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# Metal-doped carbon aerogel from sodium alginate for supercapacitor

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**Abstract.** In this paper, different metal-doped carbon aerogels are prepared by one-step carbonization with sodium alginate as raw material. It was known by SEM and TEM that the metal was uniformly dispersed into the carbon aerogels. Cr-doped carbon aerogel has a rich pore structure with a specific surface area of up to 497.4 m<sup>2</sup> g<sup>-1</sup>. The prepared samples were used in the field of supercapacitors, and the test results showed that the Cr-doped carbon aerogel has the highest specific capacitance (312.5 F g<sup>-1</sup>). This study not only develops new directions for the utilization of marine biomass resources, but also provides a simple method for preparing metal-doped carbon material.

## 1. Introduction

Carbon aerogel is a new carbon material with multi-stage pore network structure. It has the advantages of low density, high specific surface area, high porosity and low electrical resistivity, and is widely used in water treatment<sup>[1-3]</sup>, catalysis<sup>[4-6]</sup>, energy storage<sup>[7-10]</sup> and other fields<sup>[11]</sup>. Conventional carbon aerogel is prepared from resorcinol and formaldehyde by sol-gel, solvent exchange, drying and high-temperature carbonization. However, its raw materials are harmful to the environment and humans, and the preparation process is complicated and the production cycle is long. These shortcomings limit the mass production of conventional carbon aerogel. In recent years, researchers have been working on the development of carbon aerogel using biomass (such as cellulose<sup>[12]</sup>, chitosan<sup>[13,14]</sup>, glucose<sup>[15]</sup>, sodium alginate<sup>[16]</sup>) as a raw material. The preparation of carbon aerogel from biomass is more in line with the concept of environmental protection, and the preparation process is simple and the production cycle is short, so it has a good prospect for development.

Supercapacitor is a new type of energy storage device between traditional capacitors and rechargeable batteries. It has the advantages of high power density, long cycle life and wide operating temperature limit. According to different energy storage mechanisms, supercapacitor can be divided into electric double layer capacitor and pseudo-capacitor. Electric double layer capacitor mainly store electric energy by forming an electric double layer by electrostatic interaction between electrolyte ions and electrode materials. Pseudo-capacitor is based on the surface or the interior of a two-dimensional space of the electrode material that the underactive deposition of the electroactive substance causes a rapid reversible redox reaction for energy storage. However, the electric double layer capacitor has a lower specific capacitance, while the pseudo-capacitor has a shorter cycle life. Therefore, many studies



are devoted to the development of metal-doped carbon materials, which solves the shortcomings of the lower specific capacitance of electric double layer capacitor and the problem of cycle life of pseudo-capacitor.

Sodium alginate is a polysaccharide polymer extracted from marine biomass resources, which can rapidly chelate with polyvalent metal ions in aqueous solution to form hydrogel. In this paper, sodium alginate-based hydrogels rich in metal ions ( $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ) was prepared by using the characteristics of sodium alginate, and then freeze-dried and high-temperature carbonization to obtain metal-doped carbon aerogels. The metal-doped carbon aerogels were applied in the field of supercapacitor and exhibited good electrochemical performance. Among the metal-doped carbon aerogels, the Cr-doped carbon aerogel shows a specific capacitance up to  $312.5 \text{ F g}^{-1}$  at a current of  $2 \text{ A g}^{-1}$ . This paper not only develops new directions for the utilization of marine biomass resources, but also provides a simple method for preparing metal-doped carbon material.

## 2. Experimental

### 2.1. Materials

Sodium alginate,  $\text{CrN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ ,  $\text{CoNO}_3$ , and  $\text{FeN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$  were purchased from Aldrich Co. KOH and polyvinylidene fluoride (PVDF) were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co.

### 2.2. Materials preparation

Metal-doped carbon aerogels were prepared by the following steps:

- (1) 1 wt% sodium alginate solution was added to 3wt% metal salt solution ( $\text{CrN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ ,  $\text{CoNO}_3$ , and  $\text{FeN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ ) by a syringe to obtain sodium alginate hydrogels.
- (2) The hydrogels were rinsed with purified water until the metal ions on the surface were removed.
- (3) The hydrogels were placed in a freeze dryer, frozen for 12 hours, and dried for 48 hours to obtain sodium alginate aerogels.
- (4) The aerogels were heated to  $900^\circ\text{C}$  with a heating rate of  $5^\circ\text{C min}^{-1}$  and held for 2 hours under nitrogen atmosphere in a carbonization furnace to obtain metal-doped carbon aerogels. The carbon aerogels are identified as Cr-CA, Co-CA, and Fe-CA, respectively.

