A novel approach to the construction of 3-D ordered macrostructures with polyhedral particles†

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A novel and facile approach was developed for the fabrication of 3-D ordered macrostructures of polyhedral particles through coating and packing of monodisperse polystyrene-*co*-poly[3-(trimethoxylsilyl)propyl methacrylate] (St-*co*-TMSPM) microspheres with the amphiphilic triblock copolymer F127 and phenolic resol by centrifugation, and subsequent thermosetting treatment of the deposited microspheres. The polyhedral particles possess a regular shape of rhombic dodecahedra (~1 μm) due to the spontaneous deformation of the fcc packed polymeric microspheres coated with resol–F127 composites during the thermosetting process. The amphiphilic triblock copolymer F127 plays a vital role in the formation of the ordered macrostructured polyhedral particles with compatible poly(St-*co*-TMSPM)–resin composites. The simplicity of the fabrication method should open up a new door to the synthesis of nonspherical particles and the construction of ordered macrostructures that possess unique properties for potential application in various fields such as photonic crystals.

Introduction

Two or three-dimensionally (2-D or 3-D) ordered macrostructures made of colloidal particles have recently attracted enormous interest in both fundamental study and practical applications. The variability in the diameter and composition of the building blocks of the ordered structures enables them to exhibit many useful properties, which may find applications in microelectronic and optoelectronic devices,[1–4] biological and chemical sensors,[5] templating synthesis of ordered porous materials,[6] and so on. Self-assembly is currently the most efficacious methodology for the fabrication of ordered structures of colloidal particles, particularly for photonic crystals. A variety of self-assembly techniques have been developed to fabricate ordered macrostructures by the utilization of external forces including electric fields, flow fields, capillary forces, temperature gradient, *etc.*[7–13]

To date, considerable advances have been achieved toward the fabrication of ordered structures of colloidal particles, in which spherical particles have played a predominant role.[14–26] However, spherical particles are not the best option for all studies associated with colloidal particles. For example, self-assembled ordered macrostructures of spherical particles cannot achieve complete band gaps when used as photonic crystals due to the degeneracy of the polarization models induced by spherical symmetry.[27–29] Nonspherical particles provide direct advantages over their spherical counterparts for the construction of ordered structures with high complexities and crystalline lattices of low symmetries, because they can break the symmetry-induced degeneracy.[30,31] Therefore, the fabrication of ordered macrostructures of nonspherical particles is of interest and importance. Until now, although many methods have been used to prepare monodisperse nonspherical particles, it remains a challenge to organize these particles into highly ordered macrostructures. Lu *et al.*[32] developed a "thermal stretching" method to fabricate 3-D ordered structures of spheroidal particles. It is very complicated including the steps, packing polystyrene (PS) microspheres to the colloidal crystals, infiltration with polydimethylsiloxane (PDMS) into the voids, thermal curing at 50 °C and uniaxial stretching at 190 °C for the transformation of microspheres to spheroidal particles. The reactive ion etching (RIE) technique has recently been applied to fabricate ordered arrays of nonspherical particles with various shapes by using the top layer as a mask.[33] However, this method is only suitable for thin colloidal crystal films, and requires a special device with high cost. Yang and coworkers[34] reported a "thermal pressing" approach by pressing the PS spheres colloidal crystals at 110 °C in to 3-D ordered structures made of quasi-rhombic dodecahedra. The formation of such a unique structure is due to the deformation of polystyrene microspheres during the process and its face-centered cubic (fcc) packing. By using a special approach combining disassembly and self-assembly syntheses, Stein and coworkers[35] fabricated simple-cubic 3-D arrays of uniform polyhedral nanoparticles.

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† Electronic supplementary information (ESI) available: FT-IR spectrum and DSC thermogram of the monodispersed poly(St-*co*-TMSPT) microspheres. SEM images of the packed polymer microspheres obtained by the centrifugation of the poly(St-*co*-TMSPT) microspheres dispersed in ethanol solution containing phenolic resols or triblock copolymer F127. SEM images of the packed poly(St-*co*-TMSPM) microspheres after impregnation with resols, followed by thermosetting at 90 °C. SEM image of the ordered macroporous carbons obtained by pyrolysis of the resol-impregnated colloidal crystal. See DOI: 10.1039/b714288a

In this paper, we report a novel thermopolymerization induced pressing approach with the assistance of amphiphilic triblock copolymer F127 to fabricate 3-D ordered macrostructures of polyhedral particles. The process is very simple and involves two main steps: the coating and packing of monodisperse polystyrene-*co*-poly3-(trimethoxylsilyl)propyl methacrylate (St-*co*-TMSPM) microspheres with amphiphilic triblock copolymer F127 and phenolic resol by centrifugation, and subsequent thermosetting treatment of the deposited microspheres. SEM and TEM characterizations show that the polyhedral particles possess a uniform shape of rhombic dodecahedron and arrange into a 3-D ordered macrostructure due to face-centered cubic (*fcc*) packing of the resol-coated microspheres after centrifugation. Our results show that the amphiphilic triblock copolymer F127 plays a vital role in the successful fabrication of the ordered macrostructure of the polyhedral particles. More interestingly, the polyhedral particles can be changed back to uniform microspheres by hot toluene swelling. Since this approach is realized by resol thermosetting-induced "automatic" pressing without external force, it represents a way that allows a convenient and direct fabrication of 3-D ordered macrostructures of polyhedral particles with a high degree of periodicity over large domains.

