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Preparation of movable 3D periodic structures of silica spheres*

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Abstract: Monodispersed silica spheres were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of water and ammonia in ethanol medium. The net negative charge on the surface of SiO_2 spheres was enhanced after ageing silica spheres under suitable condition. Thus, a novel viscous liquid composed of mono-dispersed silica spheres was obtained. Due to the existing net repulsive forces between particles, the viscous liquid can quickly form a movable 3D periodic ordered structure with vivid color, indicating a high degree of ordering of the particles.

Key words: Silica spheres, Three-dimensional, Colloidal
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INTRODUCTION

Monodispersed nanoparticles show various interesting properties and might form 1D, 2D or 3D periodic structures, which can be treated as if they were atoms (Dushkin *et al*., 1993; van Blaaderen *et al*., 1997; Ozin and Yang, 2001; Park and Xia, 1999). In the past two decades, fabrication of 3D periodic ordered structures constructed with monodispersed particles have received considerable attention due to their diverse applications ranging from high performance LEDs, low-power microlaser and novel types of optical fibers to high speed switches (Nihei amd Okamoto, 2002), optical filters and photonic very large scale integrations (VLSIs) (Yoshiyama *et al*., 1984). Furthermore, the inverse 3D periodic porous materials (Jiang *et al*., 1999c) can be used as filters, catalyst supports (Schroden *et al*., 2001) and selective membranes (Jiang *et al*., 1999b). Therefore, it is very important to develop the precise particle assembly techniques for utilizing the novel properties of these 3D structured nano particles for future devices. A wide variety of methods have been used to fabricate the periodic ordered structures including the assembly methods (Gates *et al*., 1999), two-photon lithography (Cumpston *et al*., 1999), multi-exposure of two-beam interference technique (Lai *et al*., 2005), E-beam lithography (Knight *et al*., 1996) and etching methods (Golubev *et al*., 2002). Some of them are more suitable for 1D and 2D photonic crystals; others are suitable for fabricating 3D structures. Till now, solvent evaporation (Hsiao *et al*., 2005), sedimentation (Donselaar *et al*., 1997) and self-assembly (Pileni, 1997) base on electrostatic repulsion are the three most successful methods employed for producing 3D ordered structures from meso and nanoscale particles. It is well known that artificial silica opal photonic crystals have been prepared using various procedures (Jiang *et al*., 1999a; Mayoral *et al*., 1997). However, it is recognized that, as photonic crystal materials, the particle packing can hardly be perfect on a large scale (Griesebock *et al*., 2002); thus, these 3D photonic crystals usually give broad diffraction bands because of particle packing defects. Furthermore, 3D ordered structures of silica spheres still suffer from problems, such as too small domain sizes of the assemblies, long

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fabrication time, too many cracks (Kuai *et al*., 2004) in the obtained product and difficulty in shaping the structures, all of which limit their practical applications.

Here, we show a newly developed synthesis procedure, in which a viscous liquid of spherical silica particles forms well-defined 3D structures by a simple shaking of the mixture. In the above procedure, due to the highly ordered particle arrays in the viscous liquid sample, a vivid color can be observed with naked eyes. This procedure, in which the viscous movable packed structure can be formed, is not only applied to plane substrate but can also be applied to curved surfaces/substrate such as fibers. The main advantage is that this technique does not need special devices and reaction conditions. The above materials were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

DETAILS

Preparation of monodispersed silica spheres

Monodispersed SiO_2 nanoparticles with mean diameter 210 nm were prepared by hydrolysis of TEOS in an alcohol medium in the presence of water and ammonia, similar to the procedure reported by Stöber *et al*.(1968). In a typical synthesis, given amounts of water, ethanol and ammonia solution were introduced into a 250 ml three-neck round flask with gentle stirring at room temperature. Then, tetraethyl orthosilicate (TEOS) was introduced continuously to the medium at a precise rate (1 drop per 15 s). Reaction occurred at room temperature under continuous stirring for over 12 h, during which hydrolysis was the main reaction. The final reaction mixture contained 8.89 mol/L water, 1.47 mol/L ammonia, and 1.05 mol/L TEOS. After finishing the above hydrolysis reaction, 20 ml water was added, followed by evaporation of ethanol and ammonia in the mixture solution under vacuum at 45 °C for 30 min. SiO_2 particles were collected from the resulting white suspension caused by the centrifugation (3000 r/min). The obtained silica spheres are called primary silica spheres. In order to obtain good quality monodispered spheres, the primary silica spheres were redispersed in ethanol using an ultrasonicator, and recollected by centrifugation. The above washing process was repeated three times in order to remove impurities, such as ammonia, water, and unreacted TEOS. The final product was dispersed and stored in the mixture solution of water and ethanol (80:20 v/v).

