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ORIGINAL CONTRIBUTION

General synthesis of hollow composite ellipsoids

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Abstract A facile and general approach towards composite hollow ellipsoids has been proposed. The parent polystyrene (PS) hollow spheres are embedded in a matrix, for example, poly(vinyl alcohol), and stretched into the corresponding ellipsoids. The aspect ratio of the ellipsoids is tunable by stretching extent. Accordingly, sulfonated PS hollow ellipsoids are achieved by sulfonation of the PS hollow ellipsoids, which will facilitate an easy complexation with functional materials. Composite hollow ellipsoids, with varied composition ranging between polymer, metal and oxides, and inorganic materials, are synthesized against the polymer ellipsoids as templates. By controlling growth of the functional materials at specific sites, structure of the composite hollow ellipsoids is controlled such as surface-pillared, single-shelled and double-shelled. This approach avoids traditional removal of polymer templates, thus guarantees the shell integrity of the composite hollow ellipsoids.

Keywords Hollow ellipsoids · Elongation · Polymer · Template synthesis · Composite

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Introduction

Hollow spheres and capsules have attracted increasing interests due to their broad potential applications such as controlled delivery systems, artificial cells, light weight fillers, catalysis, and vessels for confined reactions [1–5]. Hollow structures with some special morphologies have superior properties [6–8]. As an example, the polymer hollow sphere with a movable gold nanoparticle core has shown an optical sensing of the chemicals diffused into the cavity [6]. Polyelectrolyte capsules with a shell-in-shell structure exhibit an enhanced mechanical strength and preserved permeability [7]. Photonic crystals composed of capsules with materials inside the cavity of a monodispersed hollow sphere have displayed interesting optical properties dependent on the aspect shell thickness/cavity ratio [8]. Recently, non-spherical ellipsoids have gained increasing interests. Anisotropic diffusion behavior of an isolated ellipsoid can be directly visualized under microscopy, which will help to understand transport in membranes and motion of anisotropic macromolecules [9]. Ellipsoids display more complex aspect-ratio-dependent phase behavior such as from translational ordering to jamming, which will help to design more complex materials [10, 11]. Photonic crystals of ellipsoids have exhibited unique optical properties different from the counterpart spherical ones [12, 13].

It is interesting to develop a facile approach to synthesize hollow ellipsoids and their composites. Using hematite spindle as template has enabled one to synthesize silica hollow ellipsoids with a tunable shell thickness [14, 15]. It is still a challenge to control particle size and core/shell aspect ratio of the hollow ellipsoids, as the template hematite spindles lack structural and geometrical control [14–16]. Recently, polymer ellipsoids have been synthesized by different methods. Laser irradiation of azopolymer colloids

has synthesized polymer ellipsoids [17]. Seo et al. [18] have reported continuous synthesis of polymer colloids with tunable shapes in microfluidic laminar flow reactors. However, it is still a challenge to synthesize submicron ellipsoids thereby. Colvin et al. have reported template synthesis of ordered materials composed of submicron ellipsoids including solid and hollow ones [19]. A general method has been proposed to synthesize monodispersed polymer ellipsoids by mechanically stretching spherical colloids embedded in a proper polymeric matrix [12, 13]. The aspect ratio of these ellipsoids can be precisely controlled by altering stretching extent [20–22]. It is speculated that composite hollow ellipsoids will be derived by layer-by-layer assisted deposition onto the polymer ellipsoidal templates [23]. It should be noticed that apertures or fragmentation in the shell is usually resulted by the osmotic pressure during removal of the template cores. Recently, we have proposed a general method to synthesize composite hollow spheres using polystyrene (PS) hollow spheres as templates [24, 25]. Traditional removal of template core is avoided thus to guarantee the shell integrity in principle.

Herein, we employ the similar way [12, 13] to mechanically stretch PS hollow spheres instead of solid ones to prepare PS hollow ellipsoids with tunable aspect ratio. Similar to using PS hollow sphere templates [24, 25], the ellipsoids are further modified to introduce functional groups that will be conducive to formation of composite shells. The composition can be varied ranging between polymers, inorganic materials, metal, and 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 composition and structure.

