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Preparation of silica thin films with macropore holes from sodium silicate and polymethacrylate: An approach to formation mechanism of diatomaceous earth like silica hollow particles

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ABSTRACT

Silica hollow particles (microcapsules) are one of the exciting subjects in materials chemistry in both basic and applied researches. Our previous paper reported a new preparation method of silica hollow particles having unique shell with macropore holes, which resemble diatomaceous earth in morphology, by interfacial reaction method using W/O/W emulsion as a reaction field. The preparation procedure of these unusual silica particles inherently requires the addition of suitable amounts of sodium polymethacrylate to the sodium silicate solution as the internal water phase of the W/O/W emulsion. For revealing the detailed mechanism of the formation of the shells with macropore holes, silica thin films using the similar solutions were examined as a model system of the interfacial reaction method, because both processes produce silica thin matrices such as shell or as film, respectively. Some silica thin films with macropore dents were formed by immersing dip-coated films of sodium silicate and sodium polymethacrylate into NH_4HCO_3 aqueous solution. FE-SEM/EXD observation indicated that the modest phase separation of sodium silicate and the polymethacrylate occurred in the dip-coated films before the immersion into NH_4HCO_3 solution. Moreover, infrared spectrometry studies revealed that the addition of sodium polymethacrylate to sodium silicate changed the bonds of the silicate significantly to promote the condensation. The experimental observations in these model studies strongly suggested that the shell with macropore holes in diatomaceous earth like silica hollow particles are formed by the removal of the aggregated and the phase-separated polymethacrylate during the formation of silica matrix of the particle shell.

1. Introduction

Silica materials having hollow structures are receiving particular attention as a new class of functional materials [1,2]. Recently, not only the formations of hollow particles but also the fabrications of unique shell structures are studied intensely. Diatomaceous earths are interesting natural siliceous hollow products formed from fossilized diatoms as water plants [3–10]. Their wide usefulness in various practical applications and the morphological uniqueness impress a number of materials chemists, who are impelled to create artificial systems or materials resembling the diatomaceous earths. On the other hand, tailor-made materials with specific structures of both particles and shells are also requested, which are generally hard to be obtained from diatomaceous earths as natural products. Therefore, artificially fabricated diatomaceous earth-like materials have been prepared by a variety of synthetic approaches including biomimetic and/or bio-inspired methods [11–19]. Purely artificial approaches to synthesize silica materials having the morphologies similar to diatomaceous earths are also examined [20–30]. We recently reported a leading research on an artificial production of diatomaceous earth-like materials by our own reaction process [31,32], the interfacial reaction method using W/O/W emulsion [33–37].

SEM and TEM images of a typical diatomaceous earth-like silica particle are shown in Fig. 1A and B, respectively (the weight ratio of sodium polymethacrylate solution/sodium silicate solution = 0.45). In this preparation method, a sodium polymethacrylate was added to the aqueous solution of sodium silicate used as the inner water phase (IWP) of W/O/W emulsion. This silica hollow particle contained several macropore holes in the shell [31]. The strong dependence of the formation of the macropore holes on the ratios of sodium silicate and the polymethacrylate demonstrate the

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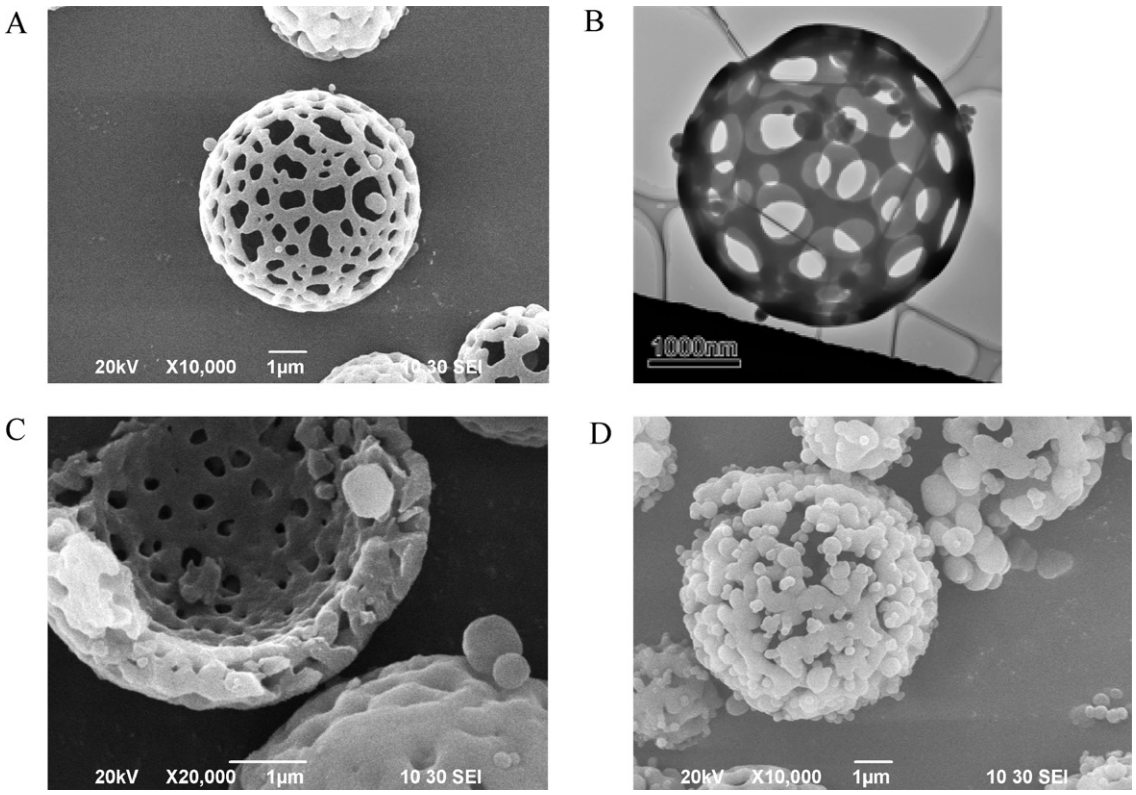

