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Short communication

Fabrication of raspberry-like polymethylsilsesquioxane microspheres mediated by tinny calcium carbonate particles

Baiyu Li *, Xiaogang Gao, Jieqiong Zhang, Yan Sun, Zaiman Liu

The School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

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ABSTRACT

The particle formation behavior of methyltrimethoxysilane (MTMS) was researched in the presence of a small amount of inorganic calcium carbonate particles. MTMS was first hydrolyzed in water under the catalyzation by hydrochloric acid to produce hydrolyzate and then neutralized by base sodium hydroxide. Under the neutral condition, the hydrolyzate of MTMS was mixed with a small amount of newly-prepared precipitation of calcium carbonate. Following this, hydrolytic polycondensation reaction catalyzed by adding ammonia to the mixture was conducted. The results show that polymethylsilsesquioxane (PMSQ) particles with raspberry-like morphology were obtained by this method, while those without addition of calcium carbonate are of smooth surface, which was confirmed by scanning electron microscopy (SEM) micrographs. The static water contact angles changed from 136.2 ± 0.9° of pure PMSQ particles with smooth surface to 146.3 ± 1.1° with raspberry-like morphology, showing a great increment in apparent hydrophobicity.

1. Introduction

Hierarchically structured raspberry-like particles with rough surface and large surface-to-volume ratios have drawn widespread attention these years, due to their excellent physiochemical properties and versatile uses. Raspberry-like hollow Au nanospheres coated with a layer of Pd grains possess improved catalytic property toward methanol oxidation [1]. Particles of this type are more widely used to fabricate surfaces with special wettabilities, e.g. superhydrophobic [2,3], superhydrophilic [4,5] or surface with gradient wettability [6].

A variety of methods has been developed to prepare raspberry-like particles. Nano-sized particles could be grafted on much larger ones through chemical bond formation to give particles of dual size roughness, i.e. raspberry-like morphology [7,8]. In this method, the particles of different sizes have to be pretreated to bear different reactive groups on surface, and a separation process is often employed to remove the ungrafted particles. Therefore, this way of preparing raspberry-like particles is somewhat sophisticated and time consuming. Emulsion polymerization, especially of Pickering emulsion, has also been used to prepare raspberry-like particles, whereas the particles are usually of organic polymers [9–11]. A more simple way to this type of particle with rough raspberry-like morphology is through coagulation of nano-sized particles onto larger core particles. The driving force for this coagulation may be hydrogen-bond interaction [12], weak acid–base interaction [13], and electrostatic force [14] between the core and corona particles. Coagulation method is a straightforward way to raspberry-like particles.

Polymethylsilsesquioxane (PMSQ) is a kind of polymeric siloxanes usually formed through hydrolysis and condensation of monomers like methyltrialkoxysilane or methyltrichlorosilane. It could be thought as an organic–inorganic hybrid material of organically modified silica. In addition to the excellent properties of inorganic silica, such as good thermal stability, weatherability, and high hardness, it is hydrophobic and has good compatibility with organic materials when compared with silica. Using the hydrophobicity, PMSQ has been used to modify the surfaces of hydrophilic materials, and superhydrophobicity can be reached when combined with special morphology [15].

In this work, we want to report a modified coagulation method, where the primary particles are of the same surface property. Newly formed tinny calcium carbonate particles act as nucleation center for primary PMSQ particle formation, then these nano-sized primary particles coagulate together with hydrolyzate of MTMS to form larger submicron-sized particles with rough raspberry-like morphology. In this process, it is unnecessary for the primary particles to be pretreated to bear special reactive groups. The process is simple to use and the obtained PMSQ particles show a great increase in apparent hydrophobicity when compared with their counterparts with smooth surface, which were prepared in the absence of calcium carbonate.

2. Experimental

2.1. Materials

Methyltrimethoxysilane (MTMS) was purchased from Qufu Chenguang Chemical Corporation Ltd. (Shandong, China), and used as received. Hydrochloric acid (38 wt.%), sodium hydroxide, calcium

* Corresponding author.
E-mail address: baiyuli@mail.lzjtu.cn (B. Li).

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chloride, sodium carbonate and ammonia (25 wt%) are all of analytical grade and used as received. Deionized water was used throughout the experiments.

2.2. Preparation of raspberry-like PMSQ particles

In a 250 mL round-bottomed flask, 90 mL of water and 5 mL MTMS were added. Then 0.5 mL of hydrochloride solution (1 mol/L) was added for MTMS to hydrolyze under magnetic stirring for a period of 30 min. After this, 0.5 mL of sodium hydroxide solution (1 mol/L) was added to neutralize the mixture.

In another 250 mL round-bottomed flask, 1 mL of calcium chloride solution (0.01 mol/L) was added. Then sodium carbonate solution (0.01 mol/L) was added dropwise and stopped adding when precipitation was observed (ca. 0.3 mL sodium carbonate solution). The above prepared hydrolyzate of MTMS was poured into this precipitate under continuous stirring. After slight stirring at ambient temperature for 2 h, ammonia was added until the pH increased to 11. The obtained white precipitate of PMSQ spheres was collected by filtration and rinsed first with water and then ethanol before drying in air.

For the preparation of the sample with a larger amount of calcium carbonate, 4 mL of calcium chloride solution (0.01 mol/L) was used; the corresponding sodium carbonate solution is about 1.2 mL, with other conditions keeping unchanged.