Experimental

Synthesis of polymer hollow ellipsoids

A desired amount (0.03∼0.4 g) of the commercially available polystyrene hollow sphere HP-433 dispersion (purchased from Rohm & Haas, ~37.5 wt% solid content) was mixed with 20 g of poly(vinyl alcohol; PVA) aqueous solution (6 wt%) and cast into a thin film about 0.1 mm in thickness. The film was cut into stripes about 3×1 cm. A stripe was stretched at a rate about 4.1 mm/min with a home-built apparatus at a given temperature 150~200 °C to a stretching ratio. Afterwards, the stretched stripe was quickly cooled by spraying liquid nitrogen. When the stripe was gradually recovered to room temperature, it was immersed in water at 80 °C for about 6 h to dissolve PVA under stirring. The PS hollow ellipsoids were obtained after being washed and centrifuged.

Synthesis of hollow composite ellipsoids

Surface pillared titania composite hollow ellipsoids: 1 mg of PS hollow ellipsoid was centrifuged and rinsed with a large amount of ethanol to substitute water from inside cavity and dispersed in 1 ml of ethanol. One milliliter of tetrabutyl titanate (TBT)/ethanol (1:1 *v*/*v*) mixture was dropped to the dispersion under stirring to allow a sol–gel process for 4 h. Titania/polystyrene composite hollow ellipsoids were obtained after cycled centrifugation, rinsing with ethanol. *Titania composite hollow ellipsoids with double shells:* 1 mg of the freeze-dried sulfonated PS ellipsoid was immersed in 0.5 ml of TBT/ethanol (1:1 vol/vol) for 24 h. After being centrifuged and rinsed with ethanol, the TBT-contained ellipsoid was transferred to 0.5 ml of ethanol at ambient temperature. An amount of 0.5 ml of water was added to the dispersion under stirring to initiate the sol–gel process for 4 h. A titania composite hollow ellipsoid with double shells was obtained after centrifugation and rinsing with ethanol. The corresponding titania hollow ellipsoid was obtained after the polymer template was removed by dissolution with *N*,*N*-dimethylformamide (DMF) or calcination in air at 450 C. *Silica composite hollow ellipsoids:* After 1 mg of the PS hollow ellipsoid was dispersed in 1 ml of ethanol, a desired amount of 25 wt% aqueous ammonia was added to adjust pH to 9. One milliliter of tetra-ethyl-ortho-silicate (TEOS)/ethanol mixture (1:1 *v*/*v*) was dropped into the dispersion to allow a sol–gel process under stirring for 24 h. Finally, a silica composite hollow ellipsoid was obtained. The corresponding silica hollow ellipsoid was obtained after the template was removed by dissolution with DMF. *Hematite composite hollow ellipsoids:* 1 mg of PS hollow ellipsoid was immersed in 2 ml of 2.5 wt% $FeCl_3$ aqueous solution for 48 h. After centrifugation and rinsing with water, the salt-contained ellipsoid was transferred to 1 ml of water at ambient temperature. An amount of 0.2 ml NaOH solution (1 M) was then added to the dispersion under stirring at 65 °C for the reaction for 4 h. A hematite Fe_2O_3 composite hollow ellipsoid was obtained after centrifugation, rinsing with ethanol. After removal of the polymer template by dissolution with DMF or calcination at 450 °C, the corresponding Fe_2O_3 hollow ellipsoid was obtained. *Magnetite composite hollow ellipsoids:* 1 mg of the sulfonated PS hollow ellipsoid (or the PS hollow ellipsoid) was immersed in 1 ml of aqueous ferrous chlorides/ferric chlorides (1:2 mol/mol) for 48 h in a nitrogen atmosphere. After centrifugation and rinsing with water, the salt-contained ellipsoid was transferred to 1 ml of water at ambient temperature. An amount of 0.2 ml of NaOH solution (1 M) was then added to the dispersion under stirring at 65 °C to allow the reaction for 4 h. A magnetite composite hollow ellipsoid was obtained after centrifuga-

