



A simple method of preparing ordered and three-dimensionally-interconnected macroporous carbon with mesoporosity by using silica template

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ABSTRACT

A simple and cost-effective method for the production of porous macro-meso structures is proposed. The approach involves using of monodispersed silica particles and in situ polymerized silica network as a removable template, and using resorcinol-sucrose derivative polymer as a carbon source. The three steps – carbon precursor, silica particles, template – are synthesized simultaneously through sol-gel reaction in one-pot system. The sample prepared by this method was characterized by scanning electron microscopy (SEM) and nitrogen adsorption and desorption, and the results present us a well long-ranged ordered structure and three-dimensionally interconnected macroporous carbon with mesoporosity.

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1. Introduction

Because micro-structured porous carbon has potential applications in catalysis, separation, coating, sensors, separation and chemical filtration, photonics, microelectronics, electro-optics, environmental engineering, adsorbents, chromatographic, insulators, biomaterials engineering, controlled released, nanolithographic template for etching [1], and so on, it is currently the object of an intense research effort owing to their outstanding properties. In order to optimize its macroporous structure, people have proposed various production methods up to now for their synthesis [2]. A typical example is using aggregates of polystyrene and silica particles as templates to fabricate ordered macroporous carbon with hierarchical pore structure. Although the use of organic templates to control the structure of inorganic solids has proven very successful for designing porous materials with pore sizes ranging from angstroms to micrometers, the preparation method is somewhat too complex because it requires a long time to prepare the template. In this regard, the present work is aimed at exploring the easy preparation method of ordered and interconnected macroporous carbon (MaMeC, macro-mesoporous carbon). For this purpose, we have now developed a method to use the combination of monodispersed silica particles and in situ polymerized silica network as a removable template, and resorcinol-sucrose derivative polymer as a carbon source. The three steps – carbon precursor, silica particles and template – are synthesized simultaneously through sol-gel reaction in one-pot system. The preparation method is very simple and efficient [3].

2. Experimental procedure

Monodispersed silica particles are obtained by putting the 0.28 mol/l of tetraethoxysilane in reaction with various concentrations of water and ammonia in ethanol while the solution was agitated by a magnetic stirrer. In order to induce acid sites, we impregnate them with aluminum trichloride (A. R.) at the mole ratio of Si/Al = 10, and then they are dried and calcined at 550 °C for 5 h. The mole ratios of reactants were the key factor to produce different sizes of monodispersed silica particles. Before being used, the synthesized silica particles are washed with high-purity ethanol by repeated centrifugation and ultrasonic dispersion in order to eliminate the unreacted tetraethoxysilane (TEOS) and ammonia. Then the silica particles are dissolved in an aqueous solution containing resorcinol (A.R.), sucrose (A.R.) and tetraethoxysilane (TEOS, A. R.), and polymerized to obtain ordered and three-dimensionally interconnected macroporous carbon. The mixture of reaction is stirred at 100 °C for 4 h, and filtered. The solid leftover is processed at 80 °C for 5 h and dried at 100 °C for 12 h. The dried sample is carbonized under an N₂ flow at a heating rate of 5 °C/min to 850 °C and held there for 5 h. The macroporous carbon composition prepared through these methods were marinated with aqueous HF solution of about 30% concentration at room temperature for 8 h to dissolve the silica framework, then filtered and washed the insoluble fraction washed away with copious de-ionized water. Finally the resultant, insoluble carbon was vacuum-dried at 80 °C overnight. Fig. 1 shows the overall synthesis procedure for the macroporous-mesoporous carbon.

Analysis of the surface physical properties of the carbon includes detection of the total surface area and characteristics of the pore size distribution. The surface morphology was characterized by scanning

