Supplementary Files Effect of electrical conductivity on the formation and annihilation of positronium in porous materials

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1. Preparation of ordered porous silicon and OMC

The ordinary procedure for the synthesis of OMC is as follows: First, 1 g SBA-15, 0.25 g sucrose, 5 g distilled H₂O and 0.14 g H₂SO₄ are mixed homogenously, then they were placed at a constant temperature of 100 °C for 6 h, and 160 °C for another 6 h. Afterwards, 0.8 g sucrose, 0.09 g H₂SO₄ and 5 g distilled H₂O was added, and they were again placed at 100 °C for 6 h and 160 °C for another 6 h. The obtained C/SBA-15 compound was carbonized in the tube furnace at 900 °C for 5 h under N₂ atmosphere. Then, the template SBA-15 was removed by 5 wt% HF solution at room temperature for 72 h. Finally, the ordered mesoporous carbon solution was filtered, washed with distilled water (EtOH) and dried at 100 °C for 24 h.

2. SAXS measurement

Small-angle x-ray scattering (SAXS) measurements were carried out using an X-ray diffractometer (X'Pert Pro, PANalytical, Netherlands) with $CuK\alpha$ radiation operated at 40 kV and 40 mA. The incident X-ray wavelength λ is 1.5406 Å and the scanning angle 2θ is from 0.6123 to 10° with the step of 0.001°.

Fig.1 represents the small-angle X-ray scattering results of the silica template and ordered mesoporous carbon. The silica template has the symbolic diffraction peaks of ordered 2D hexagonal P6mm symmetry, which was indexed as (100), (110) and (200). The same diffraction peaks were also observed for mesoporous carbon, which verifies the same regular pore structure with that of the silica template. The synthesized carbon almost copies the pore structure of the ordered mesoporous silica template (SBA-15), with rode-like shape similar to that of carbon nanotube.

The periodic interval of the ordered pores for silica template and porous carbon can be estimated by the Bragg's equation using the position of the main diffraction peak (100):

$$2dsin\theta = n\lambda\tag{1}$$

The obtained intervals of ordered pores are labeled in Fig.1, which are 8.90 nm and 8.34 nm for the synthesized ordered mesoporous carbon and silica template, respectively. The larger interval of porous carbon indicates a little collapse of the ordered pore structure from its copy of silica.

3. SEM measurement

To check the morphology of the synthesized samples, scanning electron microscope (SEM,XL 30 (Philips), Amsterdam, Netherlands) and electron diffraction spectrum(EDS) measurements were performed. Fig.2 shows the SEM image of SiO₂ template and porous carbon. The EDS of porous carbon is also plotted in the bottom of Fig.2. The two SEM images of SiO₂ template and porous carbon show very similar particle morphology, with beaded chain of about 0.6 μ m in length and 0.2 μ m in width. This indicates that the synthesized ordered mesoporous carbon is microsized particle. The SEM images further confirm the perfect copy of the morphology of ordered mesoporous carbon from SiO₂ template. In addition, the EDS spectrum of porous carbon shown in Fig.2 indicates that the sample is mainly composed of carbon element, with very little residual silica particle in the wall of the pore. This confirms successful synthesis of the ordered mesoporous carbon without existence of the silica template.

4. HRTEM measurement

High resolution transmission electron microscope (HRTEM) (JEOL JEM-2010FEF (UHR), Tokyo, Japan) were performed with acceleration voltage at 200 kV to characterize the pore structure of the sample. The TEM images of SiO2 template and the porous carbon were shown in Fig.3, which were measured from two specific directions (perpendicular and parallel to the channel directions) to intuitively demonstrate the pore structure of the synthesized samples. It is clear that the two samples all possess ordered mesoporous pores. This coincides with the results from SAXS measurements. As shown in the left part of Fig.3, the ordered 2D hexagonal symmetric pore structure of the synthesized carbon and SiO_2 template can be clearly observed. The diameter of the pore is about 3.8 nm and 8 nm for the synthesized ordered mesoporous carbon and its silica template, respectively. The ordered mesoporous pore structure is reflected in the right part of Fig.3. Compared with the distinct ordered pore structure of SiO_2 template, the mesoporous carbon has a slight collapse of the pore wall. This might be the results of pore damage during process of calcination or removing of the template by HF, and is also possibly related with the carbon source arrangement in the synthesized mesoporous carbon.

5. N_2 adsorption-desorption measurement

The N_2 adsorption-desorption isothermals were also measured at 77 K for the synthesized ordered mesoporous carbon and its SiO₂ template by using a Micromeritics ASAP 2020 gas-sorption analyzer. The method can get more information about the pore parameters, such as pore size, pore

volume and surface area. The sample was degassed in a vacuum at 180 °C for the desorption process. Pore size distribution and the average pore size were estimated from adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method [1]. At the same time, the specific surface area was calculated from the Brunauer-Emmett-Teller (BET) method [2] over the relative pressure P/P_0 range of 0.05-0.25. The results were shown in Fig.4. According to the classification of IUPAC [3], the two isothermals are both the typical IV curves, with clear capillary condensation step at the relative pressure P/P_0 of 0.4-0.8, which was the symbolic characteristic of mesoporous pore. The pore size distribution of OMC and its SiO_2 template derived from the adsorption isothermal by BJH model [1] are shown in the right part of Fig.4. The average pore size of ordered mesoporous carbon and the SiO_2 template are about 3.3 nm and 7.5 nm and the corresponding relative pore volume are about $1.276 \text{ cm}^3/\text{g}$ and $11.125 \text{ cm}^3/\text{g}$, respectively. Derived by the BET model, the specific surface area of OMC is up to $1214.94 \text{ m}^2/\text{g}$, which is much higher than the SiO₂ templates (597.92 m^2/g). The results of SAXS, SEM-EDS, TEM, and N₂ adsorption-desorption measurements all indicate that the synthesized carbon contains ordered mesoporous structure with relatively high pore volume and specific surface area. Therefore, as a new allotrope of carbon with ordered mesopores, OMC might possess its specific applications in the future.

- E. P. Barrett, L. G. Joyner, P. P. Halenda, J. Am. Chem. Soc., 1951, 73, 373-380.
- [2] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc., 1938, 60, 309-319.
- [3] M. E. Davis, Nature, 2002, **417**, 813-821.

Figure captions

Fig.1. Small-angle X-ray Scattering patterns measured for the SiO_2 template(black line) and ordered mesoporous carbon(red line). The index of three symbolic diffraction peaks were marked and the period of the ordered mesopores was indicated on the curve.

Fig.2. Scanning electron microscope images measured for the SiO_2 template (left) and ordered mesoporous carbon (right) and the Electron diffraction spectroscopy measured for the ordered mesoporous carbon(bottom). The EDS spectrum of porous carbon confirms that the sample is mainly composed of carbon element.

Fig.3. High resolution transmission electron microscope images measured for the SiO_2 template and ordered mesoporous carbon from directions perpendicular (left) and parallel (right) to the channel.

Fig.4. Nitrogen adsorption-desorption isothermals measured for the SiO₂ template(upper left) and ordered mesoporous carbon(lower left) and their relative pore size distributions (right part). The two isothermals are both typical IV curves, with clear capillary condensation step at relative pressure P/P_0 of 0.4-0.8, which indicates existence of mesoporous pores.



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