

Short Communication

Catalytic Graphitization Strategy for the Synthesis of Graphitic Carbon Nanocages and Electrochemical Performance

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An exquisite structure of graphitic carbon nanocages (GCNCs) with high surface area was fabricated by catalytic graphitization route at low temperature (650 °C). Bio-renewable lignin was used as the carbon precursor. X-ray diffraction XRD pattern and Raman spectrum indicated that the GCNCs had a high degree of graphitization crystallinity. TEM and nitrogen adsorption-desorption isotherms showed that the GCNCs possessed mesoporous and micropore structure with high surface area. The higher graphitization carbon nanocage may promote charge transfer, giving potential wide application in electrode material.

Keywords: Carbon materials; Graphitic carbon nanocages; Catalytic graphitization; Hierarchical pore; Lignin.

1. INTRODUCTION

Carbon based materials such as graphene, carbon nanotubes and mesoporous carbons have received much attention due to their high surface area, unique pore structure and good hydrothermal stability for many potential applications such as catalyst supports[1], adsorbents[2] and energy-storage materials[3]. In addition to high surface area and unique pore structure, the carbon materials are required to possess a high degree of graphitization crystallinity, since such a graphitic structure indicates to high chemical stability and excellent electrical conductivity[4]. However, meeting the requirements is a challenge because the large-scale practical techniques for preparing high surface area carbon with graphitic frameworks at a low temperatures have not been ripe.

To date, carbon materials with high surface area and unique pore structure, various synthesis approaches, such as activation route[5, 6] and template method[7, 8] had been developed to active carbons, carbon nanotubes, and porous carbons. Conventional activating agents such as KOH and H₂O[9], which are used to fabricate high specific surface area but fail to graphitic crystalline structure. Template method using ordered mesoporous silica or surfactants as sacrificial scaffolds, which can provide a high surface area, whereas an obvious disadvantage of template method is the low degree of graphitization. Chemical vapor deposition, high-temperature carbonization, arc discharge and laser evaporation are the general techniques to synthesis of carbon materials with graphitic frameworks[10], but high temperature, high energy consumption and low specific surface area are the drawbacks of these methods. Heat treatment is able to form well developed graphitic frameworks, but the surface areas and pore volume will drop sharply when the temperatures higher than 2000 °C. To solve these issues, transition metals were used to catalyze the graphitization of amorphous carbons at a lower temperatures[4]. In this paper, lignin was used as carbon precursor taking advantage of its bio-renewable, low cost, and non-toxic. Therefore, a large-scale in situ synthesis route was presented to prepare graphitic carbon nanocages with high surface areas by catalytic graphitization process.

Herein, we report a simple method for the synthesis of graphitic carbon nanocages (GCNCs) via catalytic graphitization route. The synthesis was obtained using iron nitrate nonahydrate (Fe(NO₃)₂·9H₂O) and lignin as iron source and carbon precursor, respectively. The structural properties of the achieved GCNCs were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and nitrogen adsorption-desorption isotherms. Furthermore, the electrochemical properties of the obtained GCNCs were investigated.

2. EXPERIMENTAL

2.1. Chemicals

Pluronic P123 was purchased from Aldrich. Fe(NO₃)₂·9H₂O and nitric acid were purchased from Shanghai Chemical Corp. Alkali lignin was purchased from Nanjing Forestry University, Prof. Liu group. All the chemicals were used as received without further purification.

2.2 Materials preparation

The GCNCs was synthesized by a catalytic graphitization process. In a typical procedure, 1g P123 was added into 10 g lignin (30wt% water solution) stirring for 60 min, subsequently, 1g Fe(NO₃)₂·9H₂O was added to the system. After stirring for another 30 min, the mixture was dried in a clean flat Petri dish at 100 °C for 12 h, and then peeled off, calcined at 650 °C under Argon flow for 3 hours with a heating ramp of 5 °C /min. Finally, the produced material was refluxed in 1 M HNO₃ at 120 °C for removing iron. The obtained nanocomposite material is denoted as GCNCs.

