

# Fabrication of Two- and Three-Dimensional Silica Nanocolloidal Particle Arrays

Wei Wang,<sup>\*,†</sup> Baohua Gu,<sup>†</sup> Liyuan Liang,<sup>†,‡</sup> and William Hamilton<sup>†</sup>

*Environmental Sciences and Condensed Matter Sciences Divisions, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831, and School of Engineering, Cardiff University, P.O. Box 925, Cardiff CF24 0YF, U.K.*

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Monodispersed silica spheres with diameters of 100–500 nm were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of water and ammonia in ethanol medium. Silica colloidal sphere sizes were controlled by changing ammonium concentration at fixed TEOS and water concentrations. These silica spheres settle out from their alcoholic dispersion to form closely packed three-dimensional (3-D) particle arrays—i.e., photonic crystals that exhibit vivid optical diffraction due to a high degree of ordering of the particles. The lattice constant of the opal photonic crystal structure, as determined by optical diffraction, was found to be in a good agreement with that observed by SEM measurements. Highly purified silica nanospheres could also self-assemble to form 3-D crystalline colloidal arrays (CCAs) in water, which give narrow and continuously tunable diffraction peaks in the visible range. By grafting hydrocarbon chains on silica surfaces using the silane coupling agent octadecyltrimethoxysilane, hydrophobic silica nanospheres were obtained, and they readily self-assemble at the air–water interface to form closely packed two-dimensional (2-D) particle arrays. Such 2-D particle arrays could be collected onto solid substrates to form monolayer or multilayer thin films with controlled film thickness according to the particle size.

## I. Introduction

Materials with spatially ordered features on the mesoscale of 50–500 nm have important applications in optical information processing and storage, advanced coatings, catalysis, and other emerging nanotechnologies.<sup>1–5</sup> Colloidal crystals are a promising class of such materials. Colloidal crystals are formed via self-assembly of particles in a size range from nanometers to micrometers into crystalline arrays that exhibit unusual optical<sup>2,6,7</sup> and thermodynamic properties.<sup>8–10</sup> A key element in successfully producing crystalline colloidal arrays is the preparation of highly monodispersed colloids, which generally relies on manipulating the chemistry of colloid formation. A simple method for creating colloidal crystals is gravity sedimentation of colloids from dispersion.<sup>11–15</sup> Another method applied to polymer colloids uses the flow of a solvent through micromachined channels to create dense colloidal arrays of multilayers.<sup>16</sup> A self-assembly technique that relies on capillary forces to organize colloids is used to fabricate colloidal crystal multilayers.<sup>17</sup> In this paper, we present a modified process for producing surface-functionalized monodispersed silica (SiO<sub>2</sub>) nanoparticles based on the Stöber method<sup>18</sup> and describe a method to self-assemble three-dimensional (3-D) CCAs in water and two-dimensional (2-D) colloidal arrays either at water–air interfaces or on solid substrates. Because of the high degree of ordering of the particles, these colloidal particle arrays diffract light in the visible region. The diffraction is tunable by changing the colloidal lattice constants.

## II. Experimental Section

**Materials.** Tetraethyl orthosilicate (TEOS, ≥99%) and NH<sub>3</sub>·H<sub>2</sub>O (29.4%) were obtained from Fluka and J. T. Baker,

respectively. Octadecyltrimethoxysilane (OTMOS) and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPETMOS) were from United Chemical Technologies. Absolute ethanol, chloroform, and NaOH solution (1 N) came from GE Science. All chemicals were used as received. SnakeSkin pleated dialysis tubing with a molecular weight cutoff at 10 000 was purchased from Pierce Chemical Company. Deionized water with a resistivity of 18.0 MΩ cm was obtained from a Millipore-Q Plus water purifier and used throughout the experiment.

**Measurements.** Scanning electron microscopic (SEM) images were taken with a Philips XL30 FEG electron microscope at 15 kV. Sample particles were deposited on a glass plate and coated with platinum for SEM analysis. The average particle size,  $D$ , and the standard deviation,  $\sigma$ , were determined by analyzing over 300 particles. The polydispersity from the SEM image is defined as  $\sigma/D$ .

