

## Mesoporous Silica Hollow and Solid Spheres by Templating Poly(pyrrole) Inverse Opals

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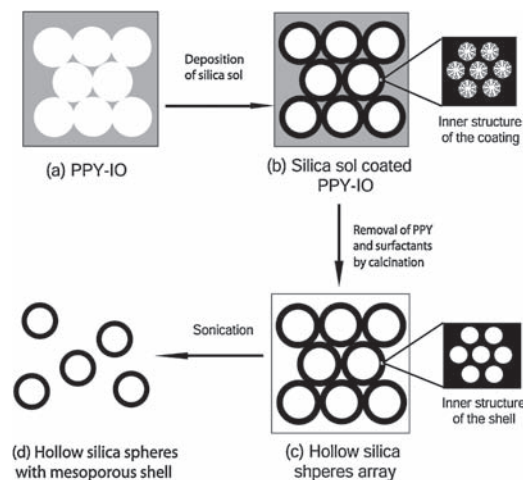
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Poly(pyrrole) inverse opals (PPY-IO) with three-dimensional (3D) network of macropores were prepared by electropolymerization of pyrrole in the voids of polystyrene (PS) colloidal crystals and subsequently removing the PS. The as-prepared PPY-IO were then served as templates to be filled with prehydrolyzed silica sols followed by calcination to synthesize mesoporous silica spheres with well-controlled diameters. It was demonstrated that the reactant composition of the silica sol played an important role in controlling the shell thickness of the hollow spheres. Solid mesoporous silica spheres could be obtained when a concentrated TEOS sol was used. The morphology and pore structures of PPY-IO and silica spheres were characterized by SEM. TEM and small-angle XRD confirmed the ordered mesostructure of the prepared silica spheres with an average pore size of ca. 6 nm.

Fabrication of materials with designed structures and morphologies has stimulated much interest in the last decade. Silica materials with various morphologies such as thin films, spheres, hollow spheres, fibers, and tubes have been prepared by carefully controlling the reactant compositions, reaction conditions, and the synthetic procedures.<sup>1</sup> Among them, spherical mesoporous silicas have received particular attention due to their easy preparation and wide applications in many fields, for example, gene and drug delivery, catalyst supports, heavy metal removal, and packing materials for high-performance liquid chromatography.<sup>2</sup> Our recent work demonstrated the use of mesoporous silica particles as both immobilization matrix and capsule templates for encapsulating biomacromolecules in biocompatible polypeptide hollow capsules.<sup>3</sup> Mesoporous silica particles were also used as templates to prepare nanoporous particles with various compositions which are difficult to achieve using normal synthetic procedures.<sup>4</sup> There have been many strategies reported for preparing mesoporous silica spheres and hollow spheres including modified Stöber method, aerosol self-assembly, acid catalysis, sonochemical methods, interfacial reactions in oil/water emulsions, and spray-drying methods.<sup>1c,5,6</sup> The main disadvantage of these techniques is the lack of control over the size of the particles, i.e., most spheres obtained are usually polydispersed in size.

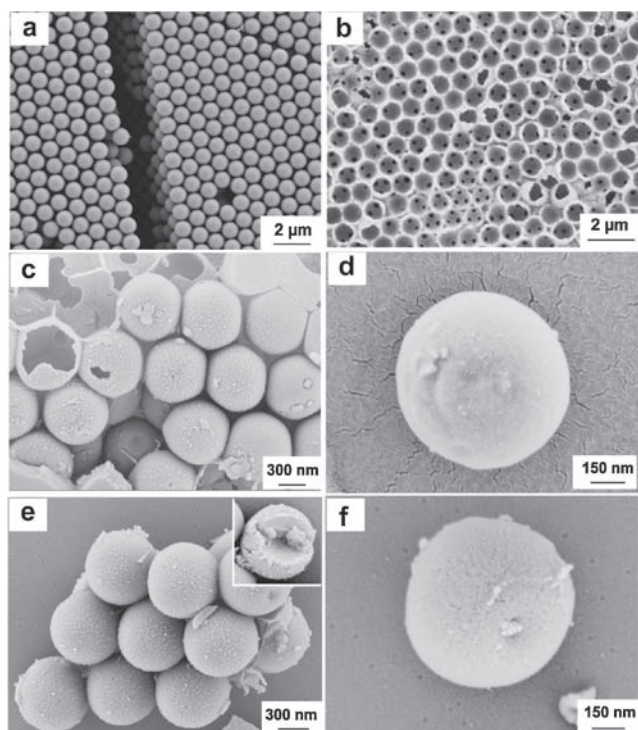
As an alternative, colloidal templating synthesis provides a facile and versatile route to prepare hollow spheres with well-defined size and morphology. For example, various inorganic and organic hollow spheres with controlled diameter, composition, and shell thickness have been prepared by layer-by-layer coating on colloid templates, followed by removal of the colloid templates by calcination or solvent dissolution.<sup>7</sup> Another interesting property of colloidal templates is the colloid particles (e.g., silica or polystyrene) could spontaneously self-organize into colloidal crystal structures with long-range periodicity.<sup>8</sup> The colloidal crystal arrays could also be used as templates to