2.3 Materials characterization

The morphology and physical characteristics of GCNCs was examined by transmission electron microscopy (TEM, JEOL JEM-2010), X-ray powder diffractometer diffraction (XRD, CuK1 radiation, $\lambda=1.5406 \text{ \AA}$), and the surface area and pore volume were determined by nitrogen sorption isotherms (ASAP 2000). The Raman spectrum was recorded on a Horiba XploRA Raman microscope using a 532 nm argon ion laser (Lab-RAM HR800). Electrochemical experiments were performed with CHI660E electrochemical workstation. Analysis was conducted using a three-electrode system with a Hg/HgO electrode as reference electrode in an aqueous electrolyte solution (1M KOH) at 25 °C. A sinusoidal ac perturbation of 5 mV was used to the electrode in the frequency range from 0.01 to 1×10^5 Hz.

3. RESULTS AND DISCUSSION

Fig.1a shows the XRD pattern of GCNCs. The strong diffraction peak located at $2\theta=26.1^\circ$ is related to the graphite (002) plane. The two weak diffraction peaks at $2\theta=42.2^\circ$ and 77.2° are indexed as (100) and (110) diffraction planes of the graphite (JCPDS Card No. 75-1621). The graphitic frameworks structure of the GCNCs is further confirmed by Raman spectrum. The Raman spectra of GCNCs (Fig.1b) produced D and G peaks at around 1332 cm^{-1} and 1581 cm^{-1} , respectively[11]. The G-band, indicative of graphitic layer of high crystallinity, is corresponding to the E_{2g} mode of graphite which is related to the vibration of sp^2 hybridized carbon-carbon in graphite. The D-band intensity is related to the number of the defects[12]. The ratio of the relative intensities of D and G bands is expressive of the crystallinity of the carbon materials[13]. By measuring the Raman spectra, the I_D/I_G of GCNCs is 0.96, indicating the high degree of structural order or higher graphitization of GCNCs, which is agree with the XRD results. It may promote the electronic conductive performance of the GCNCs[4].

