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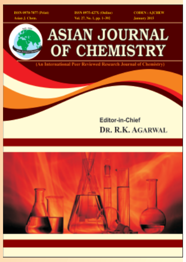

Hydrothermal Syntheses of Colloidal Carbon Nanospheres from Glucose

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Colloidal carbon nanospheres have been prepared from aqueous solutions of glucose in closed systems under hydrothermal conditions. The approach is an absolute 'green' method and the synthetic procedure involves none of the organic solvents, initiators or surfactants that are commonly used for the preparation of nanospheres. The effective reaction temperature on carbon nanospheres diameter was investigated. The obtained nanomaterials were characterized by SEM and FTIR. We find that the diameter of carbon nanospheres increasing with the rise of temperature. Most importantly, the as-formed colloidal carbon nanospheres inherit large numbers of functional groups from the starting materials and have reactive surfaces, which expand the applications fields for both fundamental study and in technical applications.

Keywords: Carbon, Hydrothermal synthetic, Nanospheres, Glucose.

INTRODUCTION

Synthesis of nanostructured materials with tunable size and shape has become a critical issue for specific applications in bioassays[1], drug delivery[2] and immunosensor[3]. In particular, colloidal carbon nanospheres are of great interest because the diffusion of guest species through the micropore can be significantly manipulated by changing their particle sizes and shapes[4,5]. Recently, carbon nanospheres have been widely used in the fields of sensor[6], supercapacitors[7] and optical[8]. The success of these applications strongly depends on the availability of colloidal nanospheres with uniform particles size distribution and good dispersion. Up to now, colloidal carbon nanospheres have been successfully prepared by using versatile approaches, for example high temperature method[9], hard template and sol-gel method[10], two-step polymerization of furfuryl alcohol[11], and microwave-hydrothermal method[6]. Although these carbon nanospheres have been documented, the method also exist several defect. First, the main obstacles in regard to high temperature processed (800-1000 °C) carbon nanospheres formed by polymerization and carbonization are aggregation of the carbon nanospheres[9] and their relatively chemically inert surfaces, which makes surface modification almost unavoidable before use as supports. Second, the polymer particles exhibit a strong tendency toward aggregation during carbonization, which makes it difficult to prepare well-dispersed carbon nanospheres[12]. Most importantly, the synthetic approach involves toxic organic solvents, catalyst or surfactants that are commonly used for the preparation of polymer nanospheres. Therefore, developing a simple and effective strategy for preparing of carbon nanospheres has become a hot and challenging topic.

In this work, we present a controllable hydrothermal synthetic method for synthesis of monodisperse colloidal carbon nanospheres in aqueous glucose solutions. The approach is an absolute 'green' method and the synthetic procedure involves none of the organic solvents, initiators or surfactants. The colloidal carbon nanospheres represent excellent candidates for application in sensors and supercapacitors by virtue of their high chemical stability and the convenient and absolutely 'green' preparation method. In particular, the as-formed colloidal nanospheres inherit large numbers of functional groups from the starting materials and have reactive surfaces, which greatly expand the applications fields for both fundamental study and in technical applications. Furthermore, we describe the detailed dehydration mechanism during the colloidal carbon formation of glucose.

EXPERIMENTAL

Synthesis of colloidal carbon nanospheres followed the process reported in the literature with a little modify[5]: Glucose (3.6 g, analytical purity, Sinopharm Chemical Reagent Co., Ltd.) was dispersed in double-distilled water (40 mL) by sonicating for 0.5 h and formed a clear solution. The resulting solution was placed in a 40 mL Teflon-sealed autoclave and maintained at 150-200 ºC for 4 h. The black or puce products were isolated by centrifugation (12000 rpm, 8 min) cleaned four times with double-distilled water and finally redissolved in double-distilled water.

Scanning electron microscopy (SEM) measurements were carried out by using a FEI QUANTA 200F microscope. The SEM samples were prepared by placing a drop of a dilute dispersion of the composites in double-distilled water on conducting glass (ITO).

