Morphology-controlled TiO_2 Nanoparticle Synthesis via Aerosol-assisted Vapor-phase Reactions

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TiO_2 particles with various morphologies have been synthesized via aerosol-assisted vapor-phase reactions. Vapor source materials and/or aerosol droplets containing source materials were fed into a quartz tube and heated in a two temperature zone electric furnace. The reaction method meant that a combination of gas-phase decomposition and crystal growth in the liquid droplet phase occurred. This resulted in the controlled formation of variously shaped crystalline TiO_2 nanoparticles varying from single crystal nanoparticles to unique dendritic nanostructures grown on a core particle.

Nanostuctured particles are expected to be applied in the future for as catalysts, controlled drug delivery systems, and electrodes. There have been many reports of nanostructured particles with various morphologies.[1–8] Since Nittmann and Stanley reported dendritic growth patterns in 1986,[1] inorganic dendritic structures have drawn much attention, and several attempts have been performed with the liquid-phase techniques.[2,8,9]

Gas-phase reaction processes are so attractive for scale-up that nanostructured particle synthesis have been investigated.[3,4,7] Haas et al. synthesized nanostructured palladium particles in an aerosol flow condenser.[3] Lao et al. exhibited a variety of nanostructures of ZnO grown by a vapor transport and condensation technique.[7] Lu et al. reported the aerosol-assisted self-assembly for mesostructured spherical silica nanoparticles.[4] They synthesized well-ordered spherical particles with stable pore mesostructures as well as layered vesicular structures. They used the method of evaporation-induced interfacial self-assembly confined to spherical aerosol droplets, which contain homogeneous solution of surfactant other than soluble silica.

In this study, we report on the production of variously shaped nanostructured TiO_2 particles by means of a homogeneous gas-phase reaction and/or reactions within aerosol droplets. TiO_2 is an important material because of its photocatalytic effects, and TiO_2 nanostructuring is expected to greatly enhance the properties for optoelectronic devices, such as photovoltaic cells.[10] Production of inorganic nanocrystals has been reported using homogeneous reactions. To the best of our knowledge, there have been no previous reports on the dendritic nanoparticle formation through heterogeneous gas-phase processes. The entire process described herein is simple and avoids the necessity of complex solvent preparation.

The experimental set up used in this work consists of a vaporizer, an atomizer, a quartz tube reactor, and an air filter. Generated particles are directly deposited on the TEM microgrids placed on a filter. The diameter of reactor is 38 mm, which has two heating zones of 300 and 150 mm in length, respectively. We conducted either the uniform temperature experiments or two-zone heating experiments. TTIP (titanium tetraisopropoxide) was chosen as a precursor. TTIP was vaporized at room temperature by nitrogen gas bubbling into the vaporizer. Aerosol droplets were formed by using the commercially available atomizer (TSI Corp., type 3076) operated in the similar manner by Lu et al.[4] According to the atomizer specifications, the droplets size was estimated from about 10 to 2000 nm with nominal 300 nm count mean diameter, and the droplet concentration was over 10^7 particles/cm^3 for nominal aerosol flow rate of 3.0 L/min. The source liquid was mixed fractionally with IPA (isopropyl alcohol) to form a diluted solution for the uniform temperature experiments. The total flow rate of the nitrogen carrier gas was maintained at 10 L/min.

Electron micrographs (TEM: JEOL JEM-4000FX, SEM: JEOL JSM-6700F) in Figure 1 reveal typical nanostructured particles formed in the two heating zones, the first having a fixed temperature of 300 °C and the second, a fixed temperature of 700 °C. The particles exhibited dendritic crystal growth features.

In Figure 1a, particles with dendritic structure were shown in various sizes from several 10 nm to about 500 nm. Also rugged particles of the order of 10 nm in size were captured on the edge of TEM grid holes. These ragged particles were synthesized through vapor-phase reactions, since the size was smaller than droplet size and the vapor source concentration was higher than droplet concentration. Figure 1b shows the particle with dendritic structure of about 10 nm scale, which corresponds to

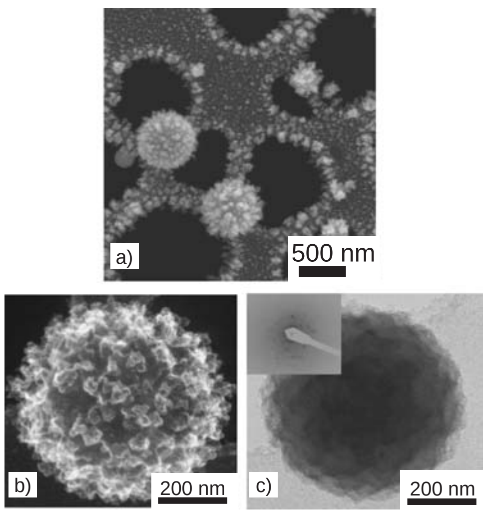

Figure 1. SEM and TEM images of nanostructured TiO_2 particles: a) SEM image of particles captured on TEM grid, b) enlarged SEM view of dendritic structured particle. c) TEM image of dendritic structured particle, top light insert in c) is SAED pattern.

