Research Article

Sol-Gel Preparation of Highly Water-Dispersible Silsesquioxane/Zirconium Oxide Hybrid Nanoparticles

Yoshiro Kaneko and Tomoyuki Arake

Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Correspondence should be addressed to Yoshiro Kaneko, ykaneko@eng.kagoshima-u.ac.jp

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Highly water-dispersible silsesquioxane/zirconium oxide hybrid nanoparticles (SQ/ZrO₂-NPs) were prepared by the following two-step reactions. First, a mixture of 3-aminopropyltrimethoxysilane (APT MOS) and zirconium tetra-*n*-butoxide (ZTB) was stirred in a mixed solvent of 0.1 mol/L methanolic hydrochloric acid and *n*-butanol at room temperature, followed by heating in an open system until the solvent was completely evaporated. Then, the aqueous solution obtained by adding water to the resulting product was heated in an open system until the water was completely reevaporated. The products (SQ/ZrO₂-NPs) obtained with a feed molar ratio of APT MOS/ZTB of more than 0.3 were dispersed well in water, and their aqueous dispersions were highly transparent, which was confirmed by UV-Vis measurements. In addition, the solid product obtained by drying its aqueous dispersion was redispersed in water. The volume-average particle sizes of SQ/ZrO₂-NPs (APT MOS/ZTB ≥ 0.3) were assessed to be ca. 4.6–23.8 nm by dynamic light scattering measurements in water. The theoretical refractive index of the SQ/ZrO₂-NP (APT MOS/ZTB = 0.3) was estimated to be 1.66. It was assumed that the water-dispersible property of the SQ/ZrO₂-NPs probably originated from the ZrO₂-SiO_{1.5}(CH₂)₃NH₃⁺Cl[−] core-shell structures.

1. Introduction

The dispersion of metal oxide nanoparticles such as those of titanium oxide (TiO₂) and zirconium oxide (ZrO₂) is an important topic for their applications, particularly the formation of transparent organic-inorganic hybrid materials with high refractive indices [1–5]. To prepare transparent hybrid materials composed of polymers and metal oxide nanoparticles, metal oxides are required to disperse well (nanoscale) in various media because interface scattering between organic and inorganic components is suppressed in hybrid materials.

Among metal oxide nanoparticles, ZrO₂ nanoparticles are attractive because they offer several advantages such as chemical inertness, excellent thermal stability, high refractive index, and high hardness. Although numerous studies have focused on surface modification to disperse ZrO₂ nanoparticles, only a few examples regarding the preparation of completely homogeneous dispersions of ZrO₂ nanoparticles have been reported [6–8].

On the other hand, we have reported the preparation of water-soluble ammonium cation-containing silsesquioxane (SQ) polymers with regular structures by the sol-gel reaction of 3-aminopropyltrimethoxysilane (APT MOS) under acidic conditions [9–14]. We determined that a salt (ion pair) prepared from an amino group of APT MOS and an acid used as a catalyst probably contributes to the water-solubility and formation of regular structures of the materials. It has also been reported that highly water-dispersible SQ/silica (SiO₂) hybrid materials have been prepared by the sol-gel copolycondensation of the mixtures of APT MOS and tetramethoxysilane under the same reaction conditions as those for the aforementioned polySQs [15]. In addition, highly water-dispersible SQ/TiO₂ hybrid nanoparticles were successfully prepared by the following two-step sol-gel copolycondensation under acidic conditions [16]. First, the mixture of APT MOS and titanium tetraisopropoxide was stirred in a mixed solvent of methanolic hydrochloric acid and isopropyl alcohol at room temperature, followed by heating in an open system until the solvent was evaporated.

Then, the aqueous solution obtained by adding water to the resulting product was heated in an open system until the water was completely reevaporated. The resulting product was dispersed well in water and its aqueous dispersion was highly transparent. These synthetic approaches have motivated us to successfully obtain highly water-dispersible SQ/ZrO₂ hybrid nanoparticles (SQ/ZrO₂-NPs) because the molecular structure of titanium tetraalkoxide as a monomer is similar to that of zirconium tetraalkoxide.

