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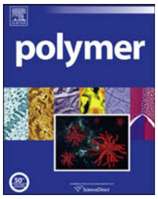

Feature Article

Composite colloids and patterning

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ABSTRACT

Over the past decade, the synthesis and application of various composite colloids and their ordered patterning have received considerable attention. We summarize the recent progress in morphology and composition control of various spherical, non-spherical composite colloids and their patterning. Hollow colloids, ellipsoidal colloids and their patterning are highlighted for their unique properties as well as broad applications.

1. Introduction

A colloid should possess at least one directional length scale within 10^0–10^3 nm [1]. The morphology of colloids can be varied in a broad scope including cube, rod, and sphere [2]. Their properties and potential applications are essentially related with the morphology, characteristic size, composition, surface property and assembled structure. It is important to develop new methods to control such characteristic features. Herein, some recent progress in controlling structure and composition of colloids and their patterning is summarized.

2. Composite hollow colloids

Hollow colloids have spurred great interest due to their potential applications in controlled release, artificial cells, light weight fillers, catalysis and confined reaction vessels [3–9]. Synthesis of hollow colloids can be roughly classified into template-free and template methods. Zeng et al. have proposed a template free "one pot" approach for inorganic hollow colloids *via* Ostwald ripening growth under hydrothermal conditions by aggregation of the corresponding nanocrystallites giving a spherical contour [10–16]. Although the template free method is obviously advantageous in avoiding the tedious step of removing templates, it remains infancy and cannot be easily extended to a broad case. Until now, template assisted synthesis is still most widely used to prepare hollow colloids owing to its simplicity and generality.

Emulsion droplets [17,18], gas bubbles [19], quasi-reverse emulsions [20] and micelles [21–27] can be used as soft templates to synthesize hollow colloids. However, they are rather weak and easily deformed and broken during the synthesis, and the template efficiency is not high.

Hard cores such as silica colloids or polystyrene latexes are commonly used as hard templates for a variety of materials (polymeric, inorganic, biological and metallic) being coated forming the core–shell structures, which is usually assisted by layer-by-layer (LBL) deposition [3–8,28–37]. The corresponding hollow colloids can be derived after the cores are removed [28–37]. In our previous work, LBL process is used to coat the surface of a polystyrene particle with polyelectrolytes rendering the shell with gel performance. Afterwards, modified carbon nanotubes (CNTs) with carboxyl groups are absorbed onto the core–shell gel particle by specific interaction forming a CNT non-woven fabric composite shell. After the core template is dissolved, CNT composite non-woven fabric cages are achieved. The shell thickness and the mesh size can be controlled [38]. The surface becomes coarse due to the protrusion of CNTs loops and their end tails. By a favorable growth of inorganic materials for example silica onto the CNTs surface *via* a sol–gel process (Fig. 1a), the inorganic/organic composite cage is significantly strengthened. This method is general. Replacing the coating material CNTs with smaller colloids, a straw raspberry alike composite colloid is simply achieved by a heterocoagulation. For example, potentially self-curable epoxy resin smaller colloids are absorbed onto the