the rugged small particle size. As shown in Figure 1c, the nanostructure was observed in the particle core. Selected area electron diffraction (SAED) pattern given in top left in Figure 1c shows that the obtained particles have polycrystalline structure corresponding to anatase. This is equivalent to the previous studies which report TiO_2 nanoparticle of anatase are synthesized at temperature above 500 °C by the thermal decomposition of TTIP.[11]

The mechanism of dendritic nanostructured particle formation can be simply explained as follows. Step 1: In the first heating zone, the droplets containing the source material from the atomizer condense to form the core TiO_2 particles. Step 2: In the second heating zone, the temperature is higher than the decomposition temperature of TTIP vapor source. Some portion of the TTIP gas source from the vaporizer homogeneously decomposes to form the nanometer-sized crystals with heterogeneous nucleation on the preformed particle flowing from the first heating zone. As a result, we obtain dendritic nanostructured TiO_2 particle.

Kinetic consideration indicates the above mechanism. Since temperature governs the rate of decomposition of the source gas, heating zone temperature may be used to control the gas-phase reaction products. We estimated the degree of the source gas homogeneous decomposition using the reported kinetic data for TTIP gas-phase reaction.[12] When the source gas is heated over 700 °C, source gas rapidly decomposes within 100 ms, whereas under 500 °C the source gas decomposes in over seconds. When the both heating zones are set at 500 °C, the dendritic particle formation in the gas phase does not take place with only particles generated from the droplets.

The above mechanism is supported by the experimental results of Okuyama et al.[13] They examined the TiO_2 particle synthesis on the seed particles by introducing the source gas containing TiO_2 seed particles in a flow reactor. They reported that the homogeneous particle formation was suppressed and that the growths on the seed particles were observed in the reactor with an increasing temperature profile. They pointed out that a lower furnace temperature results in a lower concentration of TiO_2 monomer and that the rate of homogeneous nucleation is extremely sensitive to the TiO_2 monomer concentration.

The experimental results obtained in the uniform temperature profile are shown in Figure 2. Figure 2a shows the result of homogeneous source gas decomposition at 700 °C to form the TiO_2 agglomerated nanoparticles. Figure 2b shows that the droplet reaction and gas-phase reaction at 700 °C form the large particle made from the droplet and the coagulated nanoparticles, which accumulated on the particle derived from the droplet. Figure 2c shows a typical single crystal formed from the droplet reaction. We introduced droplets of TTIP solution into the reactor uniformly heated at 500 °C. The droplet size was about 300 nm, which contained 0.001% TTIP in IPA solution. Obtained particles were single crystals, and the size was about 25 nm, which is about one tenth of the droplet size and corresponds to the droplet diameter after solvent evaporation. This indicates that the droplet evaporation and the crystal formation were taking place in series. These are in accordance with the previous study, which reports the obtained particle size was well correlated to the droplet size by the one-third power of the source material concentration in the solution.[14]

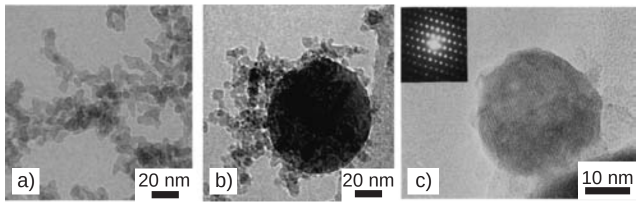

Figure 2. TiO_2 Nanoparticles formed in the uniform heating zone. a) Through homogeneous gas-phase reaction, b) TiO_2 single crystal and accumulated nanoparticles, c) HRTEM TiO_2 particle from the droplet reaction with lattice fringes observable. Top left insert in c) shows SAED pattern of single crystal.

All of these results show that the nanostructure of TiO_2 particles could be controlled by changing the degree of gas-phase reaction in a combination with aerosol droplet liquid-phase reactions.

In conclusion, we have successfully synthesized dendritic nanostructured TiO_2 particle via aerosol-assisted gas-phase reactions. The ability to synthesize the nanostructured TiO_2 particles by the vapor-phase process should enrich the applicability of these nanocrystalline particles in future optoelectronic devices.

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