Optical transmission spectra were obtained using a HP 8453 spectrophotometer. The particle size, the polydispersity, and the  $\zeta$ -potential of colloidal nanoparticles were examined by dynamic light-scattering measurement using a Brookhaven Zeta PALS  $\zeta$ -potential analyzer. Surface charge densities on the purified SiO<sub>2</sub> colloidal particles were measured by titrating the colloidal dispersion with standardized NaOH solutions, while the endpoint was determined by conductivity measurements using a conductivity meter. In principle, the total amount of the titratable charge groups ( $\equiv\text{SiO}^-$ ) would be equivalent to the amount of NaOH added when minimum conductivity was reached.

## III. Results and Discussion

**Colloid Synthesis.** Monodispersed SiO<sub>2</sub> nanoparticles with mean diameters ranging from 100 to 500 nm were prepared by hydrolysis of TEOS in an alcohol medium in the presence of water and ammonia by a modified procedure originally described by Stöber et al.<sup>18</sup>

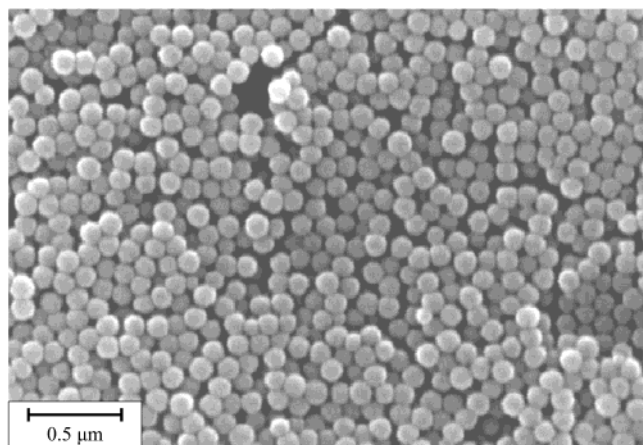
\* Corresponding author. E-mail: wangw@ornl.gov.

<sup>†</sup> Oak Ridge National Laboratory.

<sup>‡</sup> Cardiff University.

**TABLE 1: Size, Surface Charge Density, and  $\zeta$ -Potential of SiO<sub>2</sub> Spheres Prepared at [TEOS] = 0.2 M, [H<sub>2</sub>O] = 17.0 M, in Ethanol**

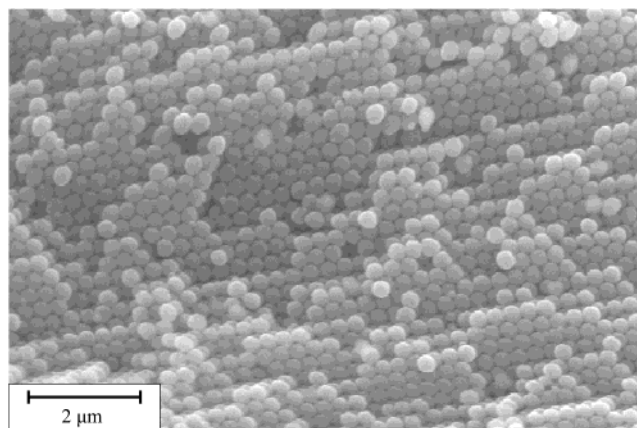
property	sample ID					
	S-30	S-31	S-33	S-36	S-29	S-35
$D$ (nm) $\pm$ polydispersity						
SEM	108 $\pm$ 4.1%	137 $\pm$ 6.0%	201 $\pm$ 5.1%	304 $\pm$ 2.4%	402 $\pm$ 3.9%	493 $\pm$ 5.8%
DLS	112 $\pm$ 4.8%		222 $\pm$ 3.8%	315 $\pm$ 5.5%	419 $\pm$ 3.4%	
[NH <sub>3</sub> ], M	0.2	0.3	0.4	0.6	0.94	1.2
surface charge ( $\mu\text{C}/\text{cm}^2$ )	0.221		0.278		0.183	
$\zeta$ -potential (mV)	−53.6		−55.5		−50.2	
SEM image	Figure 1			Figure 2	Figure 5	
diffraction spectra of particle arrays	Figure 4		Figure 3a	Figure 3b		