Therefore, in this study, we investigated two-step sol-gel copolycondensations, that is, using alcoholic hydrochloric acid in the first step and water in the second step as solvents, for the mixtures of APTMOS and zirconium tetra-*n*-butoxide (ZTB) under various reaction conditions. As a result, highly water-dispersible SQ/ZrO₂-NPs were obtained. This paper reports on the preparation method, water-dispersible behaviors, particle sizes, refractive indices, plausible structures, and formation mechanism of the nanoparticles.

2. Experimental

2.1. Materials. All reagents (APTMOs, Tokyo Kasei Kogyo Co., Ltd., Japan and ZTB, Wako Pure Chemical Industries, Ltd., Japan) and solvents (0.5 mol/L methanolic hydrochloric acid and *n*-butanol, Wako Pure Chemical Industries, Ltd., Japan) of reagent-grade quality were commercially purchased and used without further purification.

2.2. Preparation of Highly Water-Dispersible SQ/ZrO₂-NPs. A typical experiment for the preparation of highly water-dispersible SQ/ZrO₂-NPs was conducted according to the following procedure. After 0.1 mol/L methanolic hydrochloric acid (62.5 mL = 6.25 mmol) was added to APTMOs (0.269 g = 1.5 mmol), the solution was added to a solution of ZTB (85 wt% *n*-butanol solution) (2.257 g = 5.0 mmol) in *n*-butanol (125 mL). The mixture was stirred for 2 h at room temperature, followed by heating at ca. 50°C in an open system until the solvent was evaporated and further heating at 100°C for 30 min to completely remove the solvent. The obtained product was dissolved in water (100 mL) and the solution was heated at ca. 50°C in the open system until the water was reevaporated. The product was left at 100°C for 30 min and was then dispersed in water (100 mL) by stirring at room temperature for 12 h. After the resulting aqueous dispersion was filtrated to remove a slightly insoluble residue, it was heated at 50°C in an open system to evaporate water and was further heated at 100°C for 30 min to yield ca. 1.033 g of a glassy white product (SQ/ZrO₂-NPs).

2.3. Ion-Exchange Reaction of SQ/ZrO₂-NP with Sodium Laurate. SQ/ZrO₂-NP (elemental ratio of Si/Zr = 0.34, 0.173 g = 0.34 mmol of the amino group) was dispersed in 20 mL of water. This aqueous dispersion was poured into a sodium laurate aqueous solution (0.1 mol/L, 10 mL) to precipitate the product. The precipitate was collected by filtration, washed with water, and dried under reduced

SCHEME 1: Preparation of highly water-dispersible SQ/ZrO₂-NPs.

pressure at room temperature to yield ca. 0.252 g of a white powdered product.

2.4. Measurements. Elemental ratios of Si/Zr in the SQ/ZrO₂-NPs were estimated by energy-dispersive X-ray (EDX) spectroscopy using an XL30 scanning electron microscope (FEI Company). The UV-Vis spectra of the aqueous dispersions of the SQ/ZrO₂-NPs were recorded using a Jasco V-650 spectrophotometer (JASCO Corporation, Japan). A quartz cell (thickness 10 mm) containing water was used as a reference for UV-Vis measurements. The particle sizes of the SQ/ZrO₂-NPs were measured in water at 25°C using a Zetasizer Nano ZS (dynamic light scattering (DLS) apparatus) (Malvern Instruments, UK). The refractive indices of the aqueous dispersions of the SQ/ZrO₂-NPs were determined at 25°C using an RX-5000α refractometer (Atago Co., Ltd., Japan). The measurement wavelength was 589.3 nm (Na-D line).

3. Results and Discussion

3.1. Preparation of Highly Water-Dispersible SQ/ZrO₂-NPs. In the first step, intermediates were prepared by stirring the mixtures of APTMOs and ZTB (feed molar ratio = 0–1.0:1.0) in a mixed solvent of 0.1 mol/L methanolic hydrochloric acid and *n*-butanol at room temperature, followed by heating in an open system until the solvent was evaporated (Scheme 1). In the second step, after water

TABLE 1: Feed molar ratios of APTMOS/ZTB and elemental ratios of Si/Zr in SQ/ZrO₂-NPs.