RESULTS AND DISCUSSION

The carbon nanospheres were prepared by hydrothermal treatment of glucose solution in the Teflon-sealed autoclave at specific temperature and for an appropriate time and then the reactions were cooled by lowering the temperature naturally. The diameters of carbon nanospheres were influenced by reaction time, temperature and concentration of starting material. We investigated the effect of reaction temperature on the carbon nanosphere diameters. Fig. 1 presents the typical SEM images of carbon nanospheres prepared at different reaction temperature (140, 150, 160, 170, 180, 190 and 200 °C) and kept the other reaction conditions unchanged. We find that the diameter of carbon nanospheres increasing with the rise of temperature. Fig. 1A shows SEM image of the final product isolated from the glucose reaction mixtures prepared at 150 °C for 4 h followed by centrifugation at 12000 rpm. Only a small amount of unformed carbon nanospheres were observed. It is noted is that no carbon nanospheres formed when glucose solution was hydrothermally treated below 140 °C. However, the orange color and increased viscosity of the resulting solutions indicate that some aromatic compounds and oligosaccharides are formed[13], in what has been denoted the "polymerization" step. When the reaction temperature was 160 ºC, the carbon nanospheres aggregated, with an average diameter of approximately 80 nm (Fig. 1B). When increasing the reaction temperature to 170 ºC, the resulting sample shows a monodisperse distribution with a very narrow size distribution (80-100 nm in diameter). Fig. 1D and 1E show the SEM images of the carbon nanospheres prepared at 180 and 190 ºC, respectively. They show homogeneous carbon nanospheres with a very narrow size distribution (125-175 nm in diameter). Fig. 1F show that colloidal carbon nanospheres prepared at 200 ºC showed a monodisperse size distribution with an average dimension of 180 nm.

In this study, it is observed that higher reaction temperatures produced more homogeneous sample sizes than found at lower temperatures and the isolated carbon nanospheres without aggregate. According to present experimental results, the growth of carbon nanospheres seems to conform to the La Mer model[14], shown schematically in **Scheme-I**. The aromatic compounds and oligosaccharides are formed as the reaction proceeded, in what has been denoted the "polymerization" step. Upon subsequent dehydration (polymerization), microscopic nonpolar carbon-containing nanospheres were found to spontaneously assemble in a manner analogous to the mechanism by which a detergent emulsifies a mixture of oil and water. Subsequent loss of water by these assemblies leads to further coalescence of microscopic nanospheres to larger nanospheres,