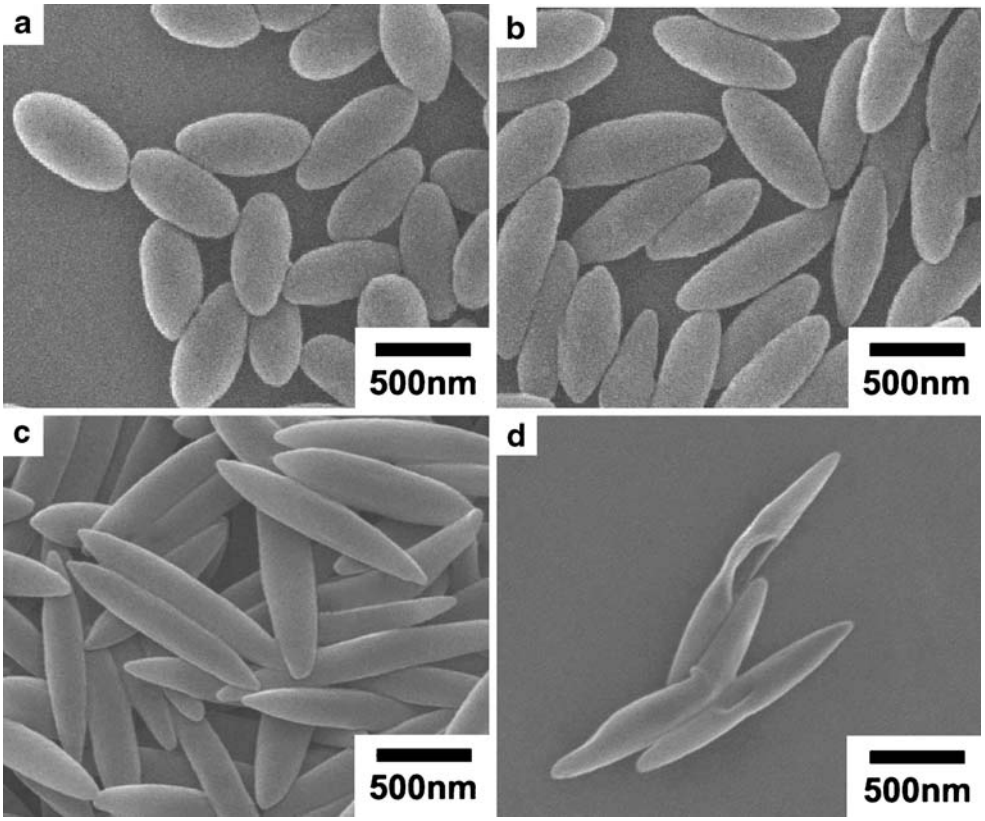

Fig. 1 SEM images of some representative PS hollow ellipsoids prepared at different stretching ratio. **a** 50%; **b** 75%; **c** 150%; and **d** 300%

tion, rinsing with ethanol. The corresponding magnetite hollow spheroid was obtained after the template was removed by dissolution with DMF. *Polyaniline composite hollow ellipsoids:* 2 mg of the sulfonated PS hollow ellipsoid (or the PS hollow ellipsoid) was dispersed in 1 ml of water containing 2 mg of monomeric aniline under stirring. After 2 h, 10 μl of aqueous sodium hyposulfite (1 M) was added to initiate a polymerization at room temperature for 24 h. A polyaniline hollow ellipsoid was obtained after centrifugation and treatment with DMF to dissolve the polymer template. *Silver composite hollow ellipsoids:* 1 mg of the sulfonated PS hollow ellipsoid was immersed in aqueous silver nitrate for 24 h. An aqueous solution of hydrazine hydrate (50 wt%) was added to reduce silver nitrate, forming a silver composite hollow ellipsoid.

Characterization Morphology of the ellipsoids was characterized by transmission electron microscopy (TEM; JEOL 100CX instrument operated at 100 kV) and scanning electron microscopy (SEM; Hitachi S-4300 instrument operated at an accelerating voltage of 15 kV). The ellipsoids were diluted with ethanol and deposited onto carbon coated copper grids for TEM observation. The ellipsoids were ambient dried and vacuum sputtered with Pt for SEM observation.