Experimental

Chemicals

Amphiphilic triblock copolymer poly(ethylene oxide)-*b*-poly-(propyl oxide)-*b*-poly(ethylene oxide) (PEO_{106}-PPO_{70}-PEO_{106}, F127), 3-(trimethoxysilyl)propyl methacrylate (TMSPM) and polyvinylpyrrolidone (PVP, M_w = 30 000) were purchased from Aldrich and used as received. 2,2-Azobisiso-butyronitrile (AIBN) was purchased from Acros and recrystallized from methanol. Styrene (St) and ethanol were purchased from Shanghai Chem. Corp. Polymerization inhibitor was removed from the styrene by filtration through an Al_2O_3 column. Low molecular-weight resol ($M_w < 500$) was synthesized by base-catalyzed polymerization of phenol and formaldehyde according to the previously reported method.[36] Distilled water was used in this study.

Synthesis of monodisperse polymer microspheres

Monodisperse poly(St-*co*-TMSPM) microspheres with a size of 1.0 μm were prepared through a dispersion polymerization approach. For a typical preparation, 10 g of styrene, 8.0 g of polyvinylpyrrolidone, 2.5 g of 3-(trimethoxysilyl)propyl methacrylate and 0.2 g of 2,2-azobisiso-butyronitrile (AIBN) were dissolved in a mixture of ethanol (140 mL) and H_2O (10 mL). The obtained solution was then added into a 250 mL four-neck round bottom flask equipped with a mechanical stirrer, a refluxing condenser, and a nitrogen inlet. After sealing in a nitrogen atmosphere, the reactor was submerged in a water bath and the polymerization was carried out with a stirring speed of 100 rpm at 70 °C for 24 h. The resulting polymer microspheres were repeatedly washed with an ethanol–water mixture (1 : 1 volume ratio) by centrifugation and then dried at 30 °C for further use.

Fabrication of 3-D ordered macrostructures of polyhedral particles

The 3-D ordered macrostructure of polyhedral particles was fabricated through a simple thermopolymerization induced pressing approach. Typically, 0.2 g of poly(St-*co*-TMSPM) microspheres were well dispersed in 20 g of an ethanol solution containing 0.2 g of F127 and 0.4 g of resol by sonication and magnetic stirring at room temperature for 1 h, the solution was subjected to centrifugation at a speed of 3000 rpm for 1 h, and the supernatant liquid was removed. The obtained colloidal crystals were dried at 25 °C for evaporation of the residual ethanol, and thermoset at 90 °C for 24 h to obtain plastic flakes made of nonspherical particles.