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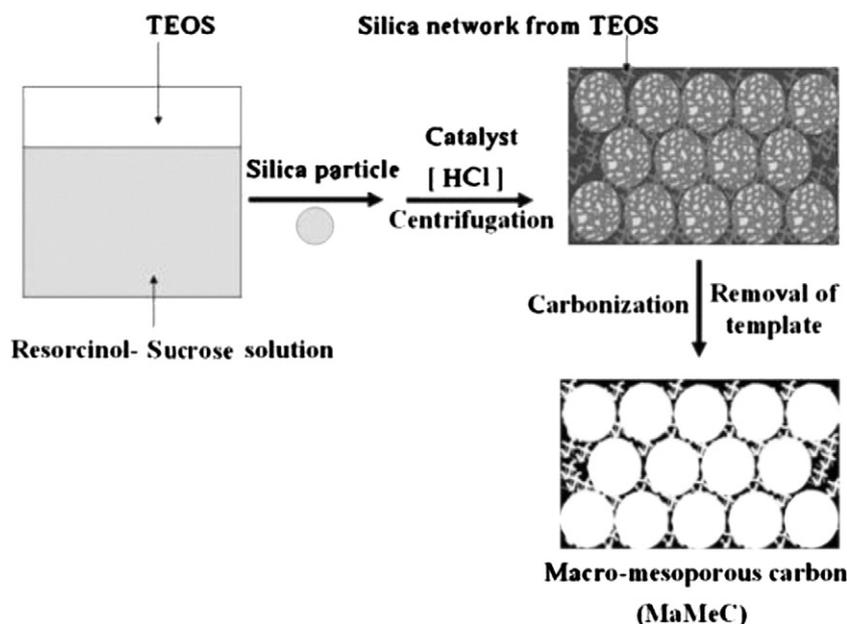


Fig. 1. A schematic illustration of the synthesis of a periodically ordered macroporous carbon framework with mesoporous wall.

electron microscopy (FEI Quanta200, Holland). The pore structure of 3DOM carbon was analyzed by means of nitrogen adsorption by utilizing Micromeritics ASAP 2010 sorption analyzer [4].

3. Results and discussion

At the initial stage of synthesis, hydrochloric acid naturally hydrolyze sucrose into fructose that is reactive for the addition (additional) reaction of resorcinol, leading to phenolic hydroxyl group derivatives [5,6]. In the presence of protons, the phenolic hydroxyl group derivatives undergo condensation reaction into three-dimensional cross-linked polymer. In our case, the surface of modified silica particles provides strong acid sites for the condensation of phenolic hydroxyl group derivatives. Furthermore, TEOS can be naturally polymerized into silica network on the acid sites of modified silica particles [7]. Therefore, it can be concluded that in the process of fabrication of well-organized macroporous carbon material with mesoporous framework, the polymerization of TEOS and the simultaneous formation of hydroxymethyl derivatives are key factors. And in the process, if there is absence of acid sites, TEOS is very slowly hydrolyzed and condensed into silica sol. Large silica aggregates from TEOS will destroy the formation of templates so as to spoil the macropore orderedness of porous carbon, and consequently, they cannot serve as templates for small framework mesopores. Fig. 2 shows the scanning electron (electronic) microscopy

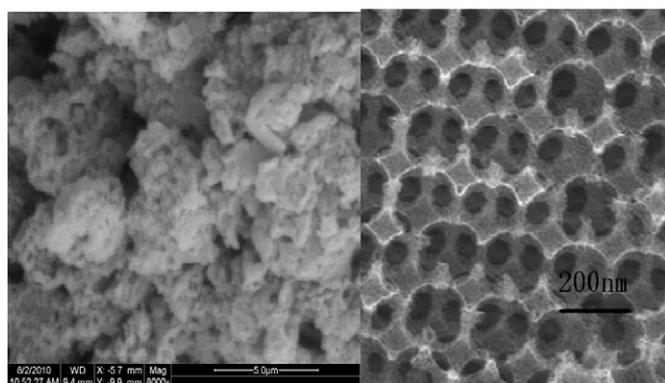


Fig. 2. The scanning electron microscopy (SEM) images of macro-porous carbon.

(SEM) images of macroporous carbon. In the SEM image of macroporous carbon material, large orderly-distributed macropores are clearly seen. Moreover, disordered small mesopores in the framework can also be observed at high magnification.

Fig. 3 shows the nitrogen adsorption–desorption isotherms and pore size distributions of macroporous carbon material. The significant adsorption at low relative pressure indicates that this carbon material has micropore that would result from the carbonization of carbon precursor. It was also found that the isotherm rose continuously at above 0.02 of relative pressure due to volume filling of mesoporosity, and at above 0.9 of relative pressure there is a capillary condensation indicating the surface coverage of macropores. From the adsorption branch of isotherm, the pore size distribution shows that the macroporous carbon material is of similar-sized framework mesopores with pores ranging between 3 and 5 nm, in good consistent with the SEM results. BET surface area of this macroporous carbon material is $890 \text{ m}^2/\text{g}$ and total pore volume is $1.95 \text{ cm}^3/\text{g}$. The mesoporosity, defined as the ratio of BJH surface area with respect to BET surface area [8], was 0.93 in this

