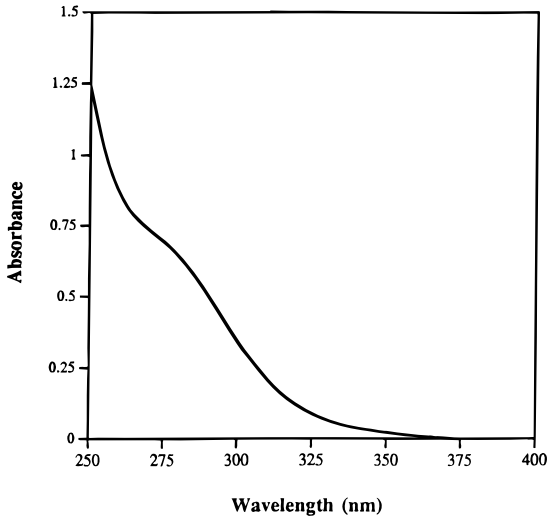

Figure 1. Optical absorption spectrum of the dilute nanosized TiO_2 colloidal solution.

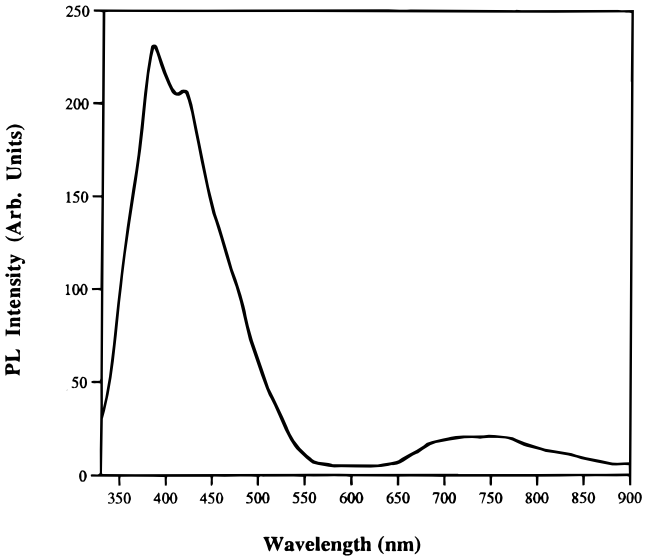

Figure 2. Photoluminescent spectrum of the dilute nanosized TiO_2 colloidal solution observed by illumination at 252 nm.

The photoluminescence of the TiO_2 colloidal solution was observed under excitation of the sample by UV light at 252 nm in air with a Perkin-Elmer LS-50 luminescence spectrometer at room temperature. Figure 2 shows the photoluminescence spectrum obtained from a dilute TiO_2 colloidal solution. There are three important characteristics visible here. First, the direct band-to-band transitions are observed with a monochromator; the peak at 420 nm is in agreement with those obtained for bulk TiO_2 powders.[12] A more striking peak occurs at 383 nm. This is, to the best of our knowledge, the first time that this type of band-to-band transition (blue light) has been observed in titanium dioxide. Second, a peak at 750 nm is observed, and the luminescence between 600 and 900 nm is associated with transitions of electrons from the conduction band edge to holes, trapped at an interstitial Ti^{3+} site.[12,13] Here, it is noted

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that the usual observed luminescence of bulk TiO_2 ranges from 700 to 1000 nm with peaks at around 850 nm.[13,14] Third, most of the luminescence of the TiO_2 colloidal solution occurs in the blue range of the visible spectrum, and decreases to the green portion of the spectrum.

We also have recently reported that such nanoparticle TiO_2 colloids can be used to fabricate monolayer and multilayer thin films by an ionic self-assmbly process,[15] which will make it possible for us to synthesize blue-light-emitting TiO_2 thin films and to characterize their photoluminescent and electroluminescent properties. The quantum yield of photoluminescence and electroluminescence and the relation between luminescence and the colloid particle size, as well as the process parameters of the colloidal, are being investigated.

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Supporting Information Available: A picture of the solution of nanosized TiO_2 colloids (1 page). See any current masthead page for ordering and Internet access instructions.

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