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Opal gel templated synthesis of oblate titania opal materials†

Lijun Ji, Jianhua Rong and Zhenzhong Yang*

State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China. E-mail: yangzz@iccas.ac.cn

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Ordered arrays of oblate titania bodies were template synthesized using opal gel templates under uniaxial compression at ambient temperature during the favorable titania sol/gel process. The aspect ratio was controllable by the compression degree.

Non-spherical colloids and their ordered arrays may be more attractive in applications such as photonic crystals than their spherical counterparts due to their lower symmetries,[1] which has been proved for example by periodic lattices assembled from polystyrene ellipsoids in a rubber matrix.[2] A variety of chemical methods have been used to directly synthesize cubic, ellipsoidal, and rod-shaped colloids.[3–7] By ion irradiation, both isolated oblate and prolate particles have been obtained.[8] But in most cases, the particles do not self-assemble into well-ordered structures, attributable to insufficient uniformity of the particle size and shape. Recently, monodisperse ellipsoidal colloids have been prepared by stretching self-assembled polymeric colloids in a matrix of a different polymer above the glass transition temperature of the colloids.[9] Titania has been extensively studied because the material refractive index and photocatalytic properties can be conveniently varied by varying the titania crystalline. By stretching ordered macroporous polymeric templates at high temperature above their glass transition temperatures, Colvin *et al*. prepared ellipsoidal inverse opals and used them as templates to prepare ellipsoidal titania spheres arrays.[10] By compression, they also obtained polypyrrole hollow capsules with the regular shape lost, much like deflated soccer ball. They have also studied the important mechanical properties of the inverse opal material by applying an exceedingly high stretching ratio till the polymer skeleton breaks and the window channels collapse.

Here, we report the preparation of ordered arrays of oblate titania bodies using acid group contained hydrogel opal templates by applying uniaxial compression in situ of a titania sol/gel process. The process is carried out at ambient temperature. The titania was found to be favourably formed in the template gel spheres. The aspect ratio of the oblate spheres was conveniently controllable by varying the spacer height and thus compression degree. Since the template gel spheres were quite malleable to begin with, the compression even at ambient temperature is thus easily achievable with a simple setup. The advantage of the present approach lies in its simplicity and easiness to carry out. The formation of the ordered oblate titania array is accomplished in a single step, with no need for temperature variations.

Polystyrene inverse opal was template synthesized using silica opals as reported by Colvin et al.[10] Monodisperse silica spheres with diameter of 300 nm were obtained by alkaline hydrolysis of tetraethyl orthosilicate according to Stöber *et al.*[11] As shown in Scheme 1 of the supplementary information,† a silica opal was obtained by ambient drying of the silica dispersion, followed by sintering at 800 °C for 3 h to promote neck formation between the silica spheres. After the silica template was immersed in styrene, free radical polymerization was performed at 60 °C for 12 h. The silica template was then removed with 40 wt.% aqueous hydrofluoric acid resulting in the formation of polystyrene inverse opal. Both the silica template and the polystyrene inverse opal are colourful, indicating the presence of long-range ordering in the structure. Scanning electron microscopy (SEM) was used to confirm the structure of the polystyrene inverse opal (Fig. 1a).

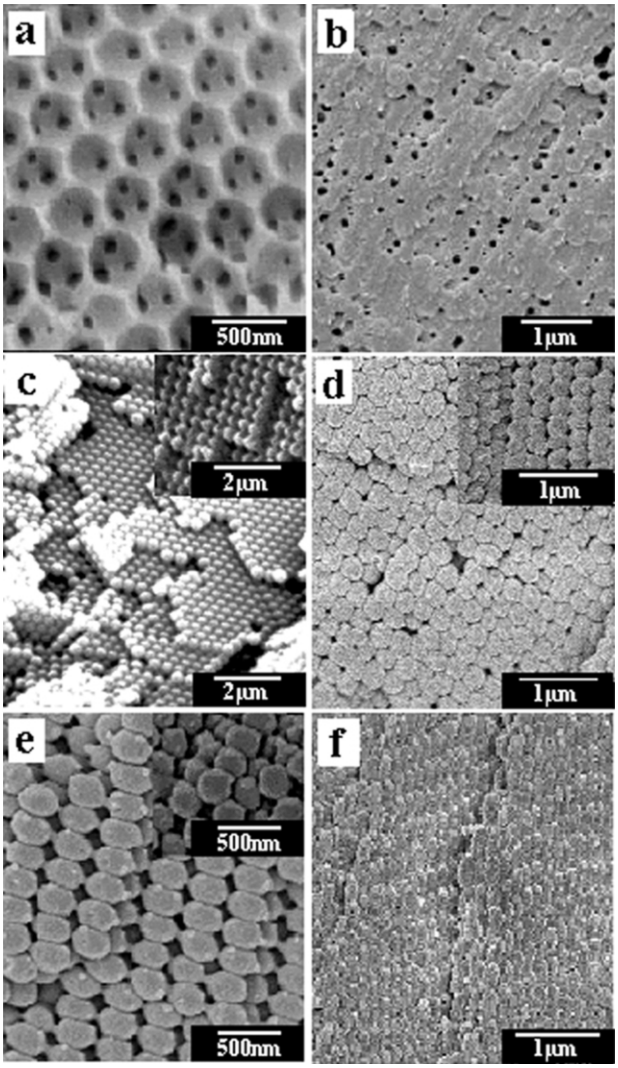

Fig. 1 Scanning electron micrographs of the representative mesostructured materials. (a) the inverse polystyrene opal. (b) The hydrogel opal after freeze-drying. (c) The gel/titania composite opal without compressing the opal gel template during the sol/gel process. (Inset) Image of the sample after calcined at 450 °C for 3 h. (d–f) (Main panel) Oblate titania opal materials after calcined at 450 °C for 3 h, subject to compression degree R of (d) 20%, (e) 35%, and (f) 50%. The images were taken for the fractured surfaces containing the direction of applied compression. (Inset) Image of the same sample, but with the fracture surface perpendicular to the direction of applied compression.