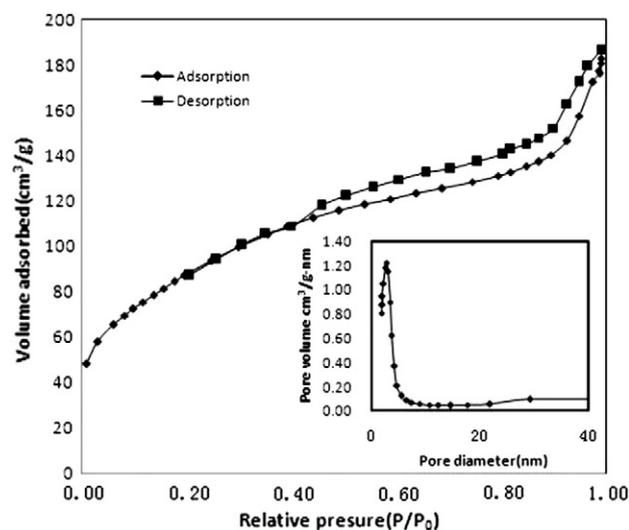


Fig. 3. N_2 adsorption–desorption isotherms and pore size distributions (insets) of macro-mesoporous carbon.

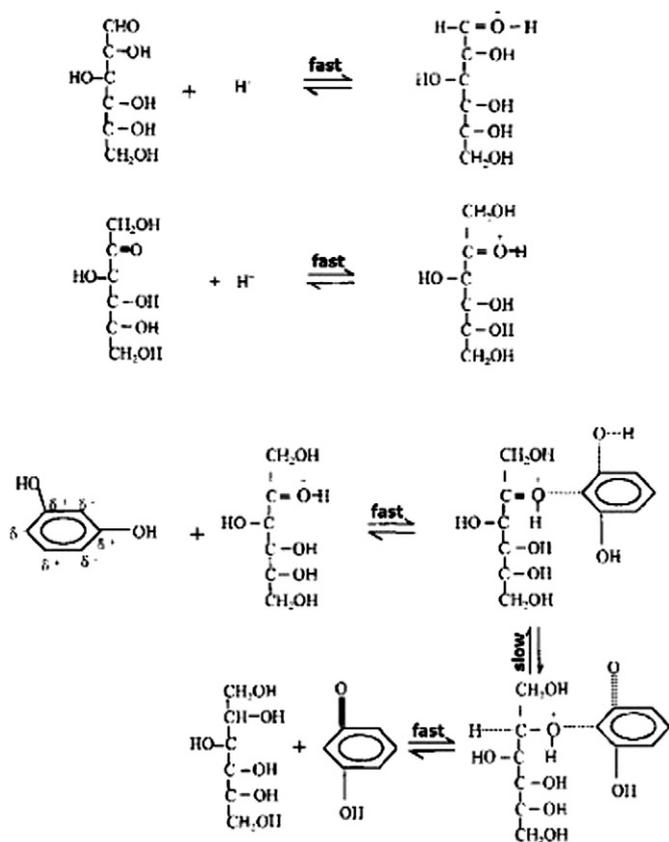


Fig. 4. Carbon precursor reaction mechanism.

material. In order to study the microporosity of the prepared carbon materials, we calculated the micropore volume using Dubinin–Adushkevitch equation (DR equation) [9–11]. The contribution of micropore volume to total pore volume is about 0.002 in macroporous carbon (micropore volume/total pore volume = 0.39/1.95). This demonstrates that the macroporous carbon has well-developed framework mesopores. The diameter of macropores could be easily manipulated by using different sizes of monodispersed silica particles.

Carbon precursor reaction mechanism is just like what Fig. 4 shows. The activator of synthesis of resorcinol and sucrose is hydrochloric acid. The hydrochloric acid that catalyzes the hydrolysis

of sucrose into glucose and fructose, and then fructose reacts with resorcinol in an aqueous in the presence of hydrochloric acid.

4. Conclusion

In this study, an ordered and three-dimensionally-interconnected macroporous carbon with mesopore was synthesized easily in one-pot system by using resorcinol-sucrose resin as a carbon precursor and unanimous sized silica particles combined with in situ polymerizable TEOS as a template. The present results obviously show that the synthesis method described in this article is a simple and time-saving way for the fabrication of ordered and three-dimensionally-interconnected-macroporous carbon with mesoposity.

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