**Figure 1.** Schematic representation of the procedure for preparing mesoporous silica hollow spheres by templating PPY-IO.

prepare hollow sphere arrays of various materials by filling the voids of colloidal crystals with the desired materials followed by removing the templates.<sup>9,10</sup> There have been also a few reports on using replicas of colloidal crystals (known as inverse opals) to prepare solid spheres by filling the inner surface of inverse opals and subsequently removing the inverse opal templates.<sup>11</sup> However, previous studies on using colloidal templates have emphasized mostly preparation of nonporous materials, and relatively few studies have focused on preparing spheres with well-defined porosity.<sup>9b,11a,12</sup>

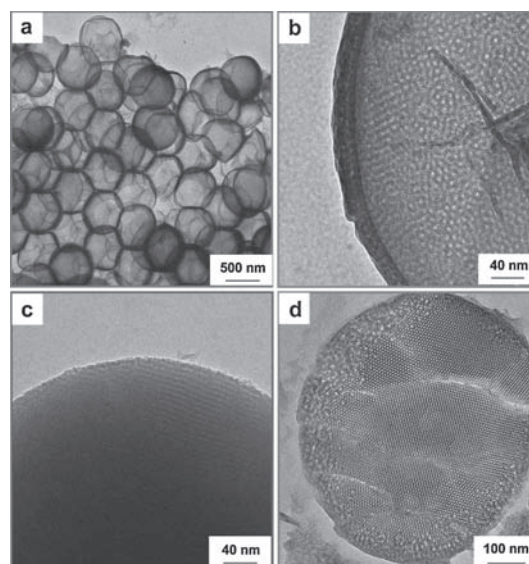
Herein we report the preparation of mesoporous silica hollow and solid spheres with well-defined diameter and mesopore size (ca. 6 nm) by templating poly(pyrrole) inverse opal (PPY-IO). A typical synthetic procedure for hollow spheres is shown in Figure 1, which includes the following steps: a) Preparation of PPY-IO templates by electropolymerization of pyrrole into the voids of the polystyrene (PS) colloidal crystals and subsequently removing the PS templates. b) Deposition of the mesoporous silica sol in the inner surface of PPY-IO templates by soaking the PPY-IO films into a prehydrolyzed silica sol with block copolymer surfactants. The surfactant allows the regulation of the porosity and structure of the resulting material. c) Removal of PPY-IO scaffolding and surfactant molecules by calcination. This process also enhances the crosslinking of the silica framework. d) Individual spheres could be obtained by subsequent sonication of the close-packed sphere array. As the concentration of the silica precursor greatly affects the formation of the spheres, we demonstrate here that mesoporous silica solid spheres or hollow spheres with variable shell thickness could be obtained by varying the molar ratio of the reactant composition of the silica sol.



**Figure 2.** SEM images of (a) a colloidal crystal self-assembled from 925 nm PS particles, (b) a PPY-IO prepared by templating colloidal crystal, and mesoporous silica spheres obtained by filling the PPY-IO templates with silica Sol I (c, d) and Sol II (e, f) followed by calcination at 550 °C for 5 h.

The PPY-IO templates were prepared using colloidal crystals as templates. PS particles were firstly self-assembled on an ITO electrode by gravity sedimentation and water evaporation at room temperature in a homemade cell. Pyrrole was then electropolymerized into the voids of the PS colloidal crystal in a 1 M KCl solution containing 0.25 M pyrrole under a voltage of 0.7 V, as with our previous report.<sup>10a</sup> PPY-IO was obtained after dissolving the PS template in tetrahydrofuran. Figure 2a shows the representative SEM image of a colloidal crystal assembled from 925-nm PS particles. It can be seen that the PS particles crystallized in hexagonal ordered packing with the (111) face parallel to the substrate, with ordered areas extending over hundreds of square micrometers. SEM observation of the cleaved edges of the samples revealed 3D ordered arrays of the crystals. Figure 2b shows the SEM image of the as-prepared PPY-IO which has a replica structure of its colloidal crystal template showing well-ordered hexagonal packing of the spherical voids. Within each spherical void, one can observe regular arrangements of smaller holes that originate from the necking points between PS spheres in the opal template. The connected small windows are essential for entirely depositing silica sol in the inner space of the inverse opal.

