Organic Solvent Dispersed TiO_2 Nanocrystal Sol: Synthesis and Characterization

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ABSTRACT

Anatase TiO_2 nanoparticles with a mean diameter of approximately 10 nm were successfully synthesized by a nonaqueous sol-gel route without the use of air-free equipment. The nanoparticles are well dispersed in common organic solvents in the form of primary particles, and the colloid is stable for more than one year. The particles and colloid were studied by X-ray diffraction (XRD), transmission electron microscope (TEM), atomic force microscopy (AFM), quasielastic light scattering (QELS), nuclear magnetic resonance (NMR) spectroscopy, and size-exclusion chromatography (SEC). The average particle size measured by several analytical methods is in excellent agreement. Moreover, NMR and SEC are able to detect the presence of an additional component comprising a second population of smaller particles with a diameter of 2 nm. The work in this paper shows that nanotechnology can benefit significantly from the new application of conventional analytical tools.

Keywords: titanium dioxide nanocrystal, colloid synthesis, characterization

1 INTRODUCTION

TiO_2 nanoparticles are of broad interest because of photocatalytic properties useful in dye-sensitized solar cells [1] and optical properties for high refractive index coatings and photonic crystals [2]. Among different synthetic routes, nonaqueous sol-gel synthesis is becoming more popular because it potentially offers better control of reaction and morpholology [3]. During the sol-gel synthesis, surface modification may be used to control the nucleation and growth of TiO_2 nanoparticles. Useful surface modification materials include carboxylates [4], silanes [5], and phosphonates [6, 7]. Despite considerable activity in the field, chemical details regarding the organic-inorganic interface and particle colloidal stability are poorly understood. It is the objective of this study to synthesize a stable TiO_2 nanocrystal colloid in common organic solvents and characterize this colloid using various analytical tools to gain understanding of the synthesis and interface of the nanoparticle and the solvent.

2 EXPERIMENTAL

The colloid synthesis was carried out largely according to ref. [8]; however, all the reactions were performed at ambient condition rather than in a glove box.

All chemicals were used as received without further purification. Typically, hexanoic acid 99% (Sigma Aldrich cat#244112) was added to titanium(IV)butoxide 97% (Sigma Aldrich cat#H12137) in a reactor (Parr Instruments Model 4843) together with 1-butanol (HPLC grade 99% Alfa Aesar) and deionized water. The reaction was run at 240°C for 5 hours. The dried precipitate was mixed with 2-butanone and 3-methacryloyloxypropyltrimethoxysilane and reacted at 68°C with ammonium hydroxide as the catalyst. The product was concentrated and hexane was added. The mixture was centrifuged at 2500 rpm for 10 minutes. The titanium oxide particles were then re-dispersed in 2-butanone forming a transparent pale yellow, colloidal solution.

The particles and colloid were studied by XRD, TEM, AFM, QELS, NMR, and SEC.

3 RESULTS AND DISCUSSION

TiO_2 nanocrystals were successfully synthesized by a nonaqueous sol-gel route. During the first step of the synthesis, titanium butoxide was first hydrolyzed and condensed into amorphous TiO_2 nanoparticles. Amorphous TiO_2 nanoparticles were crystallized at elevated temperatures and pressure and the TiO_2 nanoparticles were stabilized by hexanoic acid, which was either adsorbed or chemically bound to the particle surface. During the second step of the synthesis, the hexanoic acid surface groups were exchanged by the 3-methacryloyloxypropyltrimethoxysilane and a stronger Si-O-Ti bond was formed and the nanoparticles were further stabilized. The nanocrystals are well dispersed in common organic solvents in the form of primary particles, and the colloid is stable. The TEM photomicrograph (Fig. 1) clearly shows that the primary particle is a single crystal and the diameter is roughly 8–10 nm. XRD (Fig. 2) confirmed the TiO2 was the Anatase polymorph (PDF 21-1272). Based on the XRD peak widths, the calculated crystal size using Scherrer's equation is 8 nm, which agrees with TEM data.

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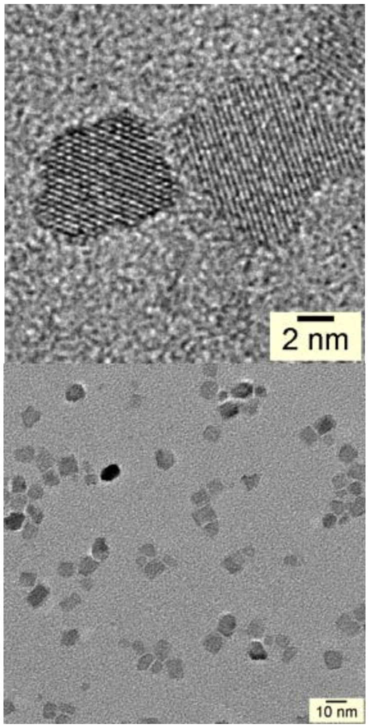

Figure 1: TEM of a stable colloid comprising a narrow size distribution of anatase TiO_2 nanoparticles.

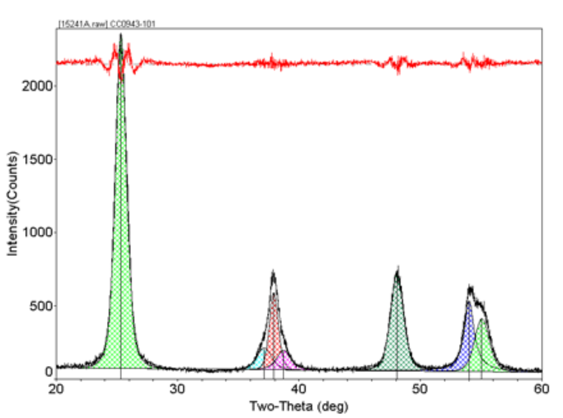

Figure 2: XRD pattern of a dried TiO_2 precipitate from the nonaqueous sol-gel reaction.

