

MESO-STRUCTURED POLYMERIC HYDROGELS*

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Abstract Meso-structured (opal and inverse opal) polymeric hydrogels of varied morphology and composition were prepared by using two methods: post-modification of the template-synthesized structured polymers and template-polymerization of functional monomers. A polyacrylic acid based inverse opal hydrogel was chosen to demonstrate its fast pH response by changing color, which is important in designing tunable photonic crystals. Template effects of the hydrogels on controlling structure of the template-synthesized inorganic materials were discussed. The catalytic effect of acid groups in the templates was emphasized for a preferential formation of TiO_2 in the region containing acid groups, which allowed duplicating inorganic colloidal crystals from colloidal crystal hydrogels (or macroporous products from macroporous hydrogels) via one step duplication.

Keywords Template synthesis, Colloidal crystals (opal), Ordered macroporous materials (inverse opal), Ordered hydrogels, Ordered inorganic materials

INTRODUCTION

Monodisperse particles can form a wealth of ordered structures (colloidal crystals, or opal structures) by self-assembly. This process could be directly “viewed” by optical microscopy; it is commonly used as a model mimicking the interaction and condensation of atoms and molecules in condensed matter physics^[1]. Single colloidal crystals and binary colloidal crystals have been created by different methods^[2]. The ordered structures are of great technological interest for example in separation and purification of macromolecules, template synthesis of ordered macroporous materials and photonic crystals. Recently, the creation of ordered macroporous materials using colloidal objects as templates has been receiving great attention because these novel structured materials have many potential applications especially as photonic crystals in optical devices. However, almost all the ordered porous materials are rigid, lacking response to environmental stimuli^[3]. Thus, their applications are greatly restricted. It is interesting to examine the ordered structures’ response to stimuli by the introduction of hydrogels, since the volume of hydrogels experiences a remarkable change with the change in some stimuli such as temperature, pH value, optical illumination and composition change^[4]. Asher *et al.* reported a kind of ordered hydrogels obtained by polymerization of water-soluble monomers to fixate polymer colloidal crystals and demonstrated their potential applications as intelligent chemical sensors^[5]. The polymer particles are not chemically associated with the hydrogels at the interface, and no macropores are present in the hydrogels. The colloidal crystals are formed by gradually decreasing the electrolyte concentration in the liquid phase, such that the ordered structure is very sensitive and easily disturbed by the introduction of monomers and polymerization. Alternatively, Hu *et al.* prepared some opal hydrogels by crosslinking the aggregates of gel nanoparticles with

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interstitial voids left between the particles. This is conducive to fast mass transportation^[6]. Therefore, it is advantageous to prepare ordered porous hydrogels in practical applications. Besides the fast mass transportation, hydrogels are also valued as templates to prepare meso-structured inorganic materials with tunable structures since the hydrogels are infiltrative^[7]. Until now, the reports of meso-structured hydrogels are scarce.

In our group, we have prepared a series of new meso-structured polymeric hydrogels, which are sensitive to a diversity of stimuli such as pH or temperature. The meso-structured hydrogels include opal hydrogels and inverse opal hydrogels. In this paper, we will introduce some advances in the study of meso-structured polymeric hydrogels from the following two aspects: (1) Preparation of the meso-structured polymeric hydrogels; (2) Synthesis of ordered inorganic materials by using hydrogels as templates.

Preparation of Meso-Structured Polymeric Hydrogels

Opal structures and inverse opal structures are reversibly template-duplicated^[3] via an intermediate ordered composite structure after removal of the template as shown in Fig. 1. Composition of the opal structures (or inverse opal structures) could be both inorganic, for example silica, and organic, for example polystyrene. Inorganic silica templates are removed by decomposition with, for example, hydrofluoric acid, while polymer polystyrene templates are removed by either calcination at high temperature or chemical dissolution. Ceramic, metal, polymer opal and inverse opal structures have been extensively created^[18, 3]. Yet, almost all the ordered structures are rigid, lacking responses. As is well known, hydrogels are commonly prepared by both polymerization of monomers and post-modification to polymers. Both opal and inverse opal hydrogels have been prepared by the two methods in our group^[8].

