Surface modification of titania nanoparticles by an evaporation-condensation process in a flow chamber

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Introduction

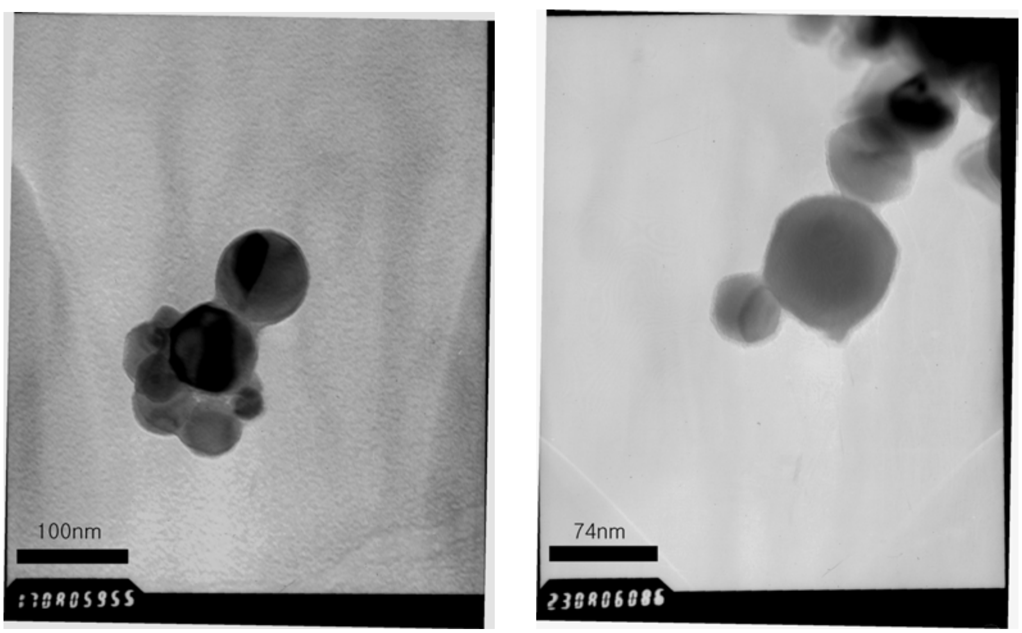
Titania (TiO_2) is an outstanding materials because of its superior physical properties but nanostructured titania films synthesized by an evaporation-condensation aerosol process can be used only for limited applications because of their low mechanical strength. In this study, the surface of titania nanoparticles (TiO_2) is modified by a heterogeneous capillary condensation process to enhance the mechanical strength of the nanoparticle film. Tetraethyl orthosilicate (TEOS) is used as precursor to form a bridge-shaped silica (SiO_2) layer between titania particles. The presence of a silica layer on nanoparticle surface is confirmed by Transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

Experimental Apparatus

A flow chamber is designed to achieve a specific supersaturation state on the basis of a laminar flow diffusion chamber for nucleation studies. The applicability of the designed chamber is verified using computational fluid dynamics calculations. These calculations, performed using FLUENT, show that the difference in radial temperature inside the chamber is sufficiently small so as to maintain stable supersaturation around the sample. The flow chamber is connected the vapor supplier, a bubbler, which is immersed in a heating bath to obtain a controlled vapor pressure. The connection lines from the bubbler to the chamber are heated to avoid any loss of vapor pressure of a precursor and the temperature of the chamber is maintained by a proportional-integral-derivative (PID) controller. Titania nanoparticles are loaded on the TEM grid directly and placed inside the chamber. The chamber is flushed with argon gas to minimize any nucleation source. Then the sample is exposed to TEOS vapor at the objective temperature and saturation ratio. The experimental conditions for capillary condensation are determined by adjusting process variables such as wall temperature, flow rate, and inlet temperature.

Results and Discussion

The surface of commercial grade titania nanoparticles (average diameter: 70 nm) were modified by an evaporation-condensation process in a flow chamber. It is thought that the capillary condensation occurs on the narrow gap between particle and the condensed TEOS molecules slowly undergo hydrolysis with the moisture in the atmosphere. In this study, various layer formations were observed at different saturation ratios as shown below in Figure 1. The relation between the coverage of the layer and the saturation ratio agrees with the theoretical prediction based on a model incorporating geometrical considerations. The modified nanoparticle compositions are analyzed by the characteristic spectra in FTIR and the specific bond energies in XPS. FTIR results are shown in Figure 2.