Fabrication of 3-D ordered pyrolytic macroporous carbon

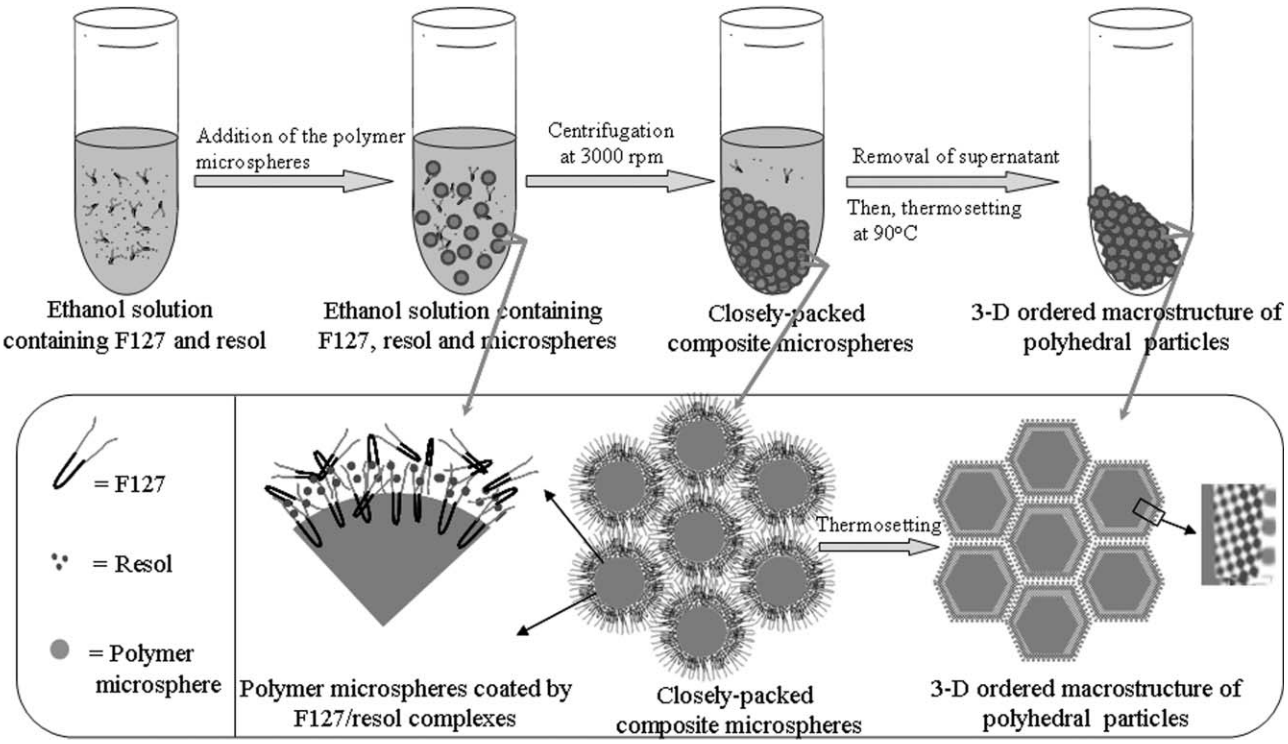
An aqueous dispersion (40 g) of poly(St-*co*-TMSPM) microspheres (5 wt% solid content) was centrifuged at 3000 rpm for 30 min to form a closely-packed colloidal crystal, followed by drying at 30 °C for 48 h for further use. 0.1 g of the obtained colloidal crystals were immersed in 20 g of ethanol solution containing 0.2 g of resol for 12 h. The impregnated colloidal crystals were then thermoset at 90 °C for 24 h and further pyrolyzed at 800 °C for 3 h to produce ordered macroporous carbons. The pyrolysis processes were carried out under a N_2 atmosphere with a heating rate of 2 °C min^{-1}.

Characterization methods

Scanning electronic microscope (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operating at 20 kV. A thin gold film was sprayed on the sample before measurements. Transmission electron microscopy (TEM) images were taken with a JEOL 2011 microscope (Japan) operated at 200 kV. For SEM or TEM measurements, the polymer microsphere samples and polymer microspheres coated with resol–F127 complexes were dispersed in ethanol by shaking and then dried on a cover glass or porous carbon film Cu grid. The dissociated polyhedal particles were prepared by vibrating the packed polyhedral particles using an ultrasonic generator (40 KHz) operating at 120 W and in a water bath maintained at 25 °C. FT-IR spectra were collected on a Nicolet Fourier spectrophotometer using KBr pellets (USA). TG analysis was carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 25 to 900 °C under air with a heating rate of 5 °C min^{-1}. DSC measurements were operated on a differential scanning calorimeter (DSC, Pyris 1 DSC, Perkin Elmer) in the range 30–200 °C with a scanning rate of 10 °C min^{-1}.

Results and discussion

Scheme 1a illustrates the fabrication procedure for the construction of a 3-D ordered polyhedral fcc macrostructure. First, home-made monodisperse poly(St-*co*-TMSPM) microspheres were prepared and homogeneously redispersed in an ethanol solution containing F127 and soluble phenolic resol (low molecular-weight phenolic resin precursors). Then the resulting dispersion was subjected to centrifugation to produce fcc close packing of poly(St-*co*-TMSPM) microspheres. As the



Scheme 1 The synthesis procedure (a) and the formation mechanism (b) of the ordered macrostructure of the polyhedral particles.

amphiphilic triblock copolymer F127 can associate with both the polymer microspheres and phenolic resols simultaneously, through hydrophobic interaction and strong hydrogen bonding, respectively,[36,37] the poly(St-*co*-TMSPM) microspheres were coated with a thick layer of F127–resol composites and packed into fcc lattices during the centrifugation process. Finally, the closely-packed microspheres were dried at 25 °C and further heated at 90 °C for 24 h for the thermopolymerization of the phenolic resols. Solid plastic flake-like products with highly ordered polyhedral macrostructures were obtained.

