

Effect of L-Arginine on the Carbon Microsphere Forming under Hydrothermal Carbonization

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Summary: Carbon microspheres (CMs) with a diameter of 5-10 μm have been synthesized by hydrothermal carbonization of starch and L-arginine. The surface property and structure of CMs were examined by FT-IR spectra, N_2 adsorption-desorption isotherms and SEM images. These characterizations indicated that the L-arginine does not connect into the CMs but it promotes the starch hydrolysis and polymerization-condensation reaction of intermediate, which accelerates the formation of CMs and improves the yield in shorter time. The surface property of CMs determines adsorption capacity for acetic acid. By contrast, the porosity resulted from the carbonization at 500 $^\circ\text{C}$ dominates the adsorption capacity for acetic acid.

Keywords: Starch; L-arginine; Hydrothermal carbonization; Carbon microsphere.

Introduction

Functional carbon materials have been a hot issue because of their wide applications in adsorbent, filter material, catalyst support, electrode and fuel cell [1-3]. Several methods, such as chemical vapor deposition [4], carbonization of polymer [5-7] and pressure carbonization [8, 9], have been widely used to synthesize carbon materials. However, these synthesis processes are complex, tedious and expensive. In particular, the carbonization is carried out at high temperature, and hence, leading to the absence of chemical functional groups over the as-prepared carbon material surface. Today, the synthesis of functional nano-materials deriving from sustainable natural precursors *via* an environment-friendly process is a highly attractive issue in material chemistry. Among these processes, hydrothermal carbonization is a shining star due to the obvious advantages, producing a variety of functional carbon materials with wide applications [10].

The carbohydrates, such as, xylose [11, 12], glucose [13-15], fructose [16], sucrose [15, 16], cyclodextrin [17], cellulose [18] and starch [18] have been used to prepare functional carbon materials through hydrothermal carbonization. The as-prepared carbon microspheres (CMs) have a core-shell chemical structure consisting of a highly aromatic nucleus and a hydrophilic surface, which contains a variety of reactively hydrophilic oxygen chemical groups (carboxylic, carbonyl, ester, hydroxyl). Hence, compared with the inert surfaces of carbon materials

prepared by other approaches, the CMs from hydrothermal carbonization are easier modified and more appropriate for catalyst support [19].

In order to improve the function of CMs from hydrothermal carbonization, the hydroxyethylsulfonic acid [20], acrylic acid [21], ovalbumin [22] were added into the solution to introduce sulfonic acid groups or nitrogen groups. The functional carbon materials showed potential application in catalysis, adsorption, and energy storage devices. L-arginine contains two amino and one carboxyl groups, which could affect the hydrothermal carbonization intermediates polymerization and condensation reaction, furthermore, modulate the morphology and structure of resultant carbon materials. As far as we know, the effect of L-arginine on the hydrothermal CMs was not illustrated in documents. Here, the L-arginine was added into the starch solution and then hydrothermal carbonization at different conditions. The effect of L-arginine on the carbon yield, morphology and surface chemical groups of CMs was researched. In addition, the as-prepared CMs were carbonized at 500 $^\circ\text{C}$ to find the structure and adsorption behavior differences between them.

Experimental

Hydrothermal synthesis of CMs

12 g starch with 0, 0.2, 0.6, 1.0, 1.2 g L-arginine was added into 30 ml deionized water and

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stirred, respectively. Then, the solution was transferred into an autoclave and statically heated at 200 °C. After the hydrothermal carbonization, the autoclave was cooled to get carbonaceous solid which was filtrated and extracted with alcohol to eliminate some soluble residues. Ultimately, the as-prepared solid was dried overnight and denoted as CM-0.2, CM-0.6, CM-1.0 and CM-1.2 according to the amount of L-arginine added, respectively. For comparison, the resultant carbon material synthesized without L-arginine was denoted as CM-0.

The dried CMs were carbonized at 500 °C for 4 h and denoted as CM-0-C, CM-0.2-C, CM-0.6-C, CM-1.0-C and CM-1.2-C, respectively.