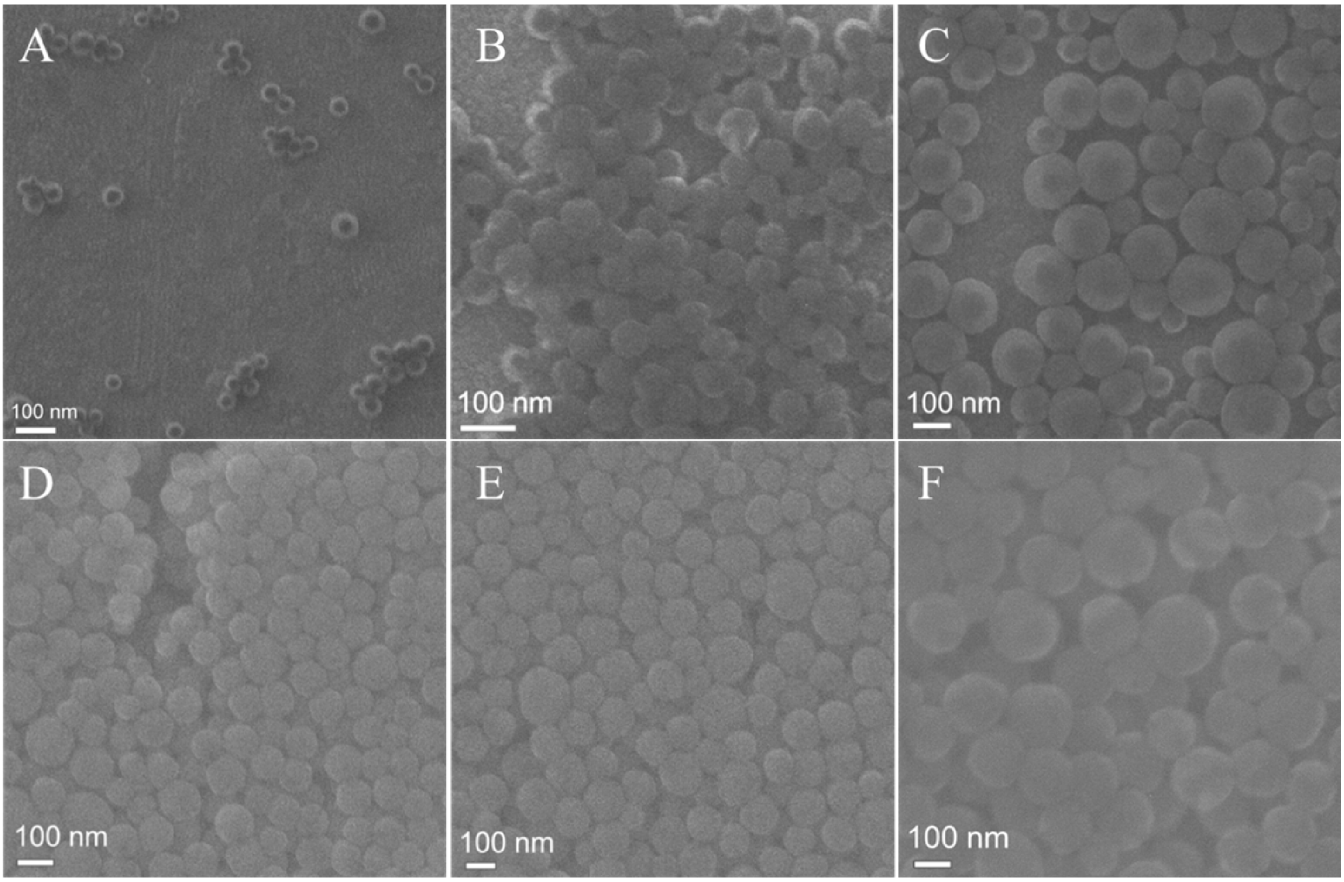
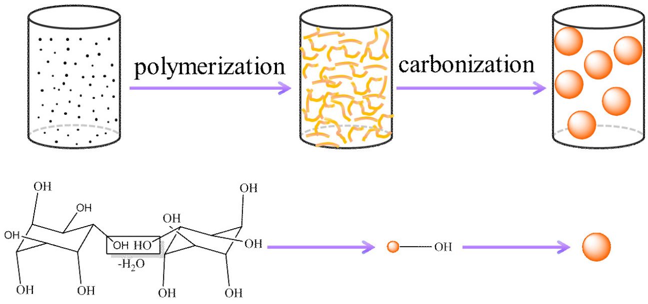


Fig. 1. SEM images of carbon spheres prepared at different temperatures: (A) 150 °C, (B) 160 °C, (C) 170 °C, (D) 180 °C, (E) 190 °C, (F) 200 °C

thereby generating a grain-like surface morphology with attendant interconnected porosity as shown in **Scheme-I**. Additionally, the carbon surface appears smooth and results from continuous intermolecular dehydration route when a glucose solution was hydrothermally treated at 150-200 ºC, which is higher than the normal glycosidation temperature and leads to aromatization and carbonization[5].



Scheme-I: Dehydration and carbonization process of glucose under hydrothermal processing

The FTIR spectrum (Fig. 2) was used to identify the functional groups present after the hydrothermal treatment. The characteristic peaks at 1713 and 1605 cm^{-1} correspond to C=O and C-C vibrations, respectively, which is a result of the aromatization of glucose during the treatment. The bands at 3780-3210 cm^{-1} were attributable to the OH stretching vibrations. The peaks at 1160 cm^{-1} were attributable to the C-OH stretching and OH bending vibration, imply the existence of large numbers of residual hydroxy groups[5,6]. Partially dehydrated residues are covalently bonded to the carbon frameworks improve the hydrophilicity and stability of the nanospheres in aqueous systems and greatly widen their potential applications.