SEM images shows that the poly(St-*co*-TMSPM) microspheres prepared *via* dispersion polymerization have a very uniform spherical shape with a smooth surface (Fig. 1a). The diameter of the polymer microspheres determined from SEM images is about 1.0 μm with a deviation of less than 4%, indicating a monodisperse size distribution. Fourier transform infrared spectra (FT-IR) of the polymer microspheres show characteristic bands at 1840–1940 cm^{-1} associated with polystyrene and bands at 1730 and 1090 cm^{-1} originating from the C=O and Si–O–C bonds of TMSPM, respectively (Fig. S1, ESI†). The disappearance of the band at 1637 cm^{-1} assigned to the carbon double bond (C=C) of TMSPM, confirmed the copolymerization of the two monomers. The synthesized polymer microspheres exhibit a glass transition temperature (T_g) of 102 °C, lower than that of polystyrene homopolymer (110 °C), as measured with a differential scanning calorimeter (DSC) (Fig. S2, ESI†). The lower T_g is due to the plasticizing effect caused by the pendant alkoxysilyl groups of the TMSPM components in the microspheres.[38]

SEM image shows that the closely-packed microspheres obtained by centrifugation with an F127–resol solution and drying at 25 °C have a typically ordered hexagonal array, corresponding to the (111) plane of a fcc macrostructure (Fig. 1b). The gel-like layers can be clearly observed around the polymer microspheres in the SEM image with high magnification and the interstitial voids in the closely-packed microspheres are fully filled up (Fig. 1c). The diameter of the microspheres is roughly measured from the SEM images to be about 1.2 μm, which is larger than that of the as made polymer microspheres. It reveals that a layer of resol–F127 composite gel with a thickness of ∼100 nm is coated on the polymer microspheres. X-Ray diffraction (XRD) measurements of the polymer microspheres coated with a thick layer of resol–F127 composite show no diffraction in the low angle region (2θ of 0.5–8°) (not shown here), indicating that the assembly of the resol and triblock copolymer F127 template to ordered mesostructure does not occur. TEM images clearly reveal that the polymer microspheres are coated with a layer of gel owing to the adsorbed F127–resol complexes (Fig. 1d), indicating the formation of core–shell composite microspheres.

After thermosetting at 90 °C for 24 h, the gel-like closely-packed microspheres were changed into a solid plastic flake caused by the thermopolymerization of the resols. SEM images show that the surface of the flake has a highly ordered macrostructure with hexagonal arrangement composed of uniform polyhedral particles, it is indexed to the typical (111) plane of the fcc close packing (Fig. 2a). It clearly suggests that the 3-D ordered macrostructure is well retained after the thermosetting and the microspheres are transformed into polyhedral particles. In order to characterize the inner structure of the ordered polyhedral packing, the solid flake was split into small particles for SEM observations. It clearly shows the highly ordered fcc macrostructure in large domains

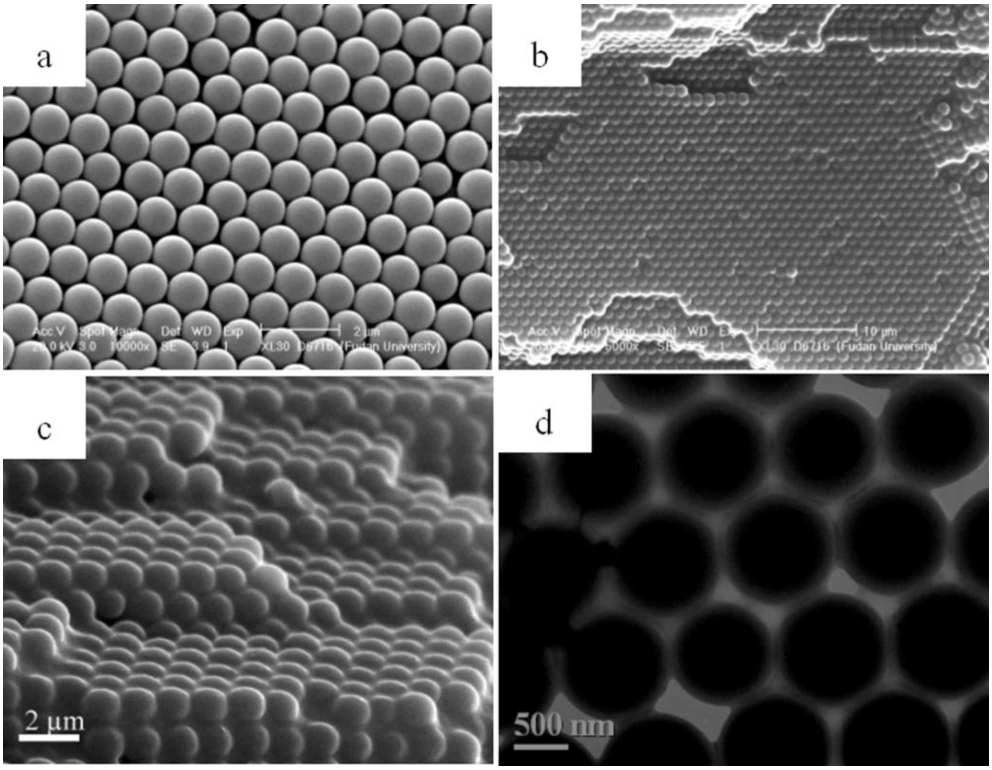


Fig. 1 SEM images of (a) the as-synthesized poly (St-*co*-TMSPM) microspheres; (b, c) the closely-packed poly(St-*co*-TMSPM) microspheres coated with resol–F127 composites after drying at 25 °C; (d) the TEM image of poly(St-*co*-TMSPM) microspheres coated with the resol–F127 composites.

