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Synthesis of Graphite Porous Carbon Sphere with Uniformly Distributed Fe₂O₃ Nanoparticles and its Properties

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Abstract: In the paper, a typical porous carbon spheres with Fe₂O₃ nanoparticles were presented by two steps of hydrothermal and calcinations method, using sucrose as template and ferrous gluconate as the provider of Fe in the process. The scanning electron microscope (SEM) shows the porous carbon spheres have diameter about 3 μm. To characterize the as-obtained porous carbon spheres, X-ray diffraction patterns were carried out, which indicate that the products the existence of Fe₂O₃. Further research on optical properties of the products is characterized by FT-IR and Raman spectrometer. With these features, the porous carbon spheres would have wide applications in the field of separation and adsorption.

Keywords: Ferrous gluconate; Hydrothermal method; Porous carbon spheres

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Introduction

Porous carbon materials have been intensively interested for various practical applications such as catalyst supports [1], adsorbents [2], lithium-ion secondary batteries [3], drug delivery [4], and gas storage media [5]. Porous carbon materials with desired morphology can be used to meet the different requirement. Recently, spherical porous carbon materials are receiving increasing attention in carbon field for their unique physico-chemical properties [6].

Up to now, a number of synthesis strategies have been developed to prepare carbon materials, including chemical vapour deposition [7], the self-generated template approach [8], pyrolysis of organometallic polymers [9], magnetron and ion-beam co-sputtering [10] and arc-discharge [11]. The ever growing need for MCSs has prompted numerous research efforts aimed at developing effective and economical synthesis techniques for

MCSs. Recently, X. Sun and Y. Li reported a way to prepare colloidal carbonspheres with a narrow size distribution by hydrothermal reaction of glucose solution at 160–180°C which is higher than the normal glycosidation temperature and leads to aromatization and carbonization of glucose; and such a hydrothermal reaction has also been employed to encapsulate Au or Ag nanoparticles in carbon nanospheres [12]. Inspired by this work, various groups have successfully prepared magnetic carbon spheres with a core-shell structure by similar multi-step synthesis processes, which require fabricating and modifying magnetic spheres before coating the carbon shell.

In our work, we have demonstrated a simple and convenient approach for the synthesis of porous carbon spheres, using ferrous gluconate and sucrose providing Fe and carbon. Furthermore, by utilizing calcination method, we believe that porous carbon spheres with Fe₂O₃ nanoparticles would provide an important per-

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spective on adsorbents, catalyst supports, and separation agents and so on.

Experimental section

Reagents and equipment

Ferrous gluconate and sucrose were purchased from Sigma-Aldrich Chemicals (St. Louis, MO). All these chemicals were used as received.

Powder X-ray diffraction (XRD) pattern of the sample was measured on 1710 X-ray diffraction with Cu K_{α} radiation ($\lambda=0.54184$ nm) (Netherlands). Scanning Electron Microscopy (SEM, Philip XL30, Holand) measurements were performed on a field emission environmental scanning electron microscope. Fourier transform infrared (FT-IR) spectra and Raman spectra were recorded on a Nexus FT-IR spectrophotometer using KBr pellets and a Renishaw in Via Raman spectrometer with an excitation wavelength of 514.5 nm, respectively.

Synthesis of monodisperse CCSs and PCSs

In a typical synthesis, 70 mg of glucose and 70 mg of ferrous gluconate were dissolved in 8 mL of deionized water to form a clear solution with the aid of magnetic stirring. The solution was then transferred to a Teflon-lined stainless steel autoclave and hydrothermally treated in an air-flow electric oven at 160°C for

16 h. After cooling down naturally, the black precipitate was separated by centrifugation, and thoroughly washed with deionized water and ethanol. After the mixture was vacuum dried at room temperature, a black powder collide carbon spheres (CCSs) was obtained.

For further carbonization, a certain amount of as-prepared CCSs was loaded into a tube furnace and calcined under a high purity argon stream at 700°C for 30 min with a temperature ramp of 5°C/min. After calcining, the black powder porous carbon spheres (PCSs) was obtained.

