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**Microstructures**

# Easy Synthesis of Hollow Polymer, Carbon, and Graphitized Microspheres**

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Hollow spheres with tailored shell structures and large internal voids are attractive materials as high-performance catalyst supports, biomaterials, photonic-band-gap materials, thermal and acoustical insulation materials, and electrode materials. Various types of hollow spheres with different compositions, such as polymer, silica, carbon, metal, or metal oxide, can be synthesized by a number of methods, using vesicles, emulsions, spray-drying, hydrothermal reduction, layer-by-layer assembly, and hard templating methods.[1] Among such systems, hollow carbon spheres (HCS), especially those with graphitic shells, are very attractive owing to their special properties, that is, good electrical conductivity, outstanding thermal stability, and satisfactory oxidation resistance at moderate temperature.

Most pathways for the production of HCS rely on hard templating[2–4] or hydrothermal reduction.[5–8] The obtained hollow spheres usually have diameters around 200–500 nm. HCS with uniform diameter can be prepared by a hard templating method, but it is difficult to obtain graphitized shells. To prepare hollow graphitic spheres (HGS), hydrothermal reduction is one option.[5,6] However, the reaction is not easily controlled, and highly nonuniform hollow spheres result. Alternatively, HGS can be prepared through thermal pyrolysis with the aid of transition-metal species[9,10] or by a microemulsion pathway.[11] The resulting HGS usually have diameters less than 150 nm, the shapes are not perfectly spherical, and the yields are quite low. These detractors severely limit their practical applications. Hence, it remains a great challenge to develop an easy approach for the preparation of HGS, especially micrometer-sized HGS, which could be interesting as reactors for three-phase (solid, liquid, and gas) reactions owing to their large central void. To our knowledge, such HGS have not been reported to date.

Herein, we demonstrate a new approach for a synthesis that can be adjusted to deliver either micrometer-sized hollow polymer, carbon, or graphitized spheres. Micrometer-sized solid polymer spheres (PS) are prepared in an alcoholic solution (see the Experimental Section) and are then hollowed out to form hollow polymer spheres (HPS) by a surprisingly simple water washing step. The HPS can be easily converted into HCS by mild pyrolysis. In the presence of a graphitization catalyst, graphitized shells are accessible. The synthesis is easily scalable to obtain large quantities of product with high purity.

The PS were prepared by the polymerization of 2,4-dihydroxybenzoic acid (DA) and formaldehyde in the presence of lysine. The non-ionic surfactant F127 is used as an additive to achieve a homogeneous, spherical product.[12] Figure 1a shows an SEM image of the obtained polymer spheres with a relatively uniform size of (1.3 ± 0.1) μm. Figure 1b, which displays a typical large-scale TEM image, reveals that these polymer spheres are essentially solid. If the center were hollow or would contain alcohol, it would be possible to detect this void in the dried spheres by TEM.[13] The pyrolyzed products (Figure 1c) consist of solid carbon materials, thus indicating the structural stability of the PS during pyrolysis. The structural transformation from polymer to carbon spheres is quite smooth, and no HCS were found in the product.

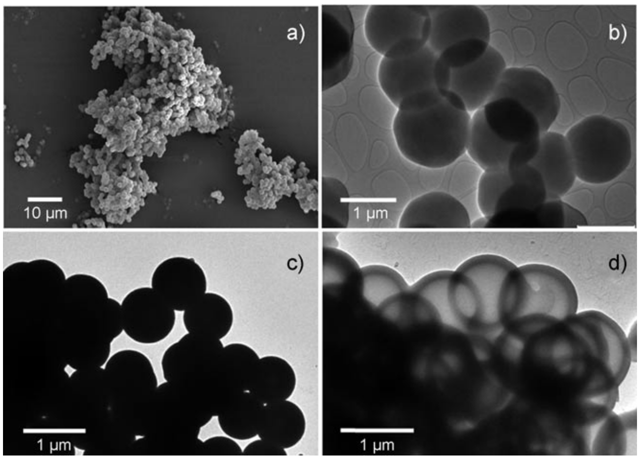

***Figure 1.*** a) SEM image of the polymer spheres; b–d) TEM images of the polymer spheres (b), the carbon spheres (c), and the hollow polymer spheres (d).