**Figure 1.** SEM image of the as-synthesized SiO<sub>2</sub> spheres with diameter 108  $\pm$  4.4 nm.

The base-catalyzed hydrolysis and condensation of TEOS monomers provided the resulting particles with negative surface charges in water due to the ionization of the surface hydroxyl groups. In a typical synthesis operation, two solutions with equal volumes were rapidly mixed to give a total volume of  $\sim$ 250 mL: one solution contained ethanol and TEOS, while the other contained ethanol, water, and ammonia. Depending on the ratio of water, ammonia, and TEOS, the reaction mixture generally turns turbid white as SiO<sub>2</sub> particles formed after  $\sim$ 2–30 min. The reaction was allowed to continue for 6 h at room temperature, with moderate stirring, for full completion.

The particle size and the polydispersity of synthesized SiO<sub>2</sub> particles strongly depend on reaction conditions, including relative concentrations of TEOS, water, and ammonia; the solvent type; and temperature. We systematically varied the reaction parameters in order to generate spherical SiO<sub>2</sub> particles rapidly with minimal polydispersity. As shown in Table 1, results indicate that the size of colloidal particles could be controlled simply by changing the concentrations of ammonia but with fixed TEOS and water concentrations in ethanol. The average SiO<sub>2</sub> sphere size increased from  $\sim$ 100 nm to  $\sim$ 500 nm when ammonia concentrations were increased from 0.2 to 1.2 M while maintaining constant concentrations of TEOS at 0.2 M and water at 17.0 M. To enhance particle charge density, for sample S-30 and S-33, we introduced additional  $-\text{SO}_3^-$  groups to the SiO<sub>2</sub> spheres by using 1 mL of CSPETMOS to replace 1 mL of TEOS in the synthesis. A typical example of the as-synthesized SiO<sub>2</sub> particles is shown in Figure 1. The SEM image of these nanoparticles exhibits their spherical shape and uniform size distribution.

**Preparation of 3-D Colloidal Arrays.** Three-dimensional colloidal arrays of monodispersed SiO<sub>2</sub> nanospheres were obtained using either the gravitational sedimentation or the CCA methodologies.

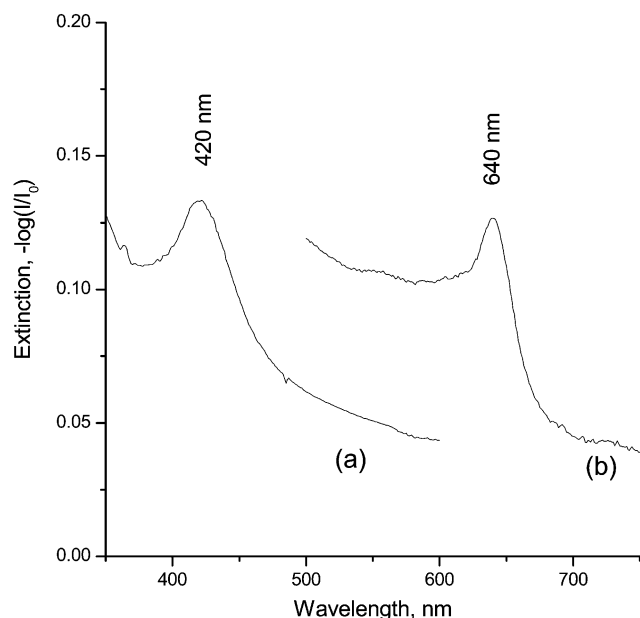
**Figure 2.** SEM image of a broken edge of a 3-D SiO<sub>2</sub> photonic crystal prepared by gravitational sedimentation. Particle diameter = 304  $\pm$  7.3 nm.

