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Synthesis of hollow silica nanoparticles using poly (acrylic acid)-3,3'-diaminodipropylamine template

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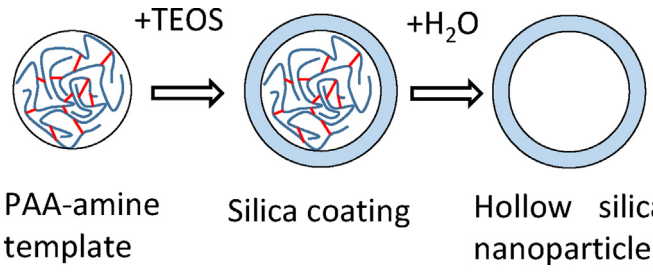
HIGHLIGHTS

- The nano-sized PAA-DDA templates were synthesized in ethanol.
- A water addition removed the template from core–shell particles.
- The DDA can work as a cross-linker of PAA and also as catalyst for sol–gel reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis of hollow silica nanoparticles using poly (acrylic acid) (PAA)-amine aggregates as nano-sized template was proposed. The PAA-amine mixtures dissolve in water, but not in ethanol, therefore the mixtures can be a template for hollow particle in ethanol and can be removed from the core–shell particle by addition of water. In order to investigate effect of amines on hollow particle formation, four kinds of amines; ethylenediamine (EDA), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TED), 3,3'-diaminodipropylamine (DDA), triethylenetetramine (TTA), which interact with carboxylic acid of PAA were chosen. The PAA-each amine nanoparticles were formed with around 200 nm by dropping of PAA/amine mixtures in ethanol under the optimum conditions. Using the PAA-DDA template, hollow silica nanoparticles with spherical form were successfully prepared for the shortest reaction time in four hours. The primary amines and secondary amine of DDA work as not only cross-linker for PAA, but also sol–gel reacting catalyst. It can be clear from that the EDA with two primary amines also worked as sol–gel catalyst while the TED with two tertiary amines didn't. On the other hands, TTA with two primary and secondary amines also provided hollow silica nanoparticles, however, the silica shell of particles were mostly collapsed. It could be thought that the four amines of TTA promote sol–gel reaction, at the same time, high water content in the template induces molecular motion.

1. Introduction

Hollow silica nanoparticles, which are composed of a solid silica shell and nano-sized hollow interior, can be expected to have unique properties of a high specific surface area [1–4], thermal insulation [5–7], optical property [8], nano-sized container [9,10], etc. A lot of synthetic routes for hollow silica nanoparticles which are categorized into soft and hard templates were reported. In these template methods, silica source is firstly coated on the template surface to form core–shell particles, and then the template is removed by suitable chemical treatments such as combustion and dissolution. From the aspect of environmental issue, development and improvement of preparation technique for hollow silica nanoparticles are also important.

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In the hard template methods, polystyrene (PS) particles were often used as the organic template because it is relatively easy to synthesis and control particle size [11]. At the same time, they have disadvantage of environmental load such as discharging waste harmful solvent to dissolve the template or carbon dioxide to burn off the template.

Fuji et al. developed inorganic template method using calcium carbonate ($CaCO_3$) or hydroxyapatite (HAp). These templates can be removed by dilute acid solution and the waste byproducts are re-used to re-synthesis the templates [12–14]. Min Chen developed one-step synthesis for hollow silica particle in which formation of silica shells and dissolution of the template particles occurs in the same medium. They controlled rates of silica coating and template removal by adjusting of ammonia amount in the medium [15,16].

We focus on polyelectrolyte aggregation as nano-sized template for hollow particle, whose dissolution property can be controlled by just addition of water. Shi et al. synthesized polymeric nanoprecipitation using poly(allylamine hydrochloride) (PAH) in ethanol [17]. In Yu's group, poly(acrylic acid) (PAA)-ammonia nanoparticles were synthesized as hollow particle's template using the properties that PAA's insolubilization in ethanol under ammonia existence and solubilization in water. The PAA powder and ammonia solution were mixed and the solution was dropped in ethanol to make PAA-ammonia template/ethanol suspension. Tetraethoxysilane (TEOS) as a silica source was slowly added in the suspension and stirred at 2 h intervals to prepare silica shell/PAA-ammonia template particles. By addition of distilled water, the PAA-ammonia template was removed. This process is simple without harmful influence on environment, however, it takes 14 h long for silica shell coating on the template. There is no mention about a reason why that such long time is required [18].

