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Hollow Microspheres

Hollow Ferrocenyl Coordination Polymer Microspheres with Micropores in Shells Prepared by Ostwald Ripening**

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Hollow microspheres with pores in their shells have received much attention owing to their hierarchically porous structures and advanced applications in electrochemical capacitive energy storage, hydrogen storage, drug delivery, sensing, and catalysis.[1] For example, Lou et al.[1h] reported that hollow SnO_2 nanospheres with nanoporous shells showed high reversible charge capacity and good cycling performance. Zhu et al.[2] investigated the drug-delivery properties of hollow silica spheres with mesoporous shells and found that the hollow microspheres were able to store significantly more molecules with higher release rates than conventional mesoporous silica.

Template synthesis[1f,3] is one of the most-used strategies to prepare hierarchically hollow microspheres, especially for pores inside the shells. Braun and co-workers[3a] have prepared hollow ZnS microspheres with mesoporous shells using dual templates assembled by lyotropic liquid crystals on the surfaces of silica or polystyrene colloidal templates. Liu et al.[3b] have produced organic–inorganic hybrid hollow nanospheres with microwindows on the shells templated by tricopolymer aggregates. The template method is general to prepare hollow microspheres with pores in the shells, but expensive and tedious post-treatment processes, such as solvent extraction, thermal pyrolysis, or chemical etching, and resultant fragile frameworks, limit or even impair its applicability.[1f,3,4] As a result, it remains an important challenge to develop a convenient and template-free method to prepare hollow microspheres with porous shells.

Porous coordination polymers are highly ordered porous multifunctional materials prepared by linking metal ions or metal oxide clusters with multidentate organic ligands without any additional template.[5] Construction of shells of hollow materials with porous coordination polymers is an especially promising approach to design hollow microspheres with porous shells through a template-free method and to endow materials with multifunctionality, such as electric, magnetic, and optical properties.[6] Herein, we report the formation of hollow coordination polymer microspheres with microporous shells by a one-pot solvothermal reaction without any additional template; the shells are constructed of iron-based ferrocenyl coordination polymers. We confirm that the Ostwald ripening mechanism is responsible for the formation of hollow cavities with controllable size.

Hollow iron-based ferrocenyl coordination polymer microspheres (Fe-Fc-HCPS) were synthesized by a solvothermal reaction of $FeCl_3{\cdot}6H_2O$ with 1,1′-ferrocenedicarboxylic acid (H_2FcDC) in *N*,*N*-dimethyl formamide (DMF; Figure 1a). The precipitate was collected by centrifugation and washed several times with DMF and $CHCl_3$. The reaction temperature, reaction time, and molar ratio of reactants play important roles in the formation of hollow spherical particles.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical microscopy (OPM) were

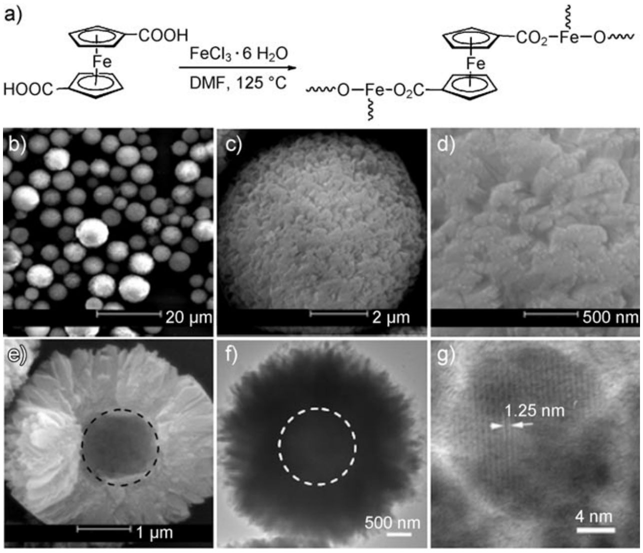

Figure 1. a) Synthetic route for Fe-Fc-HCPS. b–e) SEM images: b) low-magnification image, c) high-magnification image of a single sphere, d) local magnification of a single microsphere in (c), and e) image of a fragmented microsphere. f, g) TEM images: f) high-magnification image of a single sphere and g) local magnification of a single microsphere in (f) for Fe-Fc-HCPS (Sample 3 in Table 1). Circles in the images indicate the diameters of hollow cavities.

