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Fabrication of colloidal arrays by self-assembly of sub-100 nm silica particles

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ABSTRACT

Self-assembly of sub-100 nm spherical silica nanoparticles into ordered, tightly packed three- and two-dimensional arrays was studied. Self-assembly by vertical evaporation was investigated for particles made by two methods: an optimized Stöber method recently reported from this laboratory and a modified reverse micelle method. Ordered, close-packed, two- and three-dimensional structures were formed with spherical nanoparticles made by the optimized Stöber method. Fast Fourier transforms of top-view scanning electron microscopy images document close-packed hexagonal packing for three-dimensional arrays consisting of particles as small as 50 nm. Ranges over which evaporation temperature and suspension particle concentration can be altered as strategies for improving packing quality of 50 nm particles have been defined. Self-assembly behavior that is distinct from that of larger particles (>200 nm) is observed for these sub-100 nm particles in that the ranges over which these variables can be altered to affect array packing quality are much smaller than for larger particles. In contrast, for particles made by the reverse micelle method, only structures with poor packing quality were obtained despite the fact that such particles are typically more uniform than those made by the Stöber method. These results provide clear evidence that, in addition to particle uniformity, other particle properties deriving from fabrication method play important roles in directing self-assembly of sub-100 nm particles. Finally, a rapid self-assembly method based on horizontal evaporation was used to produce close-packed three-dimensional structures of these sub-100 nm particles spanning several millimeters. Although these arrays are not as ordered as those made by vertical evaporation, the strategy reported herein allows tightly packed, crack-free arrays up to microns in thickness to be fabricated. A mechanism for self-assembly by this process is proposed.

1. Introduction

Colloidal arrays of close-packed structures of monodisperse, sub-100 nm spherical silica nanoparticles are important in various applications including as templates for meso-porous carbon [1], polymers with ordered structures [2], and planar wave-guide materials [3]. Such arrays are also model systems for the study of fundamental phenomena such as molecular adsorption [4] and mass transport in mesopores [5–8]. Despite their potential importance, however, little systematic understanding of the variables that control self-assembly of sub-100 nm particles into ordered, three-dimensional arrays is currently in hand. Nonetheless, the elusive challenge of creating such arrays has captured the attention of several research groups recently resulting in a menu of recipes for creating arrays from nanoparticles of specific sizes without due attention to variables that might be systematically exploited to create arrays from particles in the sub-100 nm size regime.

Many methods have been reported for the fabrication of ordered colloidal arrays of nanoparticles [9]. Although several papers report fabrication of silica colloid arrays using direct pressures greater than several MPa [1,2], most methods involve self-assembly of particles due to the large area of ordered packing and control of array thickness that can be achieved [9–24]. It is generally believed that in addition to van der Waals interactions, the self-assembly behavior of silica particles is affected by electrostatic interactions and hydrogen bonding between particles [3,25–29]. Among the self-assembly methods for making silica nanoparticle colloidal arrays, one simple method for fabrication is sedimentation [10], but this method is relatively slow and usually takes weeks for completion of a single sample [11].

Wang and Gu [12] reported a method for fabrication of close-packed particle arrays through manipulation of silica nanoparticle hydrophobicity. This strategy requires particle surface modification and must be carefully controlled in order to obtain appropriate surface properties for self-assembly. The Langmuir–Blodgett method has also been used for formation of both monolayers and multilayers of silica spheres [13]. This method also requires particle surface

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modification, and in addition, multilayer structures are obtained that are not well ordered.

Okuba and co-workers introduced a rapid method for forming large area monolayers of uniform silica particles ranging in size from 25 to 100 nm using a simple wet coating process in which a suspension of silica nanoparticles is deposited onto a substrate and allowed to dry [14,15]. Hexagonal close-packed domains consisting of tens of nanoparticles can be obtained with this approach, but the arrays still contain point and line defects between these domains and do not possess long-range registry.

Self-assembly by solvent evaporation is based on attractive capillary forces operative during solvent evaporation. This method is simple, relatively fast, and can be used for particles over a wide range of sizes [16–26]. Although numerous studies describe successful self-assembly of particles >200 nm [3,16–20], relatively few reports describe self-assembly of three-dimensional colloidal arrays of silica particles <100 nm [21–23]. Indeed, to date, no systematic study of sub-100 nm silica nanoparticle self-assembly into three-dimensional structures has been undertaken.

Successful self-assembly of particles by solvent evaporation requires a monodisperse size distribution. According to Jiang et al. [24], self-assembly of three-dimensional silica nanoparticle arrays possessing long-range order requires particle size relative standard deviations (RSD) <8%. However, Wang et al. [3] demonstrated that self-assembled, two-dimensional, sub-100 nm silica particle monolayers possessing a significant fraction of close-packed hexagonal structures could still be observed using 60 nm particles with a RSD of 13%. In contrast, arrays from 40 nm particles with a RSD of 32% were not well packed [3]. Micheletto's results confirm that packing order is greatly affected by particle uniformity [16].