Fig. 1. (A) SEM and (B) TEM images of typical silica hollow particles like diatomaceous earth obtained from sodium silicate and sodium polymethacrylate by interfacial reaction method. The weight ratio of sodium polymethacrylate solution/sodium silicate solution was 0.45. (C) SEM image of a silica hollow particle mixing in the particle in (A). (D) SEM image of a silica hollow particle with an excessive addition of the polymethacrylate. The weight ratio of sodium polymethacrylate solution/sodium silicate solution was 0.53.

essential involvement of the polymer in the macropore formation. In a hypothetical scheme of our previous paper on the formation of the macropore holes, the passage of one polymethacrylate molecule from IWP to OWP (outer water phase) across the W/O/W interface creates the macropores during the silica precipitation along the emulsion interface [31]. However, the sizes of macropore holes in the silica shells are significantly larger than that of one polymer molecule with molecular weight ca. 6500. Another type of hollow particles shown in Fig. 1C is also found together with the particles shown in Fig. 1. The macropores in the particle of Fig. 1C do not permeate through the shell wall. Moreover, the excessive addition of the polymethacrylate (the weight ratio of sodium polymethacrylate solution/sodium silicate solution = 0.53) produced nanoparticles in the shell as shown in Fig. 1D, whose morphology is similar to the silica particles obtained with NaCl addition [32]. These observations suggested that the macropore holes of the particle in Fig. 1A are not simply formed by the passage of one polymethacrylate molecule across the silica shell wall.

One feature of the interfacial reaction method is the rapid mixing of two aqueous solutions, IWP and OWP, along the minute W/O/W interfaces, where the mixing areas are in the range of a few micrometers, resulting in the formation of the thin walls of silica matrix from sodium silicate. It is believed that the thin silica matrix is essential for the production of the macropore holes. On the other hand, the silica thin films are also composed of the thin silica matrix. The coated mixture of sodium silicate and sodium polymethacrylate must be very thin like the mixing area along the W/O/W interfaces of the interfacial reaction method. In addition, the reaction rate of these coated mixtures with NH_4HCO_3 aqueous solution proceeds much higher than bulk solution and comparable with that of the interfacial reaction method. Some similarities such as the thickness of silica matrix and the rapid reaction with NH_4HCO_3 solution between the silica thin shells of the hollow particles and the silica thin films suggest that the thin films play a role on a model system of the interfacial reaction method for the silica hollow particle synthesis. In this paper, we report the preparation of silica thin films with macropore dents (holes) and the formation mechanism of the macropore holes in silica hollow particles using the observations in the productions of silica thin films.

2. Experimental methods

2.1. Preparation of silica thin films with macropore dents

A typical experimental procedure of the silica thin film preparation from sodium silicate and sodium polymethacrylate was described as follows. 25 g of the sodium silicate solution (water glass No. 3: Japanese Industrial Standards, JIS K1408 obtained from Kishida Chemical Co., Ltd) was mixed with 6.8 g or 9.0 g of the sodium polymethacrylate solution purchased from Scientific Polymer Products, Inc. as 29.71 wt% aqueous solution (Mw: ~6500) and 4 g of deionized water. The double or triple diluted solutions of the above-mentioned two mother mixed solutions were also used for the experiment as well as the mother solution (stock solution). These apparently homogeneous solutions were dip-coated onto a slide glass (S2111 purchased from Matsunami Glass Ind., Ltd). All the slide glasses used for the thin film preparation were washed with deionized water thoroughly and dried at 80 °C overnight prior to coating. The washed slide glasses were drawn down at the rate of 2.0 mm per second, and were withdrawn up at the rate of 0.2 mm/s using a dip-coating machine (TD-1501 of SATUMA Communication Industry Co., Ltd.). After drying at room temperature for 12 h, these dip-coated thin films were immersed into 2 M aqueous solu-