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used to characterize the morphology of Fe-Fc-HCPS (Sample 3 in Table 1). The SEM and OPM images (Figure 1 and Figure S1 in the Supporting Information) show that the sample consists of a large quantity of micrometer-scale spherical particles with diameters around 6 μm. The formation of the hollow structure is revealed by the SEM image of a fragmented microsphere and the TEM image of a single sphere, with approximate dimensions of about 1.46 μm (shell thickness) and 1.38 μm (inner pore diameter, d_{hol}; Figure 1 e,f). The shells of spherical particles are built from nanosheets containing layered crystallites (the interplanar distance is about 1.25 nm) and amorphous phases (Figure 1 g). Control experiments of reactions of $FeCl_3$ or H_2FcDC alone and between ferrocene lacking carboxylate groups and $FeCl_3$ show that the coordination polymer microspheres will not form in the absence of the carboxylate groups (Figure S2 in the Supporting Information).

Table 1: Synthetic conditions and porosity of Fe-Fc-HCPS.[a]

Sample	t [h]	d_{sph} [μm]	d_{mic}[b] [nm]	d_{hol}[c] [μm]	d_{hol}/d_{ssph}
1	4	2.42[d]	1.01	0.00	0.00
2	8	5.18[d]	1.01	0.00	0.00
3	10	6.10[d]	1.01	1.38	0.32
4	24	4.02[d]	1.01	2.85	0.71
2 A[e]	8 + (2)[f]	4.14[c]	1.01	0.84	0.20
2 B[e]	8 + (6)[f]	4.03[c]	1.01	1.84	0.46
2 C[e]	8 + (10)[f]	4.22[c]	1.01	2.61	0.62

[a] t, d_{sph}, $d_{ssph,}$ and d_{hol} represent the reaction time, mean diameter of spheres, diameter of a single sphere from TEM, and diameter of the hollow cavity, respectively, and d_{mic} donates the micropore diameter determined from the local maximum of the micropore size distribution (from the HK method) in the shell. [b] Data from N_2 adsorption/desorption isotherms. [c] Data from a single sphere in TEM. [d] The data indicated mean diameters of spheres from SEM (Figure 1 and 3). [e] The samples were prepared by aging Sample 2 for different amounts of time at 125 °C. [f] The number in parentheses indicates the aging time.