Characterization

The porosity of CMs was measured and determined on a Micromeritics ASAP 3020 instrument. Before the measurement, the CMs were degassed in vacuum at 300 °C. The micro-structure of CMs was obtained by using scanning electron microscopy (SEM, Hitachi S-4800, Japan). Surface chemical groups of CMs were recorded by Fourier-transform infrared spectra (FT-IR, NEXUS FTIR, NIOLET)

Adsorption capacity of acetic acid (AA)

The adsorption experiment was carried out in a desiccator at room temperature. A certain amount of AA was put into the desiccator and kept for 5 h. 0.4 g CM was transferred into the desiccator to adsorb AA. The CMs with different adsorption time were weighed and the difference in weight can be considered as an indicator of the amount of surface functional groups.

Results and discussion

Porosity of CMs

The N₂ adsorption-desorption isotherms show that the specific surface area and the pore volume of the CMs are less than 7 m²/g and 0.005 cm³/g, respectively, illustrating that they are nonporous. Fig. 1 showed the N₂ adsorption-desorption isotherms of CMs carbonized at 500 °C. These isotherms are planar at the P₀/P over 0.1, indicating they are microporous. The surface areas and the pore volumes of CM-0-C, CM-1.2-C are 393, 493 m²/g and 0.20, 0.27 cm³/g, respectively, illustrating the enhancement of porosity after

carbonization at high temperature. The final CMs were prepared by hydrothermal carbonization combined with a post-step carbonization process. By introduction of air into the N₂ flow during carbonization, CMs were partially burnt off and a large number of micropores were created. Hence, specific surface area and the pore volume of CMs after carbonization were increased [23].

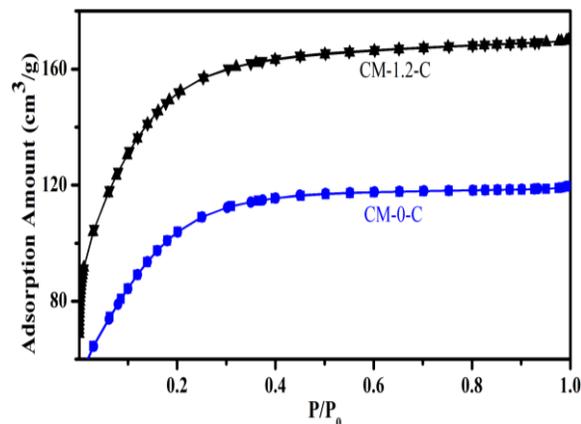
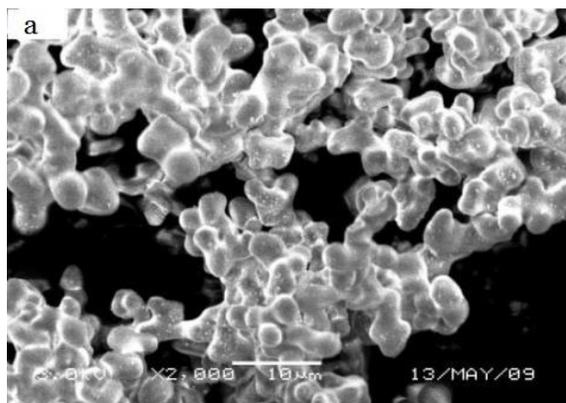


Fig. 1: N₂ adsorption-desorption isotherms of CMs carbonized at 500 °C.

Morphology of CMs

The micro-structures of CMs obtained through SEM images were shown in Fig. 2. The CM-0 is irregular agglomerate. With the addition of L-arginine, the CMs are connecting spheroids, with a diameter of 5-10 μm. The more L-arginine is added, the more piled of spheroids are obtained. This suggested that the L-arginine improves the morphology of CMs. It is presumed that L-arginine affects the acid-base and polar property of hydrothermal carbonization solution and the polymerization-condensation product is easier to aggregate to form CMs.



