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VIP **Surface Patterning**

Patterning the Surface of Colloidal Microspheres and Fabrication of Nonspherical Particles**

*Likui Wang, Linhua Xia, Gang Li, Serge Ravaine, and X. S. Zhao**

Patterning of the surface of microspheres is of great importance because of their potential applications in, for example, directed self-assembly[1] and sensors.[2] Janus spheres (spheres with two chemically different hemispheres) have been fabricated by partial modification of microspheres assembled in monolayers[3,4] or under various protections.[4,5] Microfluidic synthesis[6] and nodule-protected modification[7] have been found to be effective in relatively large-scale production of Janus particles. Recently, more complex surface patterning on microspheres of the bottom layer of a colloidal crystal (CC) has been reported.[8] Most of the previously reported methods are only suitable for the modification of those spheres pre-organized in monolayers or quasi monolayers. Thus, the modification is limited to one of the hemispheres. It is still a great challenge to pattern the whole surface of a colloidal sphere.

On the other hand, uniform nonspherical particles are highly desirable in many emerging applications.[9,10] In most cases, monodisperse nonspherical particles are fabricated by modification of spheres. Dimers and multiplets,[11] ellipsoidal particles,[10] spheres with holes,[12] snowman-like particles,[13] and colloidal clusters[14] have been fabricated from microspheres. Hybrid nonspherical particles[15] have been synthesized by using functionalized silica spheres as seeds in a polymerization process. Complex particles have also been fabricated by using colloidal lithography[16] and interference lithography.[17]

Herein, we report a method for patterning the surface of colloidal microspheres and fabrication of nonspherical particles. The method is illustrated in Figure 1. Monodisperse silica or polystyrene (PS) microspheres are first self-assembled into a CC, which is then annealed to enable connections between adjacent spheres. The CC is then immersed in a solution containing a functionalizing agent. As a result, the exposed areas of the CC are chemically functionalized while the connection areas between the adjacent spheres are protected from functionalization. After washing, the partially functionalized CC is dispersed under ultrasonication to obtain individual particles with surface pattern, in which unmodified round areas are surrounded by modified areas. When these surface-patterned spheres are used for subsequent materials growth using different strategies, two different types of nonspherical particles can be obtained. The shape of the nonspherical particles depends on the regions where the materials grow on the patterned spheres (routes a and b in Figure 1).

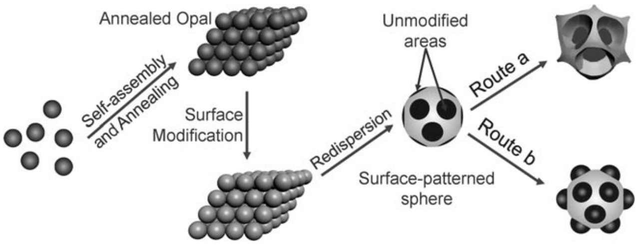

Figure 1. An illustration of patterning the surface of microspheres and two routes to fabricating nonspherical particles using the surface-patterned microspheres: a) seeded polymerization is used to obtain particles with protruding edges or arms (the polymerization mainly occurs on the light areas, i.e., modified regions of the spheres); b) a material is grown on the dark areas, i.e., unmodified areas to obtain spheres with nodules.

Let us first use PS spheres as an example. Self-assembly of PS spheres with a diameter of 984 nm and a polydispersity of 3% was conducted by using the previously reported method[18] to obtain a CC. The CC was annealed at 110°C for 15 minutes, and subsequently immersed into concentrated sulfuric acid to allow sulfonation on the exposed surfaces of the CC (the connection areas of the spheres of the CC were not sulfonated). The sulfonated CC was extensively washed with water and redispersed by ultrasonication to obtain individual PS particles patterned with sulfonic acid groups. The surface-patterned spheres were then used as seeds in a subsequent seeded-polymerization[19] step to obtain nonspherical PS particles with protruding edges (route a in Figure 1) as is seen from the SEM image shown in Figure 2a. The size of these particles was measured to be about 1.23 μm. When unmodified and completely sulfonated PS beads were respectively used as seeds in the seeded-polymerization step, the final particles were all spherical in shape, showing that the