Unlike other reported coordination polymer particles,[7] the powder X-ray diffraction (PXRD) pattern of Fe-Fc-HCPS indicates that the hollow microspheres are highly crystalline materials, which makes it possible to characterize the crystal structure of the hollow microspheres[8] (Figure S6 in the Supporting Information). The successful indexing of the PXRD pattern reveals that Fe-Fc-HCPS is isostructural with another layered zinc-based ferrocenyl coordination polymer,[9] and the experimental PXRD pattern is in good agreement with the calculated one (Figure S7 in the Supporting Information). The layered structure with the formula $[Fe_2O_2(FcDC)]$ for Fe-Fc-HCPS matches well with the high-resolution TEM image (Figure 1 g), and the plausible structure consists of two types of iron atoms in a distorted octahedral geometry bridged by oxygen atoms to form inner layers; the ferrocenedicarboxylato moiety adopts a synperiplanar conformation and tridentate bridging mode connecting three iron atoms to arrange obliquely along two sides of the layers (Figure S8 in the Supporting Information). The chemical composition of Fe-Fc-HCPS (Sample 3 in Table 1) was further investigated by energy-dispersive X-ray spectroscopy (EDX), element analysis (EA), and Fourier transform infrared spectroscopy (FTIR). The EDX pattern (Figure S10 a in the Supporting Information) of the sample shows the peaks of Fe, C, O, and Cl, thus indicating that the particles were the products of reaction between H_2FcDC and $FeCl_3$. The presence of Cl in the pattern is possibly due to the counteranion, $[FeCl_4]^-$, which balances the charge of the framework, or to other species.[10] EA results support the 2:1 ratio of Fe ions and dicarboxylate-functionalized organometallic ligands in the particles (Table S3 and Figure S8 in the Supporting Information). FTIR spectra (Figure S10 b in the Supporting Information) of Fe-Fc-HCPS and H_2FcDC confirm the formation of the coordination polymer from iron ions and ferrocenyl ligands, as evidenced by a red shift of the CO stretching frequency from 1687 cm^{-1} for the organometallic precursor to 1575.5 cm^{-1} for the coordination polymer. FTIR results are consistent with those of other reports about similar carboxylato coordination polymers, in which the CO stretching frequency shifts from 1653–1692 cm^{-1} for precursors to 1597–1613 cm^{-1} for polymers.[7a, 11] The thermal stability of Fe-Fc-HCPS, investigated by thermogravimetric analysis (TGA) in a nitrogen flow, shows that the hollow microspheres are stable up to at least 350 °C (Figure S11 in the Supporting Information).

The packing of layered ferrocenyl coordination polymers affords a two-dimensional channel structure,[5a] constructed with ferrocenyl groups and iron oxide layers, with a dimension along the *a* axis of approximately 10 Å, consistent with the results from the high-resolution TEM image (Figure 1 g). The microporosity of similar layered compounds with alternating organic and inorganic layers was also demonstrated by Johnson et al.,[12] and these species reversibly absorbed alcohol molecules. The presence of micropores in the shells of hollow microspheres was demonstrated by the N_2 adsorption/desorption isotherm, and a typical N_2 adsorption/desorption isotherm and micropore size distribution of Fe-Fc-HCPS (Sample 3 in Table 1) are shown in Figure 2. The adsorption/desorption isotherms (Figure 2 a) exhibit an intermediate mode between type I, which is related to microporous materials, and type IV, which is related to mesoporous materials.[13] The pore size distribution (Figure 2 b) shows that the shells of the sample contain mainly micropores with diameters of approximately 1 nm. The microporosity of the microsphere shells also can be analyzed by the "*t*-curve" method (Figure S12 in the Supporting Information).[13] A spot of mesopores was formed by the stacking of coordination polymer nanosheets. The BET and Langmuir surface areas of hollow microspheres are 73.4 and 114.4 $m^2 g^{-1}$, respectively; the surface areas of micropores and mesopores are 51.6 and 21.8 $m^2 g^{-1}$, respectively; and the total pore volume in the shells is 0.051 $cm^3 g^{-1}$. The surface area of the micropores is relatively low compared with other porous crystalline coordination polymers, which might be caused by the relatively compact structure (Figure S8 in the Supporting Information) or by the existence of an amorphous phase in the hollow microsphere (Figure 1 g).[14] The inherent microporosity in the shells is further supported by the existence of micropores around 1 nm in diameter for all the samples at different reaction times and the gradual increase of the percentage of micropores with increasing reaction time (Figure S12 and