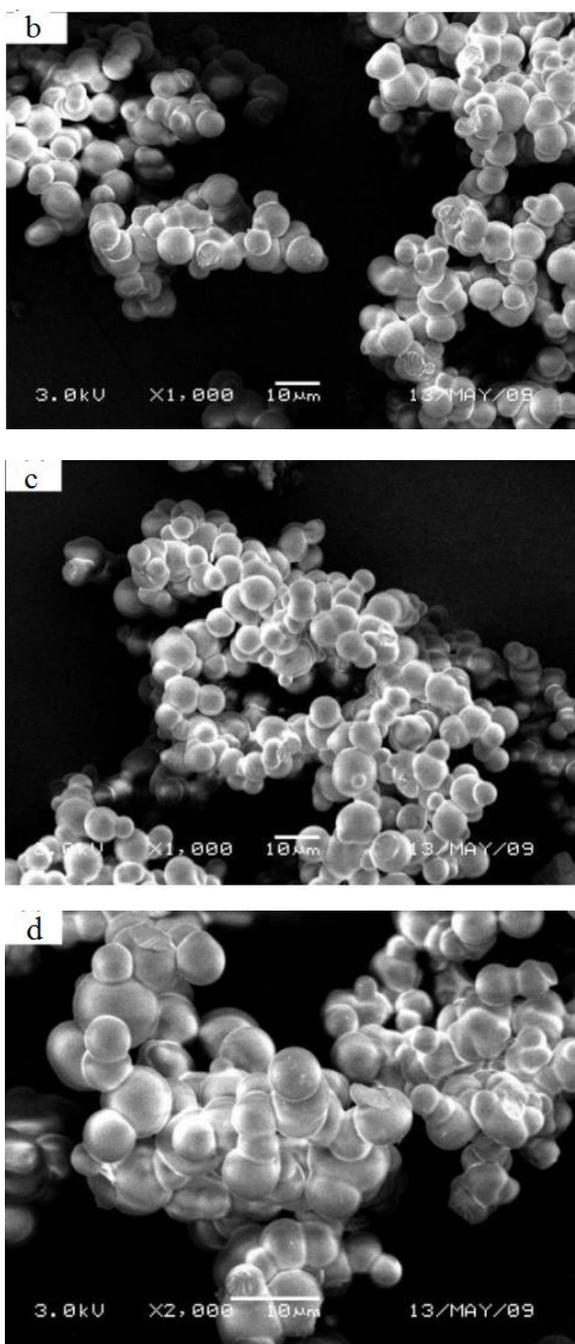


Fig. 2: SEM images of CMs for CM-0 (a), CM-0.2(b), CM-0.6(c), CM-1.0(d).

Yield of CMs

The yields for CMs at 200 °C for different time were shown in Fig. 3. The yields for all samples increase with hydrothermal carbonization time, and reach the maximum in 6 hours. The yields are

42.44%, 44.88%, 46.24%, 48.67% and 48.84% for CM-0, CM-0.2, CM-0.6, CM-1.0, and CM-1.2, respectively. For hydrothermal carbonization of starch in 1 h, the product is light brown liquid without any solid, which presumes that the starch is hydrolyzed and partly polymerization-condensation in lower degree and it could not form larger particles. However, when the L-arginine is added into the hydrothermal carbonization system, it could promote the starch hydrolysis to low molecules monomer and accelerate the polymerization-condensation of them. Hence, the solid carbon is produced. A possible formation mechanism of the CMs with the addition of L-arginine involves the dehydration of the starch into a furan-like molecule and subsequent polymerization and carbonization.

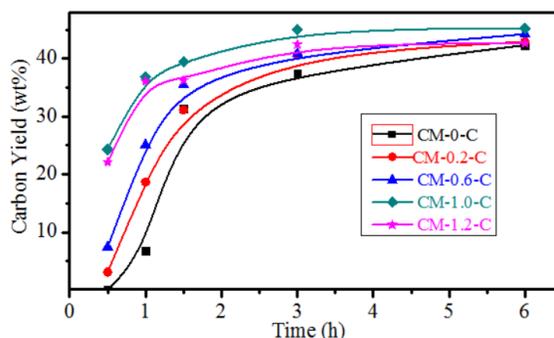


Fig. 3: Yields of CMs with different reaction time.

