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# Synthesis of ultra-small hollow silica nanoparticles using the prepared amorphous calcium carbonate in one-pot process

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ABSTRACT

The ultra-small hollow silica nanoparticles were synthesized using the prepared amorphous calcium carbonate (ACC) particles as a template. The ACC particles were firstly prepared by carbonation method, which procedure was conducted in the methanol solvent to form the $Ca(OCH_3)_2$ layers on the ACC particles. An effect of methanol concentration on the morphology of ACC particles was also investigated. The prepared ACC particles were directly coated by silica through adding tetraethoxysilane (TEOS) into the methanol solvent. Hence, the ACC-silica core-shell particles were obtained since the ACC particles have a positive charge and interact with hydrolyzed TEOS. The ACC particles could be stabilized through the reaction between methanol and calcium ions when the methanol concentration was increased over than 40 vol%.

## 1. Introduction

Hollow silica nanoparticles (HSNPs) have a unique balloon-like structure in which is air cavity and is covered by silica shell. According to their structures, HSNPs show superior properties than dense silica nanoparticles, such as a high surface area, a low thermal conductivity, a low dielectric constant and so on [1–5].

In general, the synthetic routes for HSNPs can be categorized into two methods which are template and non-template. In the non-template method, it can be divided to the electrostatic atomization method [6] and spray pyrolysis method [7]. The advantage of these methods is to be able to mass produce HSNPs. However, the obtained HSNPs are polydispersed. On the other hand, the shape of HSNPs can be easily controlled by the template method. In the template method, silica was firstly coated on the templates to form the silica shells, followed by removing the templates *via* thermal or chemical treatments [8]. However, the carbon dioxide gas and waste organic solvent are produced as the byproducts. Calcium carbonate ($CaCO_3$) [9–12] and hydroxy apatite [13] have shown a great promise as a template for synthesizing HSNPs because the templates can be easily removed by only acid treatment without calcination and organic solvent treatment. In addition, it is not necessary to adjust surface charge of particle for silica coating. Fuji et al. reported synthesis of the cubic-, needle- and sphere-like HSNPs using $CaCO_3$ template [10]. Therefore, the $CaCO_3$ template is extensively used to be synthesized for a variety of shapes including to non-sphere structure. So far, the report for synthesis of ultra-small HSNPs (<20 nm) using $CaCO_3$ template is still scant.

The methods to prepare $CaCO_3$ can be classified as two categories such as reagent method [14] and carbonation method [15–17]. The coprecipitation method which produces $CaCO_3$ particles by mixing of carbonate salt and calcium salt in solution. The carbonation method which produces $CaCO_3$ particles by bubbling of carbon dioxide ($CO_2$) gas into the calcium solvent is a conventional method for the low cost and the availability of the raw materials. Amorphous calcium carbonate (ACC) particles are well-known as ultra-small $CaCO_3$ particles of a primary phase. There are a lot of reports about the synthesis of the stabilized ACC particles such as adjusting the calcium ion, pH, temperature [14,18], and mixing with additives [19–22]. Moreover, the ACC particles are easily formed to be aggregation at pH lower than pH 9.10 [23]. They further gradually grow up. Nevertheless, the ACC particles commonly confine themselves to develop when they are synthesized in alcohol solvent [24–27].

In this work, ACC particles were prepared by a carbonation method via bubbling $CO_2$ gas into calcium ions dispersing in methanol solution. An effect of methanol concentration on the $CaCO_3$ formation was investigated. The pH of the ACC preparation was studied in a rage of 9.10–9.40. After that, ultra-small HSNPs were synthesized using the prepared ACC particles in one-pot process. The schematic diagram of the synthesis is proposed by Fig. 1.

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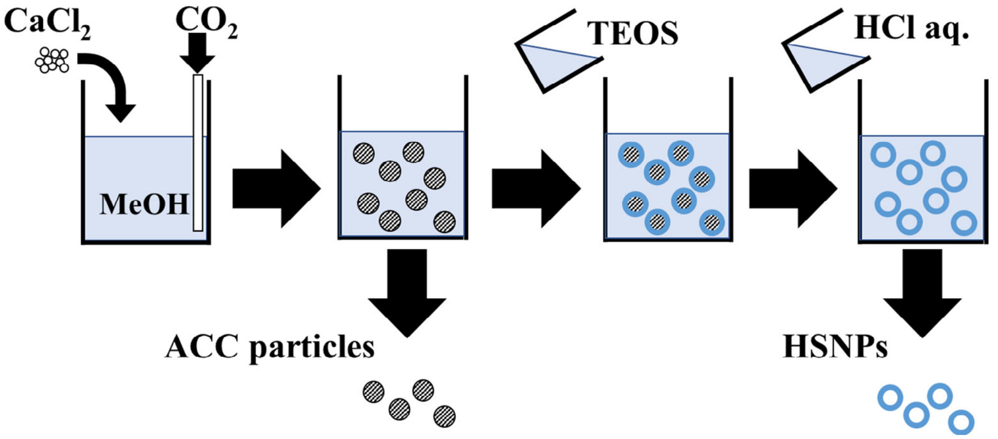

**Fig. 1.** Schematic diagram of the synthesis of HSNPs using the prepared ACC in one-pot process.

## 2. Experimental sections

### 2.1. Materials

Calcium chloride ($CaCl_2$, Wako Pure Chemical) and gaseous $CO_2$ were used as precursors for preparation of ACC particles. HSNPs were synthesized through a sol-gel reaction using tetraethoxysilane (TEOS, Wako Pure Chemical) as a silica source. For the sol-gel reaction, an ammonium hydroxide ($NH_4OH$; 25%, Wako Pure Chemical) was used as a catalyst. Hydrochloric acid (Wako Pure Chemical) was used for the ACC core template removal. Methanol (Wako Pure Chemical) was used as a reaction solvent. All chemicals were used as received without further purification.