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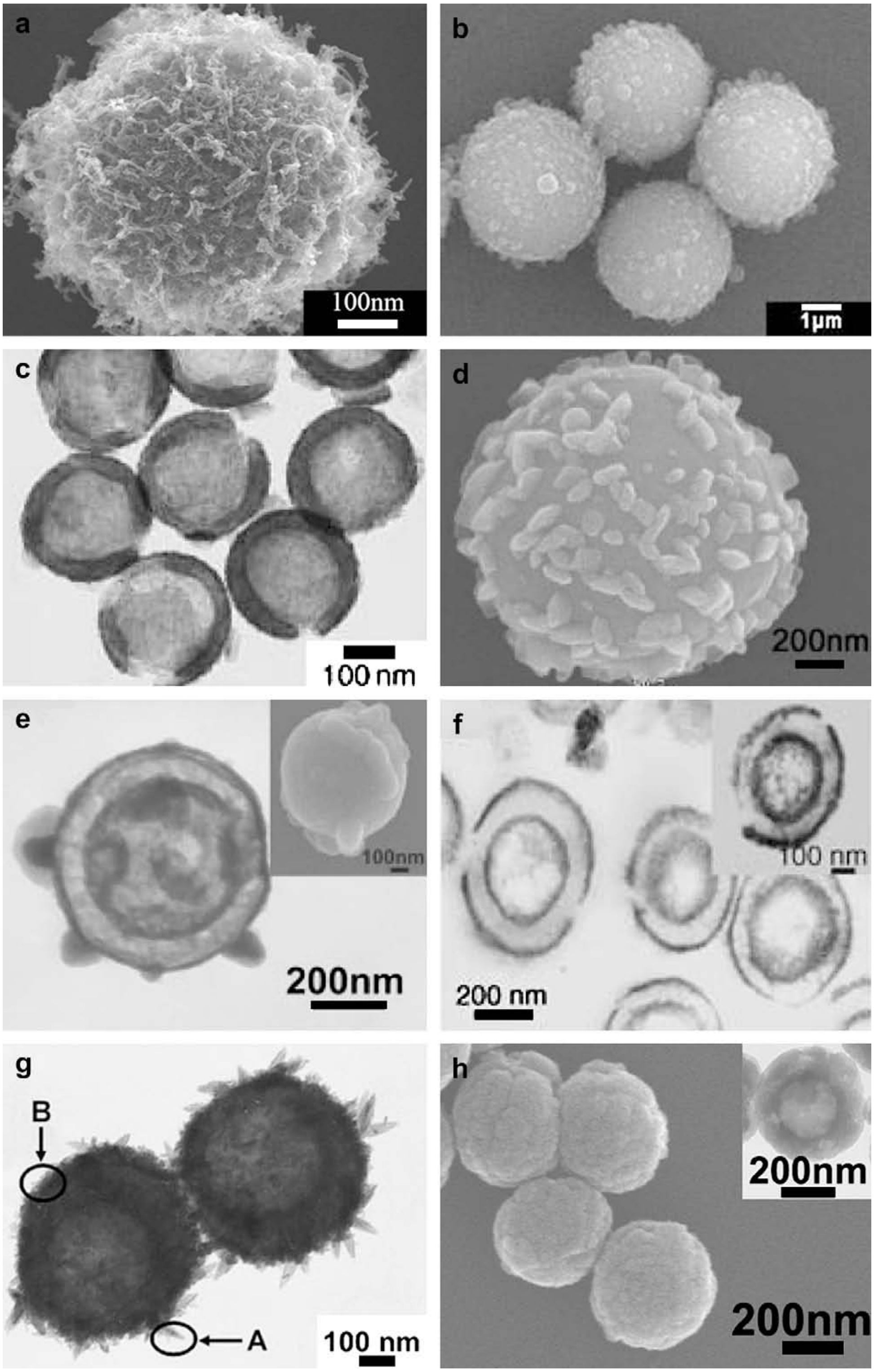

Fig. 1. Morphologies of the representative colloids: (a) silica strengthened CNTs/polyelectrolyte composite colloids; (b) PS/epoxy resin composite colloids; (c) titania hollow colloids; (d) surface-pillared titania composite colloids; (e) silica/titania composite hollow colloids; (f) cross-sectional TEM image of double-shelled titania hollow colloids; (g) titania mixture (rutile (A)/anatase (B))/gel composite hollow colloids; (h) porous carbon hollow colloids.

larger PS particle, PS/epoxy resin composite colloids are prepared (Fig. 1b) [39]. Subsequent coalescence of the epoxy resin colloids and curing leads to a typical core–shell structure and the corresponding hollow colloids. It should be noticed when the epoxy resin colloids of some crosslinking degree are used, the shell roughness can be controlled. Based on a hard core, the other approaches such as surface-initiated polymerization of polymeric brushes [40], redox replacement [41], and Kirkendall diffusion [42–44] can be used to modify the core surface rendering the shell with proper compositions.

