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Original Research Paper

## Simultaneous control of size and surface functionality of silica particle via growing method

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## ABSTRACT

Although silane treatment has been studied as a simple and powerful tool to modify the surface of silica particle, there are still several difficulties in terms of controlling surface functionality and size of nanoparticles. Here we develop a growing method to overcome above drawback. The method was processed by continuously injecting precursor using syringe pump. According to the continuous injection, the concentration of precursors in media are properly controlled, and then the continuous injection of precursor promotes the growth of silica particles. When the functional silanes (silane coupling agents) are used, the method can control the amount of surficial functional groups on the silica particle, and can adjust diameter of the particle simultaneously. Furthermore, well-controlled functional silica particles made by growing method are used for catalytic reaction, Knoevenagel reaction, as a solid state catalyst.

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## 1. Introduction

In the last two decades, various particle fabrication methods were investigated with advance of nanoscale techniques such as lithography [1,2], sol–gel reaction [3–7], emulsion [8,9], and microfluidics method [10,11]. Application fields of particle-shaped materials were extended as well and, these materials were now able to be considered in real industrial fields [12]. The crucial reason that the particle-shaped materials can be applied in various applications (particularly in catalytic application) is that the nano-sized materials provide significantly high specific surface area and easy recovery after the reaction [13–17], implying that these nano-sized catalysts contain advantage of heterogeneous catalyst and minimize disadvantage of those.

In terms of material types for the nano-particles preparation, polymers, metals, biomaterials and ceramics were often investigated in previous researches [18–26]. Among them, silica nanoparticles are the most frequently adopted in fabrication of the nano-particles, due to the properties such as easy fabrication method, convenient surface treatment, biocompatibility, uniform diameter and narrow size distribution [27–29]. However, despite the general silane treatment seems to be well studied and developed by many researchers, the methods were insufficient to apply the real industrial fields (especially in catalytic application), mainly

because of lack of enough functionality. In addition, the process still require more investigations to improve their functionality because known method for surface treatments have been failed to provide versatile controllability of functional groups, enough amount of the functional group, and control of solvent-selectivity simultaneously [30–34]. In general, hydrolysis surface treatment (HST) and direct condensation in toluene (DCT) were often used as surface treatment method. The HST was induced by condensation reaction between silane and the silanol of silica particle within homogenizing agents such as alcohols and water [35]. Therefore, the HST was available to treat in safer and easier process than DCT because the process was occurred in relatively non-toxic chemicals. However, this method was difficult to obtain high density of conjugated silane on substrate because the condensation reaction between silanol in coupling agent and particle surface could be reversible and promote esterification in these types of solvent.

On the other hand, although DCT, which was treated by non-hydrolysis condensation in toluene, can provide enough amount of functional groups on the surface [36], it required toxic chemicals such as toluene *etc.* and had limitation in controlling amount of surface functional groups. In addition, after the condensation reaction, the surface property of treated silica particle was changed from hydrophilic into hydrophobic due to absorption of organic solvents. Therefore, obtained amino-silica particle from direct condensation was difficult to be applied in aqueous medium, such as bio-, medical-fields.

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Furthermore, The size growth procedure of silica particle was also challenging. A size of silica particles usually remain on that of commercially available one (from 10 nm to few micrometer) [4,37,38]. Although the researchers expected that the nano-sized particle has shown higher catalytic activity than micron-size due to its high surface area, it seems to be difficult to use in real catalytic applications because the surface energy from higher surface area induced aggregation of the particle, and thus the aggregation of the particles caused to decrease the specific surface area of the particle. Furthermore, in the case of biological application, the particles with nano-sized diameters was difficult to be applied because the nano-sized particle can be taken by an organs and can induce a cytotoxicity [39,40]. Therefore, it is strongly required for development of simple method to control precise size of particles and their number of functional groups simultaneously.

Herein, we introduce new method for preparation of silane treated silica particle named growing method (GM). Unlike the previous silane treatment methods, the silane with specific functional groups were introduced during the growth process in order to maximize functional groups and control particle size simultaneously. With this method, we are able to produce the particle with intended diameters via continuous injection of functional precursor. Furthermore, the GM could decrease the reverse reaction of silanes because the continuous injection of silane promoted the forward reaction to produce the silane-treated particle. As a result, the new method could provide increased amount of organic functional groups on the particles, controlled quantity of the functional group, and thus enhanced catalytic activity maintaining their hydrophilic property.