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[*] L. Wang, G. Li, Prof. X. S. Zhao
Department of Chemical and Biomolecular Engineering
National University of Singapore, Singapore 117576 (Singapore)
Fax: (+65) 6779-1936
E-mail: chezxs@nus.edu.sg
Homepage: http://cheed.nus.edu.sg/~chezxs
Prof. L. Xia, Prof. X. S. Zhao
Institute of Multifunctional Materials (IMM)
Laboratory for New Fiber Materials and Modern Textile
Growing Basis for State Key Laboratory
and
College of Chemistry, Chemical Engineering and Environment
Qingdao University (P.R. China)
Prof. S. Ravaine
Centre de Recherche Paul Pascal, CNRS
Université Bordeaux-1, Pessac (France)

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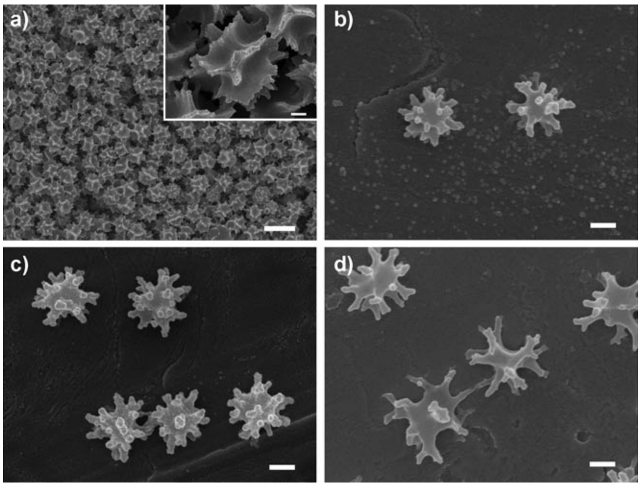

Figure 2. SEM images of nonspherical PS particles: a) nonspherical particles fabricated from 984 nm PS beads using 0.28 mL styrene in the seeded polymerization process; b–d) nonspherical particles fabricated from 400 nm PS beads, using 0.1 mL (b), 0.2 mL (c), and 0.4 mL (d) styrene in the seeded polymerization processes. The scale bar of image (a) is 2 μm. The scale bars of images (b–d) and the inset image (a) are 200 nm. Low-magnification views of samples (b–d) are presented in the Supporting Information.

formation of the protruding edges is indeed a result of surface patterning of the PS microspheres. This, in return, demonstrates that the patterning method is effective to form complex pattern on the surface of PS beads.

The X-ray photoelectron spectroscopy (XPS) results (see Table S1 in the Supporting Information) showed that the sulfur content on the surface of PS spheres was increased greatly upon sulfonation. After seeded polymerization, the sulfur content on the surface was slightly decreased, but still much higher than that of the PS beads before sulfonation. Considering the shape and the surface composition of the spheres, the mechanism of the seeded polymerization process is proposed as follows: After addition of the initiator, free radicals from the initiator react with styrene monomers to form oligomeric free radicals, most of which are captured by the existing PS beads and anchored preferentially on the sulfonated areas.[19,20] The hydrophobic chains of the radicals penetrate into the PS beads, where they react with styrene monomers solubilized in the beads. Thus, the polymerization mainly occurred underneath the sulfonated parts of the PS beads, leading to the formation of the observed protruding edges on the particles.