### 2.2. Preparation of ACC particle template

$CaCl_2$ was dissolved into 500 mL methanol aqueous solution. The methanol acts an inhibitor in the preparation of ACC particles [24]. Therefore, a concentration of the methanol was respectively decreased from 100 vol% to 40 vol%, 20 vol% and 0 vol% to study its effect on morphologies of the ACC particles. The $CaCl_2$ solution was mixed with 25% $NH_4OH$. The mixture was adjusted pH to 9.50 by hydrochloric acid (HCl). After that $CO_2$ bubbling was flow into the mixture at pH 9.50. The flow rate of $CO_2$ bubbling was set at 0.01 L/min. Through increasing $CO_2$ bubbling time, the pH of such a mixture was respectively decreased to 9.40, 9.30, 9.20 and 9.10. Because, the formed ACC particles were easily aggregated at below pH 9.10, and the aggregated ACC easily grew up [23]. The solution at each pH was collected and further used for synthesis of HSNPs. To observe morphologies of the prepared ACC particles, the solutions containing the ACC particles were dropped onto a Cu grid and observed their morphologies using a field emission scanning electron microscopy (FE-SEM; JSM-7600F, JEOL co.). The aggregation of the obtained ACC particles in the solution at various methanol concentrations was determined by a UV–vis (UV3150, Shimadzu Corp.). The crystal structure of those ACC particles was also determined by X-ray diffractometer (XRD, Rigaku, Ultima Ⅳ) with CuKα (λ = 1.5406 Å) radiation. Prior to the crystal structure studies, the ACC particles dispersing in the solutions at pH 9.20 were filtrated and then precipitated. The obtained ACC particles were washed by acetone to remove excess water. The washed ACC particles were dried in a vacuum oven at at 40 °C for 24 h. The zeta potential of the prepared ACC particles dispersing in the solution was measured by a zetasizer (Zetasizer Nano, Marvern Instruments Ltd.) in order to study an interaction between ACC particles and hydrolyzed TEOS.

### 2.3. Synthesis of HSNPs using the prepared ACC particles

The solutions containing ACC particles at which were prepared different pH was added 10 mL of TEOS. The TEOS acted as a silica source thus the silica coated on surface of the ACC particles in the one-pot process as shown in Fig. 1. The ACC particles and TEOS were mixed for 2 h to complete yield silica coating on the ACC particles. The obtained ACC-silica core-shell particles were observed their morphologies and their compositions using the FE-SEM in Energy Dispersive X-ray Spectrometry (EDS; JSM-7600F, JEOL co.). After that, HCl was added to the obtained suspension so as to decrease pH of the solution approaching to 3.00. Consequently, the ACC particles were gently dissolved into the HCl leading to produce HSNPs. The obtained HSNPs were observed their morphologies using the FE-SEM in TED-mode. The specific surface area of the obtained HSNPs was calculated from the adsorption isotherms of nitrogen ($N_2$) by Brunauer-Emmett-Teller (BET) method. The adsorption isotherms of $N_2$ at 77 K were measured in an automatic volumetric gas adsorption instrument (Belsorp-max, MicrotracBEL, Japan). Prior to measurements, the samples were outgassed at 473 K for 2 h under vacuum less than $10^{-2}$ kPa.

## 3. Results and discussion

### 3.1. Morphologies and crystal structure of the ACC particles

The effect of pH on morphologies change of the ACC particles were studied using SEM. The SEM image of the ACC particles prepared using 0 vol% methanol (pure water) at pH 9.40, 9.30, 9.20, and 9.10 was respectively shown in Fig. 2(a–d). They were found that the prepared particles gradually growth when pH of the solution was decreased. Also, the particles prepared using 20 vol% exhibit a larger size with decreasing pH of the solution that are shown in Fig. 2(e–h). However, the size of the ACC particles prepared using 40 vol% methanol at pH 9.40, 9.30, 9.20 and 9.10 in which are shown Fig. 2(i–l) seems to be smaller than other low methanol concentration. The result is an evidence to suggest that methanol possibly acts as an inhibitor of the ACC preparation process although decreasing its pH. Interestingly, the ACC particles prepared by 100 vol% methanol and with the decreasing pH as could be seen in Fig. 2(m–p) obviously show their size about 20 nm, which can be denoted as ultra-small ACC particles. These results emphasized that the methanol probably acts as the inhibitor of the ACC particle preparation [27].

Fig. 3 presents UV–vis spectra of the ACC solutions prepared using 0 vol% methanol (pure water) and 40 vol% methanol at pH

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