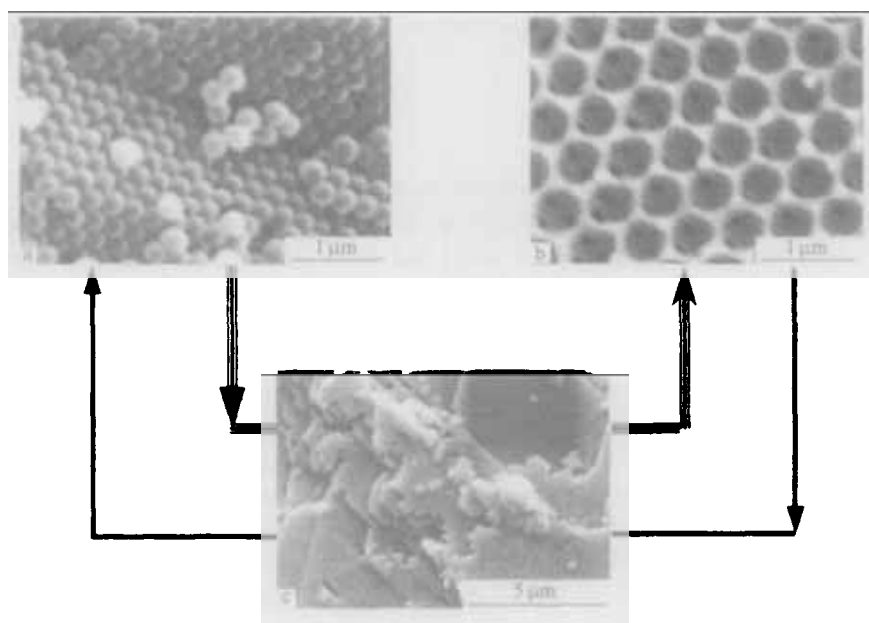


Fig. 1 Schematic preparation of opal and inverse opal structures

Route A along the zebra arrow: replication of the inverse opal structure from the opal structure via the intermediate ordered composite; Route B along the solid arrow: replication of the opal structure from the inverse opal structure via the intermediate ordered composite

a) Opal; b) Inverse opal; c) Composite

Post-modification to the as-prepared structured polymers is effective to achieve hydrogels. A dry colloidal crystal is first created by self-assembly of monodisperse polystyrene latex. After sulfonation with concentrated sulfuric acid forming hydrophilic sulfonic acid and crosslinking sulfone groups, hydrogels are formed. It is confirmed that the sulfonation occurs inwardly from the outermost layer of the sphere. Thus the ordered

core/shell hydrogels are prepared when the interior polystyrene cores are not modified. The thickness of the shell increases with the modification temperature and time. Sulfonation at the coalescence neck between the spheres is responsible for integrating the hydrogels^[9]. A typical scanning electron micrograph of the ordered core/shell hydrogels is shown in Fig. 2(a); monodisperse polystyrene cores are separately dispersed within the gel matrix. At a maximum degree of modification (conversion of the polystyrene cores), only soft hydrogel spheres are found without cores. As shown in Fig. 2(b), the spheres were too soft to retain their original spherical contour when dried at ambient temperature. After cryo-drying, the “original” morphology of the ordered hydrogel structure comprising stacked uniform spheres is clearly seen in Fig. 2(c).

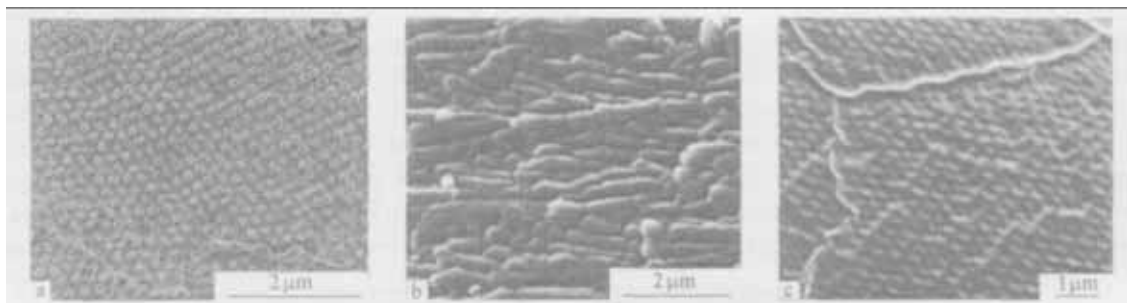


Fig. 2 Scanning electron micrographs of some meso-structured hydrogels prepared by post-modification of polymers