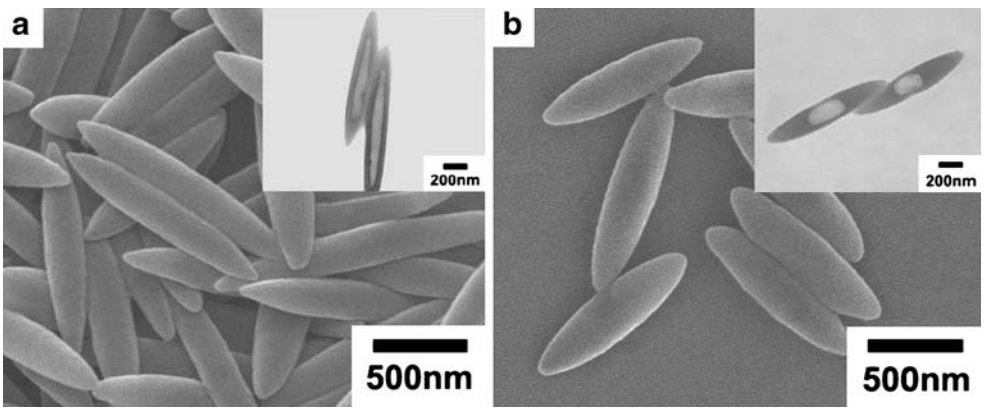

Fig. 2 SEM and TEM (*inset*) images of the PS hollow ellipsoids prepared by stretching at a given ratio 150% but at different temperatures. **a** 200 °C; **b** 150 °C

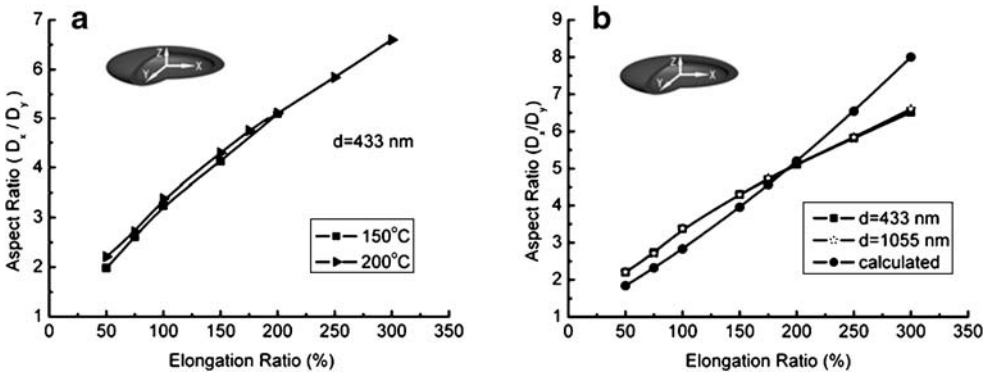

Fig. 3 Aspect ratio control of the polystyrene hollow ellipsoids: **a** by elongation at two temperature levels; **b** comparison between experimental ratio and the theoretical prediction

Results and discussion

Fabrication of polymer hollow ellipsoids by mechanical stretching

According to our previous report [24, 25], the polystyrene hollow spheres, for example HP-433 with an average diameter 430 nm, contain a thin hydrophilic interior layer and transverse channels of polymethylmethacrylate-polymethylacrylic acid, which will be conducive to be better dispersed in the aqueous solution of PVA. A temperature such as 200 °C much higher than the glass transition temperature (100 °C obtained by differential scanning calorimetry) was chosen, at which the polystyrene hollow spheres were stretched into ellipsoids according to the viscoelastic deformation mechanism [12, 13, 20–22]. Some representative PS hollow ellipsoids with varied aspect ratio are shown in Fig. 1. With stretching ratio increased, the aspect ratio increases accordingly. At a higher stretching ratio (150%), the ellipsoids have evolved into spindles with sharp tips (Fig. 1c), which will bring new plasmon resonance when complexing with functional materials. However, the ellipsoids become instable at an extremely high stretching ratio (300%), and the middle region begins to collapse (Fig. 1d).

The cavity of the hollow ellipsoids was confirmed by TEM observation (Fig. 2). It is found that stretching temperature is crucial to control the cavity structure. At