To convert the solid PS into graphitic spheres at low pyrolysis temperatures, it is necessary to introduce a graphitization catalyst (e.g. Fe species). The Fe species can be incorporated through the carboxylic acid groups. However,

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before the exchange step we decided to test the structural and morphological stability of the PS by immersion in distilled water and shaking for 24 h. After filtration and washing with distilled water, surprisingly, the TEM image of the product (Figure 1 d) reveals hollow spheres instead of the solid starting material. The diameter and shell thickness are approximately 1.2 μm and 130 nm, respectively. This process of PS synthesis and water treatment resulting in HPS was found to be highly reproducible. As mentioned above, direct pyrolysis of the PS leads to the formation of solid carbon spheres. This finding confirms that the interior part of the initial spheres contains nonvolatile compounds that were insoluble in ethanol and can be converted into carbon, forming uniform carbonaceous material. Otherwise, hollow spheres would be the product after EtOH washing or pyrolysis. Thus, the HPS are generated during the water treatment step. Water can selectively remove the interior part of the PS while leaving the exterior polymer shell undamaged. The question thus arise as to whether there are any differences between the composition of the hollow and solid PS.

To determine the differences between the PS and water-washed polymer spheres (PS-W), the samples were characterized by FTIR spectroscopy. The collected filtrates from the water treatment step (PS-W-F) and from the original synthesis medium (PS-F) were analyzed as well. For better comparison, F127, DA, and lysine were also measured with the same IR spectrometer. As seen in Figure S1 (Supporting Information), the spectrum of PS-F exhibits strong bands at 2860–2969 $cm^{-1}$ (alkyl C–H stretching in $CH_2$) and 1106 $cm^{-1}$ (C–O stretching), which indicate that F127 is present in the filtrate. The spectra of PS and PS-W are essentially identical in the range of 500–3500 $cm^{-1}$, thus indicating that the compositions of the as-made and water-treated polymer spheres are quite similar. The weak bands at 2860–2969 $cm^{-1}$ and 1106 $cm^{-1}$ reflect that the amount of F127 present is very small, if there is any. The spectra of PS and PS-W also show a strong band at 1580–1600 $cm^{-1}$ arising from an aromatic ring stretching vibration. The bands in the range of 700–885 $cm^{-1}$ are related to the out-of-plane deformation mode of C–H in substituted benzene rings. The spectrum of PS-W-F has visible bands at approximately 2866–2958 $cm^{-1}$ and a sharp signal at 1106 $cm^{-1}$, which may indicate that some F127, encapsulated in the polymer spheres, was dissolved. The bands at 1580–1600 $cm^{-1}$ and 700–885 $cm^{-1}$ indicate that some species containing DA were dissolved as well. Owing to the overlapping of bands, it is difficult to clearly identify bands belonging to lysine. However, the presence of lysine in PS-W-F was confirmed by element analysis. As seen in Table S1 (Supporting Information), the nitrogen content in samples PS and PS-W are rather similar, indicating that lysine is present in both. Clearly, PS-W-F contains more nitrogen than PS, thus indicating that lysine had been washed out from the polymer spheres and was enriched in the filtrate.

Electrospray ionization mass spectrometry (ESI-MS) was also used for analysis of the filtrate (see the Supporting Information).[14] The spectra reveal that, in addition to monomeric lysine, DA and metaformaldehyde oligomers are present as well. By comparing the intensities of the obtained signals it was shown that lysine and its condensation products with formaldehyde occur in higher intensities than DA and metaformaldehyde, respectively. This finding indicates a preferred dissolution of lysine from the PS, which had formed a salt-like complex through its amine groups and the carboxylic acid groups of DA in the solid material. In the presence of water, these complexes are easily dissolved. Other detected oligomers result from the condensation of lysine, DA, and/or formaldehyde. It is noteworthy that no signals which are attributed to condensation products of DA and formaldehyde were observed. These facts are in agreement with the chemical analysis, that is, higher N content in the water phase than in the washed solid spheres. It may thus be concluded that lysine molecules ion paired with DA act as a soft template for the formation of (hollow) carbon spheres.

