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Current
CHEMICAL RESEARCH

Received: 08/08/2010
Accepted: 07/11/2010

Preparation of hollow cobaltic carbon composite microspheres via one-pot template self-ablated process

Jie Ma[1,2]*, Shuping Zhang[1,2], Wei Liu[2], Yan Zhao[2]
[1]College of Science, University of Shanghai for Science and Technology, Shanghai - 200090, (P.R.CHINA)
[2]Green Bio- & Eco- Chem. Eng. Lab, University of Shanghai for Science and Technology, Shanghai - 200090, (P.R.CHINA)
E-mail : majie0203ch@hotmail.com

Abstract

A novel one-pot template self-ablated hydrothermal method is developed to prepare hollow carbon nanocomposite microspheres. In the system, Co_2O_3 particles are used as template reagents which are eroded by glucose at moderate conditions. The hollow contained Co^{2+} composited carbon microsphere is obtained. It is found one part of glucose coated the templates reduces Co_2O_3 into $CoCO_3$ nanoparticles. Another part of glucose is carbonized into carbon. This template self-ablated process is confirmed by some important products analysis data including XRD, FTIR, SEM, and TEM. The concentration influence of glucose on the hollow nanocomposite microsphere is discussed.

Keywords

Nanocomposite; Template self-ablated process; Hydrothermal approach; Glucose; Hollow sphere.

Corresponding author's name and address

Jie Ma
College of Science, University of Shanghai for Science and Technology, Shanghai - 200090, (P.R.CHINA)

INTRODUCTION

The hollow carbon micro/nanometer spherical materials (HCSs) have been paid close attention as they reveal diverse properties and extensive applications.[1-5] The specific properties of HCSs can be modified by change of their structure and components. These HCSs materials can be applied in various fields including lithium storage,[1] catalyst supports,[2] adsorbents,[3] template materials,[4] encapsulation materials,[5] and so on.[6] Up to now, many effective methods have been demonstrated to prepare HCSs.[6-12] Among them, template approaches are commonly adopted for they show advantages upon preparing high dispersion HCSs with controllable grain size and narrow size distributions.[4,6,7] However, these methods are either complex procedures or time-consuming, because all templates must be eliminated after the template @ carbon formation. In this letter, we report a novel one-pot process for synthesizing HCSs by using Co_2O_3 grain as template and glucose as carbon resource under hydrothermal setting. Co_2O_3 grains are eroded by the reduction of glucose, meanwhile some glucoses coated the grains are carbonized under proper hydrothermal conditions. It is worthwhile to mention that surfactants are not involved in the synthesis system. The templates self-ablated process is probably alternative route to prepare hollow micro/nanometer structure materials.

EXPERIMENTAL PROCEDURES

All reagents used in the reaction are analytical grade. The typical reaction is carried out in a 20 ml capacity Teflon-lined stainless-steel autoclave. Firstly, 2 mmol Co_2O_3 powder, 0.5 g glucose and 15 ml deionized water are added into the autoclave in turn, and the mixture is sufficient dispersed in an ultrasonic generator about 20 min. Then the autoclave was sealed

and maintained at 180 °C for 6 h in a digital type temperature controlled oven, and then allowed to cool to room temperature naturally. Dark purple product is obtained after centrifugation at 4000rpm for 20 min. Three cycles processes of centrifugation/ washing/redispersion were performed for rinsing product with water or ethanol, respectively. Finally, the as-obtained precipitates were dried in a vacuum at 60 °C for more than 5h. The micro-morphologies and nanostructure of the as-synthesized products are inspected by scanning electron microscopy (SEM) and Transmission electron microscopic (TEM). The crystal phase of product is characterized by XRD equipped with graphite monochromatized Cu Kα radiation (λ = 1.54056 Å). The power X-ray diffraction (XRD) pattern is acquired in a 2θ ranges from 5° to 70° at scanning rate of 0.02° s^{-1}. The Infrared spectrum (4000–400 cm^{-1}) of product is recorded by FTIR spectrometer with 1 cm^{-1} resolution.