Besides shell composition and surface structure, synchronous control of both cavity size and shell thickness is another key issue. Recently, we have proposed a core–shell gel colloid template approach towards composite hollow colloids. The method combines high stability of the hard core and convenient synthesis of desired materials within the gel shell. Composition and physicochemical environment of a polymeric gel can be easily tuned, which is conducive to a favorable growth of desired materials thereby. This means that the shell composition of the derived hollow colloids can be diversified (including metal, inorganic, polymeric, biological and polymeric material) [45,46]. In our previous work, a monodisperse PS colloid is treated with concentrated sulfuric acid to allow an inward sulfonation of PS colloid, thus sulfonic acid and sulfone groups are simultaneously derived in the gel shell. The sulfonic acid is responsible for a favorable growth of desired materials, and the sulfone group bridging aromatic rings makes the sulfonated polystyrene more robust. The gel-shell thickness can be controlled over the whole particle size by altering the sulfonation temperature and time, whilst the PS core size decreases to eventual zero. Many materials (polymer: polyaniline; inorganic: titania (Fig. 1c), silica; etc.) can be induced to favorably grow within the sulfonated PS (SPS) gel shell by specific interactions forming a composite shell, while the PS core is not infiltrated by the materials. After the PS core is removed, the corresponding hollow colloids are synthesized. The shell thickness and cavity size of the hollow spheres are thus controlled using such templates with different gel shell thickness and PS core size. Moreover, SPS as a kind of charged soft matter can be modulated to experience an instable fluctuation upon external electric field, which is fixated by a fast sol–gel process forming porous titania shell. SPS as a kind of strong acid can induce a favorable growth of polyaniline with *in situ* doped thereby to tune the conductivity. After incorporation of silica within the polyaniline shell, the composite hollow colloids become more robust with the conductivity less influenced. Along the similar synthesis route, titania/polyaniline and magnetic/polyaniline composite hollow colloids are synthesized thereby.

It should be mentioned that the synthesis remains essentially based on a core–shell approach, and the arisen osmotic pressure associated with molecular diffusion during removal of the core templates usually results in fracturing the shell. How to preserve the shell intact is challenging. To avoid using core templates, many hollow spheres have been recently used as templates to synthesize composite hollow colloids. As mentioned above, the shell of most hollow templates, such us polyelectrolyte capsules [47–50], viral capsids [51–53], vesicles [54–57], are soft and can hardly hold the cavity. The template synthesized products usually become deformed even collapsed during complexation with other materials.

