Effect of Acetylacetone on Morphology and Crystalline Structure of Nanostructured TiO_2 in Titanium Alkoxide Aqueous Solution System

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Network structure of single-crystal-like TiO_2 nanowires with anatase phase was synthesized at low temperature by the "oriented attachment" mechanism. The most important factor for synthesis of network structure of the TiO_2 nanowires was elucidated as the effect of acetylacetone (ACA) on the formation of nanowires. Morphology and crystalline structure of TiO_2 were varied by changing the mole ratio of ACA to Ti.

Nanocrystalline TiO_2 is one of the most attractive oxides, owing to its widespread applications in photocatalysis,[1] and solar energy conversion.[2,3]

Recently, a new mechanism for the formation of complex nanostructures has been proposed, called the "oriented attachment" mechanism.[3,4] In this mechanism, nanocrystals can join together with complete crystallographic alignment and eliminate free surfaces. We have already reported that a network structure of single-crystal-like TiO_2 nanowires formed by the "oriented attachment" mechanism using surfactant-assisted self-assembling processes.[3] Nanowires were composed of fused nanoparticles of 2–5 nm, and these make nano-network structure. The orientations of crystals of fused nanoparticles were completely aligned because the lattice images aligned perfectly. This finding is very interesting, because crystal growth by the oriented attachment mechanism is observed below 373 K while usually much higher temperature is needed, i.e., 433–523 K. This observation confirmed a remarkable characteristic of this surfactant-assisted synthesis method using acetylacetone (ACA). Here, we present the effect of concentration of ACA on morphology and crystalline structure of nanostructured TiO_2 and elucidate the important factors for synthesis of TiO_2 nanowires.

Typical synthesis of TiO_2 nanostructures is as follows: first laurylamine hydrochloride (LAHC) was dissolved in distilled water. Tetraisopropyl orthotitanate (TIPT) was then mixed with ACA in a glass vessel with desired molar ratios and immediately added to 0.1 M LAHC aqueous solution of pH 4.6. The molar ratio of TIPT:ACA:LAHC in typical synthesis is 4:4:1.[3] When the two solutions were mixed, precipitation occurred immediately. The precipitates dissolved completely by stirring the solution for several days at 313 K, and the solution became transparent. The reaction temperature was then changed to 353 K. After 4 days, the solution became precipitates or white gels with a thin yellow liquid layer. TiO_2 products were separated by centrifugation. After washing with 2-propanol and successive centrifugation, TiO_2 powders were dried in vacuum and calcined in air at 573 K for 24 h.

In this synthesis, two reagents were added to the TIPT solution, that is, LAHC and ACA. In order to examine the roles of these reagents, three samples at TIPT:ACA:LAHC = 4:0:0, 4:0:1 and 4:4:0 were synthesized. The pH of aqueous solution was adjusted to 4.6 with HCl in case of the solution without LAHC. When TIPT:ACA:LAHC was 4:0:0 and 4:0:1, white colloidal suspensions were formed immediately after mixing of two reactants. Figure 1 shows the transmission electron microscope (TEM; JEOL JEM-200CX) images and the selected area electron-diffraction (SAED) patterns of the gel samples at the different mole ratio of TIPT:ACA:LAHC after reaction at 353 K for 4 days. When TIPT:ACA:LAHC was 4:0:0 and 4:0:1, white colloidal suspension were formed immediately after mixing of reactants, and gelation did not occur. Nanoparticles with diameter of 8–10 nm are observed as shown in Figures 1a and 1b. Both of SAED patterns show the Debye–Scherrer rings which can be indexed to those of anatase phase and (121) diffraction of brookite phase of TiO_2. On the contrary, when TIPT:ACA:LAHC was 4:4:0, gelation occurred after reaction at 353 K. Nano-network structure connecting nanowires with diameter 6–9 nm is observed, and SAED pattern shows only anatase phase as shown in Figure 1c. High resolution TEM (HRTEM) image of this nano-network structure is shown in Figure 1d. Clear lattice image of (101) plane of anatase phase is aligned over several particles, which indicates that the "oriented attachment" occurred under this condition.

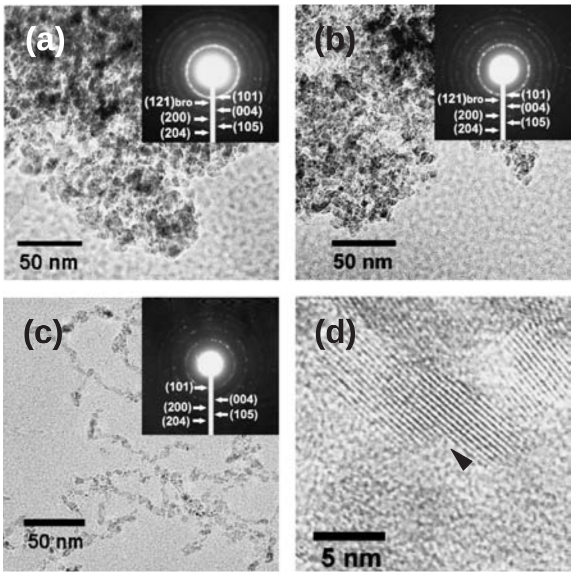

Figure 1. TEM images of TiO_2 nanostructures after reaction at 353 K for 4 days, (a) TIPT:ACA:LAHC = 4:0:0, inset: SAED patterns. (b) TIPT:ACA:LAHC = 4:0:1, inset: SAED patterns. (c) TIPT:ACA:LAHC = 4:4:0, inset: SAED pattern. (d) HRTEM image of (c).