RESULTS AND DISCUSSIONS

The typical SEM images of sample obtained via hydrothermal at 180 °C for 6 h are shown in Figure 1. The SEM images indicate that the product is consisted of various sized irregular sphere-like grains. A clear hole in a sphere shown in Figure 1A, whose high magnification image is shown in Figure 1B, unambiguously reveals the as-obtained product should be hollow structure. Figure 1B further demonstrates that the shell (ca. 50 nm thickness) is made up of many small nanoparticles. If 1.0 g glucose is added into the same system, images shown in Figure 1C and Figure 1D of the samples indicate the irregular sphere-like product is obtained still, but the hollow structure is almost never presented. Based on the above, it suggests the irregular shape of product should be attributed to Co_2O_3 template, which is common commercial powder with wide size distribution. The more concentra-

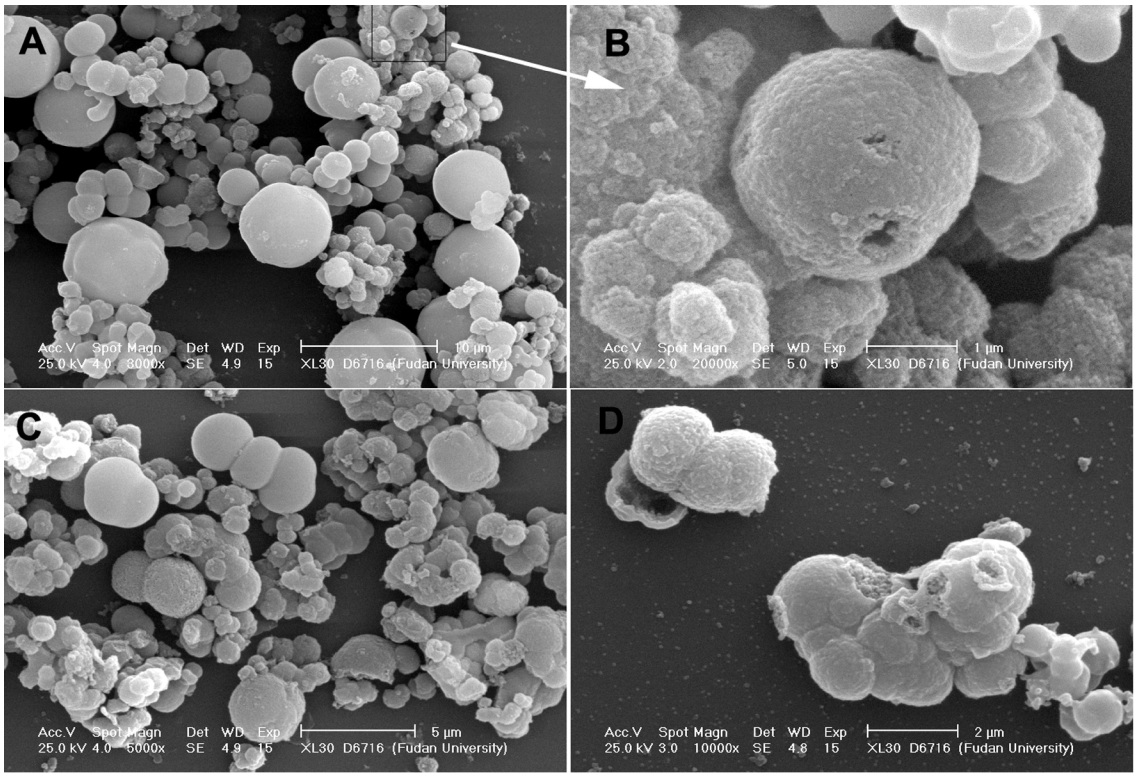

Figure 1 : The typical SEM images of samples obtained at 0.5 g (A, B) and 1g (C, D) glucose, respectively.

tion process, the more glucose is carbonized, so the size and the thickness of sphere significant increase with the amount of glucose. Figure 3D image clearly demonstrates the product include shell-like half sphere and filled particle sphere-like structures.

