UNIVERSITY OF GOTHENBURG

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

Hydrolytic Synthesis and Physicochemical Properties of TiO_2 Nanoparticles:
Fundamentals and Applications

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ABSTRACT

Titanium dioxide (TiO_2) nanoparticles were synthesized via the hydrolysis of $TiCl_4$ in order to produce clean, surfactant-free oxide surfaces. By controlling the synthesis and aging conditions, stable particles with well-defined size distributions were obtained. The particles were characterized using dynamic light scattering (DLS), electrospray-scanning mobility particle sizer (ES-SMPS), transmission electron microscopy (TEM), and X-ray diffraction (XRD) in order to gain information about the size, morphology and crystalline structure of the material. Dialysis and storage of the particles at 0°C, 5°C and room temperature gave rise to average particle sizes of around 8, 10, and 18 nm after the first 3 weeks of aging. The sizes obtained from DLS and ES-SMPS were generally in good agreement. Analysis by TEM and XRD shows that the synthesis products are composed of primary particles, about 4 nm in size, predominantly of anatase structure. A small amount of brookite (<10%) is produced. Thermodynamic calculations and experimental data reveal that the formation of the oxide particle proceeds from the condensation of titanium complexes, the first hydrolysis products, from solution. At low pH, a repeated condensation/dissolution process occurs, until an amorphous Ti-oxyhydroxide is formed, which eventually becomes crystalline TiO_2.

Experimental results from ES-SMPS and DLS indicate that the particles grow to their average measured size by the formation of stable aggregates. The effects of polydispersity on the collective diffusion detected by DLS were examined in detail, and a binary sphere model was proposed, to explain the nonlinear concentration dependence of the diffusion coefficient. The interactions between small particles and larger porous aggregates give rise to nonlinearity in transport behaviour at low volume fractions. A closer look at the surface charging of the particles was done by theoretical calculations and experiments, with indications of size-dependent behaviour.

The influence of the TiO_2 nanoparticle properties on selected applications was illustrated, using the characteristics of the porous nanoparticle surface on Ti dental implants and the interactions of free TiO_2 nanoparticles with Ca^{2+}-rich lipid bilayers. The findings of these studies validate that the direct exposure of the oxide surface to the surrounding electrolyte is significant in terms of understanding interfacial processes from the biological perspective.

Keywords: *Titanium dioxide, nanoparticles, synthesis, hydrolysis, $TiCl_4$, anatase, brookite, DLS, ES-SMPS, XRD, collective diffusion, interfacial processes.*