The preparation of Fe-doped carbon aerogels from sodium alginate

Zuozhao Zhai 1,2, Bin Ren 1,2, Yuelong Xu 1,2, Shasha Wang 1,2, Lihui Zhang 1,2, Zhenfa Liu 1,2

1Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang 050081, China
2Hebei Engineering Research Center for Water Saving in Industry, Shijiazhuang 050081, China

Abstract. In this article, Fe-doped carbon aerogels were prepared by one-step carbonization using sodium alginate as the raw material. The composition of the materials was characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results show that when the carbonization temperature is lower than 700 °C, iron mainly exists in the form of Fe3O4. When the carbonization temperature is higher than 700 °C, iron mainly exists in the form of Fe and CFe15.1.

1. Introduction
Carbon aerogel is a new type of porous carbon material, which has the advantages of large specific surface area, high porosity and good electrical conductivity. The traditional carbon aerogel uses resorcinol and formaldehyde as raw materials. However, the preparation time is long and the process is complicated [1-3]. In recent years, biomass-based carbon aerogels have become a research hotspot [4-7]. Sodium alginate is a natural polysaccharide extracted from brown algae which is composed of (1,4)-β-D-mannuronate and (1,3)-α-L-guluronate fragments. Sodium alginate is widely used in medicine, food and other industries because it is non-toxic, stable, and sticky. It is interesting that sodium alginate can chelate with polyvalent metal ions in aqueous solution to form hydrogels[8-11]. Hence, Fe-doped hydrogels can be obtained by mixing sodium alginate and iron salt solution. And, Fe-doped carbon aerogels can be obtained by carbonizing the hydrogels.

In this paper, we obtained sodium alginate hydrogels by mixing sodium alginate and iron nitrate solution. Then, the hydrogels were freeze-dried and carbonized at high temperature to obtain Fe-doped carbon aerogels. We obtained iron-loaded carbon aerogels with different carbonization temperature. The material has broad application prospects in the field of wastewater treatment because it uses non-toxic and environmentally friendly sodium alginate as raw material and the preparation process is simple.

2. Materials
Sodium alginate, FeN3O9, and isopropanol were purchased from Aldrich Co. MB was purchased from Damao Chemical Reagent Factory. H2SO4 and NaOH were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd.

2.1. Materials preparation
Fe-doped carbon aerogels were prepared according to the following steps:
(1) 5 g sodium alginate was dissolved in 500 ml deionized water to obtain solution A. 12.5 g Fe₃O₄ was dissolved in 500 ml deionized water to obtain solution B. Solution A was added to solution B through an automatic injector to obtain sodium alginate hydrogels.

(2) The sodium alginate hydrogels were washed with deionized water 6 times to remove Fe³⁺ on the surface of the hydrogel. Then, the hydrogels were placed in a freeze dryer for 48 hours to obtain sodium alginate aerogels.

(3) The aerogels were placed in a high-temperature carbonization furnace. The samples were heated to a predetermined temperature under nitrogen atmosphere and held for 3 hours. The predetermined temperatures included 500, 600, 700, 800, and 900 °C (the corresponding sample is identified as T500, T600, T700, T800, and T900, respectively).

2.2. Characterization

The X-ray diffraction (XRD) patterns of the carbon aerogels were monitored by an Ultima X-ray diffractometer under copper Kα radiation at 40 kV and 40 mA. The surface chemical groups of the carbon aerogels were determined using a Spectrum 100 Fourier transform infrared (FTIR) spectrometer. The pore structure of carbon aerogels was investigated by a Micromeritics ASAP 2460 surface area analyser at 77 K. The SSA was obtained by using Barrett-Emmett-Teller (BET) method. The pore size distribution was calculated by applying the density functional theory (DFT) model. A Hitachi S-4800 field emission scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS) was applied to examine the surface morphology and elemental distribution of the samples. A JEM-2100 Plus was used to obtain transmission electron microscopy (TEM) images. X-ray photoelectron spectroscopy (XPS) was used to measure the chemical composition.

