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LETTER

Simple morphology-controlled synthesis of hollow carbonaceous particles

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Introduction

In recent years, hollow carbonaceous particles (HCPs) have attracted great attention for their unique properties including light weight [1], thermal insulation, and chemical stability [2], and thus are desired to be applied as drug delivery [3], catalyst supports [4], gas storage [5], micro-reactor [6], and so on. At present, various approaches have been used to synthesize HCPs, such as the hard template method [7], soft template method [8, 9], hydrothermal reduction [10, 11], and so on. However, the disadvantages of these synthetic methods are that the reaction is not easily controlled and time-consuming, and it is difficult to regulate the morphology of the products. Consequently, it is necessary to develop an efficient and low cost method for synthesizing HCPs. Recently, Lu et al. [4] have reported a soft template method to synthesize HCPs through polymerization reaction. However, this study is motivated by the desire to synthesize hollow graphitic spheres, and it is hard to obtain morphology-controlled and size-regulated [12] HCPs.

In this letter, we demonstrate a simple and convenient approach for preparing morphology-controlled HCPs in a simple emulsion system. The formed products are high yield, stable, and uniform. Remarkably, it has been found that three types of HCPs, including hollow microspheres, hollow bowl-like capsules, and hollow balloons, could be easily controlled by regulating the reaction time. This simple synthesis strategy will promote a valuable way for understanding of the HCPs growth, and moreover, the as-synthesized HCPs may lead to many new potential applications.

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Experimental

All the chemical reagents were A.R. grade and used without further purification. In a typical procedure, 0.01 mol of 2,4-dihydroxybenzoic acid, 0.01 mol of lysine, 0.02 mol of formaldehyde, and 1.0 g cetyl trimethyl ammonium bromide (CTAB) were dissolved in absolute ethyl alcohol (300 mL) at the same time with magnetically stirring, and kept reacting at 80 °C for 24, 12, or 6 h, then precipitates were collected and washed with water. After that, the obtained samples were dried in a vacuum at 60 °C for 6 h.

Characterization

The morphology observation of the samples was examined with scanning electron microscopy (SEM, Philips XL-30) and transmission electron microscopy (TEM, Philips Tecnai-10). Powder XRD patterns were recorded on a MSAL-XD2 X-ray diffractometer with Cu Kα radiation (36 kV, 20 mA, $\lambda = 1.54051$ Å). FT-IR spectra were measured by an Equinox 55 (Bruker) spectrometer with the KBr pellet technique ranging from 500 to 4000 cm^{-1}.

Results and discussions

The XRD pattern of a typical sample (Fig. 1a) exhibits one broad peak at 2θ of 10°–30°, which is corresponding to the (002) plane, and results from the stacks of parallel layers. The broadening of the peak indicates the possible presence of an amorphous carbon phase within the samples [13, 14].

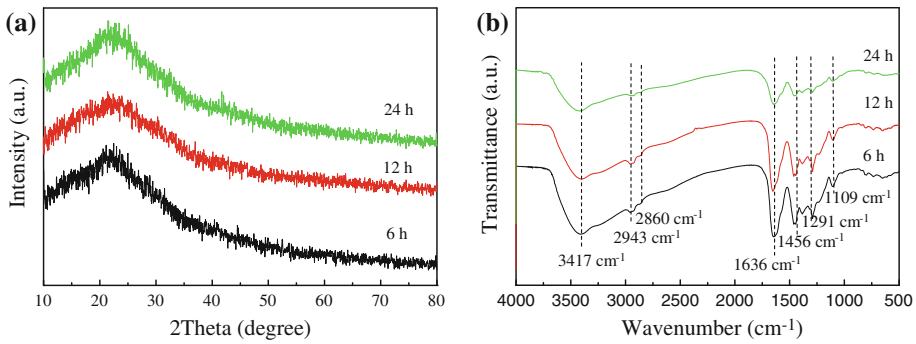

Fig. 1 XRD patterns of the as-obtained particles (**a**) and FT-IR spectra (**b**)