It was assumed that MPTMS (3-methacryloyloxypropyl trimethoxysilane) was chemically bonded to nanoparticles to stabilize organic solvent dispersions. [1]H NMR was used to confirm this hypothesis through identifying and quantifying the amounts of the various dispersion components. DECRA analysis [9–11] (VNMRJ software, Varian Inc., Palo Alto CA) was used to process the PGSE NMR data. Using DECRA analysis, separate spectra of each pure component are obtained, which enables facile spectral interpretation. In addition, the diffusion coefficients (D) of each component are obtained. The hydrodynamic diameter (D_H) of each component was estimated using the Stokes-Einstein equation,

$$D_H = \frac{2kT}{6\pi\eta D} \quad (1)$$

where k is the Boltzmann constant, T is the temperature, and η is the solvent viscosity. This relationship is strictly valid for a spherical particle with a diameter, D_H, in a continuum solvent, but is often used to estimate the size of molecules under dilute conditions.

The amount of each component was quantitatively determined using the [1]H single-pulse experiment and the external reference, TSP. DECRA analysis of [1]H PGSE NMR data (Fig. 3) of the dispersed sample provided pure component spectra, diffusion coefficients, and spectral composition. Three components are resolved: (a) low-molecular-weight impurities, (b) free, oligomeric, self-condensed MPTMS, and (c) bound MPTMS. The separation of different particles allows the identification of the chemical nature and size of different particles, as well as the quantitative concentration distribution of the particles. The analysis suggests a bimodal distribution with a population of 12 nm particles and a second population of 2 nm particles. NMR was also used to characterize chemical groups on the particle surface and their interaction with the particle. The smaller size particles in the colloid were identified as oligomers of the tri-alkoxy silane, MPTMS. SEC confirmed the existence of the second population (~2 nm) as identified by NMR (Fig. 4).

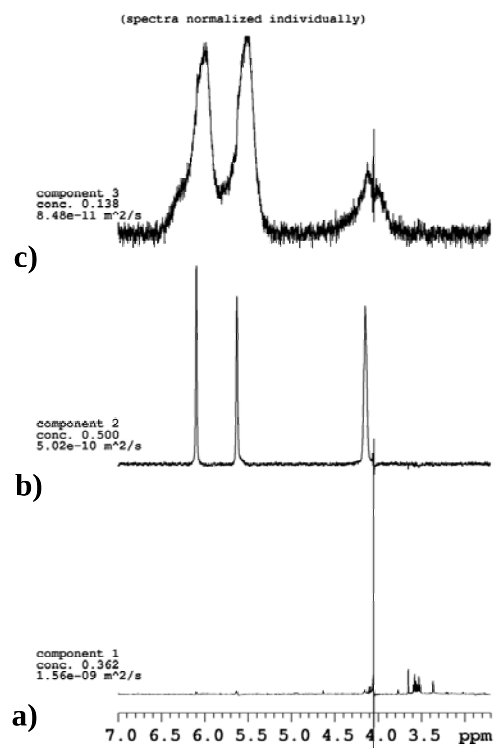

Figure 3: [1]H NMR spectra of DECRA-resolved components in a synthesized TiO_2 colloid, (a) low-molecular-weight impurities, (b) free, oligomeric, self-condensed MPTMS, and (c) bound MPTMS.

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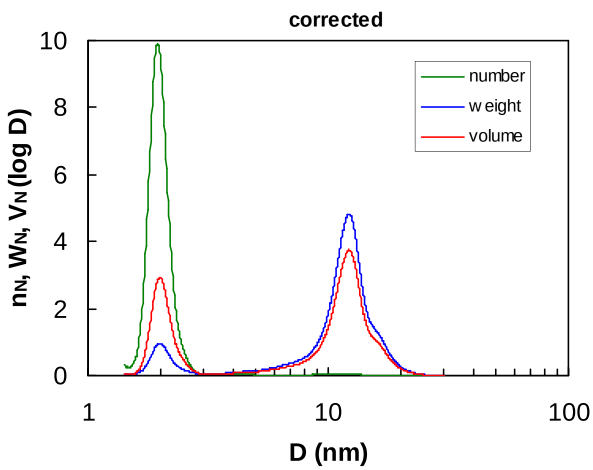

Figure 4: Differential number, weight, and volume fraction particle size distributions measured by SEC using corrected differential refractive index (DRI) detector response and equivalent hydrodynamic sphere model.

4 CONCLUSION

Anatase TiO_2 nanoparticles with a mean diameter of about 10 nm were synthesized and well dispersed in organic solvents in the form of primary particles. A tri-alkoxy silane monolayer stabilizes the dispersion. The average particle size results measured by XRD, TEM, AFM, QELS, NMR, and SEC are in excellent agreement. Moreover, NMR and SEC are able to detect the presence of a second population of particles, with a much smaller diameter of 2 nm. These particles are identified as the dimer and trimer of the MPTMS used to stabilize the TiO_2. Because of the similar chemical nature, these small particles cannot be removed using selective precipitation. Rather, a high-speed centrifugation successfully removes the smaller particles rendering a pure TiO_2 nanoparticle colloid that can be used to make high refractive index coatings. The use of NMR and SEC to characterize the nanoparticle colloid overcame the shortcoming of heavy weighting of larger particles in light-scattering measurements and allowed the characterization of the chemical group and its interaction with the particle. These characterization tools will provide essential information to understand the organic-inorganic interface and control the nanoparticle synthesis.

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