



## Synthesis of Polystyrene Template and Its Inverse Structure

HONG ZHAO<sup>1,\*</sup>, FU JUN YIN<sup>2</sup>, LI HONG ZHANG<sup>1</sup>, GUI ZHAO<sup>1</sup> and XING YOU XU<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China

<sup>2</sup>Jiangsu Marine Resources Development Research Institute of Huaihai Institute of Technology, Lianyungang 222005, P.R. China

<sup>3</sup>Huaiyin Insititute of Technology, Huaiyin 223003, P.R. China

\*Corresponding author: Fax: +86 518 85863269; Tel: +86 518 85863269; E-mail: yinfujun2008@126.com

(Received: 10 May 2012;

Accepted: 15 February 2013)

AJC-12996

A facile method for fabricating high-quality polystyrene template was reported, the optimal assembly was obtained by controlling deposition temperature and polystyrene latex concentration, which ensures a large force perpendicular to the substrate capable of overcoming thermal fluctuations and pushing particles into the substrate, leading to highly efficient assembly. The assembly mechanism is that the interfacial capillary force present during the evaporation of polystyrene latex. By silver-mirror reaction, Ag copy the polystyrene template, an inverted polystyrene template structure, that is silver nano-cavity array structure was obtained. Our results demonstrate that two-dimensional highly ordered silver nano-cavity can be formed by the chemical bath deposition method, two complementary micro-structures were generated during the self-assembly process, as indicated by the SEM images.

**Key Words:** Template, Nano-cavity, Silver, Assembly, Metal, Structure.

### INTRODUCTION

Numerous methods for producing monolayer or multi-layer of colloidal particles have been developed<sup>1-3</sup>, including spin-coating, solvent evaporation, sedimentation and self-assembly based on electrostatic repulsion<sup>4-7</sup>. Among these methods, self-assembly technique has proven to be one of the most flexible and controllable approaches. As a successful example, self-assembly of polystyrene sub-micrometer spheres has been adopted in large-scale pattern generation for quantum dots arrays or selective growth of quasi-one dimensional (1D) nanostructures. In this paper, we probe the forming mechanism of colloidal crystal experiments, by varying volume fraction of polystyrene (latex) spheres and temperature, we get different polystyrene spheres assemble pattern. Monolithic metals containing large internal surface areas have potential applications such as photonic crystal, optical applications, catalysis, substrates for surface-enhanced Raman scattering (SERS) and nano reactor<sup>8-12</sup>. Using assembled periodic structures of mono dispersive particles to create the metallic nano-cavity array has proved to be a flexible and reliable approach. Jiang<sup>13</sup> prepared three-dimensional ordered void arrays of metals and semiconductors by physical vapor deposition techniques on the assembled colloidal crystals of silica nano particles. Wang *et al.*<sup>14</sup> fabricated ordered TiO<sub>2</sub> nano bowl sheets by atomic layer deposition (ALD), ion milling and etching on the template of self-assembled polystyrene spheres. In this work,

an inverted opal structure was produced by chemical deposition of silver metal on the polystyrene template. One advantage of using electroless methods is that there exists standard recipes for the deposition of virtually any metal. We demonstrate the application of this method with silver and produce highly ordered silver nanocavity. At the same time, we revealed the mechanism of Ag eventually leads to inverted opal structure. This technique demonstrates a simple and economic approach to design monolithic metals.

### EXPERIMENTAL

Styrene was purchased from Aldrich Co. and distilled under reduced pressure. The other chemicals are all reagent grade.

**Apparatus and methods:** Polystyrene particles were synthesized according to the literature protocol<sup>3</sup>. Briefly, 20 mL of styrene and 170 mL of deionized water were mixed in a four-neck flask and the mixture was heated over a water bath at 70 °C. After the mixture being flushed with nitrogen for 20 min, 0.0674 g of potassium persulphate dissolved in 10 mL water was added to the solution to initiate the reaction. The whole reaction lasted 28 h. The aggregated polystyrene particles were removed by filtration (Fig. 1a-b). After that, the colloid was ultrasonated for 3 min or aging for several days to obtain mono- disperse colloid.