- (a) Sulfonated polystyrene core/shell opal hydrogel after ambient drying
- (b) Sulfonated polystyrene opal hydrogel after ambient drying
- (c) Sulfonated polystyrene opal hydrogel after freeze drying

Figure 3 shows the optical images of the modified samples in water. Sample (a) without modification floated at the water/air interface, indicating that the sample was not wetted by water. Sample (b) after being modified for 1 day was wetted, displaying an opaque appearance. With prolonged modification time up to 5 days, sample (e) became somewhat transparent and brilliantly colored. This means that the refractive index difference between the matrix and the dispersed phase decreased with modification time, revealing that the thickness of the hydrogel layer increased with modification time. At a modification time of 10 days, sample (f) became more transparent and colorful.

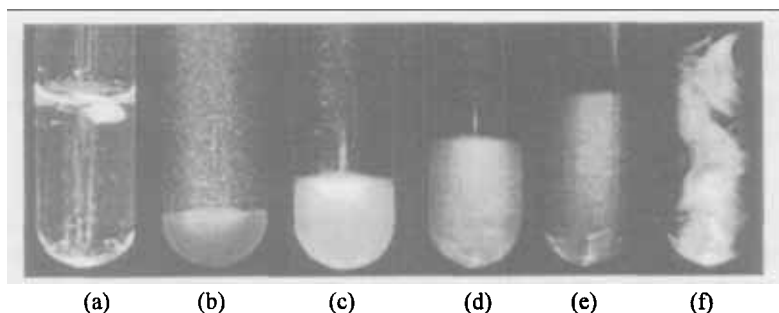


Fig. 3 Optical images of the samples after modification for different days (a) before modification, (b) 1 day, (c) 2 days, (d) 3 days, (e) 5 days, (f) 10 days

FT-IR, DSC results confirmed the composition and the core/shell structure. Elementary analysis and titration results indicated that the average sulfonated polystyrene molar fraction was 20%–50%, which was mainly determined by the modification temperature.

This idea works for the preparation of sulfonated polystyrene inverse opal hydrogels by modifying a template-synthesized polystyrene inverse opal from silica opal^[10]. After the inverse opal polystyrene was

modified with concentrated sulfuric acid, the sulfonic acid and sulfone groups were synchronously achieved, which is responsible for the hydrogels. Either modification temperature or the crosslinking agent content during the preparation of polystyrene inverse opal controlled the modulus and water uptake of the hydrogels. Pores of the sulfonated hydrogel collapsed after ambient drying, meaning that the pore wall was very soft. Freeze-drying was used to fixate the original morphology of the hydrogel. Similar to the polystyrene inverse opal, uniform pores in the inverse opal hydrogel were orderly arranged with three dimensional interconnections via the window channels^[11].

The idea of achieving hydrogels by post-modification of polymers could be extended to some other polymers, for example polyacrylonitrile (PAN). pH responsive inverse opal hydrogel was prepared by alkaline hydrolysis of PAN inverse opal, in which polyacrylic acid groups or polyanions were the active moieties for the response behavior^[12]. The formation of acrylic acid groups and acrylamide groups was verified by FT-IR results. When swollen in water, the hydrogel also displayed a brilliant color effect. Under a polarizing microscope, some colorful textures were observed as shown in Fig. 4(a). This demonstrated that the hydrogel exhibited some long-range order. An SEM image of the freeze-dried inverse opal hydrogel is shown in Fig. 4(b). Uniform pores interconnected via the window channels were three-dimensionally regularly arranged. With increasing pH value, the volume of the macroporous hydrogel increased accordingly. This means that the hydrogel is pH responsive.

