OBSERVATION OF TIME EVOLUTIONARY PHYSICOCHEMICAL PROPERTY OF SILICA NANOPARTICLES AS CRM CANDIDATES

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Abstract: The necessity for the synthesis of nanomaterials (NMs) with well-controlled physicochemical properties is emerging with the development of nano-industry and advanced applications of nanomaterials in biomedical fields. In this study, we observed time evolution of physicochemical properties of silica nanoparticles (SiO_2 NPs) as candidates of certified reference materials (CRM) for size analysis. We have validated the size stability of spherical SiO_2 NPs exhibiting diameters of 30 and 40 nm in diameter for one year.

Keywords: silica nanoparticles, UV-visible spectroscopy, DLS size, zeta potential, pH

1. INTRODUCTION

Recently, the safety of NMs has been a global issue through health and environment because they are widely used in various areas such as cosmetics, home appliances, medicines and others along with the industrial development. Therefore, many research groups throughout the world have been performing toxicity test of NMs including genotoxicity, nerotoxicity, cytotoxicity and inhalation test. However, physicochemical properties of NMs should be properly characterized in the whole process of nanotoxicity studies. In this respect, size of NMs is regarded as one of the important physical properties related with nanotoxicity. Also, the quantity of effectors, which have catalytic activities, on NM surface is closely related with the size of NMs. So, size of NM is one of the most important properties of NMs. In view of industrial requirements, CRM for NM property helps to enhance the reliability of measurement and make it easier to perform quality control of nanoproducts. Such CRM can also be used for round robin test among international laboratories to achieve global agreement on the measurement techniques of interest. It is generally required for a candidate of CRM to have homogeneity of property related with the corresponding measurand. Once the homogeneity has been established, long-term stability has to be validated for reasonable shelf-life of the CRM.

SiO_2 NPs are used in many areas such as optics, catalysis, composites, paints, biomedical analyses and drug delivery system development. In this study, we have synthesized spherical silica NPs as CRM candidates for SEM and DLS (dynamic light scattering) size measurement. SiO_2 NPs were prepared to have 30 and 40 nm in diameters, respectively, and the time evolution of physicochemical properties has been observed for SEM size, DLS size and zeta potential.

2. EXPERIMENT

In order to synthesize SiO_2 NPs, we used tetraethyl orthosilicate (TEOS) (98 %, ACROS) as the precursor and L-arginine (Sigma) as the catalyst. L-arginine was added into deionized water (DIW; 18.2 MΩ·cm) contained in the reaction apparatus. The temperature of reaction solvent was raised up to 70℃ while stirred at 1,500 rpm using a magnetic bar. After the addition of the precursor, the catalyst, the reaction mixture was maintained 24 h at 70℃ with stirring at 1,500 rpm. The quantity of TEOS and reaction time were varied depending on the target size of silica NPs (30 and 40 nm). The UV-visible absorption spectrum of SiO_2 NP in aqueous suspension was measured using a spectrophotometer (Shimadzu UV-1700). DLS size of SiO_2 NP in aqueous suspension was measured using a particle size analyzer (Ostuka Electronics, Photal ELS-Z). Synthetic SiO_2 NPs concentration was determined by measuring the weight of dried powders after dehydration of 1 mL suspension in an oven until the weight change was lower than 0.1 % for one day. Measurements of zeta potential and pH were performed using an electrophoretic laser Doppler velocimeter (Nanosizer Z, Malvern Instr. Ltd.) and a pH meter (Orion 3 star pH Benchtop, Thermo electron corporation), respectively. The size and shape of SiO_2 NPs were measure using a scanning electron microscope (SEM, S-4800, HITACHI). The individual sizes of the SiO_2 NPs were analyzed on the image displayed by graphic program. Time evolutionary observation of physicochemical properties were performed at the time points of day of synthesis (0 day), after 1 and 2 weeks, 1, 2, 3, 6, 9, and 12 months.