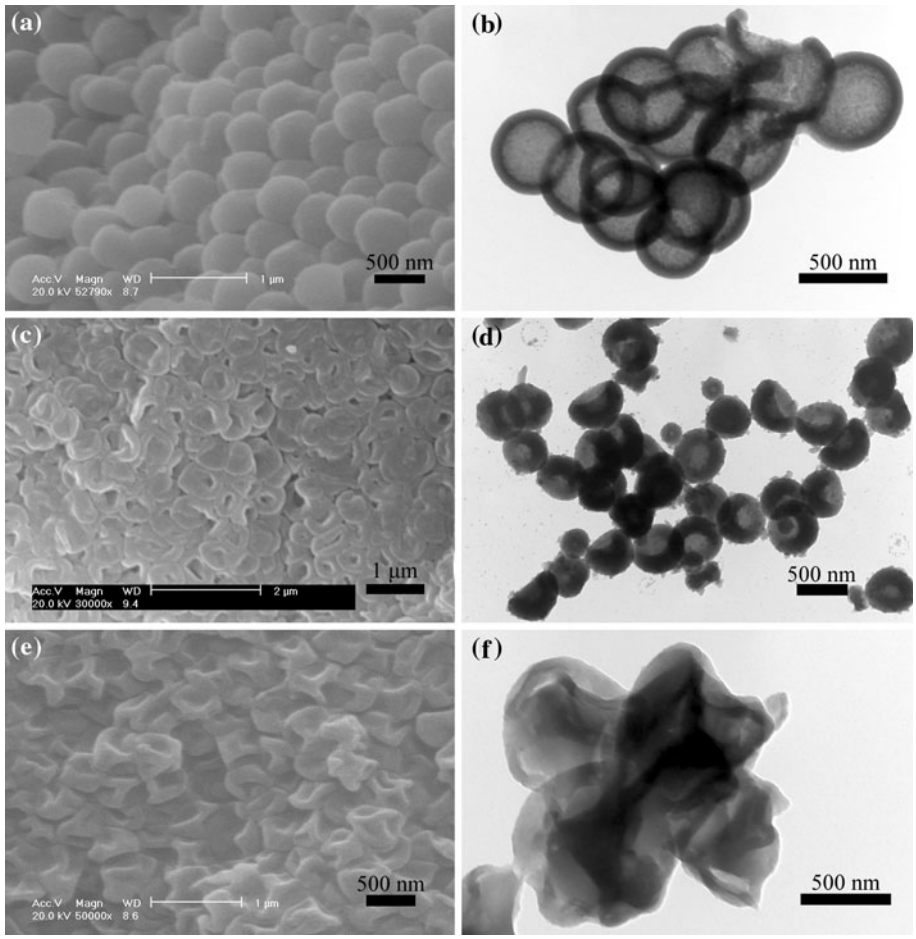

Fig. 2 The SEM and TEM images of hollow carbonaceous particles prepared for different times: **a**, **b** 24 h; **c**, **d** 12 h: **e**, **f** 6 h

The FT-IR spectra in Fig. 1b are used to characterize these HCPs. It displays that the strong peak at 3417 cm^{-1} is attributed to the O–H bending vibration [15], which implies the existence of hydroxyl groups. The infrared spectrum peaks at 1636 and 1456 cm^{-1} due to the stretching vibration of carboxyl groups and phenyl group [15], respectively, exhibiting that the composition of the HPS may be a kind of carbonaceous polymer-like phenolic resin. The absorption peak at 1109 cm^{-1} corresponds to the C–O stretching, and the peaks at 2934, 2860, and 1291 cm^{-1} originate from the methyl, methylene, and C–H stretching vibration. These results show that there are a large number of hydroxyl and carboxyl groups on the surface of the particles, which may make them utilized as confined micro-reactors and provide a potential avenue to load other functional groups, molecules, ions, and nanoparticles.

Figure 2 displays the morphology of the HCPs synthesized at 80 °C for different reaction times. The SEM image in Fig. 2a reveals that the samples synthesized for 24 h consist of a large amount of uniform microspheres with a diameter of about 500–600 nm, and the morphological yield of the microspheres is approximately 100%. Figure 2b presents the TEM image of the as-obtained microspheres. It can be observed that the microspheres are

hollow and monodisperse, and the shell thickness of the hollow microspheres is about 90–100 nm. When the reaction time reduces to 12 h, the hollow bowl-like capsules are synthesized, as shown in Fig. 2c, d. It is clear that the shell thickness of the hollow bowl-like capsules is less than 90 nm, because there is not enough polymerizing time for developing the shell to 90 nm. The formation of the hollow bowl-like capsules may be caused by the collapse of the hollow microspheres with shell thickness less than 90 nm. The collapse occurred due to the pressure difference caused by the occurrence of capillary forces during drying [16, 17]. In addition, as the reaction time declines to 6 h, hollow balloons are fabricated (Fig. 2e, f). The typical TEM image (Fig. 2f) shows that the shell thickness of the hollow balloons is approximately 40–50 nm. This morphology samples may be also shaped from collapse. These results indicate that declining the reaction time leads to thin the shell thickness of the samples [16].