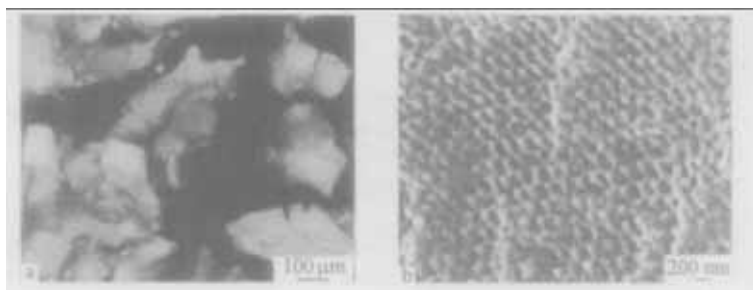


Fig. 4 (a) Polarizing micrograph of the macroporous hydrogel
(b) SEM image of hydrolyzed polyacrylonitrile inverse opal hydrogel after freeze drying

Template polymerization of functional monomers such as acrylamide, acrylic acid or *N*-isopropyl acrylamide is another effective method to prepare meso-structured hydrogels. Opal hydrogels and ordered macroporous (or inverse opal) hydrogels were successfully prepared by using silica opal and macroporous polystyrene as templates, respectively. The hydrogels were environmentally responsive to pH or temperature, when proper monomers such as acrylic acid or *N*-isopropyl acrylamide were chosen.

Template Synthesis of Ordered Inorganic Materials

When rigid templates are used, the corresponding inverse structures are commonly replicated (from pores to spheres or *vice versa*) since the rigid part is not accessible to the precursors. The case is completely different for hydrogels, because the precursors can penetrate into the pore walls or spheres. Thus structural features of the template-prepared materials are flexibly tunable.

The sulfonated polystyrene opal hydrogels containing sulfuric acid groups (Fig. 2a & 2b) were chosen as templates to prepare TiO₂ structures^[13]. Ordered arrays of hollow TiO₂ particles and solid TiO₂ particles were formed respectively (Fig. 5a & 5b). The internal cavity of the spheres in Fig. 5(a) was formed by removal of the polystyrene cores after calcination at high temperature. It is concluded that the sol/gel process was preferentially completed in the hydrogel region rather than in the interstitial voids between the template spheres. During the sol/gel process of TiO₂ in a neutralized sulfonated polystyrene opal hydrogel only continuous inorganic network was formed. It indicated that in this case the sol/gel process occurred in two regions: the hydrogel layer and the interstitial voids. Thus, the preferential sol/gel process originated from the catalytic action of the hydrogel region containing acid groups.

Structured inorganic materials could also be prepared by using inverse opal hydrogels as templates. For example, when the sol/gel process of TiO_2 was undertaken in the inverse opal hydrogel without acid groups, an ordered array of monodisperse TiO_2 spheres was formed (Fig. 5c). This resulted from the sol/gel process in the pores rather than in the pore wall. When the pore wall contained sufficient acid group (for example 30% AMPS), an inverse opal TiO_2 network was achieved due to the preferential sol/gel process in the pore wall (Fig. 5d). Thus, the catalytic effect of acid groups on the sol/gel process was the key factor for determining the sol/gel location in forming the inorganic materials. If the strongly acidic monomer AMPS was replaced by a less acidic monomer such as acrylic acid, the case was the same. WAXD spectra indicated that anatase TiO_2 and rutile TiO_2 were obtained, respectively, when the samples were calcined at low temperature, for example at 450°C , and at high temperature, for example at 900°C . Both crystal forms co-existed when calcination temperature was intermediate for example 600°C . However, the ordered structure was destroyed at high temperature, for example at 900°C , while it was well retained below 600°C .

