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Synthesis, characterization and growth mechanism of mesoporous hollow carbon nanospheres by catalytic carbonization of polystyrene

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ABSTRACT

Mesoporous hollow carbon nanospheres (HCNs) were synthesized through the carbonization of polystyrene (PS) under the combined catalysis of organically-modified montmorillonite (OMMT)/cobalt catalyst at 700 °C. The morphology, microstructure, phase structure, textural property and surface composition of the obtained mesoporous HCNs were investigated by field-emission scanning electron microscope, transmission electron microscope (TEM), high-resolution TEM, X-ray diffraction, Raman spectroscopy, N_2 sorption and X-ray photoelectron spectroscopy. It was found that OMMT not only promoted the dispersion of cobalt catalyst in the PS matrix but also affected the degradation of PS into light hydrocarbons and aromatics. The lattice oxygen of the cobalt catalyst facilitated the decomposition of light hydrocarbons and aromatics into atomic carbon during the formation of the mesoporous HCNs. A possible mechanism was proposed to explain the growth of mesoporous HCNs through the carbonization of PS under the combined catalysis of OMMT/cobalt catalyst. More importantly, this approach also offers a new potential way to transform waste polymer materials into mesoporous HCNs, which may be used as catalyst supports, adsorbents, storage media and templates for the synthesis of other useful hollow materials.

1. Introduction

Hollow carbon spheres (HCSs) with a structure of hollow core and carbon shell have attracted great attention, due to their unique physicochemical properties such as low density, large inner space and specific surface area, and wide applications in catalyst supports, adsorbents, storage media and templates for the synthesis of other useful hollow materials [1–9]. The common methods for the preparation of HCSs are chemical vapor deposition [10,11], hydrothermal treatment [7] and template-assisted method [4,7,12–16] using ethylene [10], acetonitrile [11], sucrose [11], dopamine [14], acetone [17] or furfuryl alcohol [18] *etc.* as carbon source.

From a sustainable point of view, reutilization of waste polymer materials to synthesize carbon spheres not only shows advantages with the nontoxic, cheap and abundant sources, but also provides a potential way to recycle waste polymer materials. Recently, some studies have demonstrated that virgin or waste polymer materials including polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(ethylene terephthalate) (PET) can be converted into high value-added solid carbon microspheres (SCMs) [19–23]. For example, Pol et al. converted waste PE, PS and PET into SCMs using autoclave as reactor at 700 °C [19,20]. Qian et al. converted PP into SCMs using autoclave as reactor at 700 °C [21]. Chen et al. prepared SCMs by pyrolyzing waste PET in supercritical carbon dioxide at 500–650 °C [22].

However, to the best of our knowledge, so far, there has been only one report about synthesizing hollow carbon nanospheres (HCNs) using polymer material as carbon source. Chen et al. prepared HCNs using PP as carbon source and the combined organically-modified montmorillonite (OMMT)/$Co(Ac)_2$ as catalyst at 900 °C [23]. But the HCNs showed extreme heterogeneity in the size distribution, and they did not provide information about the textural property of HCNs, nor further study the growth mechanism of HCNs. Hence, it is of great desire to synthesize HCNs with a narrow diameter distribution and further investigate the growth mechanism of HCNs using polymer as carbon source.

Herein, based on our "combined catalysis" strategy to prepare carbon nanotubes with micro/mesoporous structure [24–29], mesoporous HCNs were synthesized by catalytic carbonization of PS under the combined catalysis of OMMT and cobalt catalyst.