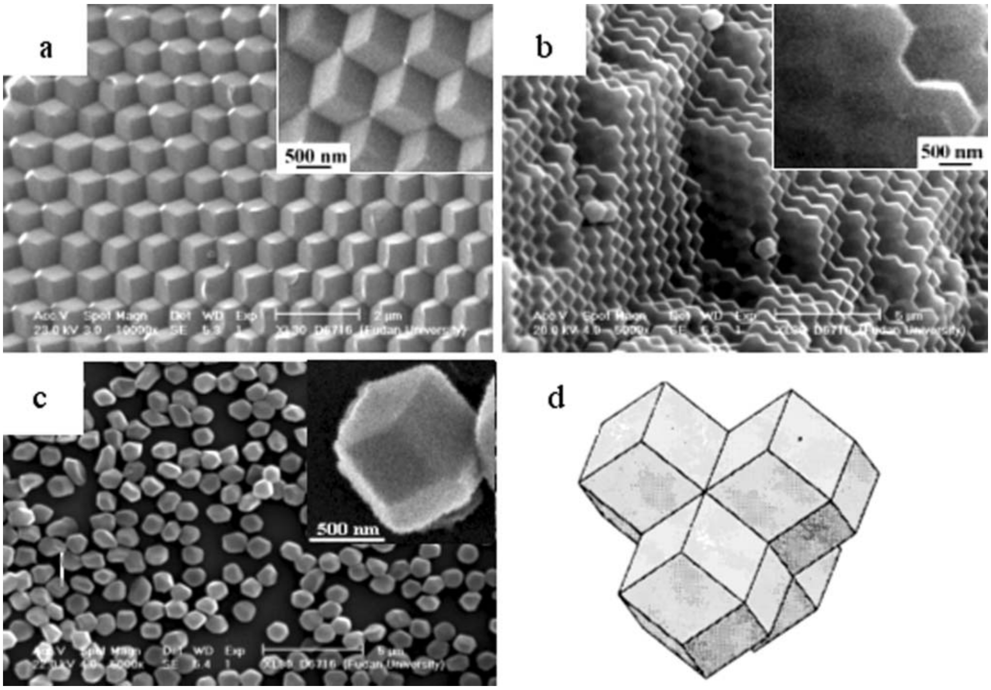


Fig. 2 (a, b) SEM images of the 3-D ordered fcc close-packed macrostructure of the polyhedral particles viewed from different faces. (c) SEM image of the individual polyhedral particles obtained by sonication in de-ionized water for 2 h. (d) The packing model of the rhombic dodecahedra. The insets in (a) and (b) are the respective SEM images at greater magnification.

from the SEM images (Fig. 2b). Remarkably, although the samples for the SEM measurements were prepared by mechanical splitting, the polyhedral particles at the fracture surface with regular polyhedron morphology were retained, suggesting the absence of strong interactions between these particles despite the close-packing. The closely-packed polyhedral particles can be dissociated and dispersed in water under intense ultrasonication. The SEM image shows that the obtained polyhedral particles are well-dispersed and the regular polyhedral morphology is partially damaged by the ultrasonication (Fig. 2c). The length values of the side and the long diagonal lines for a selected plane of the polyhedral particles from the SEM images were measured to be about 536 and 870 nm (the ratio of 1.62), respectively, agreeing well with the geometric ratio of rhombic dodecahedra. These results imply that the obtained 3-D ordered macrostructure consists of rhombic dodecahedral particles as illustrated in Fig. 2d.[34] TEM images of the polyhedral particles show uniform particles and a hexagonal morphology for each particle (Fig. 3a and b), confirming the polyhedral structure. Notably, different from the poly(St-*co*-TMSPM) microspheres coated with F127–resol composite (Fig. 1d), no visible electronic contrast was observed in the TEM image for the polyhedral particles (Fig. 3). This implies that the F127–resol complexes can associate with the poly(St-*co*-TMSPM) microspheres and blend with the copolymer microspheres after thermosetting, and thus a relatively compatible polymer composite is formed. The cross sectional SEM images (Fig. 4a and inset) clearly show typical hexagonal arrays of polyhedral particles with visible borders, further confirming the fcc packing of the rhombic dodecahedral particles. To the best of our knowledge, the ordered macrostructure of rhombic dodecahedral particles has scarcely been reported before. Very interestingly, the polyhedral particles can be restored to uniform microspheres when they were treated in refluxing toluene for 12 h, as shown in the SEM image of the obtained microspheres (Fig. 4b). FT-IR characterization indicates the presence of F127 molecules in the supernatant obtained by centrifugation of the reflux solution, but no poly(St-*co*-TMSPM) was detected. These results indicate that the resol coating on the polymer microspheres was partially cross-linked after curing at 90 °C, and relatively low molecular-weight phenolic resins are compatible with the copolymer. After treatment in toluene, the F127 molecules in the composites were extracted and microphase separation may have occurred, resulting in the rough surface of the composite particles. Meanwhile, the swelling caused by hot toluene makes the polyhedral particles deform back to the minimum surface microspheres.