Table 1. Properties of spherical SiO_2 NPs in aqueous suspension with 30 and 40 nm in diameter

Property analysis	30 nm SiO_2 NPs	40 nm SiO_2 NPs
DLS size	37.2 ± 3.8 nm	52.4 ± 0.5 nm
SEM size	31.7 ± 2.2 nm	41.7 ± 1.9 nm
Zeta potential	-81.4 ± 5.3 mV	-54.6 ± 1.4 mV
Concentration	20 mg/ml	44 mg/ml

3. RESULTS AND DISCUSSION

Preparation of SiO_2 NP suspension for time evolutionary measurement of properties

Spherical SiO_2 NPs in aqueous suspension with 30 and 40 nm in diameters were synthesized in large quantities and characterized. The results of DLS and SEM size measurements, zeta potential and concentration of NPs in suspension have been tabulated in Table 1. After the analysis of properties, the concentrations of SiO_2 NP suspensions were adjusted to be 5 mg/ml by adding proper amount of DIW. The diluted SiO_2 NP suspensions were divided into 10 ml aliquots in 20 ml glass vials with Teflon caps for the time evolutionary test of property change. The time points for the property measurements were 1 week, 2 weeks, 1, 2, 3, 6, 9 and 12 months. To see the effect of sedimentation with time evolution, we prepared two vials for each time point: the SiO_2 NP suspension in one vial was thoroughly mixed by vortex for 20 s before the property measurement, while the properties of SiO_2 NP suspension in the other vial was measured by using fraction of upper region without mixing process.

The primary particle size of SiO_2 NPs was observed using SEM and the SEM images are shown in Fig. 1.

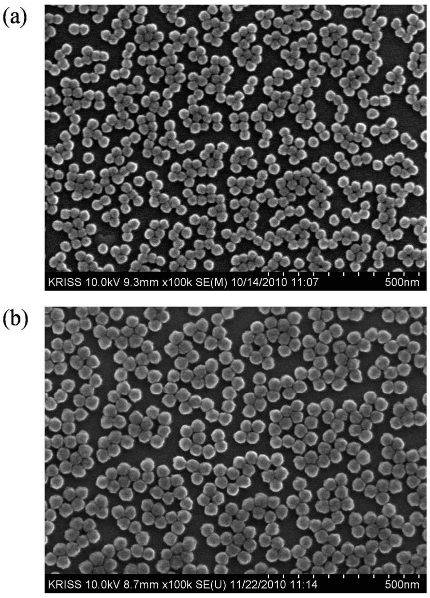

Figure 1. SEM images of SiO_2 NPs for (a) 30 nm SiO_2 NPs (b) 40 nm SiO_2 NPs

Analysis results of property measurements on SiO_2 NPs with time evolution

UV-visible (UV-vis) absorption spectra of 30 and 40 nm SiO_2 NPs in aqueous suspensions are depicted in Fig. 2. The absorption behaviour of SiO_2 NPs in aqueous suspension originates from two factors: one is reduced transmittance due to scattering and the other is electron-hole formation by the absorption of photons. In case of amorphous silica, the absorption due to electronic transition is expected to show weak band profiles, however, the absorption spectra of aqueous silica NP suspension showed monotonic decrease from the shot wavelength to long wavelength. This is an indication of the loss of transmitted light by Rayleigh scattering of which the cross section is a function of $(1/\lambda)^4$. Thus it was thought that most of UV-vis absorption spectra for SiO_2 NP suspension attributed to the scattering of light by NPs in suspension.

When we observed two UV-vis absorption spectra from mixed and unmixed suspensions with vortex, the absorption profiles showed different values after 2 months for 30 nm SiO_2 NP and 1 week for 40 nm SiO_2 NP, respectively. UV-vis absorption spectra of unmixed SiO_2 NP maintained the same profile thereafter. These results implied that a small amount of SiO_2 NP agglomerates were formed in aqueous suspension for both size of NPs. As the small amount of agglomerates in aqueous suspension sediment with time evolution, the absorption spectra of unmixed suspension showed lower value that those of mixed suspension. The rate of sedimentation for 30 nm SiO_2 NP agglomerates was much slower (~ 2 months) that that of 40 nm SiO_2 NP agglomerates (~ 1 week). The amount of agglomerates was so small that the existence of the agglomerate did not change DLS size of SiO_2 NPs (Fig. 2.)

The DLS sizes of SiO_2 NPs were almost invariant for 12 months as shown in Fig. 3a and 3b. On the other hand, zeta potentials of SiO_2 NPs were increased from highly negative values to *ca.* - 40 mV for both NPs. (Fig. 3c and 3d) As zeta potential is very sensitive to the suspension pH, we measured pH of both suspensions at each time point of measurement. pH values slightly changed toward neutral (pH 7) for both suspensions. (Fig. 3e and 3f) The isoelectric point, where the zeta potential becomes zero according to the solution pH, of SiO_2 NP is known to be between pH 1.7 and pH 3.5 [1].