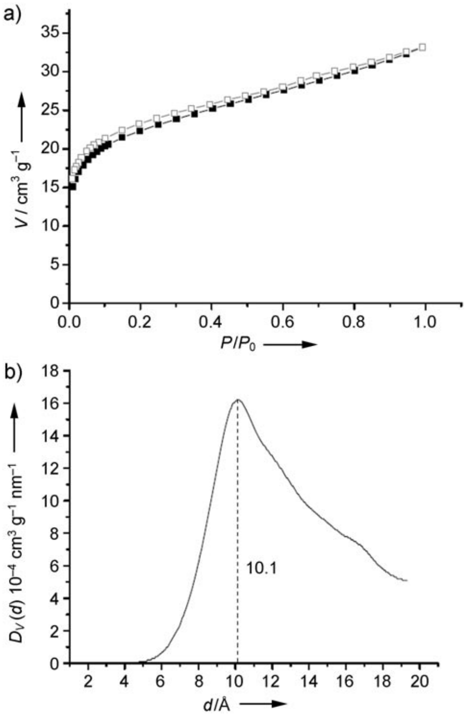


Figure 2. a) N_2 adsorption (■) and desorption (□) isotherms and b) micropore size distribution (from the HK method) of Fe-Fc-HCPS (Sample 3 in Table 1). V = volume at standard temperature and pressure, P/P_0 = relative pressure, $D_V(d)$ = differential pore volume, d = pore diameter.

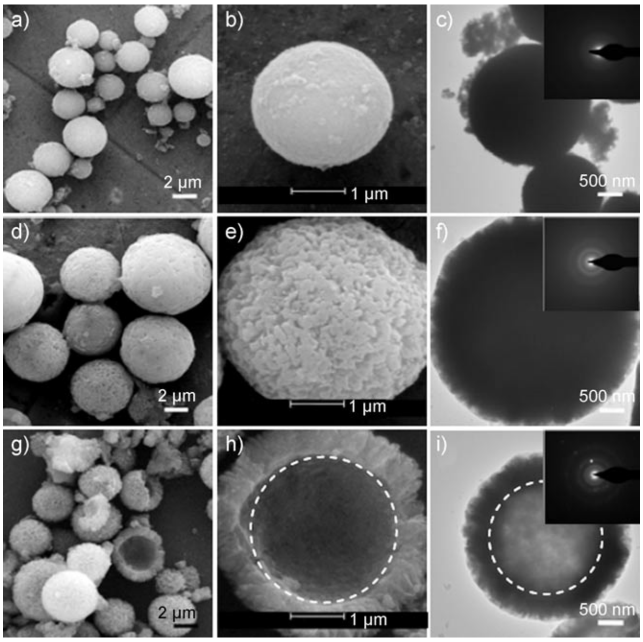


Figure 3. SEM (a, b, d, e, g, and h) and TEM (c, f, and i) images of Fe-Fc-HCPS at different reaction times: a–c) 4 h (Sample 1 in Table 1); d–f) 8 h (Sample 2 in Table 1), and g–i) 24 h (Sample 4 in Table 1). Insets are the electron diffraction patterns, and circles in the images indicate the diameters of hollow cavities.

Table S4 in the Supporting Information). These results confirm the formation of hollow coordination polymer microspheres with microporous shells by a one-pot solvothermal reaction without any additional template.

To understand the formation mechanism of hollow microspheres with micropores in the shells, we carried out the experiments for different lengths of time and monitored the reactions by SEM and TEM. As shown in Figure 3 a–c, early in the particle-formation process (4 h for Sample 1 in Table 1), both small crystallites and larger spherical particles are observed, with a mean diameter (d_{sph}) of 2.42 μm; the surface of the spherical particles is relatively rough, and even some small crystallites were adsorbed onto the larger particles. With longer reaction time (8 h for Sample 2 in Table 1, Figure 3 d–f), the diameter of spherical particles increases ($d_{sph} = 5.18$ μm), the rough surface of the microspheres is more evident, and the resultant particles are still solid. After 10 h (Sample 3 in Table 1), small cavities begin to form inside the solid spheres ($d_{hol} = 1.38$ μm), as confirmed by SEM and TEM (Figure 1). The nanosheets form at the outer layer of the spheres, and micropores appear in the shells of microspheres owing to the crystallization of coordination polymers. For the sample at 24 h (Sample 4 in Table 1, Figure 3 g–i), the solid evacuation is much more obvious and the diameter of the cavity increases to approximately 2.85 μm (Figure 3 i). The thin shell cannot withstand the stress associated with crystallization for large spheres, which possibly leads to the slight decrease of the mean diameter of microspheres ($d_{sph} = 4.02$ μm). The process of crystallization can also be confirmed by the change of the electron diffraction (ED) and PXRD patterns for samples at 4, 8, and 24 h (Figure S9 in the Supporting Information and insets of Figure 3 c, f, i).