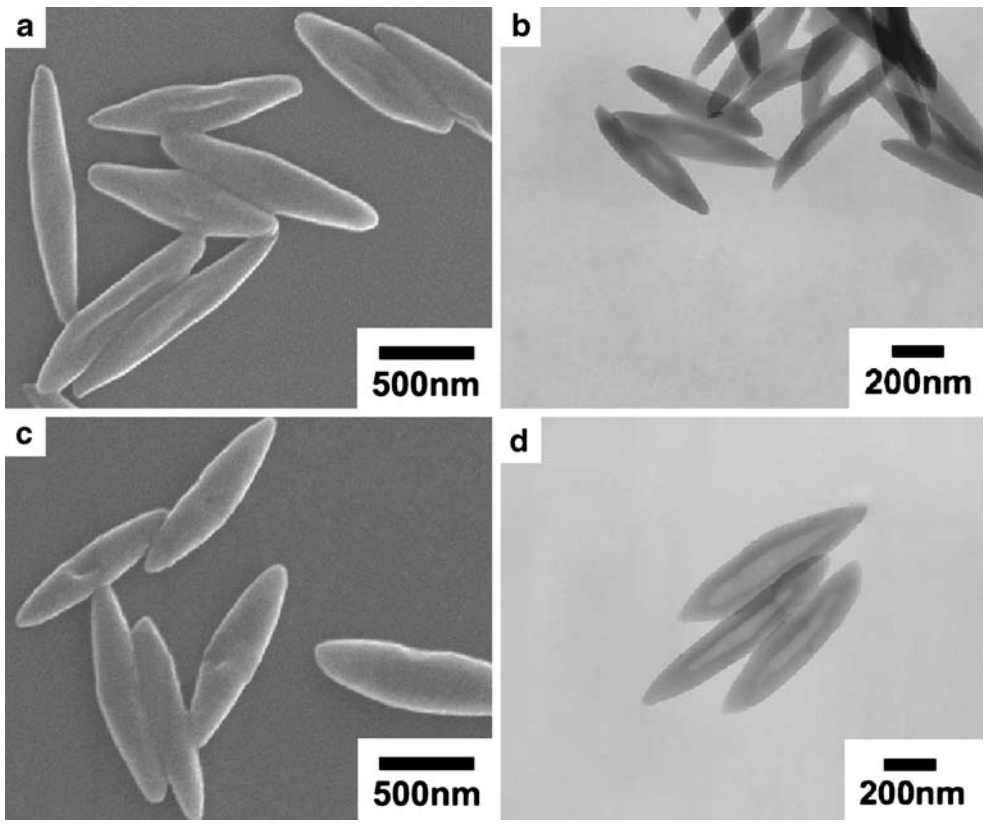

Fig. 4 SEM (**a**) and TEM (**b**) images of the sulfonated PS hollow ellipsoids prepared by stretching the sulfonated PS hollow spheres. SEM (**c**) and TEM (**d**) images of the sulfonated PS hollow spheroids prepared by sulfonation of the PS hollow ellipsoids with sulfuric acid at 40 °C for 0.5 h