**Gravitational Sedimentation Method.** In the first case, after the hydrolysis reaction was completed, SiO<sub>2</sub> particles were collected by centrifugation, followed by redispersion in ethanol using a vortexer and an ultrasonicator. The washing process was repeated three times. A drop of the colloidal alcoholic suspension was transferred to two quartz plates with a 40- $\mu\text{m}$  spacer. The quartz plates were placed vertically, and the solvent was allowed to evaporate slowly. Depending on particle sizes, the SiO<sub>2</sub> particles settled and deposited slowly between the quartz plates to form solid 3-D particle arrays in 2 to 3 weeks. The high monodispersity of the particles resulted in a highly structured ordering, and the particle thin films exhibited iridescent colors because they diffract light in the visible region. SEM images show that the SiO<sub>2</sub> particles are fairly closely packed in the 3-D architecture (Figure 2).

The optical properties of these particle arrays vary depending on the size of the nanocolloids. Figure 3 shows the transmission spectra of the SiO<sub>2</sub> photonic crystals taken at normal light incidence to the surface of the crystal plane. The 3-D closely packed particle arrays, with particle diameters of 201 and 304 nm, exhibit clear diffraction peaks at 420 and 640 nm, respectively. The spectral peak positions are related to sphere diameter because the diffraction property approximately obeys Bragg's law:

$$m\lambda = 2nd \sin \theta \quad (1)$$

where  $m$  is the order of diffraction,  $\lambda$  is the diffracted wavelength in a vacuum,  $n$  is the effective refractive index of the system (medium and colloidal particle),  $d$  is the spacing between the diffracting planes, and  $\theta$  is the Bragg glancing angle between the incident light propagation direction and the diffracting planes. The inter-planar spacing,  $d$ , can be expressed



**Figure 3.** Normal incidence extinction spectra of SiO<sub>2</sub> 3-D photonic crystals with different particle diameters: (a)  $D = 201 \pm 10.3$  nm, (b)  $D = 304 \pm 7.3$  nm.

in terms of the unit cell parameter,  $a$ , and Miller indices:

$$d = a/(h^2 + k^2 + l^2)^{1/2} \quad (2)$$

The photonic crystals are usually oriented with their (111) axes parallel to the substrate.<sup>4</sup> Theoretical calculations indicate that the face-centered cubic (fcc) structure is the most stable one.<sup>19</sup> For the fcc lattice, the diameter of the spheres,  $D$ , is related to the lattice parameter by  $a = \sqrt{2}D$ . Assuming that the volume fraction of the closely packed colloidal sphere is 74% in air and considering an amorphous silica refractive index of 1.45, calculations show that the diffraction peaks at wavelengths of 420 and 640 nm correspond to particle diameters of 193 and 294 nm, respectively. These results are in good agreement with the observed particle size of these nanocolloids using SEM (Table 1).

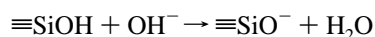
Similar SiO<sub>2</sub> opal photonic crystals prepared using various procedures have been reported by others previously.<sup>17,20–23</sup> However, it is recognized that, as photonic crystal materials, the particle packing can hardly be perfect on a large scale; thus, these 3-D photonic crystals usually give broad diffraction bands because of particle packing defects. In addition, the diffraction spectra of these closely packed particle arrays depend on the particle size—i.e., the diffraction of the photonic crystals is tunable only by changing SiO<sub>2</sub> particle sizes. This would require different photonic crystal preparations with different particle sizes; thus, the tunableness is not continuous.

**Colloidal Crystalline Array Method.** In contrast to closely packed particle crystals (hard photonic crystals), soft photonic crystal materials such as crystalline colloidal arrays (CCAs), have been developed for continuous tunability.<sup>24–26</sup> In a pure colloidal dispersion, if the colloidal particles are monodispersed and their surfaces are highly charged, the colloidal particles can be fixed, in a dynamic sense, in certain positions (with ordered, equal spacing in the colloidal suspension) by the net repulsive forces to form the CCA. Such CCA systems have been studied extensively using latex particles, such as polystyrene particles.<sup>2</sup> However, little attention has been paid to SiO<sub>2</sub> colloids for CCA preparations in water,<sup>25,27</sup> although several researchers investigated SiO<sub>2</sub> CCAs in nonaqueous media.<sup>28,29</sup> Perhaps a primary

reason for the lack of attention is that the surface charge on SiO<sub>2</sub> colloids is not strong enough to “fix” the colloidal particles in an ordered pattern. In particular, the particle density of a typical CCA needs to be as high as  $10^{13}$  cm<sup>-3</sup>; at this density, coagulation of SiO<sub>2</sub> particles could easily take place to prevent formation of CCAs.