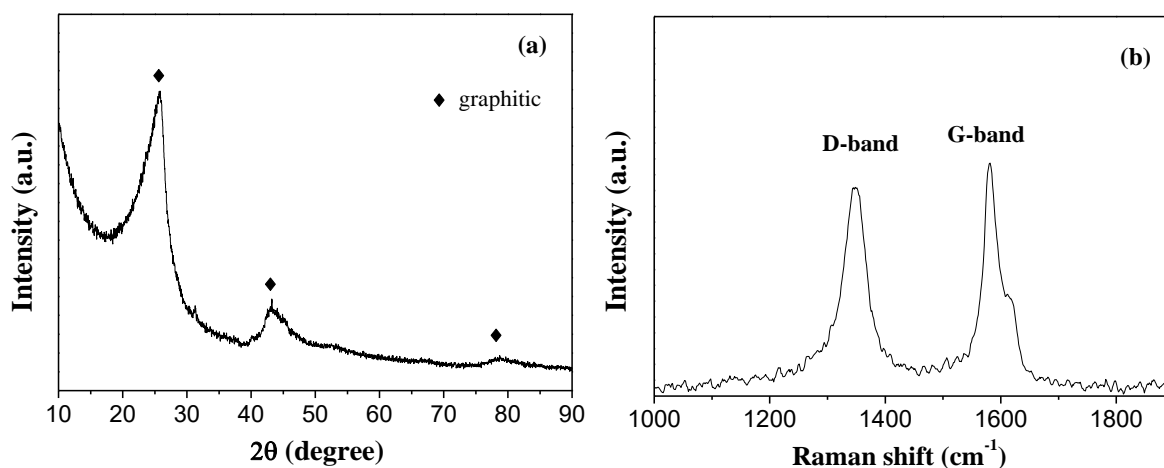


Figure 1. (a) XRD pattern and (b) Raman spectrum of the GCNCs

The microstructure of GCNCs was further characterized by TEM and HRTEM analysis as shown in Fig. 2. From Fig. 2a can be seen that the GCNCs had uniform spherical projected shapes. The size distribution of the GCNCs was concentrated at 25-35nm, and the wall thicknesses was about 2-5 nm. The graphitic frameworks structure of the GCNCs was further investigated by HRTEM. The HRTEM images (Fig. 2b) exhibited that the GCNCs is composed of well-defined graphitic layers with a spacing of 0.34 nm, which is correspond with the (002) plane of hexagonal graphite[14]. The result is agree with the analysis of XRD pattern.

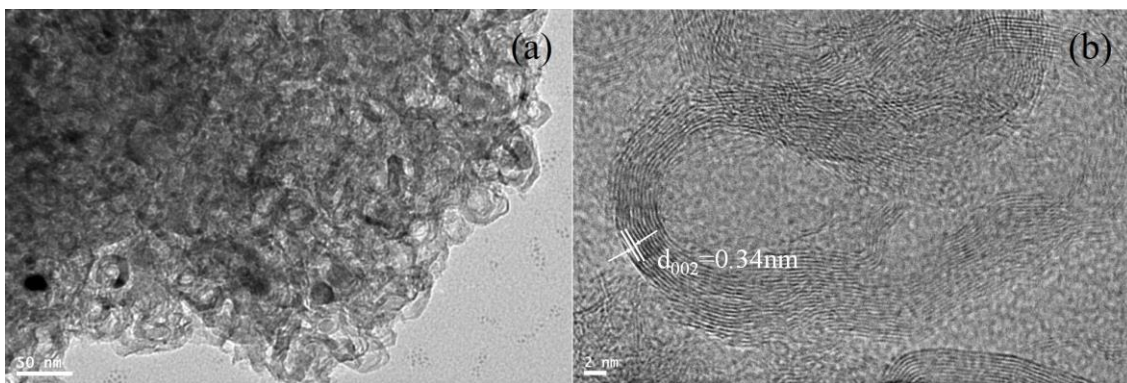


Figure 2. (a) TEM image and (b) HRTEM image of GCNCs

Fig. 3 gives the nitrogen adsorption-desorption isotherm and corresponding pore size distribution curve of the GCNCs. The isotherms exhibit a strong uptake of the HPC is located at P/P_0 0.01-0.05 suggesting the micropores characteristics. In addition, another isotherm is typical type-IV curve with an obvious hysteresis loops at relative pressures of 0.45-0.73, indicating mesoporous feature. The BET surface areas and pore volumes of GCNCs is $435.1\text{m}^2\cdot\text{g}^{-1}$. The pore size distribution obtained by BJH method applying the adsorption branches of the isotherms is shown in Fig.3b. It can be seen that the GCNCs sample has bimodal pore size distributions centered at about 0.61, 1.3, 2.4 and 3.7 nm.