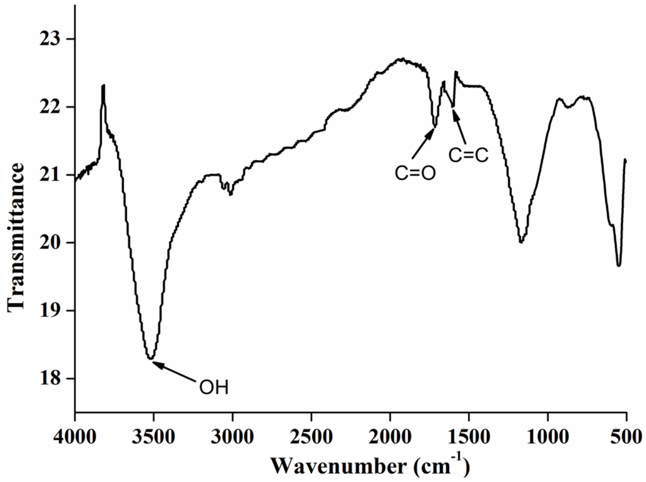


Fig. 2. FTIR spectra of carbon nanospheres

Conclusion

Colloidal carbon nanospheres have been successfully prepared from aqueous solutions of glucose by a hydrothermal method. The approach is simple, effective and absolute 'green' method. Most importantly, the as-formed colloidal carbon nanospheres inherit functional groups from the starting material and have reactive surfaces. That make the carbon nanospheres have greatly interesting for applications in nanoscience and nanotechnology fields.

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REFERENCES

1. R.J. Cui, H.C. Pan, J.J. Zhu and H.Y. Chen, *Anal. Chem.*, **79**, 8494 (2007).
2. H.G. Zhu and M.J. McShane, *J. Am. Chem. Soc.*, **127**, 13448 (2005).
3. D. Du, Z.X. Zou, Y.S. Shin, J. Wang, H. Wu, M.H. Engelhard, J. Liu, I.A. Aksay and Y.H. Lin, *Anal. Chem.*, **82**, 2989 (2010).
4. H.T. Wang, B.A. Holmberg and Y.S. Yan, *J. Mater. Chem.*, **12**, 3640 (2002).
5. X.M. Sun and Y.D. Li, *Angew. Chem. Int. Ed.*, **43**, 597 (2004).
6. R.J. Cui, C. Liu, J.M. Shen, D. Gao, J.J. Zhu and H.Y. Chen, *Adv. Funct. Mater.*, **18**, 2197 (2008).
7. J.H. Zhou, J.P. He, C.X. Zhang, T. Wang, D. Sun, Z.Y. Di and D.J. Wang, *Mater. Charact.*, **61**, 31 (2010).
8. Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, **12**, 693 (2000).
9. H. Hu and R.G. Larson, *J. Am. Chem. Soc.*, **126**, 13894 (2004).
10. J.T. Wang, Q.J. Chen, X.J. Liu, W.M. Qiao, D.H. Long and L.C. Ling, *Mater. Chem. Phys.*, **129**, 1035 (2011).
11. J.F. Yao, H.T. Wang, J. Liu, K.Y. Chan, L.X. Zhang and N.P. Xu, *Carbon*, **43**, 1709 (2005).
12. C.H. Yao, Y.S. Shin, L.Q. Wang, C.F. Windisch, W.D. Samuels, B.W. Arey, C.M. Wang, W.M. Risen and G.J. Exarhos, *J. Phys. Chem. C*, **111**, 15141 (2007).
13. T. Sakaki, M. Shibata, T. Miki, H. Hirosue and N. Hayashi, *Bioresour. Technol.*, **58**, 197 (1996).
14. V.K.L. Mer, *Ind. Eng. Chem.*, **44**, 1270 (1952).