Figure 2a show the typical XRD pattern of the typical product obtained via the given hydrothermal. The large broad peak between 10° and 30° indicates the sample include amorphous phase, which is contributed to carbonization of glucose forming non-crystallized graphite particles[13]. Meanwhile, some peaks in the patterns are indexed to hexagonal $CoCO_3$ (spacing group R-3c (167)) with lattice constants a = 4.656(5) Å and c = 15.008(6) Å, which is comparable with the data given in JCPDS (No. 11-0692). The corresponding crystal facet indexes are labeled in the Figure 2a pattern. The average size of the $CoCO_3$ is estimated about 20 nm by the Scherrer equation. So the product is belong to nanocomposite consisted to nanoparticles.

Because the diffraction peaks of Co_2O_3 are not found in the XRD pattern, Co_2O_3 powder is completely exhausted in the hydrothermal system. The experiment result suggests that the Co_2O_3 powder is reduced into $CoCO_3$ by reacting with glucose. The Co_2O_3 template is gradually eroded by glucose absorbed on its surface, that is to say, the core of sphere is ablated by self internal reaction procedures.

The FTIR spectrum of the typical sample is shown in Figure 2b. Various functional groups are indentified by theirs characteristic absorption bands shown in the FTIR spectrum. The absorption band in 3500-3000 cm^{-1} with the peak at 3413 cm^{-1} indicates hydroxyl group existing in the products, which is assigned to water and remainder -OH in carbonized process of glucose[14], meanwhile, the weak absorption intensity in 1000-1300 cm^{-1} further shows only a handful of -OH is residual in the product Some remained C-H groups are detected for its characteristic absorption peaks at 2920 $cm^{-1}$and 1374 cm^{-1} present in the FTIR spectrum. The C=O group in the product is demonstrated by the absorption peaks around 1690cm^{-1} and below 800 cm^{-1} in the spectrum, which should be belong to $CoCO_3$ or aldehyde or carboxyl groups. The absorption band around 1617 cm^{-1} and 800cm^{-1} suggest some C=C maybe exist in the product. These results are confirmed that the carbonization of glucose is not complete result into some still residual functional groups in the product.

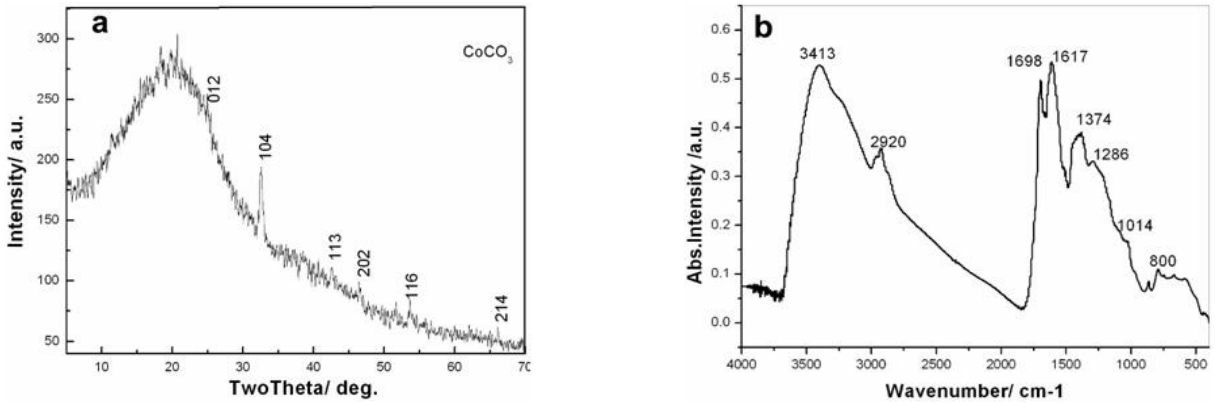

Figure 2 : The XRD pattern (a) and FTIR spectrum (b) of the typical as-obtained sample.