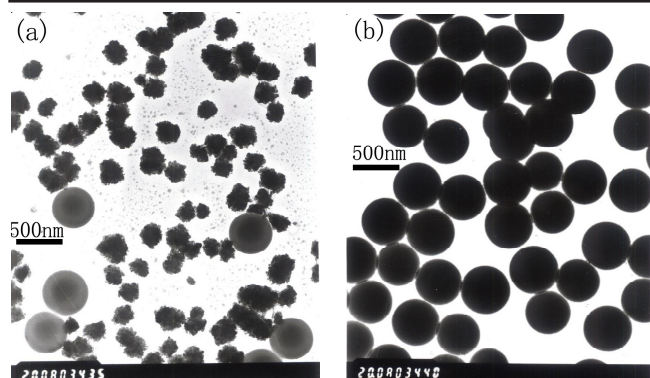


Fig. 1. TEM graphs of polystyrene sphere (a) without filtration (b) after filtration

The particle size and polydispersity were estimated by the TEM images measured on a TEM-100CXII transmission electron microscopy. The surface morphologies of the samples were measured on a Hitachi 7350G SEM microscope.

## RESULTS AND DISCUSSION

All of possible phases cubic, hexagonal, mixed or random, the cubic phase is the only stable one<sup>15</sup>. The fabrication method for polystyrene face centered cubic (Fcc) template of small lattice parameter (between 0.2 and 0.6  $\mu\text{m}$ ) has been reported in the literature<sup>16</sup>. The particles usually arrange themselves randomly. However, under favorable conditions, they form hexagonally arranged, close-packed arrays in a assembly process. Here, we discuss the optimal assemble conditions of latex spheres. Mainly, polystyrene concentration and temperature affect colloidal crystal fabrication, arrangement of polystyrene change from typical wire to a typical close-packed Fcc lattice when polystyrene concentration increased (Fig. 2a-c), which prove capillary forces draw the polystyrene spheres together as the solvent evaporate. At the same time, because of gravity, polystyrene colloid was dripped onto glass dried into film of mono- or multi- ordered arrays. Typical wire of 10 wt % prove the weak dispersion force between latex spheres. Also, temperature plays an important role in the crystallization process, because it influences the particle diffusion in the suspension and velocity of solvent evaporation. Too high temperature will left air voids among polystyrene template (Fig. 2d). In fact, perfect template require that the polystyrene spheres be able to freely diffuse across the substrate, seeking their lowest energy configuration. So a suitable temperature and concentration is critical to the crystallization. In this study, we adjusted the volume fraction of 50 wt % and temperature at 50 °C. And indeed these samples exhibit striking iridescence under white light illumination because of Bragg diffraction of the periodic distribution of particles. Moreover, the amount of defects is decreased efficiently in system with controlled temperature and concentration. The following mechanism is suggested. First, a nucleus is formed when the thickness of the solvent layer (generally water) approaches the diameter of the particles. When the tops of the particles protrude from the water surface, due to surface tension effects, the spheres are pulled together. In the second step, evaporation of the solvent from within the micro-menisci between the spheres causes water influx from outside, which is related to convective

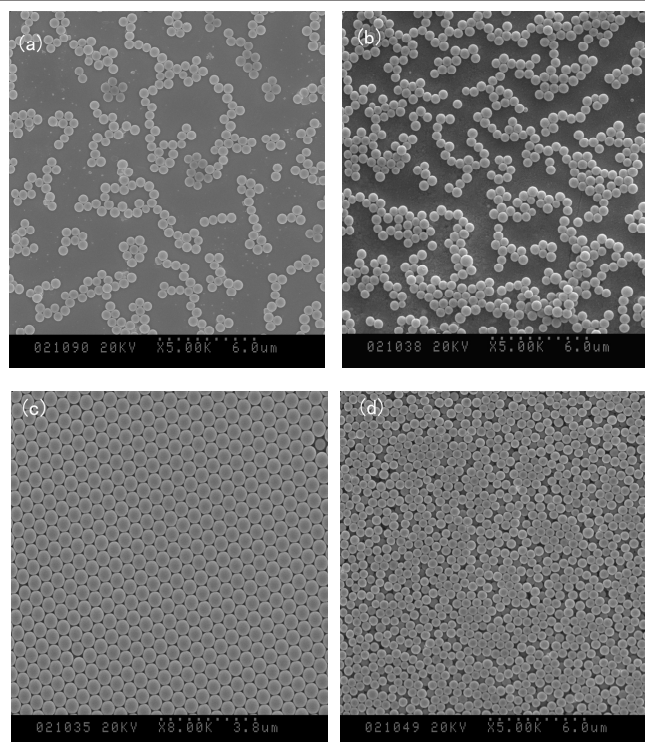


Fig. 2. SEM graphs of polystyrene nanoparticle templates formed with different polystyrene colloid concentration (a) 10 wt %, 50 °C (b) 30 wt %, 50 °C (c) 50 wt %, 50 °C. (d) 50 wt %, 80 °C