Figure 2 shows the X-ray diffraction (XRD; Rigaku RAD-IIC) patterns of TiO_2 nanostructures after reaction at 353 K for

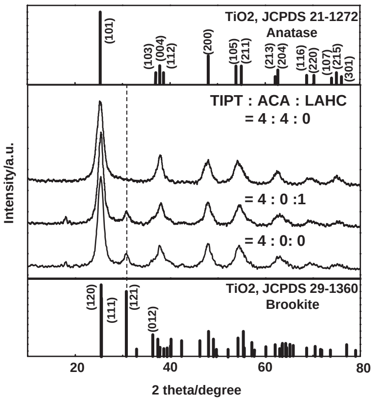

Figure 2. XRD patterns of TiO_2 nanostructures at TIPT:ACA: LAHC = 4:4:0, 4:0:1 and 4:4:0 after reaction at 353 K for 4 days.

4 days. The peaks of nanostructures at TIPT:ACA:LAHC = 4:0:0 and 4:0:1 could be indexed to anatase phase (JCPDS file No.21-1272) and (121) diffraction of bookite phase of TiO_2 (JCPDS file No. 29-1360). However, the peaks at TIPT:ACA: LAHC = 4:4:0 could be indexed to only anatase phase. These results coincide with the results of TEM images and SAED patterns. In addition, an increase in the peak height ratio of (004)/(200) and a sharpening of the (004) peak are observed, which indicates the presence of nanocrystalline anatase with a typical anisotropic growth pattern along the [001] direction.

ACA has often been used in sol–gel processing as a chemical additive to reduce the reactivity of metallic alkoxides.[5] The binding of ACA to titanium and slowdown of reactivity lead to oriented attachment. In this synthesis, the nanostructure of TiO_2 is affected by ACA considerably. First, TIPT without ACA systems, i.e., TIPT:ACA:LAHC = 4:0:0 and 4:0:1, give only TiO_2 nanoparticles. Whereas TIPT with ACA systems, i.e., TIPT:ACA:LAHC = 4:4:0 and 4:4:1,[3] gives a network structure of TiO_2 nanowires. Thus, big morphology change is induced by ACA. Second, the hydrolysis and condensation reactions are significantly decreased by modification of TIPT with ACA. This decrease in reaction rates might enable the occurrence of the oriented attachment, because nanoparticles produced by reaction of TIPT has enough time to select the crystalline face to fuse with each other. Third, the crystalline structure of nanosize TiO_2 changes, i.e., a pure anatase phase is formed in the system including ACA, whereas some amounts of brookite phase are included in the products when ACA is not included in the reactants. This effect also might be attributed to the decrease in reaction rates, because TiO_2 can select most stable structure when they react with nanocrystals. Thus, it is revealed that ACA plays an important role of not only making hydrolysis and condensation reactions slow, but also controlling the morphology and crystalline structure of TiO_2.

In order to investigate the role of ACA and LAHC in detail, the TIPT:ACA:LAHC is changed from 4:4:1 to 4:8:1. When TIPT:ACA:LAHC = 4:8:1, nano-network structure which is similar to the structure of TIPT:ACA:LAHC = 4:4:1[3] and 4:4:0, is observed and SAED pattern shows anatase phase as shown in Figure 3a. This structure is composed of a little longer and thicker nanowires than that of structures reported in Figure 1c. It is found that this nano-network structure is also formed by the oriented attachment mechanism from the HRTEM image as shown in Figure 3b.

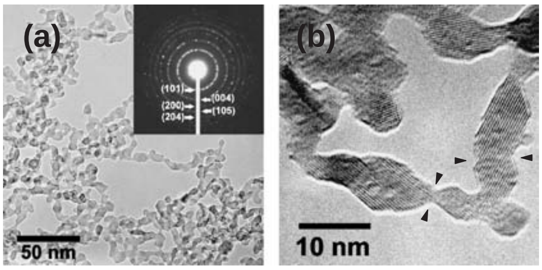

Figure 3. (a) TEM image and (b) HRTEM image of TiO_2 nano-network structure after reaction at 353 K for 4 days at TIPT: ACA:LAHC = 4:8:1, inset: SAED pattern.

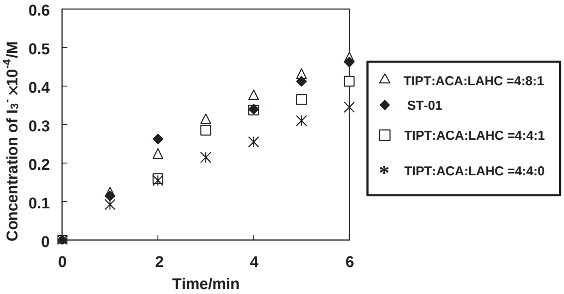

Figure 4. Photocatalytic activity of TiO_2 nanostructured materials together with ST-01.

Photocatalytic activity of TiO_2 nanostructured materials after calcinations at 573 K for 24 h was measured through the formation rate of I_3^- due to the oxidation of I^- to I_2 in excess I^- condition. 10 mg of TiO_2 samples were suspended by magnetic stirring in 10 mL of 0.2 M KI aqueous solution, and the solution was irradiated with 365-nm ray (UV-lamp 15 W). Figure 4 shows the results of photocatalytic activity in the case of comparison based on the weight of the TiO_2 samples, together with the standard TiO_2 powders: ST-01. The activity at TIPT:ACA: LAHC = 4:4:1 is higher than that at TIPT:ACA:LAHC = 4:4:0. The activity at TIPT:ACA:LAHC = 4:8:1 shows higher value among these nano-network structures and is nearly equal to that of ST-01. The specific surface areas of TiO_2 samples at the TIPT:ACA:LAHC = 4:4:0, 4:4:1, 4:8:1 and ST-01 are 126.0, 133.2, 121.9, and 300.0 m^2/g, respectively. These results including TEM images imply that LAHC and ACA would greatly affect the morphology and photocatalytic activity.

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