Run	Feed molar ratio (APTMO/S/ZTB)	Elemental ratio in SQ/ZrO ₂ -NPs ^(a) (Si/Zr)
1	1.0	1.10
2	0.8	0.99
3	0.6	0.79
4	0.3	0.34
5	0.2	0.29
6	0.1	0.22

^(a) Estimated by EDX measurements.

was added to the resulting intermediates, these aqueous solutions were also heated in an open system until the water was completely reevaporated to obtain SQ/ZrO₂-NPs (Scheme 1). These materials were almost quantitatively obtained by this reaction system.

The values of Si/Zr elemental ratios in the SQ/ZrO₂-NPs estimated by EDX measurements are listed in Table 1. These results indicate that the Si/Zr elemental ratios were almost consistent with the feed molar ratio of APTMOS to ZTB in all cases.

3.2. Water-Dispersibility of SQ/ZrO₂-NPs. The transmittances of the 1.0 w/v% aqueous dispersions of the SQ/ZrO₂-NPs obtained with various feed molar ratios of APTMOS/ZTB were measured by UV-Vis spectroscopy (Figure 1). For the aqueous dispersions of the SQ/ZrO₂-NPs obtained with a feed molar ratio of APTMOS/ZTB greater than 0.3, high transmittances were observed in the visible wavelength region (>95%, transmitted light > 380 nm), indicating that the SQ/ZrO₂-NPs (APTMO/S/ZTB ≥ 0.3) dispersed well in water and the resulting aqueous dispersions were highly transparent (Figure 1). The photographs of the aqueous dispersions also support their transparencies (Figures 2(a) and 2(b)). These high transparencies of the aqueous dispersions did not change, and precipitates were not generated even after standing for several weeks, indicating that the SQ/ZrO₂-NPs (APTMO/S/ZTB ≥ 0.3) were stably maintained in water without aggregation.

On the other hand, the transmittance of the aqueous dispersion of the SQ/ZrO₂-NP (APTMO/S/ZTB = 0.2, concentration = 1.0 w/v%) was lower than those of the aforementioned nanoparticles (Figure 1). In addition, those of SQ/ZrO₂-NPs (APTMO/S/ZTB ≤ 0.1, concentration = 1.0 w/v%) were considerably low, indicating that these products did not disperse well in water (Figure 1). Their turbidities were also confirmed by visual observation (Figures 2(d) and 2(e)). On the basis of the aforementioned results, the products were found to be highly dispersed in water with ca. 75 mol% incorporation of the ZrO₂ component. In the case of the SQ/ZrO₂-NPs (APTMO/S/ZTB ≤ 0.2), the compositional ratio of the SiO_{1.5}(CH₂)₃NH₃⁺Cl⁻ components was relatively low. Therefore, it is assumed that the

FIGURE 1: UV-Vis spectra of aqueous dispersions (1.0 w/v%) of SQ/ZrO₂-NPs obtained with various feed molar ratios.

FIGURE 2: Photographs of aqueous dispersions (1.0 w/v%) of SQ/ZrO₂-NPs obtained with various feed molar ratios for APTMO/S/ZTB: (a) 1.0, (b) 0.3, (c) 0.2, (d), 0.1, and (e) 0 and (f) solid state of SQ/ZrO₂-NP (feed molar ratio of APTMO/S/ZTB = 0.3).

SiO_{1.5}(CH₂)₃NH₃⁺Cl⁻ components, which play an important role in high water-dispersibility, could not completely cover the nanoparticle surface.

The transmittances of the aqueous dispersions of the SQ/ZrO₂-NPs (APTMO/S/ZTB = 0.3) with various concentrations were investigated through UV-Vis measurements (Figure 3). For the aqueous dispersions up to 5.0 w/v%, relatively higher transmittances were observed (>90%, transmitted light > 380 nm).