### 2.3. Characterization

The microscopic and elemental distribution of the metal-doped carbon aerogels were observed by a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The nanostructure of samples was examined by a transmission electron microscopy (TEM). The crystalline structure of the samples was obtained by a X-ray diffraction (XRD) under  $\text{Cu K}\alpha$  radiation at 40 kV, 40 mA. The Micromeritics ASAP 2460 surface area analyser were used to obtain the pore structures of the samples.

### 2.4. Electrochemical measurements

The electrochemical measurements were monitored by GAMRY Interface 100E in a three electrode system with the electrolyte of 6M KOH. The metal-doped carbon aerogels were mixed with PVDF at a mass ratio of 95:5. Then, the mixtures were pressed on nickel foil to obtain the working electrode. The Pt and Hg/HgO electrode were used as counter electrode and reference electrode. The cyclic voltammetry (CV) test and galvanostatic charge-discharge (GCD) test were applied to evaluate the electrochemical performance of the samples.

## 3. Results and discussion

### 3.1. Material characterization

The microscopic and elemental distribution of the metal-doped carbon aerogels were characterized by

SEM and EDS. Figure 1a shows the SEM and EDS of Cr-CA. It can be seen that the Cr-CA has a three-dimensional network structure and the Cr element is uniformly dispersed in the sample. Figure 1b shows the SEM and EDS of Co-CA. Compared with Cr-CA, the surface of Co-CA sample is relatively dense, and no obvious pore structure can be found. Figure 1c shows the SEM and EDS of Fe-CA. Fe-CA has many large holes and the Fe element is uniformly dispersed in the sample. The uniformly dispersed of Cr, Co and Fe is own to the chelation of sodium alginate with metal ions.

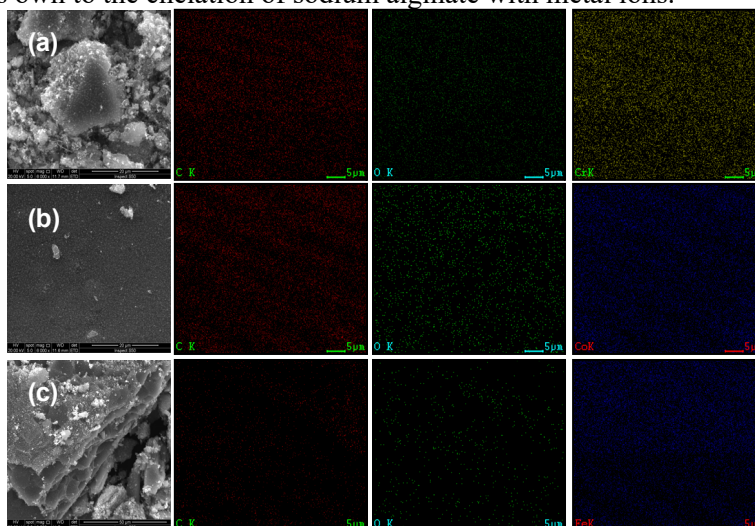


Figure 1. SEM and EDS of the samples: (a) Cr-CA, (b) Co-CA, (c) Fe-CA.

Figure 2 shows the TEM of the metal-doped carbon aerogels. It can be seen from figure 2a that Cr element is evenly distributed in the sample in different shapes. As shown in figure 2b, Co element is uniformly distributed in the sample in a spherical shape. Fe element is distributed in the sample in a spherical shape with the size of 50-100 nm and some Fe element has accumulated as shown in figure 2c.