Silica particles are negatively charged in water at a pH > ~3 because of the surface Si—OH groups. However, the net repulsive forces between particles are usually weak, depending on the pH of the solution and the screening effect of counterions. For amorphous SiO<sub>2</sub> (such as the SiO<sub>2</sub> spheres prepared herein), the zero-point of charge is around  $2 \pm 0.5$ .<sup>30</sup> To enhance particle surface charges, we purified the SiO<sub>2</sub> colloids extensively as follows.

After washing the SiO<sub>2</sub> colloids by ethanol, we washed the particles with deionized water for an additional three times. The collected particles were redispersed in deionized water with the desired particle concentration and dialyzed in a dialysis tube to exchange the nonaqueous solvent molecules and to remove any solvated impurities. We changed the deionized water daily until there were no changes of its conductivity with time. We then dialyzed the colloids against dilute NaOH solution at pH 9 for 3 days. An increased solution pH is necessary to increase the net negative charge on SiO<sub>2</sub> surfaces, as illustrated below:

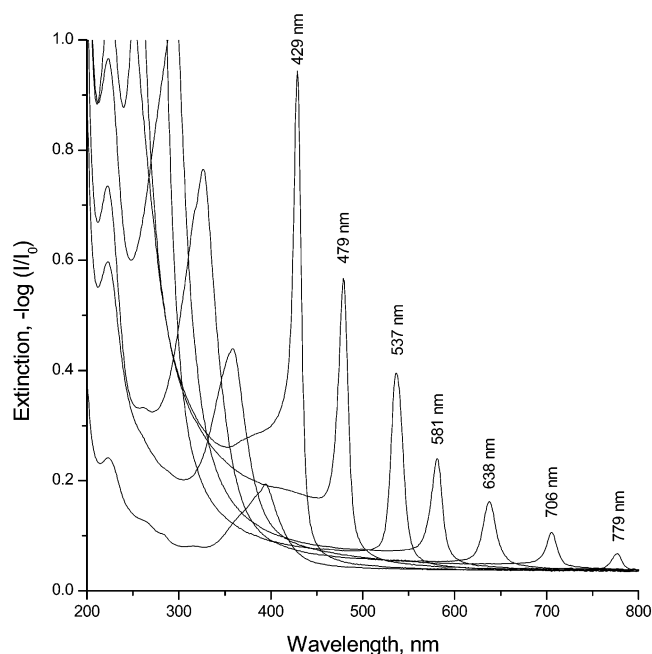


We kept the pH at or below ~9 because the solubility of amorphous SiO<sub>2</sub> increases substantially at pH > 9.<sup>30</sup> On the other hand, an increased solution pH also increases the concentration of counterions, Na<sup>+</sup>, in the colloid suspension; these ions screen the surface charge or electric double layer thickness. To reduce the screening effect of Na<sup>+</sup>, we further purified the colloid suspension by adding mixed-bed ion-exchange resins to substitute cationic and anionic ions with H<sup>+</sup> and OH<sup>-</sup>. The final pH of the colloid suspension was ~8. The purified colloidal particles readily self-assemble to form 3-D CCAs, stabilized by strong net repulsion forces.

Titration measurements showed that the purified SiO<sub>2</sub> colloids had relatively high surface charge densities, ranging from 0.18 to 0.28  $\mu\text{C}/\text{cm}^2$ , and a  $\zeta$ -potential as high as about -55 mV (Table 1). Thus, a delicate balance between ionic strength and solution pH provided a maximum repulsive force between SiO<sub>2</sub> colloid spheres, which is essential for the formation of SiO<sub>2</sub> CCAs in aqueous suspensions.

