Preparation of Anisotropic Silica Nanoparticles Using Seed-Mediated Growth Method

1. Introduction
There has been growing interest in the synthesis of anisotropic colloidal particles in sub-micrometer scale by mimicking molecular assembly behaviors [1, 2]. Great progress has been made to date; however, preparation of anisotropic silica nanoparticles (ASNPs) in high yield remains a major challenge. Here we report a facile method for fabricating ASNPs with a chain-like shape which is based on the seed-initiated growth approach.

2. Experimental
An appropriate portion of the silica NPs seeds [3] with an average diameter of about 2 nm was taken and added to the alcohol-water mixture. A specific amount of arginine was added to the suspension to achieve 15 mM. Subsequently, a required amount of TEOS was added to the suspension and the reaction was allowed to proceed at 60 °C with constant stirring of ca. 500 rpm. Electron microscopic images were obtained using a Hitachi S-900 and JEOL JEM-2000EX II.

3. Results and discussion

Growth of ASNPs is confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A representative SEM image of the ASNPs prepared by seed-initiated growth method is shown in Figure 1a. This image shows that the sample is composed of a large quantity of ASNPs with diameter of up to about 26 nm along with no or few spherical NPs. In addition to SEM, the ASNPs were investigated with TEM (Figure 1a, inset), giving similar results.

The NP aspect ratio \( \phi = L/D \) (where L and D denote the particle length and thickness, respectively) can be controlled within the range of \( \phi = 2-20 \) by changing the amount of TEOS and/or reaction condition. The average anisotropy \( \phi \) is found to decrease with increasing the dosage of TEOS, mainly due to increasing the thickness D (Figure 1b). Additionally, the dispersion of ASNPs remained stable for several months with high \( \phi \) and several weeks with low \( \phi \). Even if the ASNPs deposit from the colloidal dispersions, gentle shaking enable the redispersion of the precipitate.

ASNPs formation was sensitive to the concentration and size of seeds; in other words, the shape anisotropy changed dramatically depending on the seed concentration and size. At low seed concentration, the NPs were typically found as monomer, dimers and trimers. At high seed concentration, ASNPs with high \( \phi \) were formed and a small extent of aggregates also can be seen. These results are in agreement with the case that the higher number density of NPs leads to higher collision frequency between them. With increasing the seed size, the yield of ASNPs decreased. This result agrees with DLVO theory, which reveals that the repulsive barrier for smaller NPs is lower when the same potential curve is involved [1].

Figure 1. SEM images of ASNPs with high aspect ratio \( \phi \) (a) and low \( \phi \) (b)

The wormlike morphology of the ASNPs indirectly demonstrates that the silica seeds self-assemble into one-dimensional (1D) NP chains in the dispersion before growth. To help understand the process of self-assembly in the present system, the growth mechanism of these ASNPs was studied in detail. We discovered that the concentration of arginine and ethanol in seeding suspension was the key to the preparation of ASNPs. As the arginine and/or ethanol concentration increases, four distinct morphologies can be identified: monodisperse NPs (Figure 2a), bimodally dispersed NPs (Figure 2b), chain-like NPs (Figure 1) and aggregates (Figure 2c). To elucidate the role of ethanol in this system, comparative experiments were carried out by replacing ethanol with methanol, n-propanol, 2-propanol and t-butanol. The similar chain-like ASNPs could be synthesized in these alcohol-water mixtures at the condition of approximately the same dielectric constants as ethanol-water mixture. It was speculated that a decrease in the dielectric constant of the medium surrounding charged NPs caused the self-assembly of the seeds into 1D NP chains and then ASNPs were formed by the deposition of silica derived from TEOS.

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References

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