Surface property of CMs

The surface chemical properties of the CMs were examined by FT-IR and shown in Fig. 4 (a). It is shown that two prominent features are found. One is the O-H absorption in the range of 3400 to 3100 cm^{-1} and the other is C=O stretching absorption at 1704 cm^{-1} . It is reported that the C=O groups could exist at cross-links between furanic rings and levulinic acid embedded inside the carbon [24]. In addition, the bands at 2965 and 2930 cm^{-1} are aliphatic hydrocarbons (-C-H) while the absorption peak at 1618 cm^{-1} is the C=C stretching of furanic rings and aromatic rings. Two peaks at 1290 and 1211 cm^{-1} are the C-O-C stretching absorption. The peaks at 1023, 795 and 760 cm^{-1} are the out-of-plane C-H deformation of furanic rings [25]. These results proved that the CMs contain an aromatic core and shell with resident functionalities. However, there is no characteristic band of nitrogen-containing groups in FT-IR spectra, illustrating that the L-arginine does

not join the carbon forming reaction, but it changes the solution property and promotes starch hydrolysis and polymerization and condensation reaction. The surface functional groups are markedly decreased when the CMs are carbonized at 500 °C, which is shown in the FT-IR spectra in Fig 4 (b). There are only broad bands between 1469 and 1377 cm⁻¹, including a lot of overlapping absorption peaks attributed to carboxyl-carbonates.

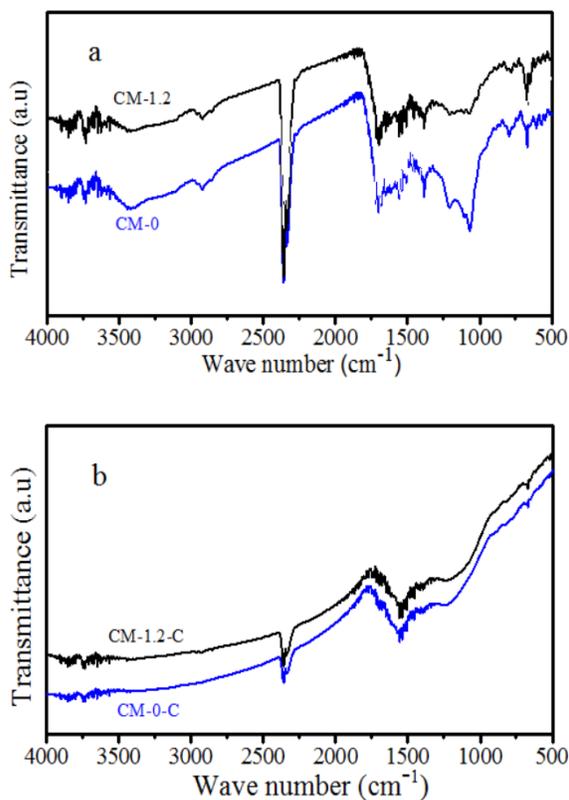


Fig. 4: FT-IR spectra of CMs before (a) and after (b) carbonization.

The adsorption capacity patterns of AA over CMs before (a) and after (b) carbonization at 500 °C were displayed in Fig. 5. The adsorption capacities of AA for CMs without carbonization are relatively low, and the equilibrium values are from 0.09 to 0.18 g/g. Because of their poor pore volume and specific surface area, the surface chemical groups will determine the adsorption capacity of AA. Therefore, the external surface and accumulation level of CMs affect the diffusion rate and adsorption capacity of AA. The CM-0 is tightly piled up and has less external surface, therefore, it shows slower diffusion rate and less adsorption capacity of AA. The CM-1.2 is loosely aggregated and has larger external surface,

therefore, it shows faster diffusion rate and higher adsorption capacity of AA. After the CMs are carbonized at 500 °C, the surface chemical groups are markedly decreased and more micro-pores are formed. It is inferred that the adsorption capacity for AA depends on their pores, and the adsorption capacities of AA vary between 0.25 and 0.3 g/g. The adsorption capacity of AA depends on the pore structure of carbonization samples, which is processed in the pattern of physical adsorption with a low velocity.