As was observed in the polystyrene system,<sup>2</sup> the SiO<sub>2</sub> CCA in water exhibits unique photonic properties. We injected the CCA into a cell consisting of two quartz plates, separated by a 125- $\mu\text{m}$  Parafilm spacer, for the UV–visible spectroscopic measurement. Figure 4 shows the extinction spectra of the CCAs of 108-nm SiO<sub>2</sub> colloids at different colloidal concentrations. The CCA normally self-assembles with its highest particle density planes [the fcc (111) or bcc (110) planes] parallel to the surface of the quartz cell.<sup>2</sup> In comparison with the spectra of hard SiO<sub>2</sub> photonic crystals (Figure 3), the transmission spectra of CCAs in water show narrower diffraction peaks. These narrower peaks imply a higher long-range ordering of the particles in suspension. The weak light absorption in background was a direct result of a lower particle density in the CCA suspension than in solid SiO<sub>2</sub> photonic crystals. An important property of soft CCAs is that the wavelength of the diffracted light is continuously tunable from blue to red in the entire visible region, simply by diluting CCAs with deionized water. This property may allow the materials to serve as tunable optical filters.



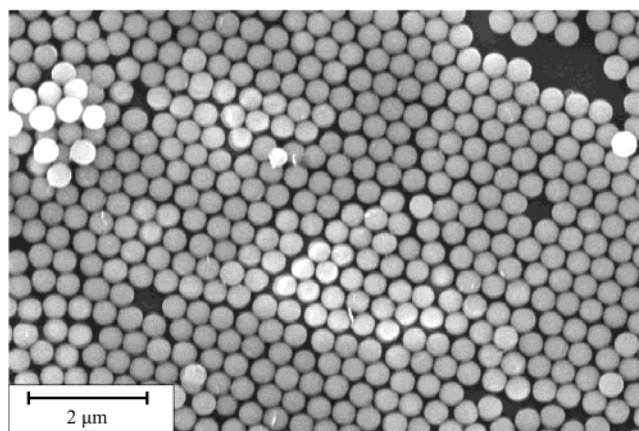


**Figure 4.** Normal incidence extinction spectra of SiO<sub>2</sub> crystalline colloidal array (CCA) at different colloidal concentrations. The CCA was placed in a 125- $\mu$ m-thick quartz cell. The SiO<sub>2</sub> nanoparticle size is  $108 \pm 4.4$  nm, as determined by SEM. Note that increasing dilution produced a red shift and that the diffraction peak can be tuned continuously.

The disadvantage of soft CCAs is their sensitivity to ionic impurity. Even low concentrations of ionic impurities could destroy CCAs by screening the static repulsion among SiO<sub>2</sub> colloid particles. However, the resistance of CCAs to external disturbance may be increased by polymerizing the CCA in hydrogels; this step permanently locks the ordered colloid particles into position.<sup>2</sup> Lee and Asher<sup>31</sup> have developed a polymerized CCA (PCCA) sensor using polystyrene colloids to monitor pH and ionic strength. Compared to polystyrene or other polymeric colloids, the SiO<sub>2</sub> colloids have better resistance to solvent and temperature changes, and therefore SiO<sub>2</sub> CCAs have the potential to be fabricated as PCCA sensors for a range of chemical detection.

**Preparation of Hydrophobic SiO<sub>2</sub> Colloids and Two-Dimensional Particle Arrays.** Methods for preparing 2-D colloidal arrays on thin films with controlled thickness are still under intensive investigation. Under the proper conditions, a closely packed colloidal thin film could be prepared by the spin-coating technique.<sup>32,33</sup> Convective self-assembly of wetting solutions is also a route for making ordered monolayers and structures of nanocrystals on a variety of substrates.<sup>34,35</sup> However, the thickness of such a 2-D particle array thin film is not easy to control. In addition, a thick particle film greatly reduces the optical transmission efficiency of the photonic crystals. Although Langmuir–Blodgett deposition has been used for fabricating silica particulate monolayers,<sup>36</sup> the hydrophilic SiO<sub>2</sub> particles, capped by a water-soluble surfactant, result in poor packing orders. Here, we report a new method for rapidly growing 2-D silica colloidal thin films or arrays on glass substrates. The procedure involves the modification of SiO<sub>2</sub> surfaces and the fabrication of 2-D self-assembled particle arrays.