PS beads of a smaller diameter (400 nm) were also used to fabricate nonspherical particles. It was found that the final particles had protruding arms rather than protruding edges (see Figure 2b–d). This morphology difference might be due to the small size of the beads. With the small beads, the thickness of the edges was so thin that they separated to form independent arms during the polymerization process. The length of the arms can be controlled by adding different amounts of styrene monomer in the seeded-polymerization step. As can be seen from Figure 2b–d, the sizes of the PS particles were 490 nm, 510 nm, and 650 nm when the amounts of monomer added were 0.1 mL, 0.2 mL, and 0.4 mL, respectively.

The surface of silica spheres can be patterned as well. In our work, a CC of silica spheres of 415 nm in diameter was fabricated using the method of Jiang and co-workers[21] and annealed at 750 °C for 5 hours to allow connections between adjacent spheres. Subsequently, the CC was immersed in a solution containing 3-(trimethoxysilyl)propyl methacrylate (MPS) to functionalize the exposed surfaces of the spheres in the CC. Washing and redispersion yielded individual spheres, the surfaces of which were patterned by MPS (the connection areas were not modified by MPS). The surface-patterned silica spheres were then used as seeds in a subsequent particle-growth process.[22] Silica was deposited only on the unmodified areas, that is, the connection areas (route b in Figure 1). Eventually, silica spheres with nodules on their surfaces were obtained as can be seen from the SEM images shown in Figure 3.

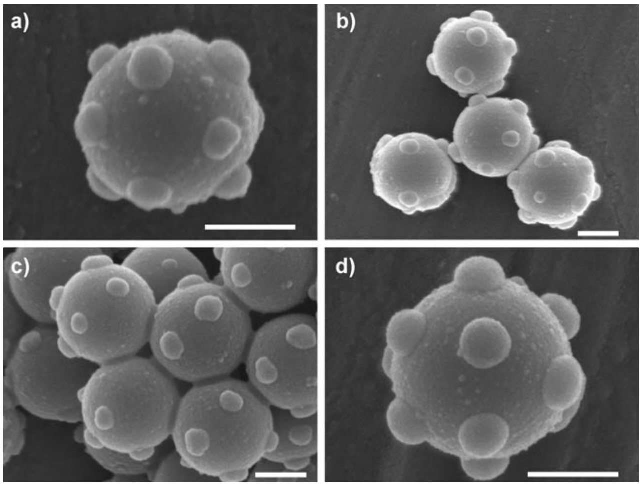

Figure 3. a,b) SEM images of nonspherical silica particles obtained from a silica CC annealed at 750 °C for 5 h. c) SEM image of a surface-modified silica CC after silica growth. d) SEM image of a silica particle obtained from a CC annealed at 750 °C for 8 h. Low-magnification views of the particles are presented in the Supporting Information. All the scale bars are 200 nm.

By using a surface-modified CC instead of surface-modified individual spheres to grow silica, it was observed that the growth of nodules occurred only on the connection areas (see Figure 3c). This observation, again, proves the successful patterning on the surface of the silica spheres. It was also observed that only part of the particles had twelve nodules connected to them. This is due to the imperfect structure of the CC and the size deviation of the spheres, leading to some of the spheres not completely connected after annealing. Through improvement of the monodispersity of the silica spheres and the uniformity of the CC structure, it is believed that a high yield of nonspherical silica particles with a 12-fold symmetry can be achieved. Figure 3d shows the SEM image of a particle obtained from a CC annealed at 750 °C for 8 hours. It can be seen that the average nodule diameter was increased from 95 ± 13 nm to 115 ± 17 nm,

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demonstrating that by adjusting the annealing time, the size of the nodules can be controlled. In addition, the number of unmodified areas on the patterned spheres and the nodules on the nonspherical particles are limited by the CC structure. In CCs with face-centered cubic (fcc) structure, as is used in this experiment, each sphere, except those in the outmost layers, is surrounded by 12 spheres. Thus, the arrangement and number of the unmodified areas and the nodules are limited to an fcc configuration. Through altering the structure of the CCs, the arrangement and number of spheres surrounding one sphere can be changed. For example, if CCs with a body-centered cubic (bcc) structure[23] is employed, the configuration of the 12 unmodified areas can be changed. In a CC with non-close-packed spheres in the same layers,[24] each sphere is contacted by six spheres. Additionally, in a monolayer of close-packed spheres, each sphere is touched by six surrounding spheres and the substrate. Thus, it is expected that particles with six or seven unmodified areas or nodules can be obtained by using these CC structure in the fabrication processes (see Figure S2 in the Supporting Information).