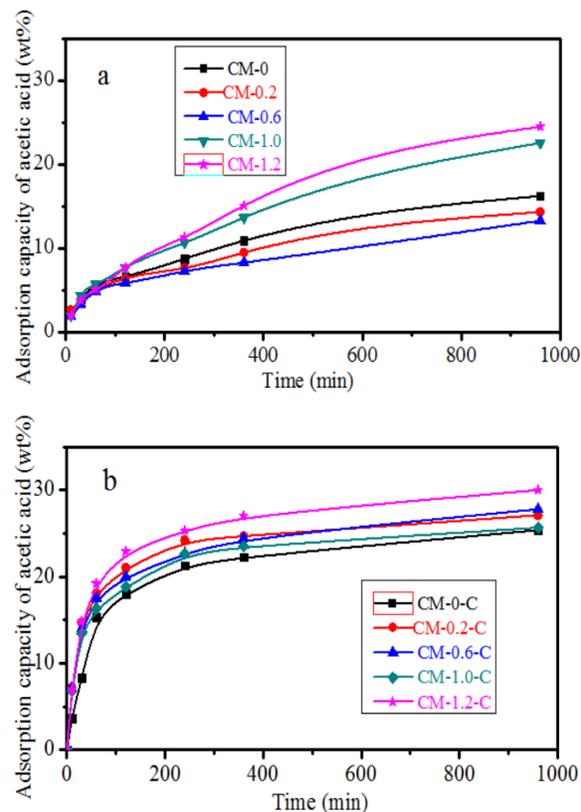


Fig. 5: Adsorption capacity of acetic acid by CMs before (a) and after (b) carbonization.

Conclusion

CMs were synthesized by using starch and L-arginine under hydrothermal carbonization process. The L-arginine could promote the CMs forming and improve the yield in shorter time. The morphology of CMs is more spheroids in the presence of L-arginine. The characterization results showed that the L-arginine does not connect into the CMs but it promotes the starch hydrolysis and the polymerization-condensation reaction of intermediate. The surface functional groups of CMs determine

adsorption capacity of AA. By contrast, the porosity resulted from the carbonization at 500 °C dominates the adsorption capacity for AA.