For the preparation of pure PMSQ particles, the pH of the above neutralized hydrolyzate of MTMS was adjusted directly with ammonia to 11, followed by washing the obtained precipitate with water and ethanol, and then dried in air.

2.3. Characterization

The morphology of the obtained PMSQ spheres was observed with a scanning electron microscope (SEM, JSM-6701F, Japan). The samples of PMSQ spheres for SEM observation were dried at 120 °C for 2 h and then coated with gold by vacuum spraying. The hydrophobicity of the obtained PMSQ spheres was investigated by measuring the static water contact angle (WCA) using a DSA100 contact angle analyzer (Kruss, Germany). For these measurements, the PMSQ sphere samples (before drying) were dispersed in a 1 wt.% MTMS solution in a mixture of water and ethanol; the volume ratio of water to ethanol is 8 to 1. The dispersion was dropped on a glass slide, which was pretreated by sonication in ethanol, and dried at 120 °C for 2 h. About 8 μL of water drop was applied for each measurement, and 5 measurements were performed for each sample at different positions to obtain an average result. X-ray photoelectron spectroscopy (XPS) characterization was performed on PHI5702 X-ray photoelectron spectroscopy, using Mg Kα X-ray for photoelectron excitation. Powder form sample of above PMSQ particles prepared in the presence of a smaller amount of calcium carbonate was used.

3. Results and discussion

Fig. 1a shows the SEM micrograph of PMSQ particles prepared in an aqueous medium catalyzed by ammonia. It can be found that without the addition of calcium carbonate the PMSQ particles are in good spherical morphology with smooth surface. Fig. 2a is the SEM micrograph of PMSQ particles formed in the presence of tinny calcium carbonate particles, of which the surface is rough and consisting of nano-sized particles, resembling the rough surface of a raspberry.

The well-established base- or acid-catalyzed hydrolysis and condensation reactions of monomeric silane precursors are shown below:

$$\text{Hydrolysis}: \equiv \text{Si–OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Si–OH} + \text{ROH} \quad (1)$$

$$\text{Water condensation}: \equiv \text{Si–OH} + \equiv \text{Si–OH} \rightarrow \equiv \text{Si–O–Si} \equiv + \text{H}_2\text{O} \quad (2)$$

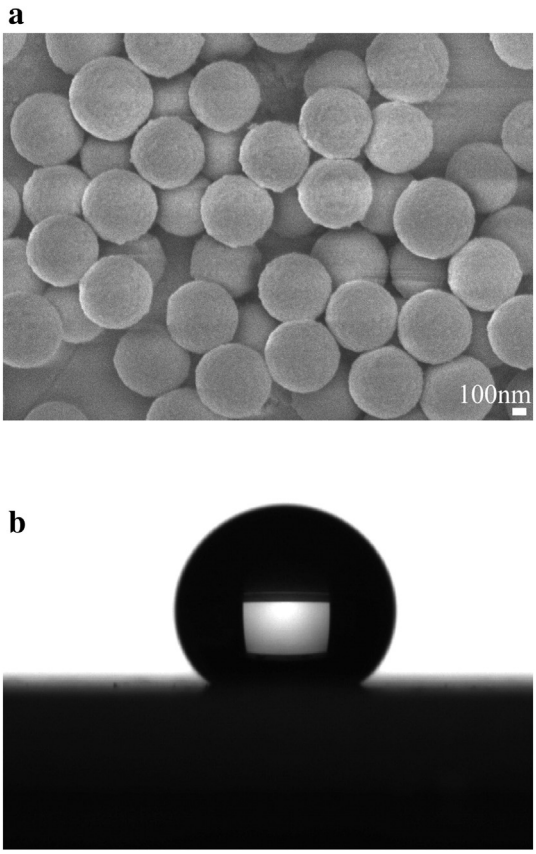

Fig. 1. SEM micrograph and WCA detection image of PMSQ particles prepared in the absence of calcium carbonate. a. SEM micrograph. b. WCA detection image.

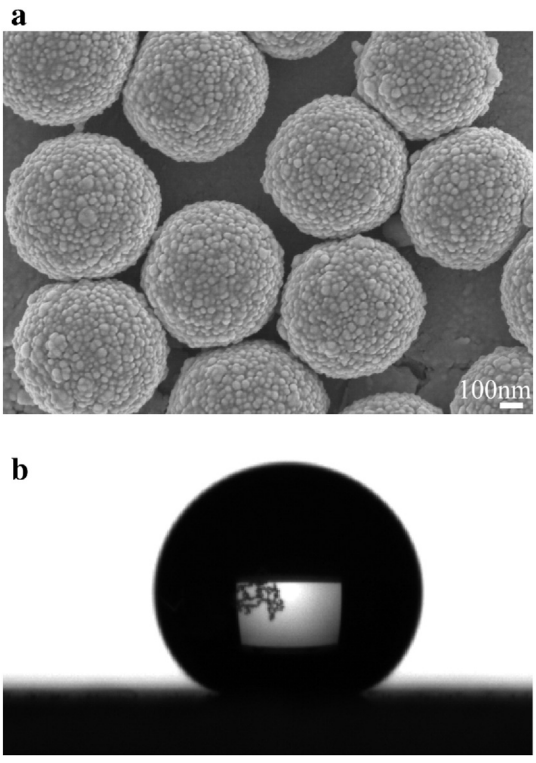

Fig. 2. SEM micrograph and WCA detection image of PMSQ particles prepared in the presence of calcium carbonate. a. SEM micrograph. b. WCA detection image.