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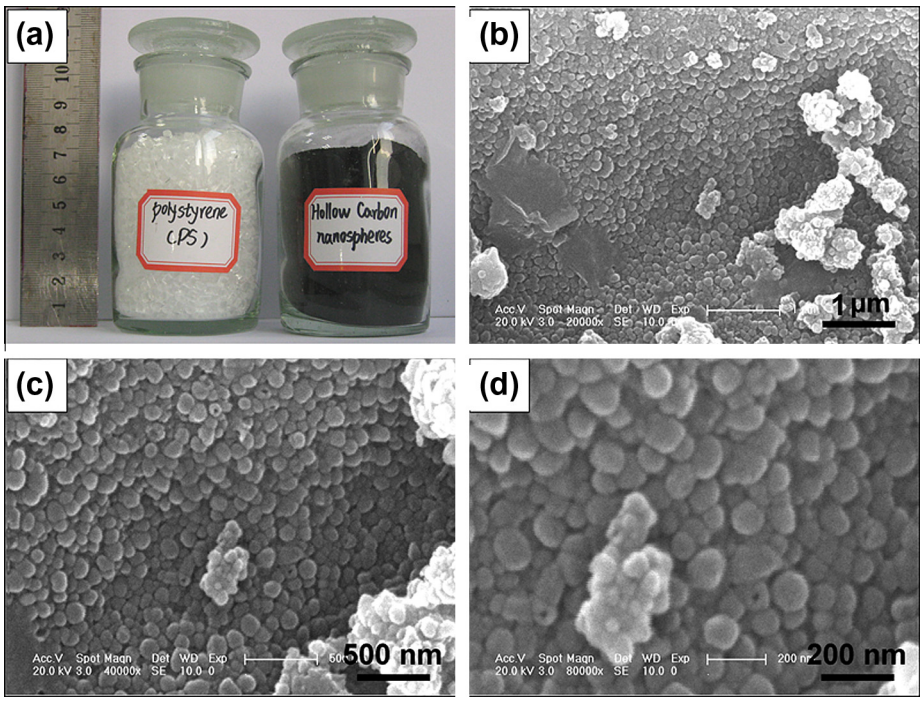

Fig. 1. Photographs of PS pellets (a, middle) and the HCN-1 (a, right) synthesized by pyrolyzing PS/10OMMT-10Co_2O_3 at 700 °C and typical SEM images of the HCN-1 (b–d) at various magnifications.

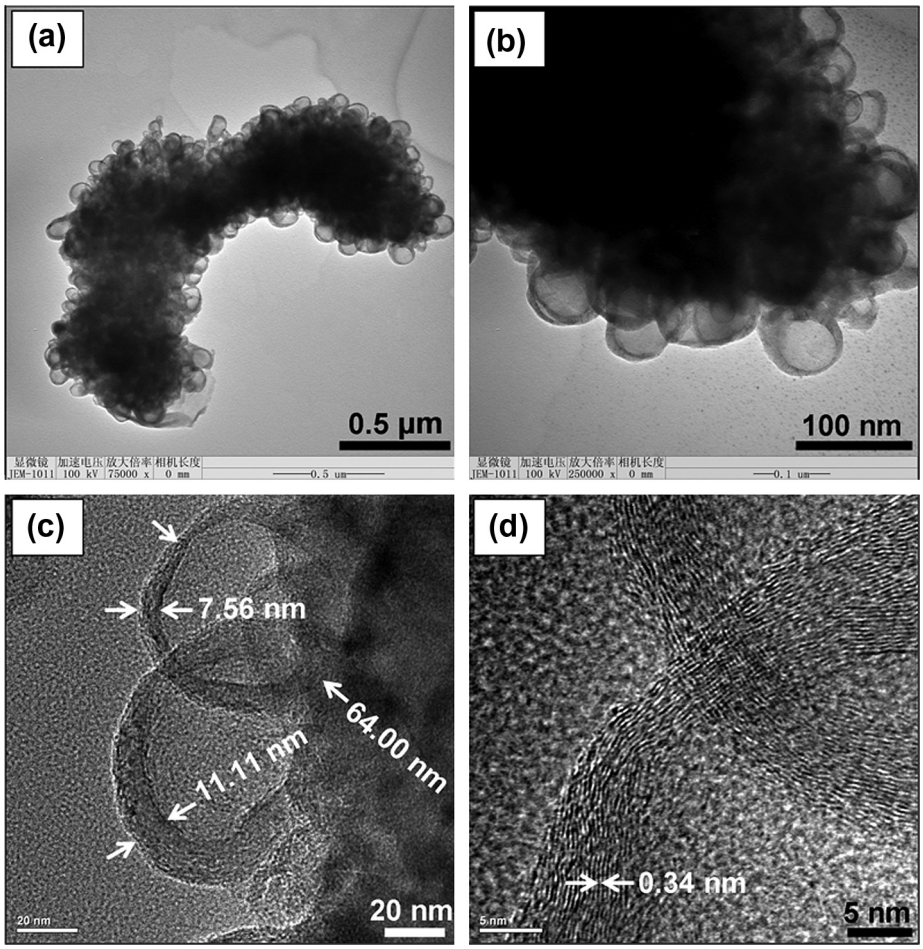

Fig. 2. Typical TEM (a and b) and HRTEM (c and d) images of the HCN-1.