We realize that some commercial polymer hollow latexes with specific composition and structural characteristics can be used as robust hollow templates [58–60]. A representative hollow colloid is composed of a PS shell skeleton with nanosized transverse polymeric gel channels connecting the interior polymeric gel surface. Some precursors can diffuse inwardly through the channels and favorably grow within the interior gel forming a composite hollow colloid. The conventional removal of core templates is avoided. When the exterior polymer shell is removed from outside, the interior composite shell is less influenced by the osmotic pressure thus giving an intact shell. Additional precursors can further grow within the channels, and the composite hollow colloids with nanosized pillars protruding from the surface are prepared (Fig. 1d). If another material is further deposited onto the composite hollow colloid, double-layered hollow colloids are prepared (Fig. 1e) [58]. Such hollow colloids have enhanced performances in strength, photo catalysis [61]. For example, sphere-in-sphere structure allows multiple reflections of electromagnetic waves (such as ultraviolet and visible light) within their interior cavities [61], and some enhancement in performances is resulted. However, many steps are involved during the current synthesis routes for double-layered hollow colloid. How to synthesize such double-layered hollow colloids in one step remains a question. Similar to the sulfonation of a PS colloid, shell of the PS hollow colloid can be transformed into SPS/PS/SPS sandwiched gel, and composite/PS/composite sandwiched hollow colloids are thus derived by a favorable growth of desired materials within the gel. After removal of the polymer template, the corresponding double-layered hollow colloids for example of titania are obtained (Fig. 1f) [59]. The shell thickness and the gap between the shells can be tuned by controlling the sulfonation degree, and a single-layered hollow colloid is eventually achieved. This approach can be extended from inorganic materials to polymers for example phenolic resin. After the double layer phenolic resin hollow colloids are carbonized at high temperature, they are converted into carbon hollow colloids. During the carbonization, small molecules are released resulting mesoporous shell [60]. It is interesting to incorporate functional materials within either mesopores or inside the cavity of the carbon colloids. The PS hollow colloid as a container can be loaded with some reagents in the cavity by diffusion through the transverse channels. Under proper conditions, the reagents diffuse outwardly accompanied by solidifying, which is equivalent to polymerization extrusion of nanofibers through the channels. Some hierarchically structured composite hollow colloids are formed. Especially, nanosized needles and their wrapped network are formed onto the exterior surface. For example, a composite hollow colloid with hairy polyaniline onto the exterior surface is formed by diffusion-limited polymerization of aniline through the channels in the presence of oxidative catalyst $FeCl_3$ in the exterior aqueous medium.

Besides loading materials inside the cavity, the PS shell skeleton can be swelled with proper monomers, and a series of polymer hollow colloids with interpenetration network (IPN) shell can be generated by swelling polymerization [62–66]. Many monomers such as acrylate, acrylonitrile, vinylbenzyl chloride and divinylbenzene can be used to tune the composition of the IPN shell. For example, when the swollen monomer divinylbenzene is crosslinked within the PS shell, the IPN hollow colloid becomes more robust and insoluble in solvents. After being completely sulfonated, the derived SPS gel hollow colloid can well preserve their spherical shape. This provides a good template forming some composite hollow colloids with tunable shell composition for example magnetic, tin-doped indium oxide (ITO), crystalline titania (Fig. 1g), nanoparticles catalysts of Pd, Rh, Pt and light emission material of Eu_2O_3 [63,65–68]. Especially, for titania hollow colloids, their crystallinity can be tuned from amorphous, anatase to rutile by simply altering pH values at normal pressure and low temperature. The composite hollow colloids are expected to have higher refractive index and higher dielectric constant. In contrast, when the linear PS hollow colloid is completely sulfonated, the colloid becomes rather weak even disintegrated in water. The sulfonic acid acts as an acidic catalyst, and automatically catalyze the crosslinked SPS into carbon at high temperature, giving a mesoporous hollow carbon colloid (Fig. 1h) [64]. Similarly, mesoporous carbon/silica, carbon/metal and carbon/ceramic composite hollow colloid are derived, which are promising in fuel cell and hydrogen storage. Besides modification of a polymer shell in order to derive hydrogel, swelling polymerization of water soluble monomers can also be used to directly give hydrogel. Location of the polymerized hydrogel can be controlled by changing the interaction between monomers and PS shell *via* adding proper swelling agent [69]. This will be conducive to absorption or growth of other materials in desired location of hydrogel hollow colloids.