As the PS are very sensitive to water, and during the synthesis the addition of formaldehyde solution (37%) brings in a small volume of water (ca. 0.3 vol% of the total volume of EtOH), the influence of the water content on the structure of the polymer products was studied. When the water volume fraction exceeds 4 vol% of the total the solvent, the resulting product consists of raspberry-shaped particles. No HPS were obtained by a water treatment step. Furthermore, crotonaldehyde (99%, no water; pure formaldehyde alcoholic solution is difficult to obtain) instead of formaldehyde solution was used to carry out an otherwise identical synthesis. In this case, only solid spheres were obtained, even though the obtained PS were washed intensively with water. This result indicates that the right water content is very crucial for the preparation of homogeneous solid and hollow spheres.

We suggest that the small amount of water in the system facilitates the protonation of the amine groups to $NH_3^+$ groups, which then interact with the negatively charged carboxylate counterions, while the stable polymer shell is preferentially formed on the exterior of the solid spheres by the copolymerization of DA and formaldehyde. The interior may consist of ion-paired salt-like oligomers, which are soluble in water but sufficiently stable to be converted into a carbonaceous solid during pyrolysis.

To convert the polymer into graphitized carbon, $Fe^{3+}$ cations were introduced into PS (denoted as PS-Fe) through the carboxylate and amine groups.[15,16] The product obtained after pyrolysis and HCl washing is denoted as CS-Fe. The TEM image in Figure 2 a shows sample PS-Fe consisting of hollow spheres with a diameter of approximately 1 μm and a shell thickness of (60 ± 10) nm. The TEM image of CS-Fe in Figure 2 b shows that this sample retained the hollow shell morphology. The microstructure of these spheres is graphitic, as shown in Figure 2 c. The average thickness of the graphitic sheet is estimated to be 10 nm. The diameter of the CS-Fe is around 900 nm, the shell thickness is about (85 ± 10) nm. Pyrolysis results in approximately 10% linear shrinkage from polymer to carbon spheres. The increased shell thickness after pyrolysis is due to the formation of mesopores (as revealed by $N_2$ sorption), which cause the shell expansion. Notably, the growth of graphitic carbon seems strictly confined within the shell. To verify that no graphitic carbon had grown on the inside, the sample was ground in a mortar to expose the interior part of these HGS; this sample was then analyzed with STEM. As seen in Figure 2 d, e, the broken parts indicate

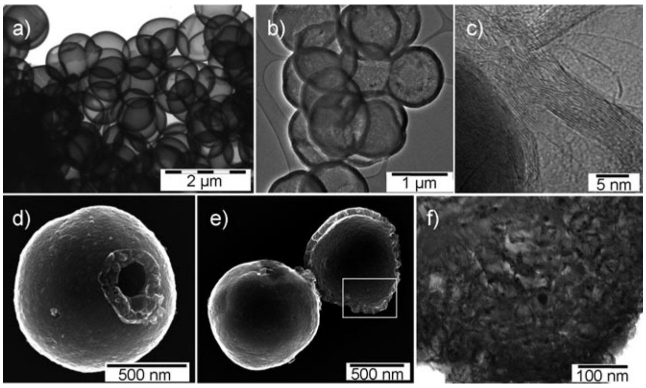

*Figure 2.* TEM images of a) Fe-chelated hollow polymer spheres (PS-Fe) and b,c) the resultant hollow graphitic spheres (CS-Fe) after acid leaching. d,e) SEM and f) STEM images of CS-Fe after acid leaching and grinding.

that these spheres are hollow. The external and internal surfaces of the spheres are rather smooth, there are no visible cavities, and no other carbon nanostructures exist on both internal and external surfaces. This result is in good agreement with the TEM observations. By visualizing the same area by STEM at a higher magnification (Figure 2 f), well-developed turbostratic graphite structures can clearly be observed in the shells. Notably, the confined growth of graphitic structures within the carbon shell is responsible for the pseudomorphic transformation from polymer to graphitic carbon. The black dots correspond to the remaining Fe-based particles, which are tightly protected by the graphitic carbon against leaching by concentrated HCl.