particle transport towards the nucleus. These templates are relatively fragile and easily disrupted during deposition. So it is necessary to anneal the colloidal crystals and make the polystyrene spheres closely contact with each other. The polystyrene template was sintered at 105 °C for 1 h<sup>17</sup>, which is just below the glass transition temperature of polystyrene. No morphological change could be detected in either colloidal template using a scanning electron microscope. The optimal assembly was obtained by controlling temperature and concentration, which ensures a large force perpendicular to the substrate capable of overcoming thermal fluctuations and pushing particles into the substrate while maintaining the effective sliding action, leading to highly efficient assembly.

Once the ordered opal is formed, it can be infiltrated with nano-sized crystallites or a precursor of insulators, semiconductors or metals<sup>4</sup>. The bottom-up deposition of Ag have been realized by the electron beam deposition (EBD)<sup>18</sup>. Here chemical bath deposition (CBD) method<sup>19</sup> is adopted to deposit Ag, put the polystyrene template in reaction solution to produce silver, silver film was chemically generated on the top of polystyrene nanoparticles, then the sample was exposed to the atmosphere until the sample was completely dry, template with deposition Ag was stuck off the glass substrate by adhesive tape and putted into toluene solution to remove the polystyrene template while leaving the silver film unaffected. To ensure the remaining spheres were completely removed, the silver film was normally sonicated in toluene for 2-3 min until bright optical diffraction from the ordered structure became clearly visible again. In the end, we obtain ordered monolayer inverse opal structured films (Fig. 3). These nano-cavity are highly ordered and separated from each other, forming a two-dimensional nano-cavity array. These cavities match the size of the

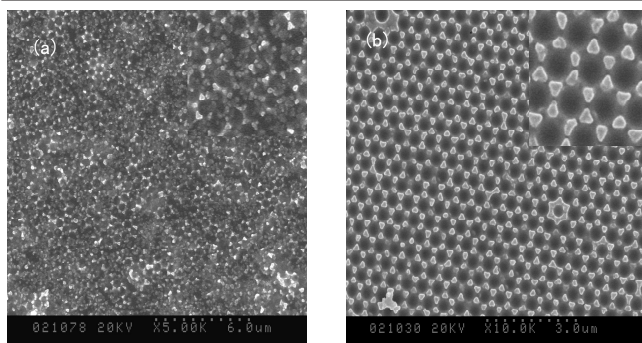


Fig. 3. SEM graphs of silver nanosphere cavity by chemical deposition (a) one (b) two

starting polystyrene colloids and retain their close-packed ordering. On the edge of every regular silver hemispheres there is six identical and perfect small triangles was formed at the contiguity of three polystyrene spheres. An important issue to address is the extent to which the metals infiltrate the template during deposition, polystyrene template is multilayer, however, silver only grow in the first half-layer of template. Fig. 3(B) provide ample evidence that these samples are uniform silver nano-cavity and structural integrity of the samples.

After one time silver-mirror reaction, a few of silver core can be seen from Fig. 3(A), which show silver fill the nanochannels of the opal incompletely. To ensure a larger filling ratio of silver amine solution in the interstitial space of the colloidal crystals, filling process is repeated two times (Fig. 3b), compact silver nano-cavity is presented. It should be pointed out that polystyrene is made of emulsifier-free emulsion polymerization, Ag growth does not seem to depend on either opal order or specific position on the sphere surface, as homogeneous distribution of the Ag core. Instead of small grains fuse together to form the three-dimensionally ordered macroporous solid<sup>20</sup>. These samples are two-dimensional highly ordered metal films with half spherical cavities, this phenomenon results from the jam of nanochannel by silver core, reaction velocity is so rapid that larger silver core in the nanochannel prevent reaction solution more infiltration, at the room temperature, it was happen to stop growing at the point where the half nanochannel of the first layer of multi-layer template. Therefore, more infiltration process is failure when silver core grow up. One hand, the infiltration of reaction solution into polystyrene opal was based on capacity which the nanochannel contain, in another hand, surface chemistry of the sphere templates influences framework formation, strong wetting interactions aid penetration and formation of a continuous network. Density of silver can be increased by multiple complementary of reaction solution. It is important that quick reaction and larger core eventually block the penetration of