The TEM images further indicate the morphologies and structure of as-obtained samples shown Figure 3. The TEM images from Figure 3A to 3C show the samples obtained at 0.5 g glucose in the given system. The hollow structure of as-obtained sample is confirmed by the Figure 3A image. Low magnification images of the sample shown in Figure 3B further demostrate that the sample is consist of many various sized hollow structures. On the other hand, the high magnification image shown in Figure 3C further indicates the shell of sample composed of many small nanoparticles. The TEM images of the sample obtained at 1 g glucose are shown from Figure 3D to 3F. The high magnification image shown in Figure 3D indicates the sample composes of solid microspheres, which is self-assembled by many nanoparticles. Meanwhile, some spheres with relative smooth surface are appeared in the product (Figure 3f), which is probably attributed to self-carbonization of glucoses without template presentation due to more easy formation of unmixed carbon crystal seed at high concentration glucose hydrothermal conditions.

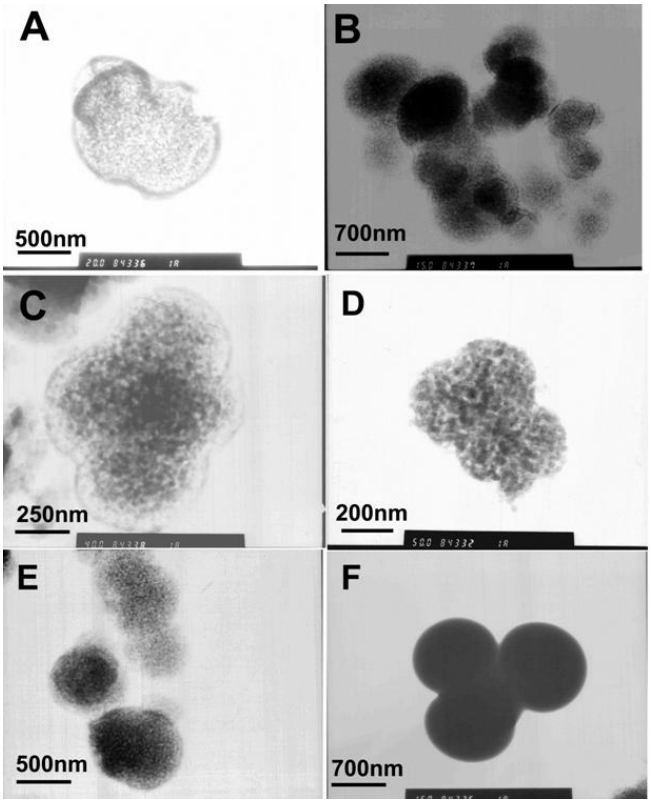

Figure 3 : The TEM images of samples obtained at 0.5g (A,B,C) and 1g (D,E,F) glucoses in the hydrothermal conditions

Based on above experiment results, at given hydrothermal conditions, the formation mechanism of HCSs

can be described as follow: Firstly, glucose is absorbed on the surface of Co_2O_3 particles. Then Co_2O_3 is reduced to Co^{2+} by the inner glucose, meanwhile, the outer glucose is in situ carbonized via hydrothermal decomposition. Third, the produced carbonic nanoparticles and $CoCO_3$ nanoparticles co-form the shell layer. The size of the cubage mainly depends on the Co_2O_3 size. With the amount of glucose increasing, the formed shell thick is boosted. When the electron beam does not transmit the thick, it is not evident whether the composed sphere is hollowed by TEM. Meanwhile, some glucose is carbonized to generate single carbon crystal seed which further forming relative unmixed smooth solid carbon spheres.

CONCLUSIONS

In the letter, we find a novel one-pot template self-ablated hydrothermal method for preparing hollow carbonic nanocomposite microsphere. The HCS nanocomposite is consisted of carbon and $CoCO_3$ nanoparticles. In the synthesis system, the concentration of glucose is an important factor for the hollow structure for some carbon sphere is formed at high amount of glucose. Now we are further investigating them to accomplish more optimal synthesis procedures.

ACKNOWLEDGEMENTS

The authors are thankful to the National '11th-five' Science & Technology Plan Key Project Foundation of China (No.2007BA62B04), the National Natural Science Foundation of China(No. 20906061), and the Shanghai Excellent Young Foundation (slg08021) for financial supports.

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