

One-pot spontaneous formation of submicron hexane-dispersible silica particles with the aid of amphiphilic reaction solvent

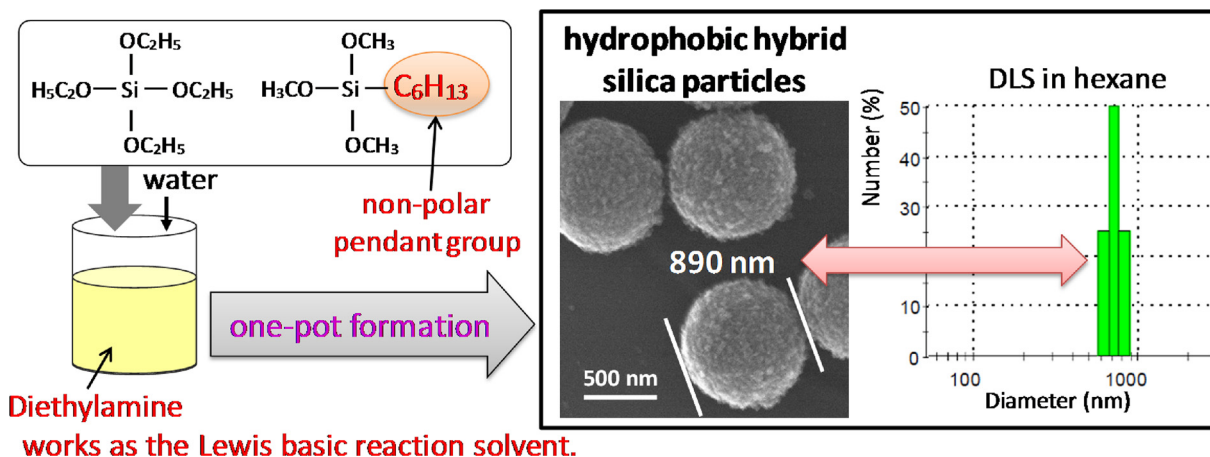
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GRAPHICAL ABSTRACT



Diethylamine works as the Lewis basic reaction solvent.

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ABSTRACT

Hydrophobic submicron hybrid silica particles were spontaneously formed in the mixture of tetraethylorthosilicate (TEOS) and hexyltrimethoxysilane (HTMS) dissolved in diethylamine, which works as a catalytic Lewis basic amphiphilic reaction solvent. The obtained hybrid silica particles were stably dispersed in non-polar solvent such as hexane in the form of the primary-particle dispersion. The solvent diethylamine functioned not only as the catalyst for the silanol polycondensation but also as a superior dispersant for the primary-particle dispersion of the hydrophobic hybrid silica particles throughout the formation process. After the addition of TEOS, HTMS and water in diethylamine, the particle nucleation was promoted the ultrasonication for 30 s. Then, the uniform-sized submicron hydrophobic hybrid silica particles were spontaneously formed after the dispersion of the nuclear was kept still for 24 h. The surface of the hybrid silica particles became increasingly hydrophobic. This is because of the higher density of the non-polar pendant groups (hexyl groups) in the vicinity of the surface, which results from the lower reactivity of trifunctional HTMS than that of tetrafunctional TEOS. The merits of using diethylamine are summarized as follows; 1) Since diethylamine strongly catalyzes silanol condensation, the particle surface was thoroughly hydrophobized. 2) Since the hydrophobized particle had good affinity with

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diethylamine, the hybrid silica particles remained stably dispersed in it. Furthermore, even after the hybrid silica particles are air-dried, they are redispersed in hexane in the form of the primary-particle dispersed.

1. Introduction

Surface-hydrophobized silica particles are industrially widely used in producing such important chemical products as fillers for elastomer reinforcement [1,2] and stationary phases for reversed-phase liquid chromatography [3]. The surface-hydrophobized silica particles are also effective for rendering glass surface hydrophobic by surface coating [4]. This technology has been proved efficient for obtaining self-cleaning glass surface.

For the above purpose, two-step preparation methods of silica particles surface-hydrophobized with trifunctional or bifunctional organosilane have been reported [5–16]. Lee et al. [5] prepared silica particles by adding TEOS and catalytic ammonia to mixed solvent of water and ethanol, where the silica particles were surface-hydrophobized by the following addition of various trifunctional organosilanes. The layer of the obtained surface-hydrophobized particles showed prominent water repellency as seen in the contact angle as large as 140°. Ebrahimi et al. [6] prepared silica particles surface-hydrophobized with dichlorodimethylsilane, which were stably dispersed in octane. Ogihara et al. [7] used dodecyltrichlorosilane for surface-hydrophobizing silica particles, which exhibited stable dispersability in 1-butanol in contrast to noticeable tendency to aggregate in ethanol.