silver amine into more than half opal. During this procedure, Ag grows mostly inside the half layer opal structure.

### Conclusion

This communication describes forming conditions of ordered colloid crystal template. It also demonstrates how mono-layer inverse opal structured films of metals can be conveniently and easily fabricated by the use of colloidal crystal templates. This morphology will be of value in applications which rely on the chemical activity of metal surfaces. At the same time, this technique demonstrates a simple and economic approach for producing various designed patterns by a combination of physical and chemical method. Moreover, long-range ordering of the nano-cavity array endows the samples with striking optical properties which are the subject of ongoing study.

### ACKNOWLEDGEMENTS

This work was supported by the Science Foundation of Jiangsu Marine Resources Development Research Institute (JSIMR11B03).

### REFERENCES

1. A. Stein and R.C. Schroden, *Curr. Opin. Solid State Mater. Sci.*, **5**, 553 (2001).
2. P. Jiang, F. Bertone, K.S. Hwang and V.L. Colvin, *Chem. Mater.*, **11**, 2132 (1999).
3. B.T. Holland, C.F. Blanford, T. Do and A. Stein, *Chem. Mater.*, **11**, 795 (1999).
4. D.J. Norris and Y.A. Vlasov, *Adv. Mater.*, **13**, 371 (2001).
5. B. Frank, C. Schäfle, B. Keilhofer, C. Bechinger, J. Boneberg and P. Leiderer, *Adv. Mater.*, **10**, 495 (1998).
6. Y. Cui, M.T. Björk, J.A. Liddle, C. SoInnichen, B. Boussert and A.P. Alivisatos, *Nano Lett.*, **4**, 1093 (2004).
7. J. Xu, E.S. O'Keefe and C.C. Perry, *Mater. Lett.*, **58**, 3419 (2004).
8. O.D. Velev and E.W. Kaler, *Adv. Mater.*, **12**, 531 (2000).
9. S.H. Park, B. Gates, D. Qin and Y. Xia, *Adv. Mater.*, **11**, 462 (1999).
10. M.C. Netti, S. Coyle, J. Baumberg, M.A. Ghanem, P.R. Birkin, P.N. Bartlett and D.M. Whittaker, *Adv. Mater.*, **13**, 1368 (2001).
11. P.M. Tessier, O.D. Velev, A.T. Kalambur, A.M. Lenhoff, J.F. Rabolt and E.W. Kaler, *Adv. Mater.*, **13**, 396 (2001).
12. J.E. Barton and W. Teri, *Nano Lett.*, **4**, 1525 (2004).
13. P. Jiang, *Angew. Chem. Int. Ed.*, **43**, 5625 (2004).
14. X. Wang, C. Lao, E. Graugnard, C.J. Summers and Z. Wang, *Nano Lett.*, **5**, 1784 (2005).
15. H. Míguez, F. Meseguer, C. Lopez, A. Mifsud, J.S. Moya and L. Vázquez, *Langmuir*, **13**, 6009 (1997).
16. F. Zeng, Z. Sun, C. Wang, B. Ren, X. Liu and Z. Tong, *Langmuir*, **18**, 9116 (2002).
17. A. Stain, *Micropor. Mesopor. Mater.*, **44-45**, 227 (2001).
18. C.L. Haynes and R.P. van Duyne, *J. Phys. Chem. B*, **105**, 5599 (2001).
19. R. Torrecillas, A. Blanco, M.E. Brito, C. Lopez, M. Míguez, F. Meseguer and J.S. Moya, *Acta Mater.*, **48**, 4653 (2000).
20. P. Jiang, J. Cizeron, J.F. Bertone and V.L. Colvin, *J. Am. Chem. Soc.*, **121**, 7957 (1999).