A solid product was recovered by the evaporation of the aforementioned aqueous dispersion (Figure 2(f), e.g., SQ/ZrO₂-NPs (APTMO/S/ZTB = 0.3)), indicating that the product's water-dispersibility is not due to the decomposition of Zr–O and Si–O bonds. Even after repeating the treatment of dispersion in water and the evaporation

FIGURE 3: UV-Vis spectra of aqueous dispersions of SQ/ZrO₂-NPs (feed molar ratio of APTMOS/ZTB = 0.3) with various concentrations.

FIGURE 4: Volume-average particle size distributions of 2.0 w/v% aqueous dispersions of SQ/ZrO₂-NPs measured by DLS at 25°C. Feed molar ratio of APTMOS/ZTB = (a) 0.3, (b) 0.6, (c) 0.8, and (d) 1.0.

of water three times, the high transparency of the aqueous dispersion of the SQ/ZrO₂-NP was maintained, as confirmed by visual observation. Here, the dispersion treatment was performed by adding water to the SQ/ZrO₂-NP (concentration, 1.0 w/v%) and stirring at ca. 50°C. These results strongly indicate that SQ/ZrO₂-NPs exhibit high water-dispersibility and redispersion is possible.

The volume-average particle sizes of the SQ/ZrO₂-NPs (APTMO/S/ZTB = 0.3, 0.6, 0.8, and 1.0) estimated by DLS measurements in water (2.0 w/v%) at 25°C were assessed to be 4.6 ± 2.4 , 6.9 ± 3.1 , 15.2 ± 5.7 , and 23.8 ± 7.3 nm, respectively (Figure 4), indicating that the SQ/ZrO₂-NPs (APTMO/S/ZTB $\geq$ 0.3) were well-dispersed, relatively small nanoparticles.

FIGURE 5: Correlation between refractive indices and concentrations of aqueous dispersions of SQ/ZrO₂-NPs (feed molar ratio of APTMOS/ZTB = 0.3).

3.3. Refractive Indices of SQ/ZrO₂-NP Aqueous Dispersions.

To estimate the refractive indices of the SQ/ZrO₂-NP (APTMO/S/ZTB = 0.3) by the Abb refractometer, we attempted to prepare a film on a flat glass substrate. However, a stable film could not be obtained. Therefore, various concentrations (0 (only water), 19.6, 41.7, 60.6, and 64.7 wt%) of the aqueous dispersions of the SQ/ZrO₂-NP were prepared, and the refractive indices of these dispersions were estimated by the Abb refractometer to be 1.333, 1.367, 1.420, 1.481, and 1.496, respectively. These values were plotted on a graph and their fitted curve was calculated as follows: [$y = -7.0178 \times 10^{-10}x^4 + 1.8343 \times 10^{-7}x^3 + 5.7152 \times 10^{-6}x^2 + 0.0015738x + 1.333$]; y and x denote refractive indices and concentrations of the aqueous dispersions of the SQ/ZrO₂-NP (APTMO/S/ZTB = 0.3), respectively (Figure 5). From this fitted curve, the theoretical refractive index of the SQ/ZrO₂-NP, that is, that for 100 wt%, was calculated to be 1.66.

3.4. Investigation of Necessity of Two-Step Sol-Gel Copolycondensation.

The highly water-dispersible SQ/ZrO₂-NPs were obtained by the aforementioned two-step sol-gel copolycondensation; that is, alcoholic hydrochloric acid in the first step and water in the second step were employed as solvents. Here, to investigate the necessity of this two-step reaction, a comparative sol-gel copolycondensation experiment was performed using 0.1 mol/L aqueous hydrochloric acid as a substitute for methanolic hydrochloric acid in the first step. The Si/Zr elemental ratio of the resulting product obtained with a feed molar ratio of APTMO/S/ZTB = 0.3 was estimated by EDX measurements to be ca. 0.38. The transmittance of the aqueous dispersion of this product decreased compared with that of the SQ/ZrO₂-NPs obtained by the aforementioned two-step sol-gel copolycondensation (Figure 6). Its turbidity was also confirmed by visual observation (Figure 6, inset). Use of aqueous hydrochloric acid in the first step probably resulted in the formation of

FIGURE 6: UV-Vis spectrum of aqueous dispersion (1.0 w/v%) of the product obtained using 0.1 mol/L aqueous hydrochloric acid as a substitute for methanolic hydrochloric acid in the first-step reaction. The inset shows a photograph of this aqueous dispersion.

a larger particle size because the progress of the sol-gel reaction of ZTB was considerably faster than that using methanolic hydrochloric acid. These results indicate that the two-step reaction is required for the preparation of highly water-dispersible nanoparticles.