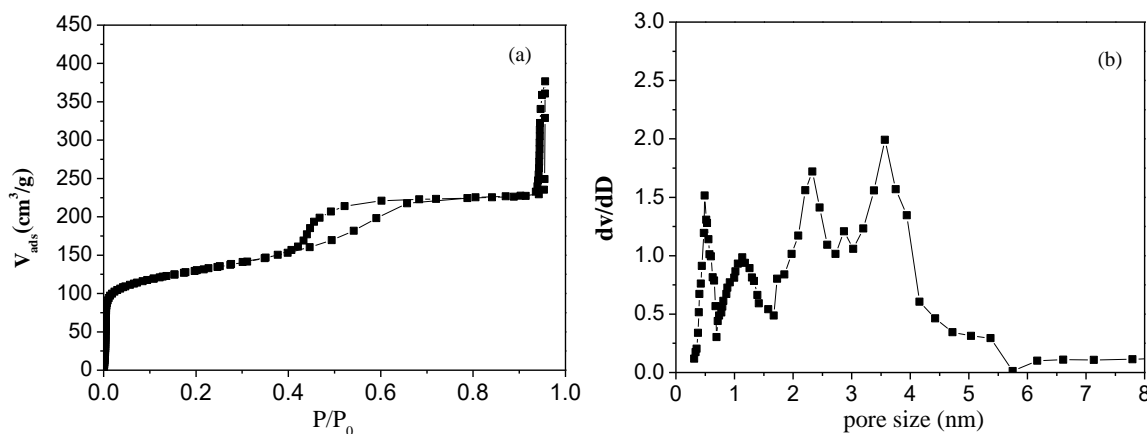


Figure 3. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curves of the GCNCs

As electrode material, lower electrical resistance of electrode is preferred for a higher electrochemical efficiency. Electrochemical impedance spectroscopy (EIS) measurement was carried out to understand the superior electrochemical performance of GCNCs. The EIS spectra of the GCNCs were recorded (Fig. 4a) and the inset is the equivalent circuit. Fig. 4a shows the Nyquist plots obtained from GCNCs electrodes is constituted by one depressed semicircle at high frequency and an inclined line segment in the low frequency region. The semicircle at high frequencies corresponds to the charge-transfer resistance, while the incline line is associated with the diffusion resistance of active ion (Ex. lithium ions). The intersection point with the real axis in the high-frequency range is the internal resistance (R_s), which includes the contact resistance at the electrode interface. The diameter of the semicircles represent the faradic charge transfer resistance (R_{ct}) at the interface between the current collectors. The values of R_s and R_{ct} for the GCNCs electrode are 15.6 and 8.9 Ω , which are closed to the natural graphite electrodes[15]. As expected, it indicates that the GCNCs possess a high electrical conductivity. The electrochemical performance of the GCNCs was evaluated through CV analyses in 1.0 M KOH aqueous solution by using a three-electrode system. The CV curves of GCNCs at different scanning rate ranging from 5 to 100 mVs^{-1} are shown in Fig. 4b. All of the CV curves exhibit a rectangular shape, suggesting the capacitance behaviour from the formation of an electric double layer[16]. Further the GCNCs also show the strong peaks at 0.8V and indicates that the retainment of the similar rectangular shape from 20 to 100 mVs^{-1} confirms the consistency of the capacitance behaviour prevailing, irrespective of the change in voltage potential.

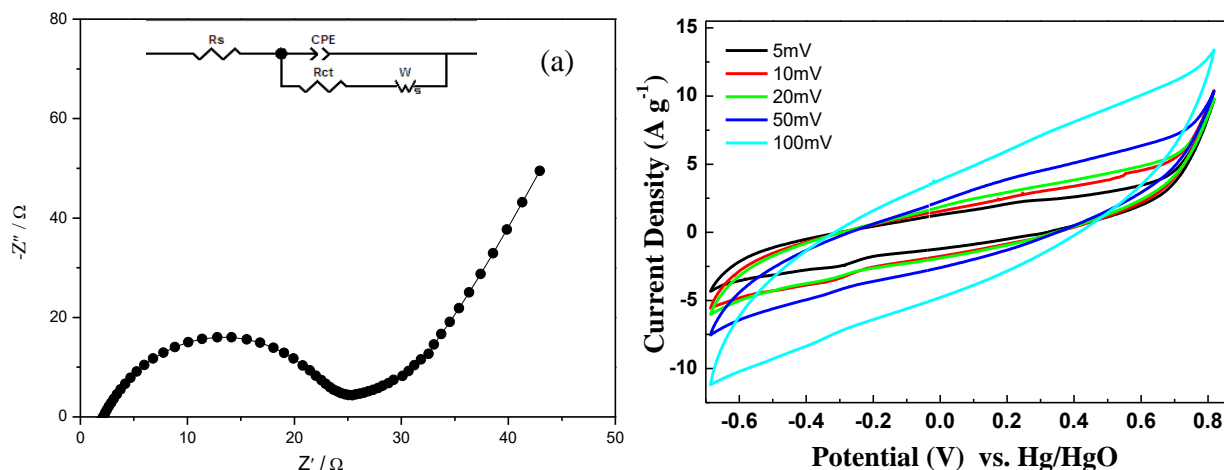


Figure 4. (a) EIS Nyquist plots and (b) CV curves at different scanning rate ranging from 5 to 100 mVs^{-1} of the GCNCs