In conclusion, we have demonstrated a chemical approach to patterning the whole surface of colloidal microspheres and subsequent fabrication of nonspherical particles. The mechanism of the formation of the nonspherical particles was discussed. Such surface-patterned spheres and nonspherical particles may find applications in directed self-assembly,[1] fabrication of superhydrophobic surfaces,[25] and sensing devices.[2,26]

Experimental Section

Non-cross-linked PS spheres of 984 nm in diameter were synthesized by an emulsifier-free polymerization method.[19] A CC self-assembled from these spheres was annealed at 110 °C in an oven for 15 min. Then the CC (6 g) was ground into small pieces and put in a conical flask. A concentrated H_2SO_4 solution was poured into the flask (the weight ratio of CC over H_2SO_4 was about 1:20). The flask was then placed in an oil bath at 40 °C. The mixture of the CC and H_2SO_4 was mildly stirred for 2.5 h to allow sulfonation[27] of the CC. Subsequently, the CC was washed with water four times. Upon redispersion of the sulfonated CCs in water by ultrasonication for 8 h in a Transonic 460/H bath (Germany; frequency: 35 kHz), functionalized PS beads (about 4.0 g) were obtained. In the seeded regrowth process, surface-sulfonated PS sphere suspension (15 mL, containing 0.29 g of PS spheres) was mixed with H_2O (50 mL) and styrene monomer (0.28 mL) under stirring for 60 min at 60 °C under the protection of N_2 flow. Then, a solution of potassium persulfate (0.016 g in 10 g H_2O) was added to the above mixture. After polymerization for 24 h, nonspherical PS particles were obtained after centrifuging and washing. The detailed experimental procedures of patterning 400 nm PS spheres and subsequent fabrication of nonspherical particles are given in the Supporting Information.

Silica spheres of 415 nm with a polydispersity of 3 % were synthesized using a modified Stöber method.[22] A vial containing a 0.75 wt % colloid of the silica spheres was placed in a desiccator connected to a vacuum pump with a piece of cleaned silicon wafer placed vertically[21] near the vial wall. The desiccator was heated to 50 °C and kept at a pressure of 115 mm Hg for 24 h to allow the formation of colloidal crystals (CCs) on the silicon substrate. A CC containing 0.05 g of silica spheres (the weight of the spheres were calculated by subtracting the weight of the substrate) was first annealed at 750 °C for different periods of time. Subsequently, the CC film was placed in a solution containing ethanol (40 mL), H_2O (1.5 g), 3-(trimethoxysilyl)propyl methacrylate (MPS; 0.5 mL), and ammonia solution (25 %, 1 mL) for 24 h. Then, the CC film was taken out and washed with ethanol five times to remove residual MPS. The washed film was dried at room temperature and the mass was measured. Finally, the CC film was redispersed in ethanol by ultrasonication. After drying, patterned silica spheres (about 0.04 g) were obtained. The surface-patterned silica spheres (0.02 g) were added to a mixture of ethanol (40 mL), H_2O (5 g), and ammonia solution (25 wt %, 1 mL) under stirring for 30 min. Then, a solution of tetraethyl orthosilicate (TEOS, 40 μL) in ethanol (40 mL) was dropped into the mixture containing silica spheres at a speed of $3.6\,\mathrm{mL\,h^{-1}}$ still under stirring. After completion, the system was stirred for another 2 h. The final solid (nonspherical silica particles) was collected by centrifuging.

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