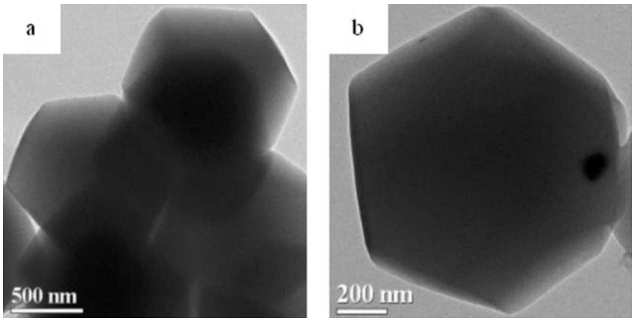


Fig. 3 (a, b) TEM images of the dispersed rhombic dodecahedral particles prepared using the thermopolymerization induced pressing method after being ultrasonically dispersed in water.

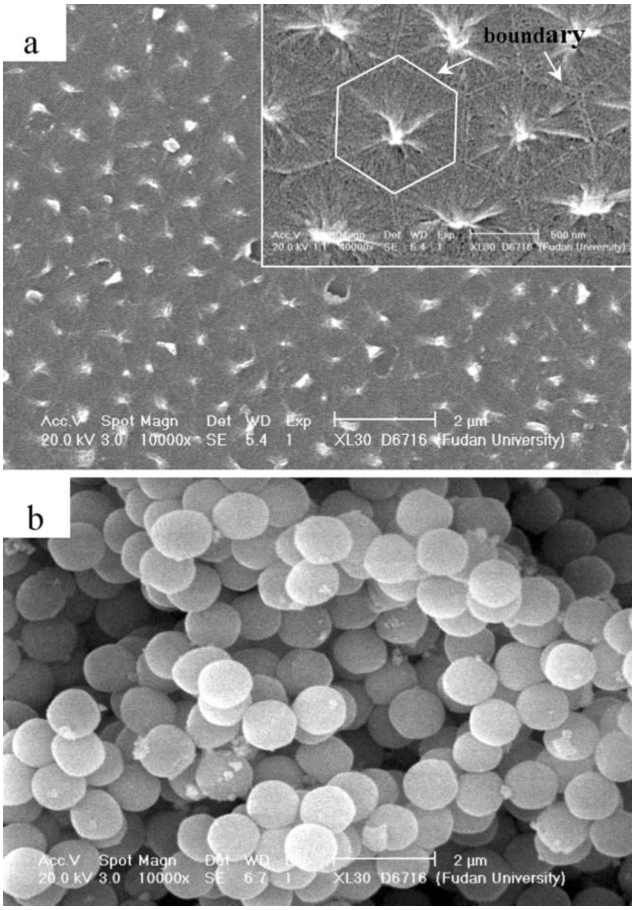


Fig. 4 (a) Cross sectional SEM images of the 3-D ordered macrostructure of polyhedral particles. (b) The SEM image of the individual polymer microspheres obtained by treatment of the polyhedral particles in refluxing toluene for 12 h. The insert is the image at higher magnification.

It is worth noting that, if the poly(St-*co*-TMSPM) microspheres were dispersed in an ethanol solution containing only the phenolic resol or F127, by using the above procedure, 3-D colloidal crystals of spheres were obtained instead of the closely-packed polyhedra particles (Fig. S3, ESI†). In addition, the interstitial voids were not fully filled. These results clearly indicate that amphiphilic F127 plays a vitally important role in the formation of 3-D ordered polyhedral arrays. To further understand the formation of the 3-D ordered polyhedral arrays, an experiment was performed where the pre-formed colloidal crystals of the polymer microspheres were impregnated with the resol in ethanol solution, followed by heating at 90 °C for thermosetting (see Experimental section). The SEM image of the obtained sample shows that, although the interstitial voids can be fully filled by phenolic resins without triblock copolymer F127, the obtained ordered macrostructure is constituted of polymer microspheres and phenolic resin (Fig. S4a, ESI†) rather than the uniform polyhedral particles. Furthermore, as shown in the fractured area (Fig. S4a inset, ESI†), obvious phase separation occurs between the poly(St-*co*-TMSPM) microspheres and their surrounding phenolic resins. Since the sample for the SEM image (Fig. S4a) was obtained by mechanical grinding, some polymer microspheres embedded in the phenolic resin were cracked and cut, and defective or hemispheric microspheres remained in the