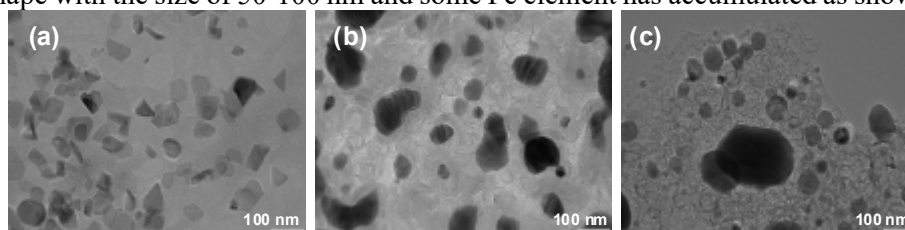


Figure 2. TEM of the samples: (a) Cr-CA, (b) Co-CA, (c) Fe-CA.

XRD patterns of the metal-doped carbon aerogels are shown in Figure 3. The peaks at  $2\theta \approx 24.5^\circ$ ,  $33.6^\circ$ ,  $36.2^\circ$  and  $54.9^\circ$  are corresponding to [012], [104], [110], and [116] planes of  $\text{Cr}_2\text{O}_3$ . The peaks at  $2\theta \approx 42.5^\circ$ ,  $44.2^\circ$ , and  $50.2^\circ$  are corresponding to [112], [115], and [222] planes of  $\text{Cr}_7\text{C}_3$ . The peak at  $2\theta \approx 26.6^\circ$  is corresponding to [006] peak of graphitic carbon. The peaks at  $2\theta \approx 44.2^\circ$ ,  $51.5^\circ$ , and  $75.9^\circ$  are corresponding to [111], [200], and [220] planes of Co. The peaks at  $2\theta \approx 44.7^\circ$ ,  $65.0^\circ$ , and  $82.3^\circ$  are corresponding to [110], [200], and [211] planes of Fe. The peaks at  $2\theta \approx 43.3^\circ$ ,  $50.4^\circ$ , and  $74.1^\circ$  are corresponding to [111], [200], and [220] planes of  $\text{FeC}_{15.1}$ .

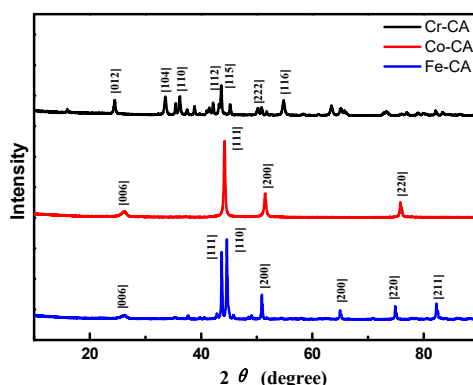


Figure 3. XRD patterns of the samples

Figure 4 shows the pore structure of the samples. As shown in figure 5a, All samples show the type IV isotherms. The appearance of the hysteresis loop indicates the presence of mesopores in the samples. At the low pressure ( $P/P_0 < 0.01$ ), the adsorption curve of Cr-CA rapid increase indicating the existence of micropores. Figure 5b shows the pore distribution of the samples. It can be seen that Cr-CA has many micropores at 0.5-1.0 nm, and Co-CA, Fe-CA have little micropores. Table 1 shows the detail porosity property. The specific surface area (SSA) of Cr-CA is  $497.4 \text{ m}^2 \text{ g}^{-1}$  and the SSA of Co-CA is only  $82.5 \text{ m}^2 \text{ g}^{-1}$ .

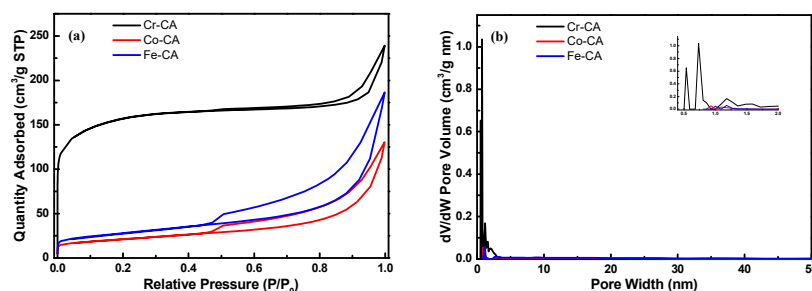


Figure 4. Pore structure of the samples

Table 1. Detail porosity property of the samples

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$S_{\text{m}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_{\text{T}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{m}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$D_{\text{ave}}$ (nm)
Cr-CA	497.4	288.7	0.3035	0.1542	2.4
Co-CA	82.5	13.8	0.1234	0.0070	6.0
Fe-CA	179.9	17.9	0.3429	0.0083	7.6