This formation process of the hollow coordination polymer microspheres is similar to those in the preparation of hollow TiO_2 and Sn-doped TiO_2 nanospheres by Zeng and coworkers,[15] in which Ostwald ripening controlled the growth of spherical particles and formation of hollow interiors. Ostwald ripening[16] is a facile template-free strategy for the preparation of hollow materials in which the formation of a hollow structure is induced by mass diffusion from the interior of solid aggregates, where crystallites are smaller and less compact, to the exterior with larger crystallites. The time-dependent SEM images, ED patterns, and PXRD patterns (Figure S9 in the Supporting Information) of hollow microspheres indicated that the formation of hollow structures took place after the crystallization of coordination polymers, which is consistent with the Ostwald ripening process.[16] Furthermore, Jung et al.[11a] proposed another formation mechanism of coordination polymer tubes without any additional template, in which the initially formed solid lumps acted as the template for the formation of new shells and subsequently dissolved to produce the final hollow structure.

To fully verify that the hollow microspheres were generated through the Ostwald ripening process instead of the self-template-directed mechanism,[11a] the aging of the solid spheres (Sample 2 in Table 1) in pure DMF at 125 °C was performed for different lengths of time: 2, 6, and 10 h. TEM images of samples (Figure 4) indicate that the hollow structure forms even without initial reagents (metal salts