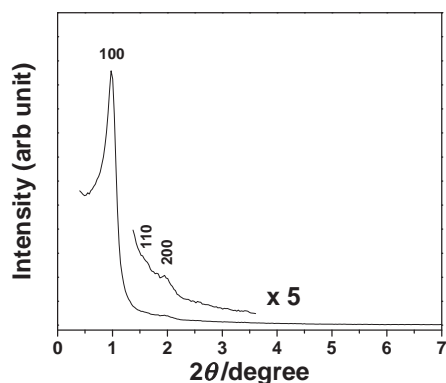
The mesoporous silica sols used for deposition were prepared by first dissolving TEOS in ethanol. After adding a dilute HCl solution and prehydrolyzing for 30 min at room temperature, an ethanol solution of P123 surfactant was added. The molar ratios of the reactants were varied for obtaining different products. Specifically the following two reactant ratios



**Figure 3.** TEM images (a, c) and cross-section images (b, d) of the mesoporous silica spheres obtained by filling the PPY-IO templates with silica Sol I (a, b) and Sol II (c, d) followed by calcination at 550 °C for 5 h.

were defined as silica Sol I (TEOS:P123:H<sub>2</sub>O:HCl:EtOH = 1:0.0095:5:0.0089:22) and silica Sol II (TEOS:P123:H<sub>2</sub>O:HCl:EtOH = 1:0.0095:6:0.04:10.4). The mixed solution was then aged at room temperature for 3 h. The PPY-IO films were soaked into the aged mesoporous silica sols for 1.5 h followed by calcination at 550 °C for 5 h. The heating process was carried out to burn the PPY templates as well as the organic surfactant molecules in the system. It also promotes the crosslinking to enhance the silica framework. Figure 2c shows the SEM image of a sample prepared by using a mesoporous silica Sol I. Ordered assembly of spheres is observed with hexagonal packing structure similar to the original colloidal crystal template. From some of the broken spheres, it can be concluded that the as-prepared spheres using silica Sol I are hollow inside with shell thickness in the range of 30–50 nm. The spheres are connected with each other due to the connecting windows within PPY-IO film. Subsequent sonication can facilitate the separation of the connected spheres (Figure 2d). Further experimental results indicate that the morphology of the resulting spheres can be controlled by varying the molar ratio of the reactant composition in the silica sol. For example, when silica Sol II is used, solid silica spheres can be formed. Figure 2e shows the SEM image of a sample prepared using silica Sol II. Spheres with solid inside are clearly seen from some of the broken particles (Figure 2e, inset). An individual sphere obtained after sonication is also shown in Figure 2f. The diameters of the above hollow and solid spheres, as calculated from SEM, are about 770 nm for hollow spheres and about 780 nm for solid spheres with a narrow size distribution of ca. 5% which can be considered to be copied from the initial PS particles used. These diameter values correspond to ca. 16% shrinkage relative to the original diameter of the polystyrene particles (925 nm) due to calcination.

The as-prepared spheres were further characterized by transmission electron microscopy (TEM). Figures 3a and 3c



**Figure 4.** Small-angle X-ray diffraction (XRD) patterns of calcined mesoporous silica hollow spheres obtained by using silica Sol I.

show TEM images of the samples obtained by filling the PPY-IO templates with silica Sol I (a) and silica Sol II (c), respectively. The electron contrast between the center and the edge of the spheres, showing that the spheres are hollow when using silica Sol I and become solid when silica Sol II was used, which is in agreement with the SEM results (see before). From the cross-section images of high-magnification TEM (Figures 3b and 3d), well-ordered hexagonal pore arrays for both hollow and solid spheres are observed. However, disordered pore arrays were also observed in some areas of the particle. The mesopore size of hollow spheres measured from TEM is around 6 nm which is consistent with the value (5.8 nm) calculated from the nitrogen sorption isotherm by the Barrett–Joyner–Halenda (BJH) model (data not shown).

The small-angle X-ray diffraction (XRD) patterns of mesoporous silica spheres obtained after calcination are shown in Figure 4. Two peaks are observed, which can be indexed to (100) and (200) reflections of the 2D hexagonal space group ( $p6mm$ ), similar to that observed for the original SBA-15. The intense (100) peak reflects a  $d$  spacing of 8.94 nm, corresponding to a cell parameter  $a$  of 10.32 nm.

In summary, we have demonstrated a template-direct route to prepare mesoporous silica spheres by templating PPY-IO. Depending on the reactant composition ratio of the silica sol used to fill the template, hollow and solid spheres with well-defined mesostructures could be prepared. The method also allows the fine control over the shell thickness of the hollow spheres. Another advantage of this approach is that both hollow and solid silica spheres have well-controlled particle sizes which are completely affected by the colloidal templates, thus transferring this burden to the original polystyrene colloids for which high-quality samples are commercially available. This method can also be extended to prepare hollow spheres and solid spheres of other materials for a variety of applications.

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