An alternate method for fabrication of uniform silica particles in the sub-100 nm range is the reverse micelle method, which can be used to make very uniform particles with perfect spherical shapes in the range of 30–70 nm [30,31]. The RSDs of the particles can be controlled to within 4% [30,31], which would appear to satisfy the uniformity requirement [3,16,24] for successful self-assembly of ordered, close-packed structures over large areas. Significantly, however, systematic study of the self-assembly behavior of such particles has not been reported. Indeed, three-dimensional, close-packed structures consisting of nanoparticles made by the reverse micelle method have only been successfully formed as pellets requiring high pressure [2]. The lack of successful self-assembly of these particles into ordered, three-dimensional arrays despite their excellent monodispersity makes them interesting systems to compare with particles formed by the Stöber method.

The work reported here involves self-assembly of sub-100 nm silica particles into three- and two-dimensional arrays. Using a fast (<2 h) batch Stöber method with reaction conditions optimized by a protocol developed previously in this laboratory, monodisperse, spherical silica nanoparticles with controlled size in the range from 50 to 120 nm with RSD < 9.5% can be produced [32]. This strategy provides large quantities of particles of sufficient quality for systematic study of their macroscopic self-assembly behavior. The effects of particle properties, including particle size distribution, fabrication method, evaporation temperature, and particle concentration, on the packing quality of the resulting arrays are discussed. To the best of the authors' knowledge, the effects of these variables on the self-assembly of nanoparticles in the sub-100 nm size range has not been previously reported.

This work seeks to answer two questions: First, do sub-100 nm particles exhibit the same self-assembly behavior as larger (>200 nm) particles? Secondly, how do operational parameters associated with the self-assembly process affect packing quality of the resulting arrays? Answers to these questions are obviously critical for applications and technologies requiring self-assembly of silica nanoparticles in this size range. Finally, array formation using a fast self-assembly method based on horizontal evaporation is discussed. This method not only provides a rapid protocol for self-assembly as an alternative to the widely used vertical evaporation method, but also provides new insights into the self-assembly behavior of sub-100 nm spherical silica nanoparticles.

2. Materials and methods

2.1. Fabrication and purification of silica particles

An optimization protocol for synthesis of sub-100 nm silica particles by the Stöber method has been described recently from this laboratory [32]. With the exception of a single study in which packing of particles made by this optimized Stöber procedure were compared with packing of particles made by a conventional Stöber approach, all particles herein designated as Stöber particles were fabricated by this optimized method. After this synthesis, the particles so obtained were washed with ethanol with typically 4 cycles of centrifugation at 8000 rpm followed by ultrasonic redispersion in ethanol, and then finally sintered at 600 °C for 4 h prior to self-assembly.

A modified reverse micelle method based on those proposed by Arriagada and Osseo-Asare [30,31] was used to scale reactions from 5 to 50 mL to produce silica nanoparticles in sufficient quantity for self-assembly. Specifically, 47 mL hexane, 1 mL ammonium hydroxide and 4.31 mL polyoxyethylene (5) nonylphenyl ether (C_9H_{19}-C_6H_4-$(OCH_2CH_2)_nOH$ ($n \cong 5$, NP-5, Sigma–Aldrich) were transferred to a 120 mL glass bottle and mixed well by mechanical stirring. Then, 1 mL TEOS was added to the mixture and stirred at moderate rate for 3 min. The system was then allowed to react for 24 h without stirring. By this procedure, a suspension containing silica colloids of ~50 nm dia was obtained. After synthesis, the silica nanoparticles were purified by centrifugation and ultrasonic dispersion in acetone, ethanol and water to remove the surfactant and other unreacted materials.

2.2. Self-assembly by vertical evaporation

Silica nanoparticles were self-assembled using the vertical evaporation procedure reported by Jiang et al. [24] In this procedure, 0.005–0.05 g (0.05–0.5 wt%) of purified silica particles were dispersed by sonication in 10 mL ethanol in a clean scintillation vial. A clean microslide (1 × 10 cm, Fisher Scientific) was then placed in a vertical position in the scintillation vial for thin film development. The scintillation vial and microslide were covered by a 1200 mL crystallizing dish to eliminate external airflow and contamination [24].

To evaluate particle concentration effects on packing quality, Stöber silica particle suspensions with the same particle size (53 nm ± 9.5%) but different weight percentages (0.25%, 0.3%, and 0.4%) were used. All samples were placed under the same crystallizing dish to ensure identical ethanol evaporation rates. Films were allowed to develop at room temperature, measured to be 22 °C.

Stöber silica particle suspensions of the same particle size (53 nm ± 9.5%) with a 0.2 wt% particle percentage were used to study the effect of temperature on packing quality. These suspensions were developed at different temperatures (22 °C, 40 °C, and 50 °C) while keeping all other conditions the same.

2.3. Characterization of silica colloidal arrays

The resulting silica particle thin films were characterized by field emission scanning electron microscopy (SEM, Hitachi S-4800 and S-4500) in the backscattering mode after coating with a thin layer of Au–Pd. Images were acquired using an electron accelerating voltage of 15 kV. Cross sectional images were collected at 45°. Fast Fourier