(a) saturation ratio > 1 (b) saturation ratio ≈ 1

Figure 1. Silica layer coverages at different saturation ratios by TEM

Surface modification process is performed at the low temperature compared with chemical vapor deposition (CVD) and is expected to prevent some disadvantages of high temperature process such as interdiffusion of particles, loss of surface area, and deterioration of interface property. We obtained some modified nanoparticles that has the bridge-shaped silica layer on the selective area of the nanoparticle surface. The coverage of the layer is dependent on the saturation ratio of TEOS vapor supplied into the chamber. From the TEM results, the thermodynamic equilibrium model for spherical particles shows a good agreement with the experimental results. The geometrical effect for non-spherical particles should be considered for more homogeneous condensation over the various particle sizes or films composed of the different agglomerates. This selective capillary condensation process will be applied to the nanostructured titania films produced in an evaporation-condensation aerosol process in the end, and it is expected to overcome the low mechanical strength of nanoparticle film without damaging surface properties severely. The mechanical strength of the modified film will be analyzed by nanoindentation method.

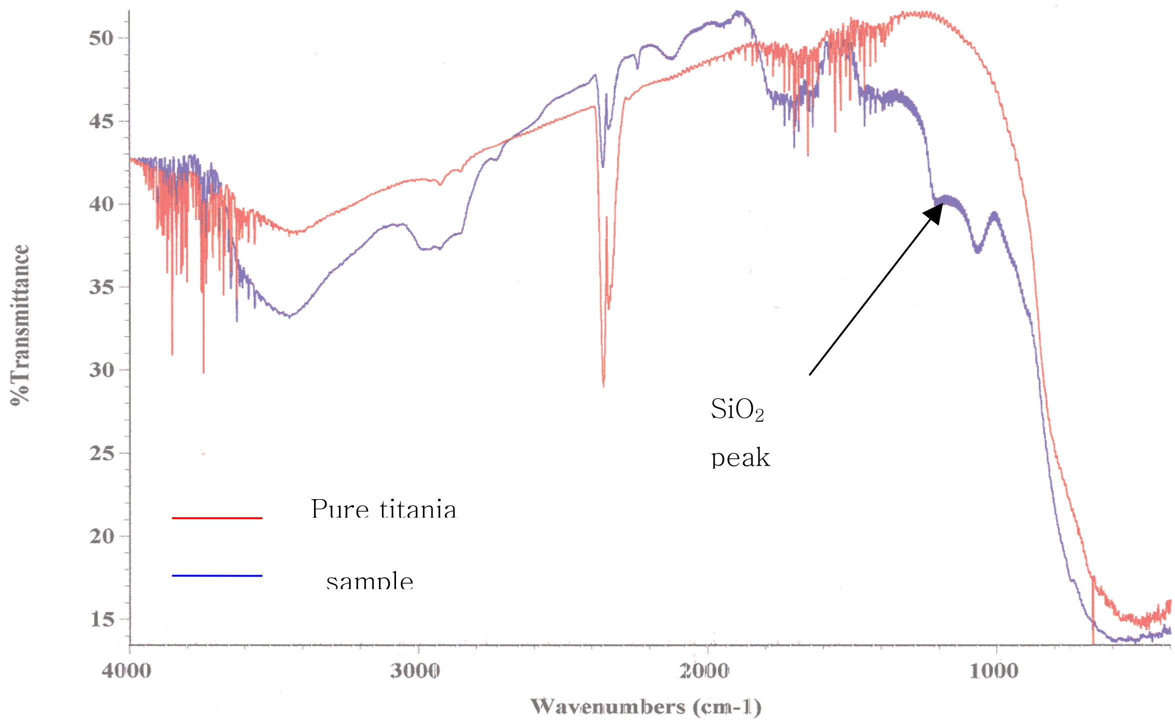


Figure 2. FTIR spectra of pure titania and modified titania particles

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