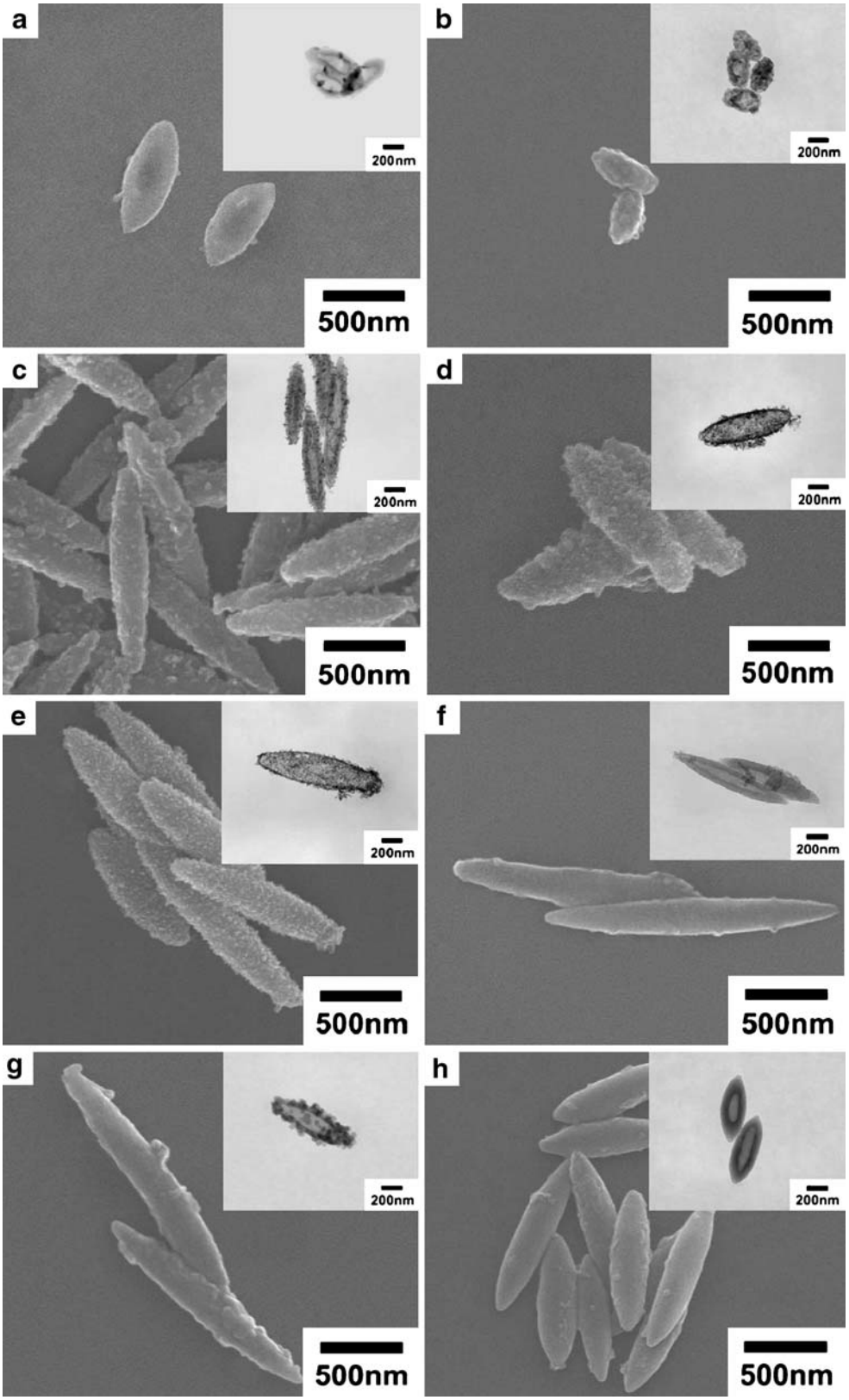

Fig. 5 Morphology of some representative ellipsoids. **a**, **b** The surface-pillared titania composite ellipsoids before and after dissolution of the polymer template with DMF; **c**, **d** the Fe_2O_3 composite hollow ellipsoids before and after dissolution of the polymer template with DMF; **e** the Fe_2O_3 hollow ellipsoids after the composite being calcined at 450 °C in air; **f** the polyanline composite hollow ellipsoids; **g** the silica composite hollow ellipsoids; **h**) the Fe_3O_4 composite hollow ellipsoids

higher temperature, for example 200 °C, the hollow cavity deforms the same ratio as that of the whole contour (Fig. 2a). At lower temperature, for example 150 °C, the cavity aspect ratio is far smaller than the contour (Fig. 2b).

The contour aspect ratio is controlled by stretching ratio. As shown in Fig. 3a, the aspect ratio is less influenced by temperature. This finding is valid for larger hollow spheres, for example HP-1055, with a diameter about 1,055 nm. For an ideal system where only one single sphere is embedded in an infinite elastic matrix and the composite film is linear elastic with no interfacial energy contribution, the aspect ratio can be predicted according to Eshelby [20–22]. At lower stretching ratio, the experimental aspect ratio is higher than the corresponding theoretical one. At higher stretching ratio, for example above 200%, the experimental aspect ratio is lower. This derivation from ideal ones is related with interfacial energy contribution and polymers relaxation in our studied system.

Sulfonated PS hollow spheres were obtained after sulfonation of the parent PS hollow spheres with sulfuric acid for 0.5 h [24]. They were stretched into hollow ellipsoids at 200 °C (Fig. 4a,b). At a stretching ratio 150%, the ellipsoids (denoted as S1) show a thicker shell and a smaller cavity. The ellipsoids begin to partially collapse. This is related with the sulfonated PS gel of the ellipsoids. As comparison, the PS hollow ellipsoids prepared under the same conditions but from the parent ones can preserve the contour better (Fig. 2a). Alternatively, the sulfonated PS hollow ellipsoids (denoted as S2) can also be derived by direct sulfonation of the corresponding PS hollow ellipsoids