4. CONCLUSIONS

In conclusion, graphitic carbon nanocages (GCNCs) with high surface area was synthesized by catalytic graphitization route at a low temperature. XRD, Raman and TEM results reveal that the GCNCs possesses a well-developed graphitic structure. Nitrogen adsorption-desorption isotherm indicate that the GCNCs exhibits high surface area and hierarchical pore structures. The EIS result reveal that the GCNCs possess a high electrical conductivity. The excellent charge transfer performance coupled with the high surface area of the GCNCs, which can be potentially applied in fields, such as catalyst supports, adsorbents, and electrode material.

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References

1. Y.T. Gong, M.M. Li, H.R. Li, Y. Wang, *Green Chem.*, 17 (2015) 715-736.
2. W.M. Hao, F. Bjornerback, Y. Trushkina, M.O. Bengoechea, G. Salazar-Alvarez, T. Barth, N. Hedin, *Acs Sustain Chem Eng.*, 5 (2017) 3087-3095.
3. B.W. Xu, Z.J. Li, *Energy*, 72 (2014) 371-380.
4. F. Wu, R. Huang, D.B. Mu, B.R. Wu, Y.J. Chen, *Electrochim Acta*, 187 (2016) 508-516.
5. Y.X. Zhai, C. Li, G.Y. Xu, Y.F. Ma, X.H. Liu, Y. Zhang, *Green Chem.*, 19 (2017) 1895-1903.
6. J.N. Wang, L. Zhang, J.J. Niu, F. Yu, Z.M. Sheng, Y.Z. Zhao, H. Chang, C. Pak, *Chem Mater.*, 19 (2007) 453-459.
7. L.F. Cui, M.C. Yao, X. Bai, L. Zhang, S.F. Kang, *Int J Electrochem Sc.*, 11 (2016) 8346-8353.
8. Y. Wang, Y.T. Chen, F. Wang, B. Li, C.L. Zhang, Y.Q. Miao, L.F. Cui, S.F. Kang, X. Li, *Int J Electrochem Sc.*, 8 (2013) 8077-8083.
9. B.Y. Xia, J.N. Wang, X.X. Wang, J.J. Niu, Z.M. Sheng, M.R. Hu, Q.C. Yu, *Adv Funct Mater.*, 18 (2008) 1790-1798.
10. H.F. Qin, B. Wang, C.Y. Zhang, B.L. Zhu, Y. Zhou, Q.F. Zhou, *Catal Commun.*, 96 (2017) 28-31.
11. X.S. Qi, J.L. Xu, W. Zhong, C.T. Au, Y.W. Du, *Diam Relat Mater.*, 45 (2014) 12-19.
12. X.Z. Xu, J. Zhou, L. Jiang, G. Lubineau, S.A. Payne, D. Gutschmidt, *Carbon*, 80 (2014) 91-102.
13. R.F. Wang, H. Wang, H. Li, W. Wang, J.L. Key, L. Khotseng, S. Ji, *Electrochim Acta*, 132 (2014) 251-257.
14. G.D. Li, H.X. Yu, L.Q. Xu, Q. Ma, C. Chen, Q. Hao, Y.T. Qian, *Nanoscale*, 3 (2011) 3251-3257.
15. S.B. Yang, X.L. Feng, L.J. Zhi, Q.A. Cao, J. Maier, K. Mullen, *Adv. Mater.*, 22 (2010) 838-842.
16. Rajagopal R R, Aravinda L S, Rajarao R, Zboril, R, *Electrochimica Acta*, 211 (2016) 488-498.

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