During a series of experiments, we find that CTAB plays a crucial role on achieving size-controlled products. It acts as the so-called controlling reagent rather than the template of shaping hollow particles. In order to confirm the role of CTAB, it was replaced by sodium dodecyl benzene sulfonate (SDBS), while the system was kept at 80 °C for 24 h and other conditions are not changed. Figure 3a, b displays that hollow carbonaceous microspheres with average size about 1.6 μm can be obtained by using SDBS. This result verifies that the role of CTAB is not as template. It is worth noting that other types of surfactants also play a vital role in controlling the size of the products. The block copolymers, such as F127 and P123, were used as surfactants. When 1.0 g F127 is used and other conditions remain the same, we get hollow carbonaceous microspheres with an average diameter of 1.2 μm, as shown in Fig. 3c, d. On further study, the surfactant is changed to P123 (1.0 g), keeping other conditions the same. A large number of hollow carbonaceous microspheres with an average diameter of 1.0 μm can be obtained (Fig. 3e, f). It is also found that in this system, the content of the used surfactants dose not significantly affect the size of the HCPs.

Consequently, regulating the reaction time can synthesize three types of HCPs. The size of products can be controlled using different surfactants while keeping other conditions the same. Of course, to control the size of the

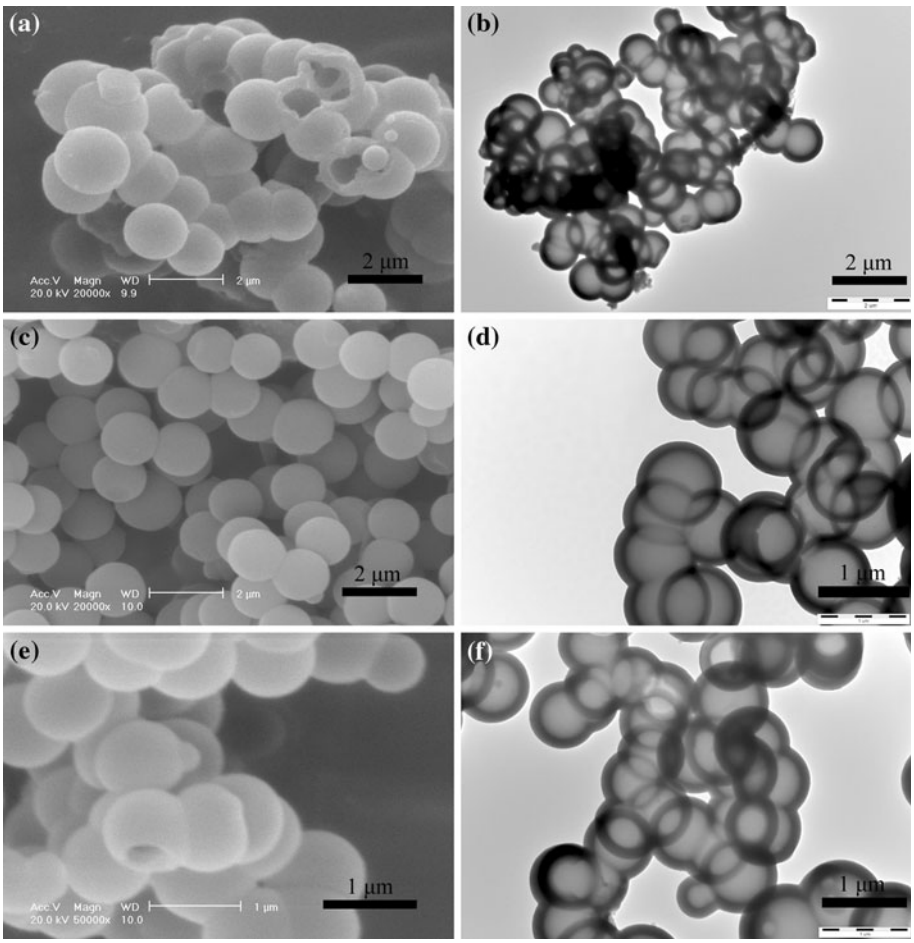

Fig. 3 The SEM and TEM images of hollow carbonaceous microspheres prepared by different surfactants at 80 °C for 24 h: (**a**, **b**) SDBS; (**c**, **d**) F127; (**e**, **f**) P123

samples accurately and its distribution, considerable kinetic and other principles in the emulsion system should be further studied. The study is now in progress.

Conclusions

In summary, morphology-controlled HCPs are successfully synthesized by a simple approach. Three types of HCPs such as hollow microspheres, hollow bowl-like capsules, and hollow balloons are tailored by controlling the reaction time. This approach is facile and convenient, and there is no need for more procedures to obtain HCPs. The as-synthesized products with hollow structure and a large number of hydroxyl and carboxyl groups may serve as drug delivery, catalyst supports, gas storage, and so on.

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