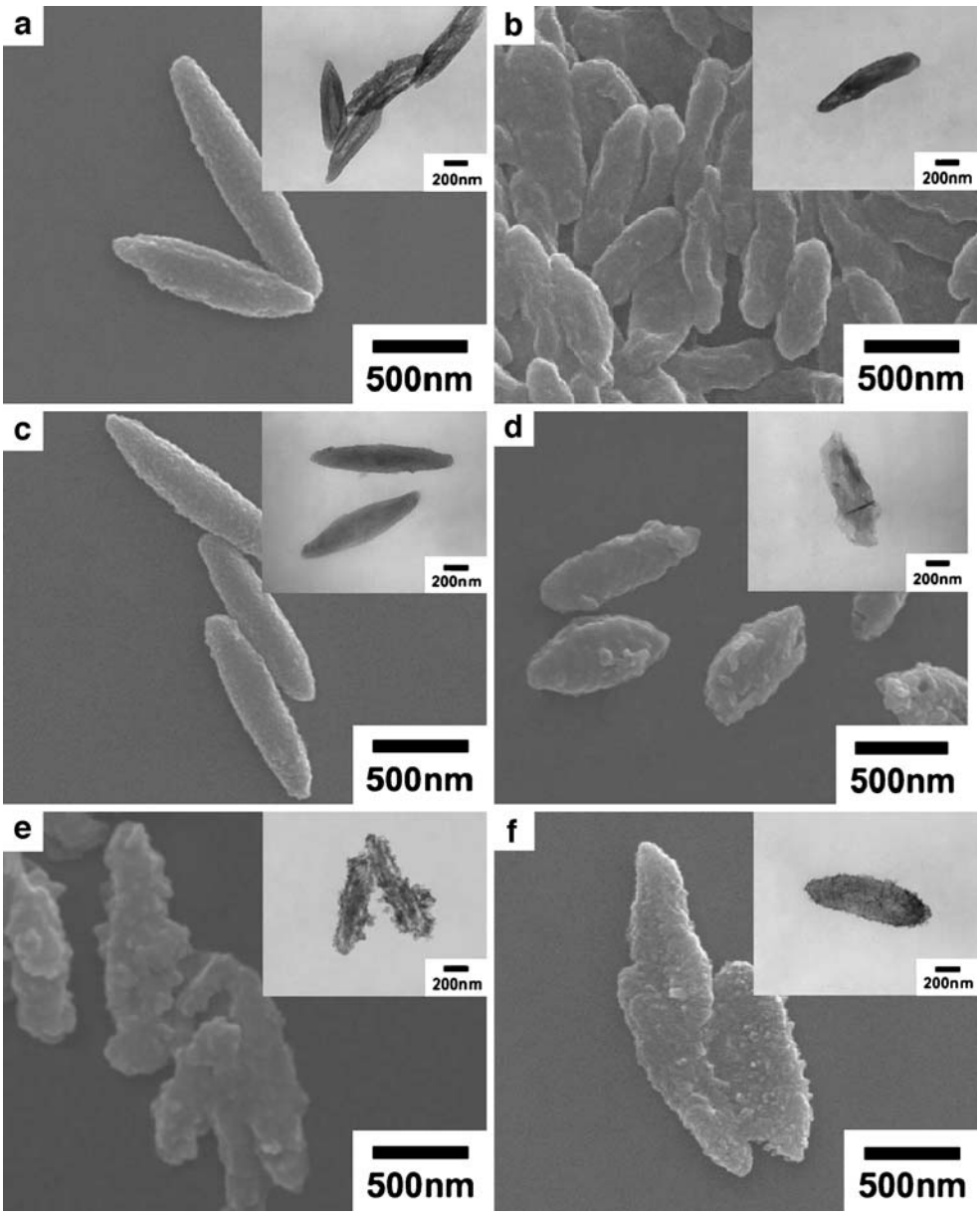

Fig. 6 Morphology of some representative double-shelled ellipsoids prepared using sulfonated PS hollow ellipsoid templates. **a**, **b** The titania composite hollow ellipsoids before and after being dissolved with DMF; **c**, **d** the polyaniline composite hollow ellipsoids before and after being dissolved with DMF; **e** the Ag hollow ellipsoids after the composite ellipsoids were treated with DMF; **f** the Fe_3O_4 hollow ellipsoids after the composite ellipsoids were treated with DMF

(Fig. 4c,d). They are also easily collapsed especially for those ellipsoids with a higher aspect ratio and higher sulfonation degree.