Result and discussion

According to the design strategy, CCSs were prepared using glucose and ferrous gluconate as precursors under hydrothermal conditions at 160°C for 16 h, as shown in Fig. 1 A and B. As can be seen from SEM photos, these discrete CCSs with an average diameter of 3 μm are still nearly monodisperse spheres. In general, the formation of CCSs during the hydrothermal reaction is by the process of aromatization and carbonization of glucose. While the SEM photos of the calcined product were shown in Fig. 1 C and D. The calcined PCSs are multihole with the diameter of 3 μm , and the surface of the product was distributed by large amount of hole, which indicate that the product have potential application in adsorbents.

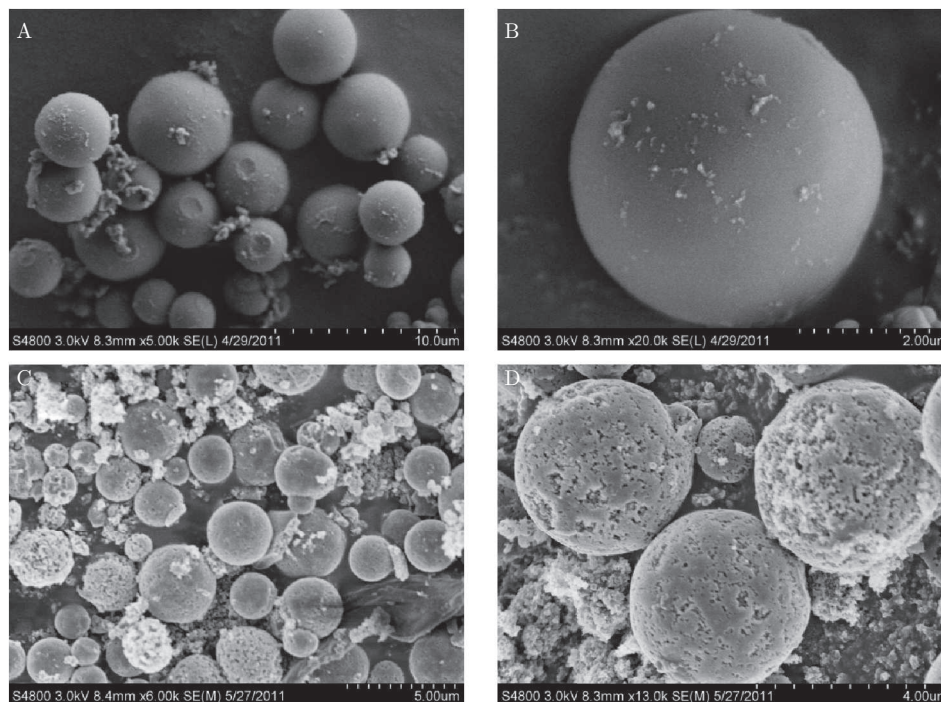


Fig. 1 The SEM morphology of CCSs (A and B) and PCSs (C and D)

The XRD patterns were used to verify the difference between CCSs and PCSs, showing in Fig. 2, a for CCSs and b for PCSs separately. In pattern b, the typical diffractions of (012), (014), (110), (113), (202), (024), (116) and (018) were detected, which were attributed to the Fe_2O_3 phase (JCPDS, No:33-0664). On the other hand, the broad diffraction at around 23° was observed (showing in pattern b), indicating the existence of amorphous graphite. It reveals after calcining in tube furnace, the functional group on the surface of PCSs help the action of Fe oxidation.