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References

1. X. Jian, D. Wang, and H. Liu, Controllable synthesis of carbon coils and growth mechanism for twinning double-helix catalyzed by Ni nanoparticle, *Compos. Part B: Eng.*, **61**, 350 (2014).
2. C. H. Wu, S. Y. Chen, and P. Shen, Polyyenes and flexible Si–H doped carbon nanoribbons by pulsed laser ablation of graphite in tetraethyl orthosilicate, *Carbon*, **67**, 27 (2014).
3. S. Dey, A. Govindaraj, and K. Biswas, Luminescence properties of boron and nitrogen doped graphene quantum dots prepared from arc-discharge-generated doped graphene samples, *Chem Phys Lett*, **595**, 203 (2014).
4. A. Jain, R. Balasubramanian, and M. P. Srinivasan, Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review, *Chem. Eng. J.*, **283**, 789 (2016).
5. M. Washiyama, M. Sakai, and M. Inagaki, Formation of carbon spherules by pressure carbonization-Relation to molecular structure of precursor, *Carbon*, **26**, 303 (1988).
6. L. Huang, Q. H Chang, and G. L Guo, Synthesis of high-quality graphene films on nickel foils by rapid thermal chemical vapor deposition, *Carbon*, **50**, 551 (2012).
7. L. Chao, Y. Yu, Y. Hu, and J. Zhang, A co-confined carbonization approach to aligned nitrogen-doped mesoporous carbon nanofibers and its application as an adsorbent, *J Hazard Mater*, **276**, 192 (2014).
8. X. Wang, H. Wang, Q. Dai, Q. Li, J. Yang, A. Zhang, and Z. Yan, Preparation of novel porous carbon spheres from corn starch, *Colloids Surf. A*, **346**, 213 (2009).
9. M. M. Bruno, N. G. Cotella, M. C. Miras, T. Koch, S. Seidler, and C. Barbero, Characterization of monolithic porous carbon prepared from resorcinol/formaldehyde gels with cationic surfactant, *Colloids Surf. A*, **358**, 13 (2010).
10. M. M. Titirici and M. Antonietti, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization, *Chem Soc Rev*, **39**, 103 (2010).
11. M. M. Titirici, M. Antonietti, and N. Baccile, Hydrothermal carbon from biomass: a comparison of the local structure from poly- to monosaccharides and pentoses/hexoses, *Green Chem*, **10**, 1204 (2008).
12. J. Ryu, Y. W. Suh, D. J. Suh, and D. J. Ahn, Hydrothermal preparation of carbon microspheres from mono-saccharides and phenolic compounds, *Carbon*, **48**, 1990 (2010).
13. Y. Mi, W. Hu, Y. Dan, and Y. Liu, Synthesis of carbon micro-spheres by a glucose hydrothermal method, *Mater Lett*, **62**, 1194 (2008).
14. M. Sevilla, A. B. Fuerts, Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides, *Chem Eur J*, **15**, 4195 (2009).
15. M. Zheng, Y. Liu, K. Jiang, Y. Xiao, and D. Yuan, Alcohol-assisted hydrothermal carbonization to fabricate spheroidal carbons with a tunable shape and aspect ratio, *Carbon*, **48**, 1224 (2010).
16. Y. Shin, L. Wang, I. T. Bae, B. W. Arey, and G. J. Exarhos, Hydrothermal dehydration of aqueous fructose solutions in a closed system, *J. Phys. Chem.*, **111**, 15141 (2007).
17. Y. Shin, L. Wang, I. T. Bae, B. W. Arey, and G. J. Exarhos, Hydrothermal syntheses of colloidal carbon spheres from cyclodextrins, *J Phys Chem C*, **112**, 14236 (2008).
18. M. Sevilla, A. B. Fuertes, The production of carbon materials by hydrothermal carbonization of cellulose, *Carbon*, **47**, 2281 (2009).
19. X. Sun and Y. Li, Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles, *Angew. Chem. Int. Ed.*, **43**, 597 (2004).
20. X. Liang, M. Zeng, and C. Qi, One-step synthesis of carbon functionalized with sulfonic acid groups using hydrothermal carbonization, *Carbon*, **48**, 1844 (2010).
21. R. Demir-Cakan, N. Baccile, M. Antonietti, and M. M. Titirici, Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid, *Chem Mater*, **21**, 484 (2009).
22. N. Baccile, M. Antonietti, and M. M. Titirici, One-step hydrothermal synthesis of nitrogen-

- doped nanocarbons: albumine directing the carbonization of glucose, *ChemSusChem*, **3**, 246 (2010).
23. L. Weihan, L. Minsi, M. Wang, L. Zeng, and Y. Yu, Electrospinning with partially carbonization in air: Highly porous carbon nanofibers optimized for high-performance flexible lithium-ion batteries, *Nano Energy*, **13**, 693 (2015).
24. D. Wu, R. Fu, and Z. Yu, Organic and carbon aerogels from the NaOH-catalyzed polycondensation of resorcinol-furfural and supercritical drying in ethanol, *J. Appl. Poly. Sci.*, **96**, 1429 (2005).
25. N. Baccile, G. Laurent, F. Babonneau, F. Fayon, and M. M. Titirici, Structural characterization of hydrothermal carbon spheres by advanced solid-state MAS ^{13}C -NMR investigations, *J Phys Chem C*, **113**, 9644 (2009).