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Effects of mole ratio of ACA/TIPT on morphology of TiO_2 nanostructured materials by surfactant-assisted mechanism

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Nanocrystalline TiO_2 is one of the most strudied oxides, owing to its widespread applications in photocatalysis[1,2], solar energy conversion[3], sensors[4], and mesoporous membrane[5]. The technological potential of TiO_2 is expected to be remarkably extended if a fine-tuning of particle morphology is achieved. In this work, TiO_2 nanostructures, such as nanorod, nanowire, and nano-network, were synthesized by surfactant-assisted mechanism using molecular assembies composed of surfactant and titanium alkoxide. The synthesized nano-network structured materials by this method showed very high photocatalytic activity, higher than ST-01 (Ishihara co. Ltd.), which is known as the highest photocatalytic active TiO_2 commercially available nano particles. The electric, magnetic, catalytic properties of TiO_2 nano-size materials are strongly depend on the morphology of the materials. Effects of mole ratio of ACA/TIPT on morphology of TiO_2 nanostructured materials were studied.

In a typical synthesis, laurylamine hydrocholoride (LAHC) was dissolved in distilled water. Tetraisopropyl orthotitanate (TIPT, $Ti(OCH(CH_3)_2)_4$ were mixed with the different moles of acetylacetone (ACA) in a glass and immediately added to LAHC aqueous solution of pH 4.6. The mole ratio of metal alkoxides to LAHC was 4. The mole ratio of ACA/TIPT was changed from 0.1 to 2. When the two solutions were mixed, precipitation occurred immediately. The solutions were stirred for several days at 313K, the temperature was then changed to 353K. After 1day**,** TiO_2 products were separated by centrifugation. After washing with 2-propanol and successive centrifugation to remove the surfactants, the TiO_2 powders were dried in vacuum.

We carried out the experiment with variation in the mole ratio of ACA/TIPT to investigate the effects of ACA directly related to the reaction rate. When TIPT was mixed with ACA, ACA coordinated to titanium atom, letting one isopropyl alcohol unbound. The coordination number of titanium atom changed from 4 to 5, resulting in a color change from colorless to yellow. The reaction rate of the hydrolysis and the condensation reactions became slow with this modification[6]. Figure 1 shows the transmission electron microscope (TEM; JEOL JEM-200CX operated at 200kV) image and the selected area electron-diffraction (SAED) patterns of the gel samples at the mole ratio of ACA/TIPT = 0.2 after reaction at 353K for 1day. TiO_2 nanorods with average diameter of 5 ± 2nm and average length of 20 ± 5nm (aspect ratio = 4) were observed as shown in Figure 1a. SAED patterns as shown in Figure 1b shows the Debye-Sherrer rings of (101), (004), (200), (105), (204) diffractions of the anatase phase. Thus, TiO_2 nanorods had very high crystallinity, even though they were synthesized at extremely low temperature, 353K for 1day. When the mole ratio of ACA/TIPT was 0.5, longer TiO_2 nanorods with average diameter of 5 ± 2nm and average length of 30 ±10nm (aspect ratio = 6) were observed as shown in Figure 2a as compared with the nanorods at the mole ratio of ACA/TIPT = 0.2. Whereas, when the mole ratio of ACA/TIPT was 1, nano-network structure consisting of the nanowires with diameter 5-10 nm were observed as shown in Figure 3a. SAED patterns as shown in figure 2b, 3b indicated that these TiO_2 nanostructures also high crystallinity.

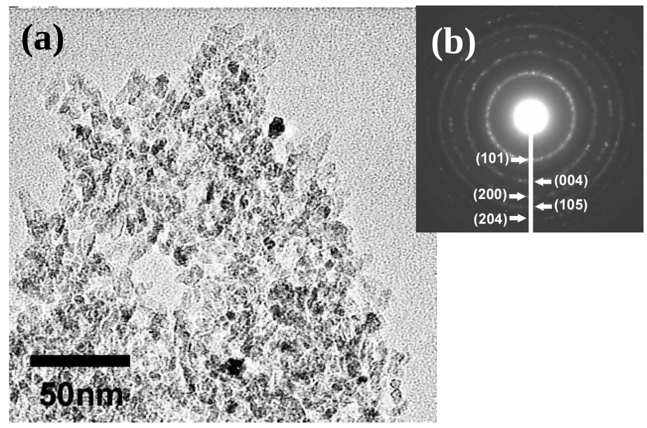

Figure 1**.** (a) TEM images and (b) SAED patterns of TiO_2 nanorods at the mole ratio of ACA/TIPT = 0.2.

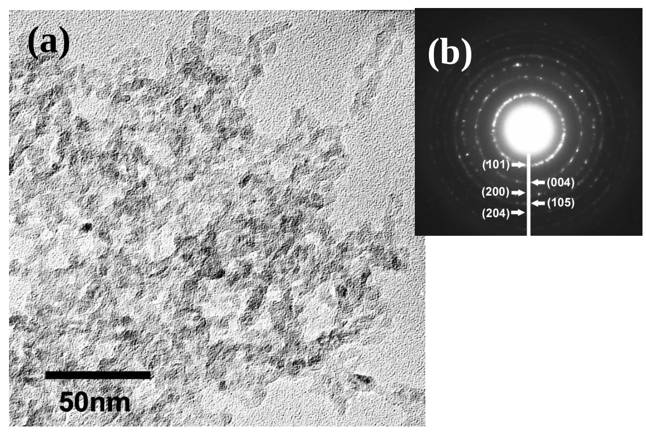

Figure 2**.** (a) TEM images and (b) SAED patterns of TiO_2 nanorods at the mole ratio of ACA/TIPT = 0.5.

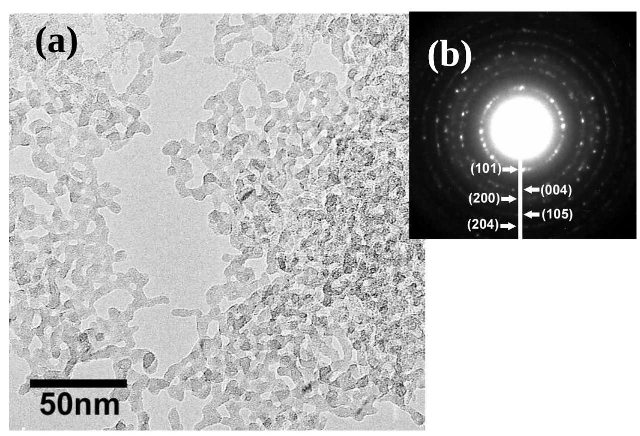

Figure 3**.** (a) TEM images and (b) SAED patterns of TiO_2 nano-network structures at the mole ratio of ACA/TIPT = 1.

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