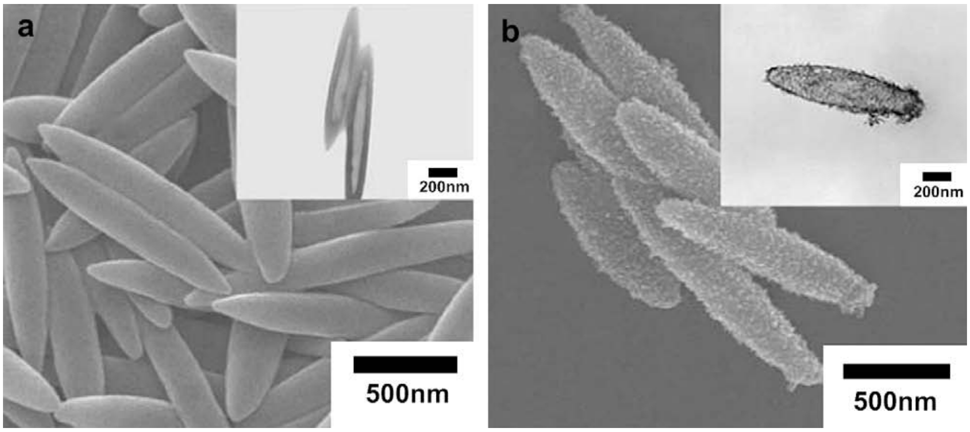

Fig. 2. Morphology of the representative ellipsoids: (a) the PS hollow ellipsoids prepared by stretching the corresponding spherical hollow colloids at a given ratio 150% and 200 °C; (b) the Fe_2O_3 hollow ellipsoids after the composite ellipsoids are calcined at 450 °C in air.

3. Unsymmetrical composite colloids

Recently, unsymmetrical colloids have gained increasing interests due to their unique properties and performances. Asymmetry herein refers to be anisotropic either in morphology or composition distribution.

Ellipsoid is a kind of typical unsymmetrical colloid, which shows an anisotropic diffusion behavior directly visualized under optical microscopy. This will help to better understand transportation in membranes of anisotropic macromolecules [70]. Ellipsoids display more complex aspect-ratio-dependent phase behavior such as from translational ordering to jamming, which will help to design more complex materials [71,72]. Polymer ellipsoids in micron size have been synthesized by different methods such as laser irradiation of azopolymeric colloids [73], and microfluidic laminar flow reactors [74]. However, it is still a challenge to synthesize submicron ellipsoids. Colvin et al. have reported template synthesis of ordered materials composed of submicron ellipsoids including solid and hollow ones [75]. It is required to break the ordered structures for obtaining the corresponding individual ones. A general method has been proposed to synthesize monodisperse polymer ellipsoids by mechanically stretching spherical colloids embedded in a proper polymeric matrix [76,77]. Their aspect ratio can be precisely controlled by altering the stretching extent. It is speculated that composite hollow ellipsoids will be derived by layer-by-layer assisted deposition onto the polymer ellipsoidal templates [9]. We employ the similar way [76,77] to mechanically stretch PS hollow colloids instead of solid ones to prepare PS hollow ellipsoids with tunable aspect ratio (Fig. 2a) [78]. Similar to using PS hollow colloidal templates, the ellipsoids are further modified to introduce functional groups, which will be conducive to the formation of composite shells. The composition can be varied ranging from polymers, inorganic materials, metal, to their compounds. Selectively growing composites at specific sites will bring in complex structures. This method is general and makes it facile to synthesize hollow ellipsoids with varied compositions and structures.

Colloids with unsymmetrical distribution of components, the so-called Janus colloids, usually display distinguished performances. Several methods have been developed to synthesize such Janus colloids [79–85]. Methodologies based on a two-dimensional plane, such as mask-protecting assisted site-selective modification [80] and template-directed self-assembly [81] have been proposed. However, their efficiency is too low for large-scale production. Microfluidic methods have also been developed to prepare Janus particles with unconventional morphologies [82]. However, a special design of the fluidic channels is required and it is difficult to synthesize nanosized colloids with a size of 10^1–10^2 nm. Recently, Pickering emulsion assisted synthesis of Janus colloids, in which the two parts of the particles are separated by the oil/water interface and protected in the two phases allowing further modification, has gained increasing interest [83]. In order to avoid the possible influence of particles rotating at interfaces, a wax solidification method has been reported where the fumed silica particles are embedded in a frozen wax/water Pickering emulsion interface, where rotation is prohibited. The unprotected part of the silica particles is then selectively modified with a silicane coupling agent to form Janus colloids [84]. Janus colloids can be prepared at a liquid/liquid Pickering emulsion interface by a fast carbodiimide coupling reaction onto one part of the microgel particles at one liquid phase [85]. The composition of such Janus colloids is rather restricted by this method. How the rotation of those particles at the Pickering interface that affects the perfection of Janus colloids is unclear.