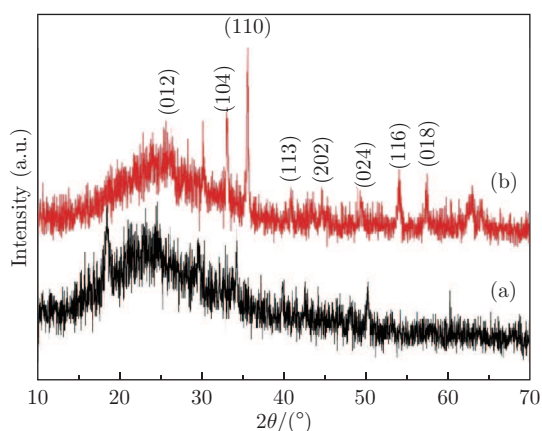


Fig. 2 XRD patterns of (a) CCSs and (b) PCSs

The carbon structure of the different types of carbon spheres is also evident in the Raman spectra shown in Fig. 3 [13]. The peaks located at 1330 cm^{-1} (D-band) and 1590 cm^{-1} (G-band) are attributed to the in-plane vibration of the disordered amorphous carbon and the in-plane vibrations of the crystalline graphite, respectively, which are the same as those of amorphous carbon. The increased intensity ratio of D band and G band is mainly attributed to the instinctive and induced surface defects (by products, catalyst and band destruction induced defects). Therefore, the Raman spectrum shows that the carbon in CCSs sample is disordered, in agreement with the XRD pattern observations. While calcining the CCSs in 700°C , the product show good

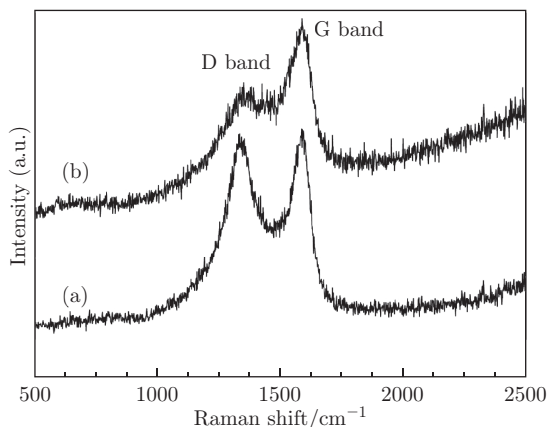


Fig. 3 Raman spectra of CCSs (a) and PCSs (b)

performance of carbonization. It well matches the hypothesis that increasing the temperature will increase the degree of graphitization.

Conclusion

In summary, we demonstrated a facile and efficient way to synthesize porous carbon spheres via synchronous hydrothermal reaction of glucose and ferrous gluconate and further carbonization. The formation of PCSs is attributed to intermolecular carbonization during hydrothermal reaction because of the similar molecular structure of glucose and ferrous gluconate. Subsequently, during further carbonization under high temperature, Fe(II) ions in the as-prepared CCSs not only work as catalysts for the graphitization of amorphous carbon, but are also oxidized to form Fe_2O_3 nanoparticles. Due to the good performance in multipole and ferrite oxidation, it will have potential use in the field of adsorbents, catalyst supports, and separation agents.

Acknowledgements

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References

- [1] V. P. Torchilin, *Pharm. Res.* 2007, 24, 1.
- [2] Klett JW, Hardy R, Romine E, Walls C, Burchell T. *Carbon* 2000; 38(7): 953-73.
- [3] Gallego NC, Klett JW. *Carbon* 2003; 41(7): 1461-6.
- [4] Samad, Y. Sultana, M. Aqil, *Curr. Drug Delivery* 2007, 4, 297.
- [5] L. Guo, L. Zhang, J. Zhang, J. Zhou, Q. He, S. Zeng, X. Cui and J. Shi, *Chem. Commun.*, 2009, 6071.
- [6] J. H. Yun and D. K. Choi, *J. Chem. Eng. Data*, 1997, 42, 894.
- [7] J. Y. Miao, D. W. Hwang, K. V. Narasimhulu, P. I. Lin, Y. T. Chen, S. H. Lin and L. P. Hwang, *Carbon*, 2004, 42, 813.
- [8] B. Liu, D. Jia, J. Rao, P. Zuo and Y. Shao, *J. Solid State Electrochem.*, 2009, 13, 497.
- [9] Y. Koltypin, A. Fernandez, T. C. Rojas, J. Campora, P. Palma, R. Prozorov and A. Gedanken, *Chem. Mater.*, 1999, 11, 1331.
- [10] T. Hayashi, S. Hirono, M. Tomita and S. Umemura, *Nature*, 1996, 381, 772.
- [11] S. Seraphin, D. Zhou and J. Jiao, *J. Appl. Phys.*, 1996, 80, 2097.
- [12] X. Sun and Y. Li, *Angew. Chem., Int. Ed.*, 2004, 43, 597.
- [13] S. Santangelo, G. Messina, G. Faggio, M. Lanza and C. Milone, *J. Raman Spectroscopy.*, 2011, 42, 593-602.