The crystallinity of CS-Fe was also characterized by XRD. Figure 3 a shows its XRD pattern, which displays typical reflections of well-developed graphitic carbon and weak reflections of Fe and $Fe_3C$. The particle sizes of the Fe particles were estimated to be approximately 20 nm by the Scherrer equation. An estimated graphitization degree of the HGS is about 50 %. This value is lower than that of perfect graphite, owing to the nanosized turbostratic graphite structures, as revealed by the TEM and SEM studies. The well-protected Fe-based nanoparticles ensure that these hollow spheres are magnetically separable by a magnet. Thus, CS-Fe can be used as magnetically separable catalyst or adsorbent.[17]

The porosity of the obtained hollow graphitic spheres was analyzed by $N_2$ sorption. Figure 3 b shows a type IV isotherm for CS-Fe, thus indicating the mesoporosity of the shells of the HGS. This finding is in good agreement with TEM and STEM observations. The specific surface area and total pore volume of CS-Fe are 444 $m^2 g^{-1}$ and 0.36 $cm^3 g^{-1}$, respectively.

In comparison, the $N_2$ sorption isotherm (Figure 3 b) of CS (CS was obtained by direct pyrolysis of PS under the same conditions as CS-Fe) is essentially of type I, revealing predominantly microporous features. Sample CS has somewhat lower surface area (351 $m^2 g^{-1}$) and smaller total pore volume (0.17 $cm^3 g^{-1}$) than CS-Fe. The sorption data thus clearly reveal that the Fe-based catalyst leads not only to the formation of graphitic nanostructures but also to the development of additional mesopores during pyrolysis.

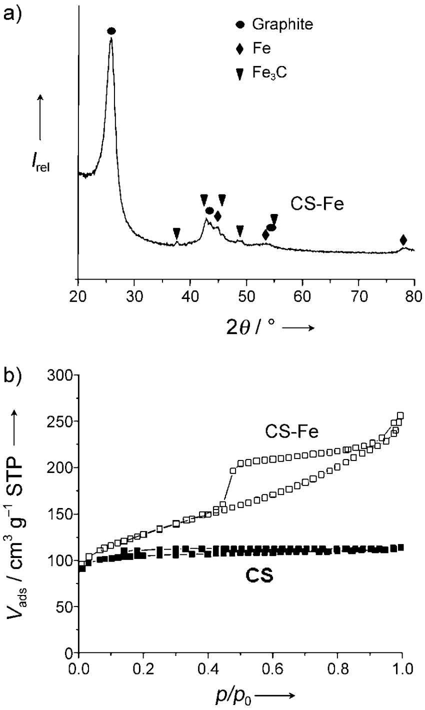

*Figure 3.* a) XRD pattern of hollow graphitic spheres CS-Fe after acid leaching. b) $N_2$ sorption isotherms of CS-Fe and CS (carbon spheres).

In summary, we have established a facile and tunable synthetic procedure for the preparation of micrometer-sized hollow spheres, including polymer, carbon, and graphitized spheres. Starting from one type of polymer sphere, diverse products, such as core–shell and solid spheres having amorphous or graphitized microstructure, can be obtained, depending on the post-synthesis treatment methods. By combining those unique properties with the inherent properties of hollow spheres, such as low density, high surface area, thermal insulation, and electronic properties, these hollow graphitic spheres have great potential for a variety of applications, such as for magnetically separable catalysts, fuel cell electrode materials, drug delivery agents, and adsorption and separation agents.

## *Experimental Section*

Polymer spheres were prepared by the polymerization of 2,4-dihydroxybenzoic acid and formaldehyde in the presence of lysine as polymerization catalyst. In a typical synthesis, DA (1.4 g), L-lysine (0.24 g), and Pluronic F127 (1.5 g) were dissolved in EtOH (500 mL) at 80 °C for 2 h under vigorous stirring. After addition of formaldehyde (1.48 g), the clear solution became turbid white in color, then beige to orange with time. After 1–3 days, the yellow polymer was collected by filtration, washed with EtOH, and dried at 50 °C. For Fe loading, the polymer product was immersed in aqueous $FeCl_3·6H_2O$ (0.24 M) overnight. Subsequently, the polymer was washed, dried, and then pyrolyzed at 850 °C for 3 h in Ar. The obtained black powder was treated with concentrated HCl (37 %) to remove the leachable Fe-based particles. Finally, hollow graphitic spheres were obtained after washing and drying. For the syntheses of other spheres, refer to the procedures given in the text. Variation of solvent amount leads to a wider size distribution. With other solvents (e.g. methanol, isopropyl alcohol, or glycerol), no spherical products were obtained under any of the conditions explored. Moreover, resorcinol and phloroglucinol as the precursors have been explored. However, no hollow spheres were obtained. Thus, DA is unique for this synthesis.

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