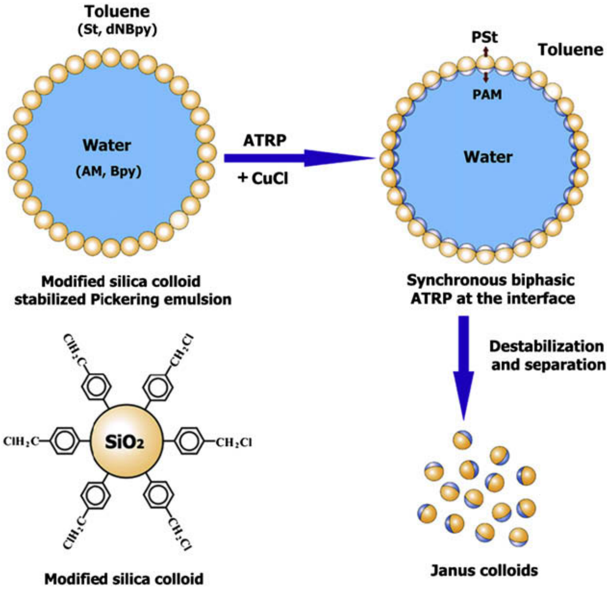

Fig. 3. Synthesis of Janus composite colloids by biphasic grafting at a Pickering emulsion interface.