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† Electronic supplementary information (ESI) available: Schemes 1 and 2. See http://www.rsc.org/suppdata/cc/b3/b300825h/

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In this study, we used monomer solutions consisting of dimethylacrylamide, acrylic acid, and methylenebisacrylamide in 1 : 1 : 0.02 weight ratios dissolved in a water/ethanol mixture (4 : 7 wt/wt), with total monomer content 30 wt.%, to demonstrate our method. Ethanol was used to facilitate diffusion of the monomer solution into the inverse opal polystyrene. After the inverse opal was infiltrated by the monomer solution containing 1 wt.% of the initiator AIBN, and followed a free radical polymerisation at 60 °C for 3 h, a solid composite resulted. The initial inverse opal polystyrene template was then removed with chloroform in a soxhlet extractor for 12 h, whereupon the opal gel was formed. Upon swelling in water, the opal gel appeared iridescent. The soft opal hydrogel particles were easily deformable and fused, and were found to quickly lose their spherical shape after ambient drying. Fig. 1b shows the SEM image of a freeze-dried opal structure from the opal hydrogel swollen with ethanol/water mixture. Ethanol can reduce the destructive effect of water crystallization on the opal structure. Upon swelling with water, the dry sample could be reversibly converted into a colourful opal hydrogel. By using different compositions of the monomer solution, hole sizes, and stacking structure of the starting inverse opal templates,[12] opal gels with correspondingly different properties can be produced. The hydrogels strength was influenced by the polymer content, molecular weight, and degree of crosslinking in the gel. When the polymer content was below 20 wt.%, the opal hydrogel is very soft and easily deformable upon contact. But in the range of 20–50 wt.%, the opal hydrogel is tough enough for easy manipulation of its shape.

Water was completely removed from the opal hydrogel by repeatedly rinsing it with a large amount of ethanol. This helps to slow down the titania sol/gel process. Afterwards, the opal gel was put into a large amount of tetrabutyl titanate (TBT) at ambient temperature for 24 h. The TBT-swollen opal gel was then immersed in an excess amount of water/ethanol (1 : 1 wt/wt) mixture for 5 h to let the titania sol/gel process proceed. Fig. 1c shows the opal structure of gel/titania composite spheres formed. After calcination,[13] titania opal with distinctive spherical contours could be found (the inset of Fig. 1c). This is explained by the favourable gelation of titania in the region containing acid groups, which is ensured by a sufficient amount of acid groups for example dimethylacrylamide/acrylic acid 1 : 1 weight ratio in this case.[14–15] Thus the titania is only formed in the opal gel spheres rather than in the interstitial voids between the spheres. Had a neutralized or lower content of acid groups contained opal gel been used, bulk titania would be formed.

As shown in Scheme 2 (see supplementary information†), when we carried out the sol/gel process confined between two substrates, non-spherical titania/gel composite opals and the correspondingly deformed titania opals were found. In this case, the substrates were compressed, which was adjusted by the spacer height. When the substrates were slightly compressed against each other to the extent of producing a 20% reduction in the thickness of the composition opal, the deformation of the template synthesized titania spheres was not substantial (Fig. 1d). When the compression degree is increased to the point of reaching 35% deformation in the opal gel, noticeably deformed titania opals could be obtained (Fig. 1e). Ellipsoidal contour with the oblate axis parallel to the direction of applied compression was clearly noticeable in the structure (Fig. 1e). The inset of Fig. 1e shows the SEM image of the same sample, but viewed from a direction perpendicular to the applied compression. Evidently, circular contours were found, confirming the deformed structure to be the oblate shape. Some indentures and pillars started to appear at the necks where the oblate spheres were broken. When the compression degree reached 50%, the titania bodies begin to coalesce with each other, but the oblate contours were still recognizable (Fig. 1f). The titania opals in structure became strongly bound to each other, and individual titania spheres could not be separated by sonication. The titania crystalline can be varied by altering the calcination temperature.[13] These oblate titania opal materials have higher refractive index contrast than the reported one,[2] study on the optical properties is in progress.

In summary, ordered arrays of oblate titania bodies were prepared by a favourable sol/gel process in the opal gel template. The aspect ratio of the oblate titania bodies is controllable by simply compressing the gel template at ambient temperature during the sol/gel process. It is key that the acid groups can induce the favourable sol/gel process in the opal spheres. By incorporating the idea presented by Colvin et al.,[10] ordered arrays of ellipsoidal titania bodies should be achievable. We further point out that it is possible to incorporate functionalized nanoparticles in the titania bodies if the monomers used in synthesizing the opal gels contain them.

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