2.3. Structure and properties

XRD was used to determine the crystalline structure of Fe-doped carbon aerogels. As shown in Figure 1a, the peaks at 2θ=30.1, 35.4, 37.1, 43.1, 56.9, and 62.5° correspond to the [220], [311], [222], [400], [511], and [440] planes of cubic Fe₃O₄, respectively [31] which indicates that after carbonization at 500 °C or 600 °C in N₂ atmosphere, the Fe³⁺ was converted to Fe₃O₄ completely. The peaks at 2θ=44.7, 65.0, and 82.3° correspond to the [110], [200], and [211] planes of cubic Fe, respectively [32]. The peaks at 2θ=43.3, 50.4, and 74.1° correspond to the [111], [200], and [220] planes of cubic CFe₁₅.₁ [33, 34], respectively which means that when the carbonization temperature rose to 700°C, Fe₃O₄ was converted to Fe and CFe₁₅.₁. It is speculated that when the temperature is higher than 700 °C, Fe₃O₄ undergoes a redox reaction with C or CO to form iron. In addition, when the temperature continues to rise, the peaks of CFe₁₅.₁ gradually increase that indicates higher temperature leads to Fe transform to CFe₁₅.₁. FTIR spectroscopy (Figure 1b) was used to understand the surface chemistry of Fe-doped carbon aerogels. The broad and strong peak at 3450 cm⁻¹ is associated with the stretching vibrations of O-H. The observed peak at 1600 cm⁻¹ is attributed to COO stretching vibrations. The absorption at 1380 cm⁻¹ corresponds to C-OH stretching or C-H in-plane bending vibrations. The peak at 1000 cm⁻¹ is attributed to C-C framework vibrations or C-O-C stretching vibrations [31-33]. From the FTIR spectra, the hydrophilic functional groups disappear after high-temperature carbonization, indicating that the carbon aerogels have good hydrophobicity. Enhanced hydrophobicity can increase the adsorption and removal efficiency of organic matter in waste water.
The pore structure of Fe-doped carbon aerogels were investigated by N₂ adsorption/desorption measurements. As shown in Figure 2a, the isotherms of all samples belong to type IV. At a relative pressure of P/P₀<0.01, the rapid rise in the adsorption curve indicates the presence of micropores in the samples. The hysteresis in the middle range of relative pressures indicates the existence of mesopores. From Figure 2a, when the carbonization temperature is higher than 700 °C, the content of micropores is significantly decreased. As shown in Figure 2b, there are many micropores at 0.7-1.0 nm in T500 and T600, and there are many mesopores at 2-30 nm in T700, T800, and T900. Detailed porosity parameters are summarized in Table 1. The SSAs of the samples are obviously increased after carbonization at high temperature. The proportion of micropores in T500 and T600 is large, and the proportion of micropores in T700, T800, and T900 is small. Moreover, when the temperature is higher than 700 °C, the SSA gradually decreases as the temperature increases, and the average pore diameter gradually increases. This result may be due to excessive temperature causing partial pore structure collapse.

The morphologies of the aerogel and Fe-doped carbon aerogels at different carbonization temperatures were characterized by SEM. Figure 3a shows that the aerogel has a coral-like three-dimensional network structure. After high-temperature carbonization, the morphology of the sample
changes. The structures of T500 and T600 become denser, and sporadic mesopores can be seen. Due to the limited SEM resolution, it is difficult to observe micropores on the surfaces of samples. When the carbonization temperature is higher than 700 °C, a large amount of mesopores appear in the samples. This abundance may be due to that at approximately 700 °C, C reacts with Fe3O4 to form CO2, which plays a role in pore formation, resulting in a large number of mesopores. Moreover, as the temperature increases, the pore size gradually decreases. The pore structure of sample T900 was severely damaged. SEM-EDS was further applied to investigate the composition of T700, revealing the homogeneous distribution of C, O, and Fe in T700.