Fabrication of 3D silica opals

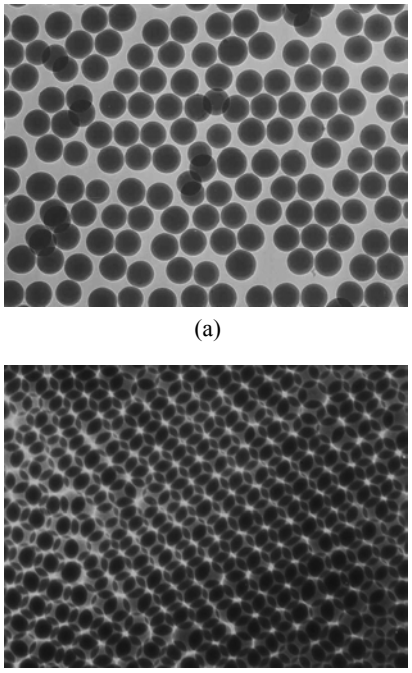
3D movable SiO_2 colloidal arrays were obtained using a gravitational sedimentation method. The mixture solution containing the silica microspheres, ethanol and water was put into a small glass bottle. The SiO_2 particles settled and deposited at the bottom of the bottle to form a movable white precipitate in 3 to 4 d. The major part of the clear solution in the bottle was carefully removed. After the glass bottle was aged at 60 °C for one and a half weeks, the white precipitate changed to a viscous liquid with obvious iridescent colors along the cross section of the sample, indicating the formation of regular 3D periodic structures due to the electrostatic interaction of the monodispered particles.

Analytical methods

TEM was conducted with a JEM-200 microscope operating at 160 kV. Samples were mounted on a microgrid carbon polymer, supported on a copper grid. SEM observations were conducted with an FEI SIRION FESEM scanning electron microscope. In the scanning electron microscope investigations, the specimens were gold-coated prior to examination.

RESULTS AND DISCUSSION

The most important parameters in determining the performance of colloidal crystals in optical applications are the crystalline quality. Spheres of either larger or smaller diameter can destroy the 3D periodic structure. Fig.1 shows the transmission electron microscopy (TEM) images of spheres with a diameter of about 210 nm. The monolayer of the silica spheres formed on the microgrid carbon polymer (supported on a copper grid) shows the well dispersed silica spheres (Fig.1a). When more droplets of the ethanol suspension containing silica spheres are deposited on the grid, two layers of regular periodic structure of silica spheres can be clearly observed in the TEM image (Fig.1b). It is clearly seen that every silica sphere (on the top) is in contact with three silica sphere (at the bottom) in this structure.



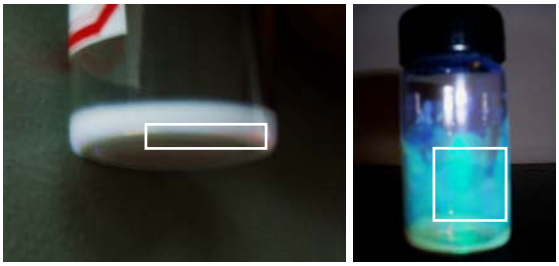
(a)

(b)

Fig.1 TEM image of monodispersed SiO_2 spheres with a diameter of 200 nm. (a) The mono-layer of dispersed silica spheres; (b) The two layers of silica spheres

In visible light, the viscous liquid sample shows a white-color and a little iridescent color at the cross section of the liquid sample (the white circle area in Fig.2a); however, when the bottle was turned over, rolled up, and returned its original position, the iridescent color was clearly observed on the glass wall, just like natural opals.

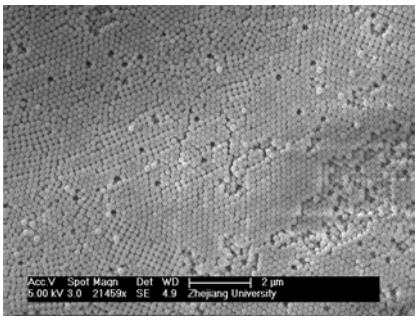
The digital camera image of the movable liquid sample shows green color on the glass walls (the white circle area in Fig.2b). As was observed in solid artificial opal system, the SiO_2 layer on the glass walls seems to exhibit unique photonic properties. This is due to a thin layer of 3D periodic structure formed as the viscous liquid returned to the bottom along the glass wall. Thus, light interacts with this periodic structure as a sub-micrometer diffraction grating to produce the color in visible spectrum. Moreover, we found the green color became weaker with increasing time, showing that the 3D periodic structure layer formed on the glass wall became thinner due to the flowing of the silica micro spheres. Here, we propose that the colloidal particles are monodispersed and that 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 crystalline colloidal arrays. Silica particles are negatively charged in water at pH>3 because of the surface Si-OH groups. However, the net repulsive forces between particles are usually weak, depending on the solution pH and the screening effect of counter ions. The increasing of pH is necessary to increase the net negative charge on SiO_2 surfaces. So, in this experiment, the final pH of the colloid suspension was about 8. We kept the pH at or below 9 because the solubility of amorphous SiO_2 increases substantially at pH>9. Thus, a delicate balance between ionic strength and solution pH provided a maximum repulsive force between SiO_2 spheres, which is essential for the formation of SiO_2 crystalline arrays in aqueous suspensions. The purified colloidal particles readily self-assemble to form 3D crystalline arrays stabilized by strong net repulsion forces.