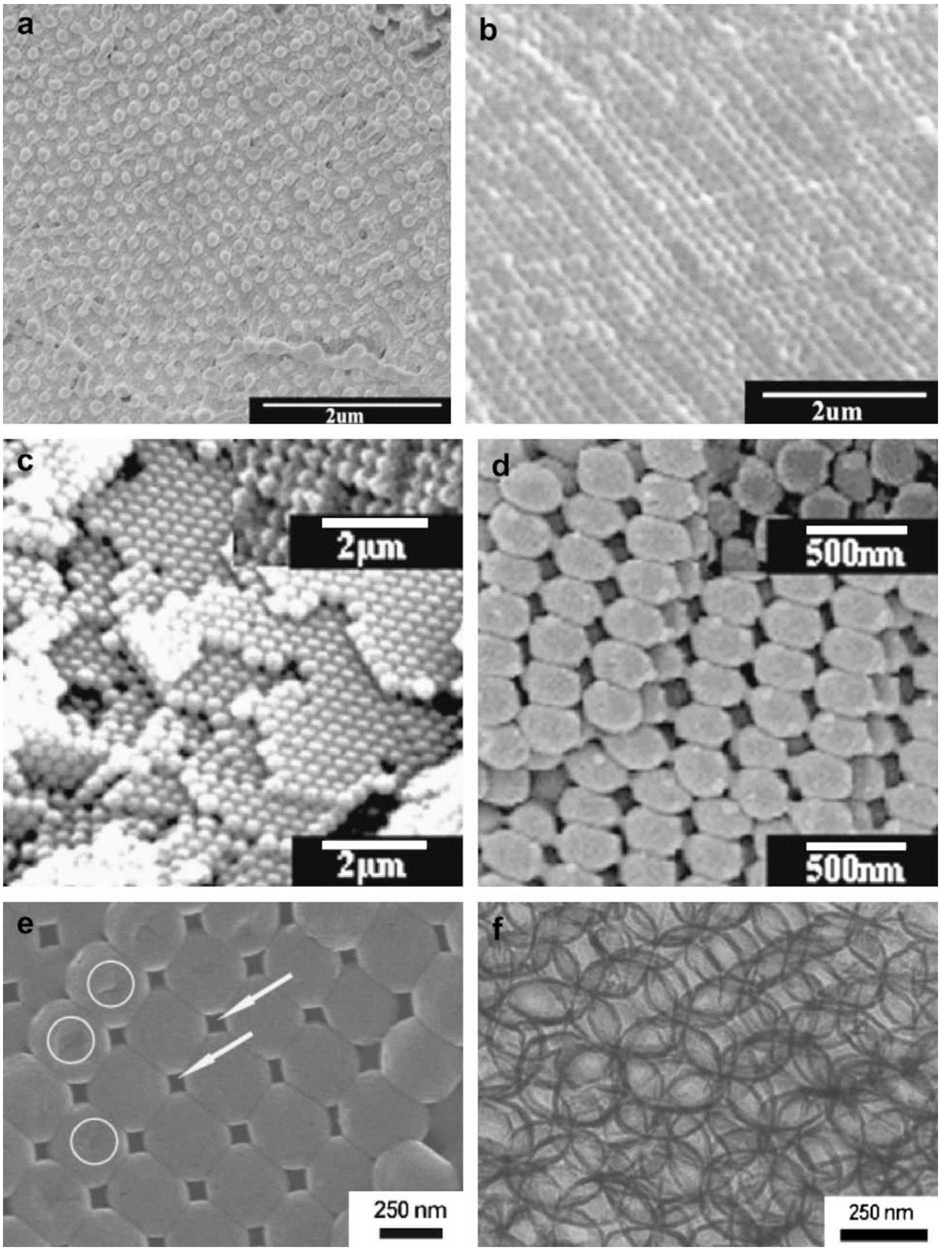

Fig. 4. Some representative opals: (a) core–shell sulfonated polystyrene gel opal; (b) silica opal by the replication of the gel opal; (c) gel/titania composite opal without compressing the opal gel template during the sol/gel process. Inset: the sample after being calcined at 450 °C for 3 h; (d) oblate titania opal material after being calcined at 450 °C for 3 h, subject to a compression degree of 150%. Inset: the fracture surface perpendicular to the direction of applied compression; (e,f) PS and PAN opal-inverse opal interlocked structures, respectively.

Recently, our group have developed a method to synthesize Janus composite colloids by simultaneous biphasic grafting of different polymer brushes onto the two parts of a Pickering colloid at a liquid/liquid emulsion interface by atomic transfer radical polymerization (ATRP) [86] (Fig. 3). Restricting the rotation of colloids by *in situ* polymerization is the key for the formation of Janus colloids. PS/poly (acrylamide), metal/silica composite colloids have also been derived to demonstrate the feasibility of this approach. Since the original colloids at the interface are hydrophobic, the inherent hydrophobic performance is not changed if only PS is grafted. The rotation of the colloids at the interface is not prohibited; therefore a core–shell (silica–PS) structure is eventually obtained. In contrast, if hydrophilic polyacrylamide is grafted, the rotation is greatly restricted, and a Janus colloid is synthesized.

4. Composite colloids patterning

Since the pioneering work of Vanderhoff on monodisperse polystyrene (PS) in 1954 [87], an increasing interest has aroused about monodisperse colloids due to their potential applications in chemical analysis, biological medicine and diagnosis, and information industry [88]. Especially, monodisperse colloids can assemble into ordered structures, which display photonic crystalline [89–103] (or opal) behavior. In reverse, they can also be used as templates to synthesize ordered macroporous materials (or inverse opals) [89–103].