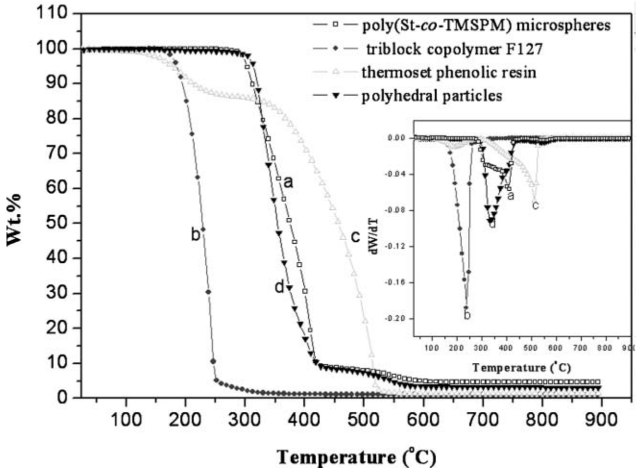


Fig. 5 TGA and DTG (differential thermogravimetric) curves of (a) poly(St-*co*-TMSPM) microspheres; (b) amphiphilic triblock copolymer F127; (c) the thermoset phenolic resin (phenolic formaldehyde, PF); and (d) the polyhedral particles prepared by the thermopolymerization induced pressing approach.

phenolic resin. In the case of the polyhedral particles, no distinct phase separation is observed as shown by the TEM (Fig. 3a, b) and the cross sectional SEM images (Fig. 4a). These results reveal that F127 molecules act not only as a bridge between the polymer microspheres and resols, but also as a compatilizer that promotes the blending of polymer microspheres and resins during the thermosetting.

Thermogravimetric (TG) analyses carried out in air (Fig. 5) show that the poly(St-*co*-TMSPM) microspheres exhibits three weight loss steps, which can be ascribed to partial decomposition of the poly(TMSPM) segments (∼15 wt% at 270–320 °C), the polystyrene segments (∼77 wt% at 320–500 °C) and the organic silane components (∼4 wt% at 500–900 °C) respectively (Fig. 5a). The minor residue (4.5 wt%) is due to the formation of silica after calcination in air. Triblock copolymer F127 shows only one sharp weight loss ascribed to the decomposition at 300 °C (Fig. 5b). The phenolic resin (Fig. 5c) displays two weight loss steps assigned to the dehydration and condensation of numerous hydroxyl groups (∼10 wt% from 100 to 200 °C), and the decomposition of the thermoset phenolic resins (∼90 wt% from 200 to 600 °C), respectively. In contrast, the ordered polyhedral particles prepared from our thermopolymerization induced pressing approach display two obvious weight loss steps (Fig. 5d). One large weight loss of ∼91.8 wt% occurs between 250 and 420 °C, due to the co-decomposition of the polymer microspheres and phenolic resins as well as the triblock copolymer F127. While another small weight loss of ∼5.0 wt% occurs at 420 to 570 °C, probably owing to the decomposition of the remaining organic silane components of the poly(TMSPM) segments. The continuous decomposition behavior with large weight loss implies a compatibility between the phenolic resin and the poly(St-*co*-TMSPM) microspheres, further suggesting the formation of relatively homogeneous polymer composites.

In fact, due to the compatibilization effect of triblock copolymer F127, the ordered macrostructure of the polyhedral particles shows poor resistance to pyrolysis at high temperature under N_2. For example, after pyrolysis at 300 °C, the 3-D ordered macrostructure was only partially retained (Fig. 6a). Pyrolysis at 500 °C could completely destroy the polyhedral macrostructure (Fig. 6b). While in the case of colloidal microsphere crystals impregnated with phenolic resin (Fig. S4a, ESI†), after pyrolysis at a high temperature of 800 °C, the ordered macrostructure was well retained and 3-D ordered macroporous carbon was obtained, because the polymer microspheres was decomposed and the phenolic resin was carbonized *in situ* into a rigid carbon framework (Fig. S4b, ESI†). It reveals that the impregnated sample possesses two discrete phases, *i.e.* the isolated poly(St-*co*-TMSPM) microspheres and the continuous phenolic resin framework, which allows the removal of the polymer microspheres and carbonization of the phenolic resin to proceed independently.

Our results show that, by using the thermopolymerization induced pressing approach through the same fabrication procedure, the ordered polyhedral macrostructure with PS–resin–F127 composites can be obtained by using PS microspheres instead of the poly(St-*co*-TMSPM) microspheres, suggesting a general route for the fabrication of the ordered polyhedral macrostructures.