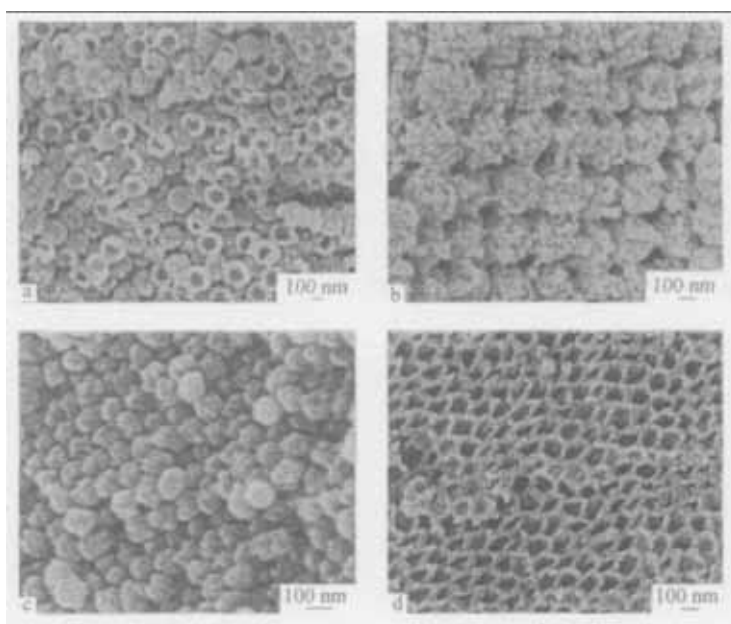


Fig. 5 Scanning electron micrographs of some ordered TiO_2 samples using different templates
 (a) Using sulfonated core/shell opal hydrogel shown in Fig. 2(a), calcined at 450°C
 (b) Using sulfonated opal hydrogels shown in Fig. 2(b), calcined at 450°C
 (c) Using PDMA inverse opal hydrogel as shown in Fig. 3(c), calcined at 450°C
 (d) Using PDMA inverse opal hydrogel containing AMPS, calcined at 450°C

In summary, opal and inverse opal meso-structured hydrogels of varied characteristic dimensions, morphology and composition were prepared by post-modification of polymers and polymerization of functional monomers. An example was given to demonstrate their potential application as templates to adjust the morphology of structured inorganic materials. Many structured and functional materials will be derived according to the idea introduced in this work.

REFERENCES

- 1 (a) Kirkwood, G., *J. Chem. Phys.*, 1939, 7: 919;
 (b) Alder, B.J. and Wainright, T.E., *Phys. Rev.*, 1962, 127: 359;
 (c) Alfrey, T.Jr., Bradford, E.B., Vanderhoff, J.F. and Oster, G., *J. Opt. Soc. Am.*, 1954, 44: 603;

- (d) Fisher, E.W., *Kolloid. Z.*, 1958, 160: 120;
 - (e) Luck, W., Klier, M. and Wesslau, H., *Die Naturwissenschaften*, 1963, 50: 485;
 - (f) Arora, A.K. and Tata, B.V.R., "Ordering and Phase Transitions in Colloidal Systems", VCH, Weinheim, 1996;
 - (g) Xia, Y., Gates, B., Yin, Y. and Lu, Y., *Adv. Mater.*, 2000, 12: 693;
 - (h) Pusey, P.N. and Megen, W., *Nature*, 1986, 320: 340
- 2 (a) Blaaderen, A. Van, Ruel, R. and Wiltzius, P., *Nature*, 1997, 385: 321;
 - (b) Vickreva, O., Kalinina, O. and Kumacheva, E., *Adv. Mater.*, 2000, 12: 110;
 - (c) Cheng, Z., Russel, W.B. and Chaikin, P.M., *Nature*, 1999, 401: 893;
 - (d) Velikov, K.P., Christova, C.G., Dullens, R.P. and Blaaderen, A., *Science*, 2002, 296: 106;
 - (e) Bartlett, P. Ottewill, R.H. and Pusey P.N., *Phys. Rev. Lett.*, 1992, 68: 3801
 - 3 Goltner, C.G., *Angew. Chem. Int. Ed.*, 1999, 38: 3155
 - 4 Jiang, P., Bertone, F. and Colvin, V.L., *Science*, 2001, 291: 453
 - 5 Tanaka, T., *Sci. Am.*, 1981, 244: 124
 - 6 Tanaka, T., *Phys. Rev. Lett.*, 1978, 40: 820
 - 7 Holtz, J.H., Holtz, J.S.W., Munro, C.H. and Asher, S.A., *Anal. Chem.*, 1998, 70: 780
 - 8 Holtz, J.H. and Asher, S.A., *Nature*, 1997, 389: 829
 - 9 Hu, Z., Lu, X., Gao, J. and Wang, C., *Adv. Mater.*, 2000, 12: 1173
 - 10 Caruso, R.A., Antonietti, M., Giesig, M., Hentze, H. and Jia, J., *Chem. Mater.*, 2001, 13: 1114
 - 11 Yang, Z.Z., China Patent Application, 2001, No. 01100392.8, 01100391.x, 01100390.x and 01118317.9
 - 12 Yang, Z.Z., Li, D., Rong, J.H. and Yan, W.D., *Macromol. Mater. Eng.*, in press
 - 13 Rong, J.H. and Yang, Z.Z., *Macromol. Mater. Eng.*, 2002, 287: 11