As a first step, we modified silica surfaces from hydrophilic to hydrophobic surfaces in order to transfer the hydrophilic SiO<sub>2</sub> particles into weakly polar and nonpolar solvents. We first functionalized SiO<sub>2</sub> spheres by using the silane coupling agent



**Figure 5.** SEM image of hydrophobic SiO<sub>2</sub> particle monolayer on a glass slide deposited from a colloid monolayer at the air–water interface. Particle diameter =  $402 \pm 15.7$  nm.

OTMOS, which has a hydrophobic octadecyl hydrocarbon chain. Briefly, after hydrolysis and condensation of TEOS were completed, we separated the SiO<sub>2</sub> particles and redispersed them in 100 mL of ethanol with 1 mL of NH<sub>3</sub>·H<sub>2</sub>O (29.5%). Ten milliliters of the OTMOS chloroform solution (10%) was added dropwise into the reaction mixture with vigorous stirring. The hydrophobic octadecyl hydrocarbon chains were grafted on the SiO<sub>2</sub> particle surface by hydrolyzing methoxy groups of the OTMOS to form reactive silane triols and then condensing on the SiO<sub>2</sub> particles surface with surface  $\equiv\text{Si}-\text{OH}$  groups. After 24 h, the particles were separated and washed by ethanol. These modified SiO<sub>2</sub> particles could readily be dispersed into various organic solvents such as chloroform or cyclohexane because of their hydrophobic surfaces.

The 2-D particle arrays were then fabricated by transferring the hydrophobic, surface-modified SiO<sub>2</sub> particles from their colloidal suspension in an ethanol–chloroform mixture onto an air–water interface. The SiO<sub>2</sub> colloid dispersion in ethanol and chloroform was added drop by drop to a deionized, water-filled Petri dish; with the evaporation of chloroform, the colloidal particles rapidly self-assemble at the water–air interface to form an approximately closely packed particle monolayer—i.e., a 2-D particle array. We optimized the quality of the monolayer by adjusting the SiO<sub>2</sub> colloid concentration and the ratio of ethanol to chloroform in the solvent. Pure chloroform is not a satisfactory solvent because of its rapid evaporation, which causes crystal growth that is too fast to obtain uniform particle film, resulting in highly concentrated particle islands. On the other hand, if pure ethanol is used as the solvent, a number of SiO<sub>2</sub> particles disperse into the bulk water phase and the particles are not closely packed at the air–water interface. Therefore, we used an ethanol–chloroform mixture as solvent for better control of the growth of the 2-D particle arrays. The particle thin film at the air–water interface is stable and readily transferred onto solid substrates such as glass slides and plastic plates by contacting the substrate with particles at the air–water interface. Figure 5 is a typical SEM image of the closely packed SiO<sub>2</sub> monolayer formed on a glass slide. The long-range order of the thin film is confirmed by the top-view SEM image. By repeatedly transferring the monolayer onto the solid substrate, we could obtain multiple layers of SiO<sub>2</sub> particles, forming a 3-D crystal architecture. Using this technique, the particle film thickness could be precisely controlled and is predictable.

#### IV. Conclusion

We have synthesized monodispersed SiO<sub>2</sub> nanoparticles with sizes ranging from 100 to 500 nm. The hard 3-D photonic crystals could be obtained simply by gravitational settling of these monodispersed SiO<sub>2</sub> particles. The particle size derived from the diffraction pattern of these colloidal crystals agreed well with data obtained from SEM and DLS analyses. We also demonstrated a method to prepare soft 3-D CCAs in water using highly purified, monodispersed SiO<sub>2</sub> colloids. Such CCA suspensions exhibit tunable diffraction properties in visible wavelength ranges. In addition, we prepared hydrophobic SiO<sub>2</sub> nanocolloids, which readily self-assemble to form monolayers—i.e., 2-D particle arrays at the air–water interface. These monolayers can be transferred onto solid substrates either as monolayers or multilayers to form 3-D photonic crystals. The method thus presents a convenient way to fabricate controlled thicknesses of particle thin film. These 2-D and 3-D particle arrays may find wide application in chemical sensing technology and optical detections.

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