In this study, we sought for a simple one-pot method to fabricate hydrophobic submicron-sized silica particles which can be easily and stably dispersed in such highly nonpolar media such as hexane. It should be stressed that the one-pot procedure in the present study requires us only to mix the starting chemicals (tetraethylorthosilicate (TEOS), hexyltrimethoxysilane (HTMS) and water) in the reaction solvent (diethylamine) which works as the catalyst for the reaction. In such cases, it is often the problem that particles strongly tend to aggregate due to the relatively high polarity of the dispersing solvent while the particles turn increasingly hydrophobic in the course of the reaction. Therefore, the solvent needs to be capable of dispersing the considerably hydrophobic particles throughout the fabrication process. In this study, hexyl-containing hybrid silica particles were formed by

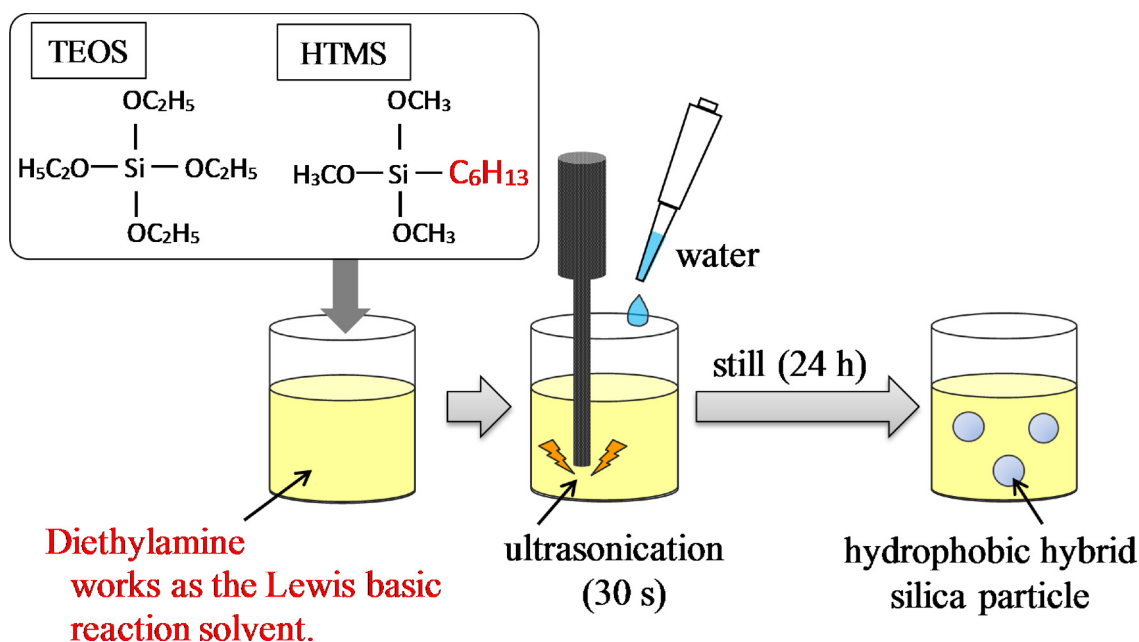
the above one-pot procedure from TEOS and HTMS dissolved in diethylamine. The low permittivity of diethylamine ($\epsilon = 3.68$) worked as the efficient catalyst for the silanol polycondensation, through which the resultant hydrophobic submicron silica particles were formed. The low permittivity of diethylamine allows the formed microparticles to be stably dispersed without the help of any other additives for maintaining the dispersability. In this regard, the authors [17] have reported that magnetite nanoparticles were readily surface-hydrophobized with polyhexylsilsesquioxane derived from hexyltrimethoxysilane dissolved in diethylamine. The obtained surface-hydrophobized magnetite nanoparticles could be stably dispersed in toluene. Owing to the low permittivity of diethylamine, the magnetite nanoparticles were surface-hydrophobized and kept dispersed from the beginning to the end of the reaction and recovery process.

In present study, the authors show the effectiveness of the use of diethylamine as the reaction solvent in which different alkoxy silanes react with each other to form the submicron hybrid silica particles without being annoyed with the aggregation due to the hydrophilic-hydrophobic inversion. In order to trigger the primary stage of the nucleation, the ultrasonication was employed since the effectiveness was proven in previous studies [18,19]. The stable dispersability in the form of the primary-particle was checked by tracing the growing particle size throughout the reaction and aging period.

2. Experimental

2.1. Materials

Tetraethylorthosilicate ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$, TEOS), diethylamine, methylisobutylketone, ethanol, and hexane were purchased from Wako Pure Chemical Industries (Japan). Hexyltrimethoxysilane ($\text{CH}_3(\text{CH}_2)_5\text{Si}(\text{OCH}_3)_3$, HTMS) was obtained from Shin-Etsu Chemical (Japan). These reagents were used as provided without further purification. Water used for the sample preparation was purified by distillation.



Scheme 1. One-pot preparation scheme of the hydrophobic hybrid silica particles.

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