Template synthesis of hollow composite ellipsoids

Similar to using polymer hollow spheres as templates [24, 25], the polymer hollow ellipsoids can also be used as templates to synthesize composite hollow ellipsoids. To confirm the presence of hydrophilic channels across the shell, their replication with TiO_2 was undertaken by a preferential sol–gel process [26]. The hollow ellipsoid (Fig. 1b) prepared at a stretching ratio 75% was used as an example template. The corresponding titania composite hollow ellipsoids are shown in Fig. 5a. Hollow cavity is clearly distinguished. In addition, some nanosized TiO_2 pillars exist onto the shell surface. Thermal gravimetric analysis (TGA) result shows that the composite ellipsoid contains 15.6 wt% of titania. After the polymers were dissolved with DMF, the corresponding hollow TiO_2 ellipsoids were obtained (Fig. 5b). They became shrunk. The shell is composed of nanoparticles about 30–50 nm (Fig. 5b). The hollow ellipsoids are intact, indicating titania dominantly grow within the interior surface of the shell. Additional TiO_2 pillars are connected with the shell surface, which are buried beneath the polymer shell. These findings conclusively reveal that there exist the hydrophilic channels across the polymer shell. The titania is amorphous. After the composite ellipsoids were calcined to remove polymers at 450 °C in air, the amorphous titania was transformed into anatase phase.

The easy binding of metal ions by polymeric gels (containing groups such as carboxylate, carboxylic acid, sulfonic acid) facilitates the synthesis of metal or metal oxides. The hollow PS ellipsoids offer excellent organic scaffolds to synthesize metal oxide nanoparticles favorably onto their interior surface. As a proof of the concept, the PS hollow ellipsoid (Fig. 1c) was used as a template to prepare Fe_2O_3 composite hollow ellipsoids (Fig. 5c). Onto the exterior shell surface, Fe_2O_3 nanoparticles are dispersed rather than continuous network. After the composite ellipsoids were exposed to DMF to remove the polymer template, Fe_2O_3 hollow ellipsoids with rough surface were obtained (Fig. 5d). This indicates that Fe_2O_3 shell is continuous, which is formed onto the interior shell surface. Fe_2O_3 hollow ellipsoids become shorter in longitudinal axis and longer in transverse axis. The synthesized Fe_2O_3 hollow ellipsoids are sufficiently robust to survive further calcination at 450 °C in air (Fig. 5e). This method can be further extended to other materials such as conducting polymer polyaniline, inorganic SiO_2 [27] and magnetic Fe_3O_4, resulting in the corresponding composite ellipsoids (Fig. 5f–h). It is noticed that the ellipsoids formed using PS hollow ellipsoid templates dominantly result in hollow ellipsoids with a single shell, as the materials are favorably grown onto the interior surface of the template shell.

According to our previous finding that double-shelled hollow spheres can be obtained when using sulfonated PS hollow sphere templates [24], it is rational to use sulfonated PS hollow ellipsoids as templates to achieve double-shelled ellipsoids. As reported previously [24], sulfonic acid group was introduced within both interior and exterior surfaces of the PS shell, which facilitates further complexation with functional materials thereby. As the first example, titania composite ellipsoids were synthesized by a sol–gel process (Fig. 6a) using the template S2. Hollow cavity is distinguished. After the composite ellipsoids were treated with DMF to remove the polymer template, the double-shelled titania hollow ellipsoids were obtained (Fig. 6b). Both the shells are around 30–40 nm in thickness, which are supported with a gap about 35 nm. Another template S1 was used to synthesize the polyaniline composite hollow ellipsoids (Fig. 6c). Hollow cavity is not clear. After being treated with DMF, the hollow cavity becomes clear (Fig. 6d). Both the shells are around 40–60 nm in thickness, supported with a gap about 20 nm. The similar process was employed to synthesize double-shelled hollow ellipsoids with varied composition such as metal Ag, metal oxide Fe_3O_4 using S2 template (Fig. 6e–f).

Conclusion

We have demonstrated a general and facile approach towards composite hollow ellipsoids with both cavity size/shell thickness and longitudinal/transverse axes aspect ratios controlled. Structure of the composite ellipsoids can be controlled in being single-shelled and double-shelled. The functional polymer gels of the templates play a key role in facilitation of an easy complexation with functional materials ranging between polymers, metals and oxides, and inorganic materials.

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