### 3.2. Electrochemical performance of the metal-doped carbon aerogels

The CV test of the samples is investigated at a current density of  $10 \text{ mV s}^{-1}$  with the potential window of -0.8 to 0 V. As shown in Figure 5, the CV curves of Cr-CA and Fe-CA show a quasi rectangular shape indicating the electrical-double-layer behavior. However, there is a sharp change in the ends of Co-CA that may be due to the decomposition of water indicating the poor electrochemical performance of Co-CA.

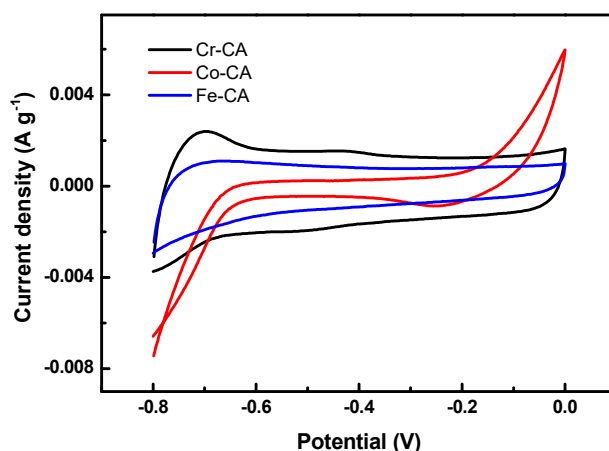


Figure 5. CV curves of the samples

Figure 6 shows the GCD curves of the samples (at a current density of  $2\text{ A g}^{-1}$ ). It can be seen that the GCD curves of Cr-CA and Fe-CA exhibit a triangular shape and the GCD curve of Co-CA shows a platform indicating the poor electrochemical performance of Co-CA. The result shown in the GCD is similar with the CV. The specific capacitance can be calculated according to the following equation :  $C = I\Delta t / m\Delta V$

Where,  $I$  is the current,  $\Delta t$  is the discharging time,  $m$  is the mass of the metal-doped carbon aerogels, and  $\Delta V$  is the voltage. The specific capacitances of Cr-CA, Co-CA, and Fe-CA at a current density of  $2\text{ A g}^{-1}$  are  $312.5$ ,  $125.2$ , and  $62.5\text{ F g}^{-1}$ , respectively.

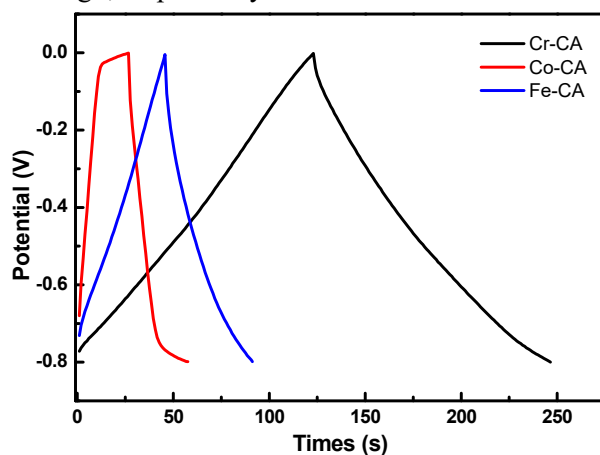


Figure 6. GCD curves of the samples

#### 4. Conclusions

In summary, We prepared different metal-doped carbon aerogels by ion exchange, freeze drying and high temperature carbonization with sodium alginate as raw materials. The metal elements were uniformly dispersed in the carbon aerogels that was confirmed by EDS and TEM. The pore structures were examined and Cr-doped carbon aerogel shows the highest specific surface (up to  $497.4\text{ m}^2\text{ g}^{-1}$ ). The metal-doped carbon aerogels were used in the field of supercapacitors. The results showed that the Cr-doped carbon aerogel has the highest specific capacitance (up to  $312.5\text{ F g}^{-1}$ ). This study not only develops new directions for the utilization of marine biomass resources, but also provides a simple method for preparing metal-doped carbon material.

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