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Size-controllable synthesis of carbon spheres with assistance of metal ions

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ABSTRACT

This is great interest in tuning diameter of carbonaceous materials for applications in energy storage, templates and separation etc. In this study, different texture and size distribution of carbon spheres were obtained in only one step by hydrothermal carbonization of glucose using metal chlorides, such as NaCl, $MgCl_2$, $CaCl_2$ and $FeCl_3$. Then, structure and chemical composition of the products were characterized by means of SEM, TEM, FTIR and Zetasizer. The combination of these results had allowed us to infer that adding metal ions was more efficient than prolonging hydrothermal treatment in promoting the formation of carbon microspheres. In addition, metal ions strength is proportional to the size of the particles. At last, through investigating the morphology transformation process of the products, a possible growth mechanism was proposed.

1. Introduction

Colloidal nano-/micro particles have attracted much attentions due to their tunable physicochemistry properties through modifying their size, composition, microstructure and crystallinity [1,2]. Among of them, as a new material, spherical carbon particles are attractive because of their broad applications in templates [3], energy storage [4], adsorption [5], separation technologies [6] and lubricants [7] etc. Up to now, various synthetic strategies have been developed to prepare carbon spheres, such as hydrothermal synthesis [8,9], chemical vapor deposition [10] and pressure carbonization [11], among of them, hydrothermal carbonization is a better choice due to its simple, economical and environmental friendly properties.

Previous studies have shown that dimension control of carbon spheres is crucial for their specific applications [12]. Although prolonging reaction time is helpful to increase their size slightly, it's time consuming and energy consumption. In this paper, we present a facile route to prepare spherical carbon particles with tunable size distribution using salts of Na, Mg, Ca and Fe. Some affecting parameters have been investigated thoroughly, and a possible growth mechanism has been proposed.

2. Experiment

All of the reagents were of analytical reagents and purchased from aladdin without further purification. In a typical synthesis, 4.58 g glucose was dissolved in 50 ml de-ionized water, and then 0.1169 g NaCl was poured into the solution, its final concentration was 40 mM. Afer stirring for 10 min, the final mixture was transferred into a teflon bottle (100 ml) held in a stainless steel autoclave. After heating at 180 °C for 4 h, the mixture was cooled naturely, and then washed three times with de-ionized water and ethanol, respectively. The final products were collected through centrifugation.

3. Results and disscussion

Reaction time had a great effect on size distribution of carbon spheres. Scanning electron microscopy (SEM) images of carbon spheres prepared from 4 h hydrothermal carbonization showed discrete and uniform spherical morphology, and their diameter was in the range of 100–200 nm (Fig. 1A(a), (a1)). Further increasing reaction time to 10 h, 1–2 μm sized carbon microspheres surrounded by nanoparticles (~200 nm) particles formed, these spherical nanoparticles were not dispersive but fused with each other. As shown in Fig. 1A(c) and A(c1), after hydrothermal treating for 24 h, irregular shaped nanoparticles mixed with carbon microspheres formed. The size of the nanoparticles and microspheres was 400 nm and 1–2 μm, respectively. Besides, almost all

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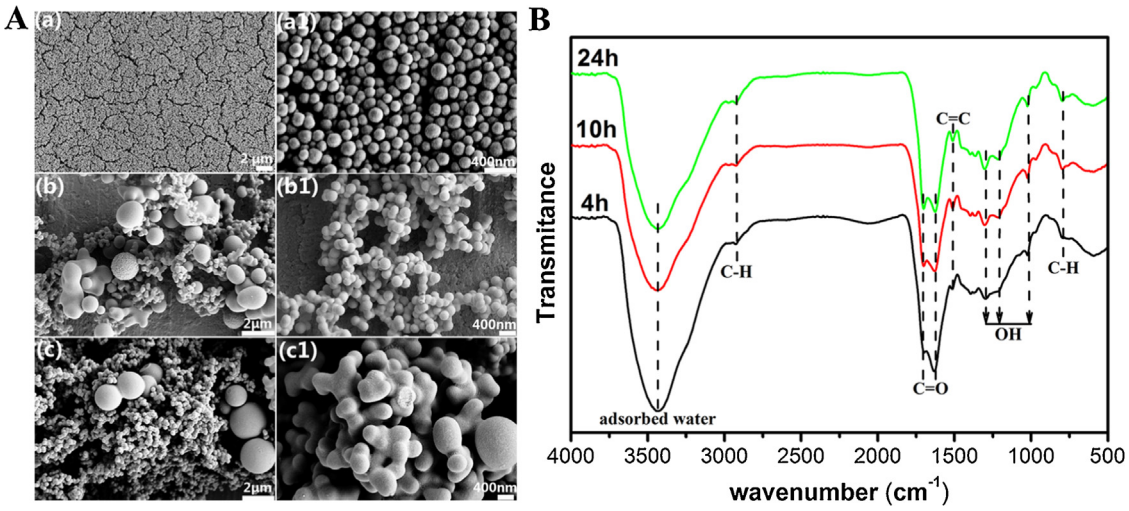