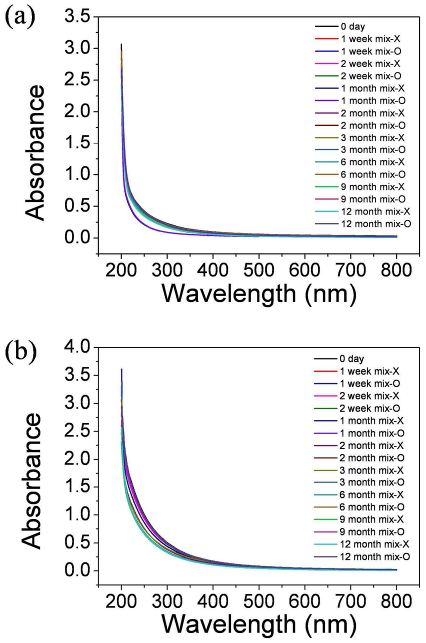

Figure 2. SiO_2 NPs UV-visible spectrophotometer results by lapse of time. (a) 30 nm SiO_2 NPs (b) 40 nm SiO_2 NPs

It is also reported that the zeta potential of SiO_2 NPs is drastically changed in the pH range of 2 to 5 [2]. In this pH range, zeta potential is known to change linearly. Therefore, the change of zeta potential is not attributable to the change of suspension pH. We presume that the increase of zeta potential of SiO_2 NPs toward neutral charges is the result of reaction between SiO_2 and CO_2. In case of DIW maintained in the air, pH of DIW decreases down to pH 5.5 due to dissolution of CO_2 gas forming carbonic acid. However, pH values of the SiO_2 NP suspensions converged to neutral (pH 7) regardless of their initial pH: pH 8 for 30 nm SiO_2 NP suspension and pH 6 for 40 nm SiO_2 NP suspension. So we suspect that the surface of SiO_2 NPs reacted with carbonic acid in a very small amount resulting in the interruption of acidification of NP suspension.

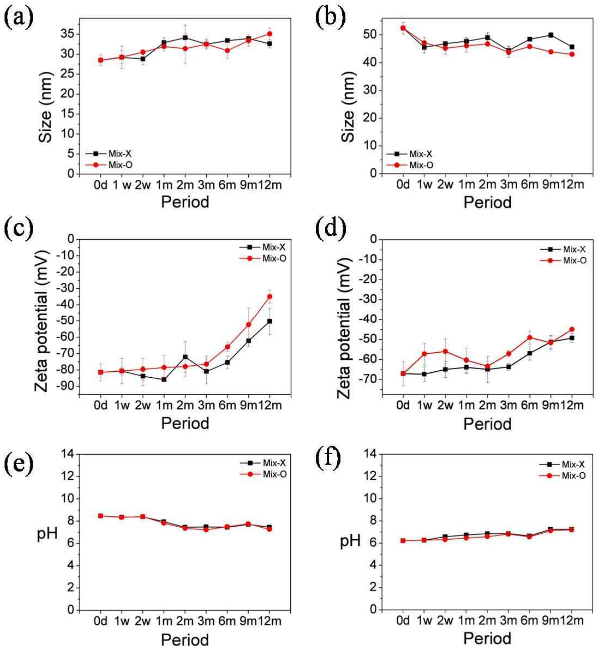

Figure 3. SiO_2 NPs DLS, zeta potential and pH observation results by lapse of time. (a) DLS of 30 nm SiO_2 NPs (b) DLS of 40 nm SiO_2 NPs (c) Zeta potential of 30 nm SiO_2 NPs (d) Zeta potential of 40 nm SiO_2 NPs (e) pH of 30 nm SiO_2 NPs (f) pH of 40 nm SiO_2 NPs

4. CONCLUSION

In this study, we observed physicochemical property of SiO_2 NPs in aqueous suspension as candidates of CRM for SEM and DLS size measurement. It was shown that the DLS size of SiO_2 NPs in aqueous suspension was almost invariant for 12 months. Zeta potential of NPs increased toward neutral charge up to *ca*. - 40 mV for 12 months. As the pH of suspensions was not much altered in this period, the change of zeta potential was not supposed to originate from the pH change. The reaction of dissolved CO_2 gases with SiO_2 NP surface might be a source of surface charge neutralization

5. REFERENCES

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