On the basis of the above results, we speculate that the formation of the ordered polyhedral macrostructures involves a coating and thermopolymerization induced pressing process, as illustrated in Scheme 1b. In the homogeneous dispersion, the PEO blocks of F127 molecules can interact with the resol

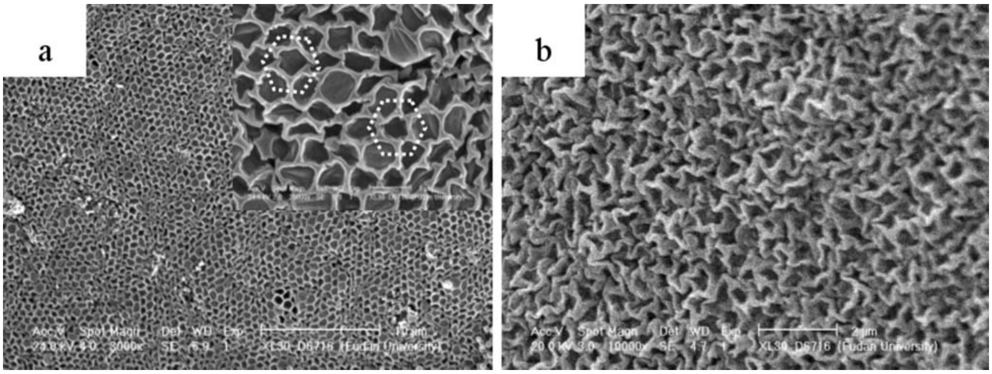


Fig. 6 SEM images of the 3-D ordered macrostructure of polyhedral particles after pyrolysis under N_2 (a) at 300 °C for 3 h and (b) at 500 °C for 3 h.

precursors *via* hydrogen bonding, a sol of F127–resol composites can be formed.[36] Meanwhile, the PPO segments of the amphiphilic triblock copolymer F127 molecules can associate with the poly(St-*co*-TMSPM) microspheres through van der Waal interactions. Therefore, the polymer microspheres are coated with a layer of F127–resol composite with the assistance of amphiphilic F127, and the core–shell microspheres are formed. The excess F127 molecules are probably adsorbed on to the surface of the microspheres and act as stabilizers to make the core–shell microspheres readily and homogeneously disperse in the uniform dispersion. By centrifugation, the microspheres are packed into an ordered fcc lattice with interstitial voids partially filled by F127–resol composites. Due to the coating process occurring at the dispersion stage, the content of F127–resol composites coated on the microspheres could not meet the requirement for the co-assembly of F127 and resols to form an ordered mesostructure through the evaporation-induced self-assembly (EISA) method,[35] therefore the ordered mesostructure could not be formed around the polymer microspheres. During the heating process at 90 °C, the thermopolymerization of the resol shells occurs, which results in uniform centripetal forces caused by the shrinkage. Meanwhile, the poly(St-*co*-TMSPM) cores would be swelled and soften by the heating because of the low glass transition temperature (T_g). The cooperation driven from the centripetal and swelling forces can press the soft microspheres and make them gradually deform into polyhedra. Due to such a thermopolymerization induced pressing process, the interpenetration network is formed between the outer phenolic resin and the inner polymer microspheres with amphiphilic F127 as an intermediate, and a compatible polymer composite is formed. On the other hand, the F127 molecules on the interface of the core–shell spheres also act as an isolator to prevent the inter-polymerization of resols on the neighboring microspheres, resulting in the formation of borderlines between the polyhedral particles. Consequently, the closely-packed polyhedral particles can be separated in to individual polyhedra due to the absence of strong interaction between these particles. By contrast, when a resol or resol–F127 ethanol solution is impregnated into the voids of the pre-formed fcc polymer microspheres, the core–shell microspheres could not be formed, because the microspheres tightly contact each other with considerable contact surface area. In a such case, the forces caused by the thermopolymerization fall in different directions. Therefore, the uniform polyhedral particles could not be formed.

In conclusion, we demonstrate a novel and facile approach to the fabrication of a 3-D ordered macrostructure of polyhedral particles. The polyhedral particles possess a regular shape of rhombic dodecahedra (∼1 μm) due to the spontaneous deformation of the fcc packed polymeric microspheres coated with resol–F127 composites during thermosetting process. The amphiphilic triblock copolymer F127 plays a vital role in the formation of the ordered macrostructured polyhedral particles with compatible poly(St-*co*-TMSPM)–resin composites. Moreover, the polyhedral particles can be changed back to uniform microspheres by hot toluene swelling. The simplicity of the fabrication method should open up a new door to the synthesis of nonspherical particles and the construction of ordered macrostructures that possess unique properties for potential application in various fields such as photonic crystals.

Acknowledgements

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