Fig. 1. Morphology (A) and FTIR spectra (B) of carbon spheres prepared at different reaction time with no additive, A(a, a1) 4 h; A(b, b1) 10 h; A(c, c1) 24 h.

of the nanoparticles fused with each other and without discrete nanoparticles existed. Therefore, according to the former results, we could infer that increasing reaction time resulted in the growth and fusing process of nanoparticles, but it's quite inefficiency for promoting the formation of large amount of microspheres. Moreover, as shown in Fig. 1B, independently of reaction time, all of the spectra contained the same FTIR bands, which indicated that they have the same chemical nature. The bands at 1500–1750 cm^{-1} could be attributed to C=O and C=C vibrations [1,13], whereas the bands in the range of 1000–1450 cm^{-1} were ascribed to O—H bending vibration. In addition, the bands at 798 and 2914 cm^{-1} were assigned to C—H vibrations [14,15].

Hydrothermal carbonization of glucose in the presence of sodium chloride resulted in shape and size transformation of carbon spheres, as shown in Fig. 2. It should be noted that the concentration of Na^+ was a key factor in controlling paritcle size.

From Fig. 2a, the particles were in the form of nano and microspheres with an average dimension at the range of 0.5–5 μm, and their size distribution remained unchanged as the concentration of Na^+ reached to 20 mM. As the concentration of Na^+ reached to 40 mM, the diameter of the carbon nanospheres increased and reached ~1 μm (Fig. 2c), while the diameter of microspheres was not changed. Further increasing the concentration of Na^+ was not helpful for facilitating the growth of carbon spheres, especially for nanoparticles' growth.

In general, different additives might affect the nucleation of carbon spheres and tune their growth process. Hence, we chose NaCl, $MgCl_2$, $CaCl_2$ and $FeCl_3$ as the corresponding additives, and investigated their influence to the size and texutre of carbon particles.

As shown in Fig. 3A(a) and B (a), the average dimension of carbon spheres was 1.4 μm for NaCl group. As the additives were $MgCl_2$ and $CaCl_2$, the majority of the products was larger particles with an average dimension of 2 and 2.5 μm, respectively. Therefore, the metal ions with different atomic radius at equal ionic strength condition would affect the size distribution of the

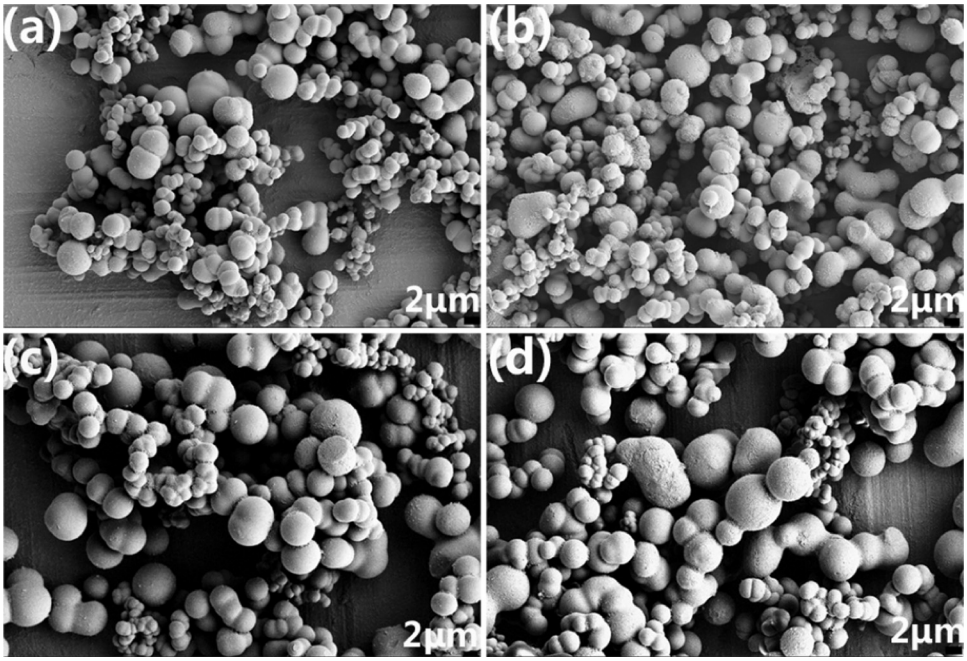

Fig. 2. SEM image of carbon spheres prepared at different concentration of NaCl. (a) 10 mM; (b) 20 mM; (c) 40 mM; (d) 100 mM. The period of hydrothermal process was 4 h.