It should be noticed that the commonly used colloidal crystal templates are rigid and diffusion of the precursors into the template colloids is prevented, thus structure of the ordered macroporous materials lacks of control [104]. New structured templates are required in order to fabricate new structured porous materials. Our and other groups have reported that those latexes with functional surface can be used as templates having good compatibility with an inorganic network [45,46,60]. The idea is feasible to their assembled structures. Using soft sponge like polymer gels as templates to modify the inorganic framework have demonstrated the perspective to tune the porous materials structure [105]. We have proposed a simple method to achieve ordered opal hydrogels by sulfonation of a PS colloidal crystal [106,107]. The sulfonation occurs inwardly from the latex surface. A series of opal hydrogels with varied structure and composition are derived by controlling sulfonation degree of the dry colloidal crystal with concentrated sulfuric acid. In the case of a partial sulfonation, the interior PS core remains. A kind of core–shell opal hydrogel is derived (Fig. 4a). In the case of a complete sulfonation, sulfonated polystyrene opal hydrogel is synthesized. Similarly, the sulfonated polystyrene hydrogel can be penetrated by desired materials. As an example, silica forms within both the interstitial voids and the hydrogel shell by a sol–gel process, and some new hierarchically structured silica materials are synthesized for example silica with isolated voids uniformly distributed (Fig. 4b). Different from formation of silica, titania can favorably form within the sulfonated polystyrene hydrogel. Arrays of both solid titania colloids and hollow titania colloids are obtained by controlling sulfonation degree. The opal titania materials could be disintegrated into the corresponding individual colloids under ultrasonication [108]. Besides inorganic materials, responsive polymer materials for example pH responsive polyacrylic acid can also be incorporated with the opal hydrogel forming IPN structure [109]. The ordered IPN opal hydrogel experiences a dimension alteration thus color change with pH values. They can be potentially used as a visible pH sensor.

Besides the ordered structures from symmetric colloids, ordered arrays of non-spherical colloids may be more attractive in applications such as photonic crystals than their spherical counterparts [110,77]. Hydrogel opals can also be directly synthesized by a free polymerization of the corresponding monomers within a rigid for example silica inverse opal, therefore composition of the opals can be easily tuned. Hydrogel can be easily compressed under stress, which may be used to further synthesize non-spherical opals. We have reported the synthesis of ordered arrays of spherical and oblate titania objects under varied stress (Fig. 3c,d) [111] using an acid group contained hydrogel opal. The key is that titania can be favorably grown only within the acid group contained hydrogel. It is convenient to control the aspect ratio by varying the spacer height thus the compression degree.

A new surface template synthesis has been reported for a complex ordered structure [112]. It is a key to grow desired materials onto the colloid surface exposed to the interstitial voids of a silica opal. After the opal template is removed, monodisperse hollow colloids are regularly arranged, which are interconnected through the window channels. This new structure is interlocked between binary opal–inverse opal structures. The new interlocked structure has displayed new properties as a photonic crystal [113,114]. Different from the other synthesis by chemical vapor deposition [112,114,115], we have reported a general facile method to synthesize opal–inverse opal interlocked materials of varied composition (Fig. 4e,f) [116]. Three main steps are involved: (1) grafting of polymer rushes onto the colloid surface of a silica opal template by atom transfer radical polymerization (ATRP); (2) modification of the polymer brushes rendering functional groups, and (3) an induced favorable growth of composite shell. After the removal of silica opal templates, opal–inverse opal interlocked structures with varied compositions of polymers, inorganic materials, and carbon are achieved. Our synthesis method is rather facial and without expensive apparatus.

5. Conclusion and remarks

In summary, we have reviewed a short progress in architectural designing and synthesis of some spherical composite colloids, unsymmetrical colloids, as well as their ordered patterning. Template synthesis is mainly used to assure the transcription efficacy. Polymeric gels with a diversity of functional groups are significant to control both macroscopic morphology and microscopic structure of the colloids and their patterning. Especially, hollow composite colloids with either interior or exterior structure tunable, ellipsoidal colloids and their arrays are emphasized since they will give new properties. The progress in structure and composition control of colloids and their arrays will bring more opportunities to systematically explore their new performances.

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