Previously, we have obtained hollow silica nanoparticles by following of Yu's technique [19]. Then, effect of water in ethanol on the silica shell microstructure was reported. In this technique, PAA molecules were aggregated with ammonium ion in ethanol to be a template for hollow particle. The added TEOS was hydrolyzed with the ammonia and coated on the aggregated PAA molecules to form a silica shell. The PAA molecules could be movable in ethanol and the template surface seems to be quite unstable for stable attachment of the hydrolyzed TEOS. To solve these problems, it is necessary to accelerate silica coating or to harden the template. As former, an increase in TEOS or ammonia as a catalyst are required, while as latter, addition of as like a cross-linker to connect PAA molecules each other. Here, four kinds of amine compounds with various combinations of primary, secondary, tertiary amines were used and the effects of these amines on hollow structure formation were discussed.

2. Experimental

2.1. Preparation of hollow silica nanoparticle

Hollow silica nanoparticles using PAA-ammonia template were prepared according to Yu's research [18]. A 0.09 g of PAA powder (molecular weight: 5000, Wako Pure Chemical Industries, Ltd.) and 25% ammonia solution (Wako Pure Chemical Industries, Ltd.) or 30% amines solutions (ethylenediamine (EDA, Wako Pure Chemical Industries, Ltd.), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TED, Wako Pure Chemical Industries, Ltd.), 3,3'-diaminodipropylamine (DDA, Tokyo Chemical Industry Co., Ltd.), triethylenetetramine (TTA, Wako Pure Chemical Industries, Ltd.) were mixed for 2 min. The solutions were completely dissolved which were visually confirmed. The mixed solutions were dropped in dehydrated ethanol (99.5%, Wako Pure Chemical Industries, Ltd.) and stirred. A 0.15 ml of tetraethoxysilane (TEOS, Wako Pure Chemical Industries, Ltd.) was added at 2 h interval. The total reaction times were from 4 to 14 h. After the desired times of stirring, the suspensions were rinsed by ethanol and water, centrifuged and dried under vacuum atmosphere.

2.2. Characterizations

For microscopic observation, the obtained samples dispersed in ethanol were immobilized on a microgrid and observed by transmission mode of a scanning electron microscope (STEM, SEM, JSM-7600F, JEOL Ltd.). The viscosity of the PAA-amines solutions were measured by HAAKE Rheo Stress 6000 (Thermo Fisher Scientific K.K.). The particle size of PAA-amines template in ethanol was measured by zetasizer (Malvern Instruments Ltd.).

3. Results and discussion

Fig. 1(a) shows SEM observation of PAA-ammonia template by dropping of PAA (0.09 g) and ammonia (1.5 ml) mixture in ethanol (30 ml). The PAA-ammonia templates were formed as gathering of large particles with over 100 nm and small ones with less than 100 nm. According to Yu's research, one of the factors to dominate the template size is PAA amount for ammonia. It can be controlled from several tens nm to hundreds nm [18]. In our experiment, mechanical treatment is also effective. The results will be appeared elsewhere.

Using the above PAA-ammonia template, effect of reaction time on hollow particle formation was investigated. Fig. 1(b)–(d) shows STEM observations of samples which were prepared for (b) 8 h, (c) 10 h, and (d) 14 h. For less than 8 h, nothing was observed by microscope. For 8 h reaction, there were very few particles observed. As shown in Fig. 1(b), partially-collapsed hollow particles which were caught on the microgrid were observed. The size of the obtained particles was less than 100 nm. For 10 h reaction (Fig. 1(c)), the number of observed particles quite increased compared to ones for 8 h (Fig. 1(b)). The large hollow particles with over 100 nm were also obtained in addition to the small ones with less than 100 nm, however, shell of the large hollow particles were broken (represented as arrows in the picture). For 14 h reaction (Fig. 1(d)), the large and small hollow particles were clearly observed without collapsed. From these results, 14 h reaction time is necessary to form hollow structures.

When TEOS were added in the PAA-ammonia template/ethanol suspension, TEOS molecules approach to the template and were hydrolyzed by the ammonia. The hydrolyzed TEOS were subsequently condensed by the ammonia and formed a silica shell at the template surface. In the PAA-ammonia template, templates can be formed by the interaction between ammonia and carboxylic acid (COOH) of PAA. The number of the added ammonia is over thousand times higher than the number of COOH of PAA. The excess of ammonia which were not used for the reaction with PAA played as a catalyst for hydrolysis and condensation of TEOS. However, the reaction of TEOS at the template surface is really slow. In addition, it can be thought that PAA molecules are movable in the PAA-ammonia solution template. The template surface could be unstable in ethanol and it seems to be difficult for quick attachment of the hydrolyzed TEOS. The driving force of silica coating on the template surface is not clear. At the unstable template surface, ethanol, water, ammonia are mixed together because they are immiscible each other. Just after TEOS addition, hydrophobic TEOS exist in ethanol. If TEOS attaches ammonia near the surface, hydrolysis will be started. The hydrolysis TEOS prefer to stay in the hydrophilic template surface.

To accelerate TEOS reaction, effect of ammonia amount on particle formation was investigated. Fig. 2 shows STEM observations