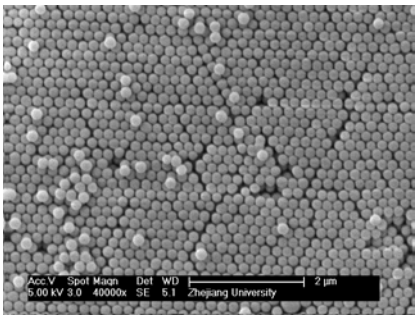
(a) (b)

Fig.2 Digital camera image of the movable liquid sample. (a) The weak iridescent color in the white circle area; (b) The green color on the glass wall in the white circle area

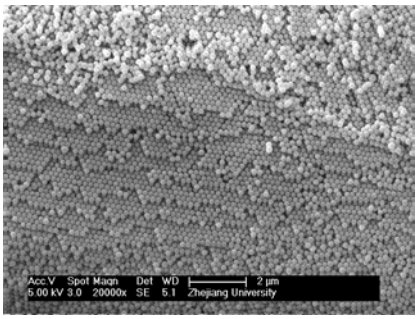
The SEM images of the dried sample further confirm the movable 3D periodic structure of the colloidal crystal. Fig.3a shows a typical SEM picture of the sample. At low magnification, the particles appear textured (Fig.3a); the magnified SEM image confirmed the silica spheres were self assembled into the hexagonally close-packed fcc structure (similar to that of a natural opal) (Figs.3b and 3c). As shown in Figs.3a and 3b, some cracks and defects are observed on the surface of the colloidal opal. Despite these defects, the opals prepared still exhibit a strong reflectance peak, centred at about 520 nm, showing that the silica periodic arrays have large tolerance to the geometric disorder. The diffraction characteristics of the system can be accurately predicted with dynamic diffraction theory, though the Bragg diffraction equa-



(a)



(b)



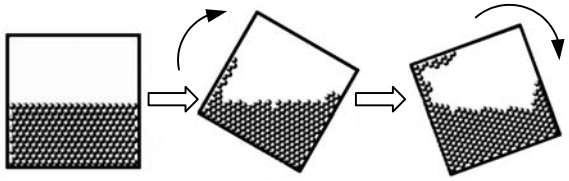
(c)

Fig.3 SEM image of the dried sample. (a) Top section; (b) The enlarged image of (a); (c) The cross section

tion ($\lambda_0/2=n_c d_{hkl}\sin\theta$, where λ_0 is the wavelength of the diffracted light in air, d_{hkl} is the interplanar spacing, n_c is the refractive index of the composite, and θ is the Bragg angle) is α reasonable approximation (Rundquist *et al*., 1989). In this experiment, the diameter of the sphere is 210 nm, the refractive index of SiO_2 is 1.5. Then, we may get the interplanar spacing d_{hkl}:

$$d_{hkl}=\frac{\sqrt{2}D}{\sqrt{h^2+k^2+l^2}}=\frac{297}{\sqrt{3}}=172\text{ nm},$$

thus, $\lambda_0=2n_c d_{hkl}\sin\theta=3\times172\times\sin\theta=516\sin\theta$. When $\theta=90°$, $\lambda_0=516$ nm. The structure obtained using the above-mentioned method obviously shows green color, optically viewed from any direction. This indicates the silica colloidal crystal film is 3D periodic face centred cubic (fcc) crystal structure (Vos *et al*., 1997; Miguez *et al*., 1997) or diamond structure, consistent with the SEM image. Interestingly, in the cross section part of the sample, a multilayer structure was clearly observed as shown in Fig.3c; every layer is composed of 2D periodic array of spheres. The formation of this multilayer structure is due to the fact that viscous liquid of colloidal silica spheres flow down along the glass wall of the bottle. Fig.4 shows the schematic for the formation of the silica spheres multilayer structure: when the bottle containing the colloidal silica spheres was turned, the thicker layer of the colloidal silica spheres was formed on the glass wall (Fig.4a); when the bottle was turned upside down, the viscous colloidal silica spheres flowed down due to the gravitational sedimentation, which results in reduced thickness of colloidal silica layer (Fig.4b). With increasing time, more and more silica spheres trend to flow down, thus the multilayer structure was formed (Fig.4c). This result is consistent with the changing of color for this sample.



(a) (b) (c)

Fig.4 Schematic of the formation of the multilayer structure. (a) Origin position, corresponding to Fig.2a; (b) and (c) When the bottle turned upside down, corresponding to Fig.2b

CONCLUSION

In summary, we have demonstrated an effective procedure for a viscous liquid composed of monodispersed silica sphere. The viscous liquid can quickly form a movable 3D periodic ordered structure due to the net repulsive forces between particles. These 3D periodic structures exhibit vivid color due to a high degree of ordering of the particles. This technique does not need special devices and conditions. Thus, some practical applications using this

viscous liquid are anticipated.

Although we have only demonstrated this procedure with 210 nm silica spheres, we believe that this method could also be applied to monodispered particles of other materials, and even to particles with different dimensions.

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