## 2. Experimental

### 2.1. Materials

Tetraethylorthosilicate (99%, Aldrich) (TEOS), ethyl alcohol (99.9%, anhydrous, Samchun chemical co.), and ammonia solution (23%, Junsei) was selected as precursor, solvent, and catalyst respectively. (3-aminopropyl) triethoxysilane (99%, Aldrich) (APS), Toluene (anhydrous, 99.8%, Aldrich) and methylene chloride (anhydrous, >99.8%, Aldrich) was used for a silane treatment. For Knoevenagel reaction, 4-Hydroxybenzaldehyde (98%, Aldrich) and ethyl cyanoacetate ( $\geq 98\%$ , Aldrich) were selected as reactants for the catalytic reaction. All reagents were used without any purification.

### 2.2. Growth of silica particle

The preparation of colloidal silica particle was based on Störber method. 20 ml of ethyl alcohol, 2 ml of ammonia solution, and 3.2 ml of distilled were well mixed in 50 ml round bottom flask using magnetic bar. To form the seed particle, 2 ml of TEOS was injected into the mixed solution and reacted for 4 h at 35 °C. To grow the size of the particle, additional precursor (TEOS) was gradually injected into the solution using syringe pump. The rate of injection of the precursor was 2 ml/h. Depending on amount of additionally injected TEOS solution and reaction time, particles were named as 1-silica (2 ml), 2-silica (4 ml), and 3-silica (6 ml) respectively.

### 2.3. Amine treatment in GM

To obtain the amino silane-treated silica particle using GM, APS was injected into the grown 2-silica particle solution using syringe pump while the particle growth procedure was progressed. Depending on its injected amounts, the silanes were introduced

using syringe pump continuously as amount per unit hour. After the reaction was finished, the products were obtained by centrifuge and washed using ethanol several times. The particles was dried at 80 °C oven before use.

### 2.4. Amine treatment on silica surface using hydrolysis surface treatment and direct condensation in toluene

To obtain APS-treated particles via HST and DCT, the 3-silica particles were obtained by centrifuge and several washing procedures. For the HST, 1.0g of prepared 3-silica particles were re-dispersed in 10 mL of anhydrous ethyl alcohol by sonication at room temperature. APS and distilled water were added into the colloidal silica solution and mixed with stirring for 24 h. The particle was obtained by centrifuge and washed using ethanol several times. To obtain APS-treated silica via DCT, 1.0g of 3-silica particles were dispersed in 50 ml of toluene using sonication and the 1.2 ml of APS was injected. The mixed solution was reacted in 110 °C oil bath with reflux for 24 h. After that, to remove the excess physisorbed silane, added methylene chloride into the reaction flask. The particles were obtained after several washing procedures using ethanol.

### 2.5. Knoevenagel reaction

In order to achieve the Knoevenagel reaction, each particle (No treated, 100 G, and 300 G) was dispersed in 2 ml of toluene by ultra-sonicator till the particles were perfectly dispersed. 0.4 ml of benzaldehyde and the same amount of ethyl cyanoacetate were injected into the reaction batch. The particles and reactants were well mixed using magnetic bar. The final products and the silica particle were divided from mixture by centrifuge in unit time and the solution was filtrated using syringe filter to remove the remaining silica catalyst.

### 2.6. Characterization

SEM images were taken using HITACHI S-4800 at an acceleration voltage of 10 kV. Confocal laser scanning microscopy (CLSM) images for confirmation of amine on the particles were obtained using ZEISS LSM5 LIVE at 532 nm wavelength for rhodamine and 488 nm for FITC-STV. Photoluminescence spectroscopy (PL) was completed using Cary Eclipse Fluorescence Spectrophotometer. The FITC treated silica particles were dispersed in 3 ml of distilled water. Emission wavelength was set as 470 nm. Gas-chromatography/mass spectrometry was performed using Perkin Elmar Clarus 600. The conversion ratio was calculated from measuring the molar amount of product divided by the total molar amount of mixture (products and reactants).

## 3. Results and discussion

### 3.1. Difficulties of general silane treatments and the growing method (GM)

As mentioned before, the surface treatment method of silica particle is still challenging task considering their final application fields. Among them, the key handicap of these treatments is that the treatments were difficult to cover either extremely high or low concentration of functional groups via single treatment. For instance, in catalytic application, while the particles produced by hydrolysis method can cover Michael reaction, which required lower concentration of amine functional groups, the particle was not suitable for high amine-required reaction such as Knoevenagel reaction [41–43]. Therefore, it is impossible that these surface

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