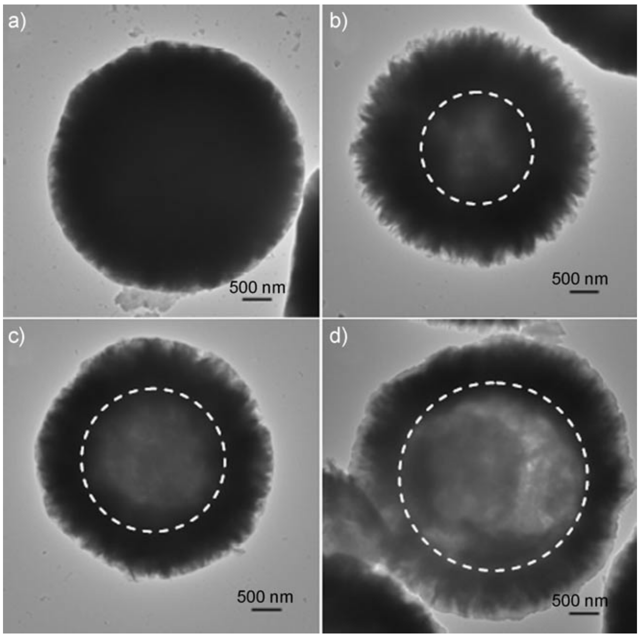


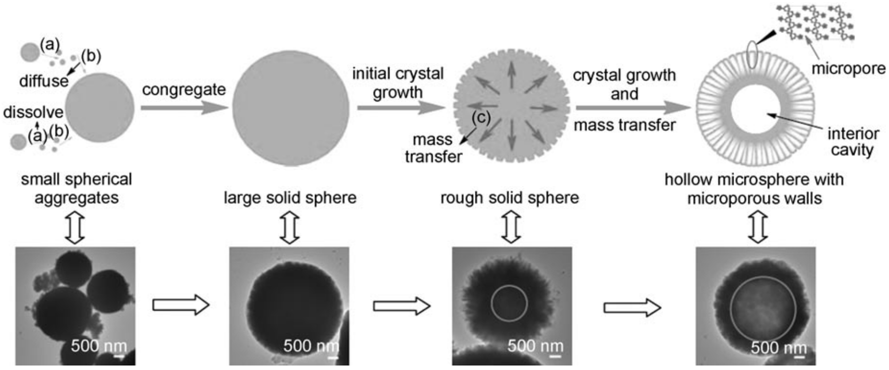
Figure 4. TEM images of samples after aging Fe-Fc-HCPS (Sample 2 in Table 1, Figure 3 d–f) for different times: a) 0 h (Sample 2 in Table 1), b) 2 h (Sample 2 A in Table 1), c) 6 h (Sample 2 B in Table 1), and d) 10 h (Sample 2 C in Table 1). Circles in the images indicate the diameters of hollow cavities.

and organic ligands), and the sizes of microspheres show no pronounced change, but the diameter of the cavity increases with prolonged aging. As a result, the formation of the resultant hollow microspheres originates from the mass transfer of small crystallites inside the spheres to the outside owing to Ostwald ripening, which does not require any additional reagent or template.

On the basis of above results and analysis, the formation of hollow microspheres with microporous shells results from the mass transfer and crystallization of small crystallites, that is, from the Ostwald ripening process. The detailed formation mechanism of hollow microspheres is depicted in Scheme 1. Firstly, owing to the coordination reaction of metal salts and dicarboxylic acid ligands, large numbers of small coordination polymer crystallites nucleate from solution and quickly congregate to larger solid spherical particles to decrease the surface energy. Under solvothermal conditions, the outer crystallites grow into larger crystals, while inner crystallites dissolve and migrate out to reduce their higher surface energies, thus finally forming the hollow cavities inside the spheres. During the solid evacuation process, the crystal structure of layered coordination polymers would induce the growth of crystalline nanosheets outside of the spheres, producing rough hollow spheres. Meanwhile, the crystallization of coordination polymers endows the shells of hollow microspheres with microporosity.

Analysis of the size of the cavities indicates that the hollow pore diameter can be tuned in the range of micrometers by increasing the reaction time or aging time (Table 1). The diameter of the hollow pore reached approximately 2.8 μm, and the ratio between the diameters of the cavity and the sphere was as high as approximately 0.7 for the sample with a reaction time of 24 h (Sample 4 in Table 1). These results suggest that the pore size of the coordination polymer can be extended to the range of macropores by increasing the reaction time. We also investigated the utility of this method for producing hollow spheres of coordination polymers with other metal ions, such as Mn^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}. Hollow microspheres can be obtained for all of these species, thus indicating that Ostwald ripening is a general method to prepare hollow coordination polymer microspheres. Although Ostwald ripening has been widely used to prepare hollow inorganic materials, such as metal oxides,[15] hydroxides,[15a] and sulfides,[15a,16] to our knowledge the application to the synthesis of hierarchically hollow coordination polymer microspheres has not been reported to date.

In conclusion, we demonstrate a general and template-free strategy for the preparation of hollow microspheres with microporous shells by a simple one-pot solvothermal method without any additional template, the shell of which is built from porous coordination polymer. The Ostwald ripening mechanism is responsible for the formation of the hollow structure, as shown by SEM, TEM, electron diffraction, and PXRD investigations. The tunability and functionality of the coordination polymer make it easy to control the size of micropores inside the shells and functionality of frameworks by choosing different metal ions or ligands, or by subsequently modifying frameworks with functional groups. The hollow coordination polymer microsphere has great potential for applications in hydrogen storage, controllable drug delivery, catalyst support, or highly efficient electrochemical capacitive energy storage.



Scheme 1. Proposed formation process of Fe-Fc-HCPS by the Ostwald ripening mechanism with corresponding TEM images. a) Dissolution of small particles; b) diffusion and redeposition of the dissolved species; c) dissolution and outmigration of inner crystallites.

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