Figure 3. SEM images of the aerogel (a), T500 (b), T600 (c), T700 (d), T800 (e), and T900 (f). EDS of T700 (g)

TEM image of T700 is presented in Figure 4a. Fe nanoparticles with diameters of 10-50 nm are firmly embedded into the carbon matrix, which is due to the chelation of Fe3+ and sodium alginate. After high-temperature carbonization, sodium alginate turns into carbon that envelops iron in the center, preventing the aggregation of iron. XPS measurement was used to further obtain the composition and elemental state of the samples. In the survey scan spectra (Figure 4b), C, O, and Fe are observed in T500 and T700. Figure 4c shows the high-resolution Fe2p XPS spectrum of T500. The spectrum shows the typical characteristic peaks of Fe3O4 at 723.5 and 711.2 eV, which refer to Fe2p1/2 and Fe2p3/2, respectively. The high-resolution Fe2p XPS spectrum of T700 is shown in Figure 4d. Compared with the spectrum for T500, a new peak located at 707.1 eV, which refers to Fe0, is observed, which further indicates that Fe3O4 was converted to Fe [34-37]. It can see the peaks of Fe3O4 in T700. It may be due to that the Fe on the surface was oxidized to Fe3O4 during the test.
3. Conclusions
In summary, we prepared Fe-doped carbon aerogel materials by one-step carbonization using environmentally friendly sodium alginate as raw material. The form of iron in the carbon aerogel can be changed by adjusting the carbonization temperature. When the carbonization temperature is under 700 °C, iron mainly exists in the form of Fe₃O₄. When the carbonization temperature is higher than 700 °C, iron mainly exists in the form of Fe and CFe₁₅.₁. These novel Fe-doped carbon aerogel materials will have broad application prospects in the field of wastewater treatment due to the environmentally friendly raw material, simple preparation process, and efficient removal of organics in wastewater.

References
[1] Hanzawa Y., Kaneko K. (1996) Activated carbon aerogels. Langmuir, 12: 6167-6169.
[2] Pekala R.W., Farmer J.C., Alviso C.T. (1998) Carbon aerogels for electrochemical applications. Journal of Non-Crystalline Solids, 225: 74-80.
[3] Tamon H., Ishizaka H., Araki T. Okazaki M. (1998) Control of mesoporous structure of organic and carbon aerogels. Carbon, 36: 1257-1262.
[4] Dai J., Zhang R., Yan Y. (2018) 3D macroscopic superhydrophobic magnetic porous carbon aerogel converted from biorenewable popcorn for selective oil-water separation. Materials and Design, 139: 122-131.
[5] Chen X., Chen C., Zhang Z. (2013) Gelatin-derived nitrogen-doped porous carbon via a dual-template carbonization method for high performance supercapacitors. Journal of Materials Chemistry A, 1: 10903-10911.
[6] Zhu L., Wang Y., Li S. (2017) An environmentally friendly carbon aerogels derived from waste pomelo peels for the removal of organic pollutants/oils. Microporous and Mesoporous Materials, 241: 285-292.
[7] Li D., Yang D., Xia Y. (2016) Double-Helix Structure in Carrageenan–Metal Hydrogels: A General Approach to Porous Metal Sulfides/Carbon Aerogels with Excellent Sodium-Ion Storage. Angewandte Chemie-International Edition, 55: 1-5.

[8] Zhao W., Yuan P., Yang D. (2015) Sustainable seaweed-based one-dimensional (1D) nanofibers as high-performance electrocatalysts for fuel cells. Journal of Materials Chemistry A, 3: 14188-14194.

[9] Wang N., Liu Q., Kang D. (2016) Facile self-crosslinking synthesis of 3D nanoporous Co3O4/carbon hybrid electrode materials for supercapacitors. ACS Applied Materials & Interfaces, 8: 16035-16044.

[10] Liu L., Yang X., Lv C. (2016) Seaweed Derived Route to Fe2O3 Hollow Nanoparticles/N-doped Graphene Aerogels with High Lithium Ion Storage Performance. ACS Applied Materials & Interfaces, 11: 7047-7053.

[11] Ma N., Jia Y., Yang D. (2016) Seaweed Biomass Derived (Ni,Co)/CNTs Nanoaerogels: Efficient Bifunctional Electrocatalysts for Oxygen Evolution and Reduction Reactions. Journal of Materials Chemistry A, 4: 6376-6384.