3.5. Plausible Structure of SQ/ZrO₂-NPs. We assume that the water-dispersible properties of the SQ/ZrO₂-NPs originated from the ZrO₂-SiO_{1.5}(CH₂)₃NH₃⁺Cl⁻ core-shell structure. Therefore, to investigate the presence of ammonium cations (–NH₃⁺) on the surface of the SQ/ZrO₂-NPs, an ion-exchange reaction of the SQ/ZrO₂-NP (APTMOs/ZTB = 0.3) was performed with sodium laurate. This was achieved by pouring the SQ/ZrO₂-NP aqueous dispersion into an aqueous solution of sodium laurate to immediately precipitate. The resulting product was not dispersed in water due to its hydrophobicity (Figure 7), although, as previously described, that with Cl⁻ was well dispersed. These results indicate the possibility of the ion-exchange reaction of the SQ/ZrO₂-NP, resulting in change in dispersibility in water due to the exchange of counter anions (from Cl⁻ to a laurate anion). Therefore, the SQ/ZrO₂-NP probably exhibits a core-shell structure with –NH₃⁺ groups on its surface. Owing to charge repulsion of –NH₃⁺ groups on the surface, SQ/ZrO₂-NPs were dispersed well in water.

3.6. Plausible Formation Mechanism of SQ/ZrO₂-NPs with Core-Shell Structures. Since ZTB is much easier to be hydrolyzed than APTMOs, a nanoaggregate composed of ZTB and oligomeric ZrO₂ components would form in the first place. Successively, hydrolysis of less reactive APTMOs probably occurred, and partially hydrolyzed material composed of (CH₃O)₃Si(CH₂)₃NH₃⁺Cl⁻ and oligomeric SiO_{1.5}(CH₂)₃NH₃⁺Cl⁻ components would stack on the surface of the ZTB/ZrO₂ aggregate. Thus, it would be assumed that the intermediate with the core-shell structure was formed (Scheme 2(a)). Subsequently, when the water was

FIGURE 7: A photograph of aqueous suspension (1.0 w/v%) of the product obtained by ion-exchange reaction of the SQ/ZrO₂-NP (feed molar ratio of APTMOs/ZTB = 0.3) with sodium laurate.

SCHEME 2: Plausible formation mechanism of SQ/ZrO₂-NPs with core-shell structures.

added to the intermediate and the resulting aqueous solution was heated in the open system, the reaction completely proceeded to probably prepare the final product (SQ/ZrO₂-NPs) with ZrO₂-SiO_{1.5}(CH₂)₃NH₃⁺Cl⁻ core-shell structure (Scheme 2(b)).

4. Conclusions

Highly water-dispersible SQ/ZrO₂-NPs were prepared by the two-step sol-gel copolycondensation of a mixture of APTMOs and ZTB, whereby *n*-butanol and methanolic hydrochloric acid were first used as a mixed solvent, followed by water. Aqueous dispersions of SQ/ZrO₂-NPs obtained with a feed molar ratio of APTMOs/ZTB of more than 0.3 were highly transparent, and redispersion was possible. The volume-average particle sizes of the SQ/ZrO₂-NPs (APTMOs/ZTB ≥ 0.3) were assessed to be ca. 4.6–23.8 nm

by DLS measurements in water. The theoretical refractive index of the SQ/ZrO₂-NP (APTMOs/ZTB = 0.3) was estimated to be 1.66. It was assumed that the water-dispersible properties of the SQ/ZrO₂-NPs originated from the ZrO₂-SiO_{1.5}(CH₂)₃NH₃⁺Cl⁻ core-shell structure.

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