



# Effect of synthesis temperature on the ordered pore structure in mesoporous silica studied by positron annihilation spectroscopy



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## ABSTRACT

Mesoporous silica with ordered pore structure was synthesized at various temperatures using TEOS as the silica source and P123 as the template. Both small angle X-ray scattering (SAXS) and high resolution transition electron microscopy (HRTEM) measurements verify the ordered pore structure of the synthesized SiO<sub>2</sub>. With synthesis temperature increasing, the pore structure has slight damage at 130 °C, while it shows ordered structure again at 150 °C. When the synthesis temperature increases to 180 °C, the ordered pore structure is severely destructed. The change of pore structure is further confirmed by scanning electron microscopy (SEM) measurements. Positron lifetime measurements reveal four lifetime components in the synthesized mesoporous SiO<sub>2</sub>, and the two long lifetimes  $\tau_3$  and  $\tau_4$  correspond to the annihilation of o-Ps in the micropores and large pores of the material, respectively. The longest lifetime  $\tau_4$  tends to increase slightly with increasing synthesis temperature. However, its intensity  $I_4$  shows an overall decrease with exception at 150 °C. At the synthesis temperature of 180 °C, the intensity  $I_4$  decreases drastically to about 17.5%. This indicates variation of the size and fraction of pores with increasing synthesis temperature, and the pore structure is seriously destructed at 180 °C. By comparing with the N<sub>2</sub> adsorption–desorption measurements, it was found that the Goworek's model is more suitable for the size estimation of cylindrical pores from the o-Ps lifetime, while Dull's and Ito's model is appropriate for the rectangular and spherical pores, respectively.

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## 1. Introduction

Mesoporous materials, from the natural materials such as diatomaceous earth, natural zeolite and polypite [1–3], to the synthesized porous materials [4–11], have found their wide applications in many fields and attracted more and more attentions. The research areas and related applications are further broadened especially after the appearance of the controllable ordered porous materials, which not only make up the deficiency of microporous zeolite materials [1] for the application in the macromolecules adsorption [4] and catalytic reaction [5], but also can be applied as the microreactor [6] of the controllable nano-materials in chemistry industries, biological technology [7], adsorption isolation [8], environment catalysis, [9], etc. The most commonly used material is ordered mesoporous silica [10–13], such as MCM-41, MCM-48, SBA-15, KIT-6, and SBA-16, which contains different pore size, surface area, pore volume and pore morphology.

Ordered mesoporous silica can be easily synthesized at lower temperatures, even at the room temperature. However, at lower temperatures such as room temperature, large amounts of terminal hydroxyl groups will be irregularly stacked, which might cause the irregular rank of the wall structure of the ordered pore and result in the collapse of the pore structure. Therefore the mesopore in silica possesses a relatively low ordering. Higher synthesis temperature might result in a more stable and ordered mesopore structure. Nevertheless, a much too high temperature will also destroy the ordered pore structure. Therefore an appropriate synthesis temperature should be chosen to attain the balance between pore structure and pore stability.

The pore structure such as pore size and their size distribution can be detected by the gas adsorption method [14]. This method is based on the fact that below the saturated vapor pressure of the adsorbate, it condenses to liquid in narrow pores. However, this method is only sensitive to mesopores (2–50 nm), and only open pores can be detected. In a closed-pore material, gases cannot enter the pore, so the adsorption method fails to work. Mercury intrusion porosimeter [15] is another approach to estimate the pore size. However, this porosimeter is sensitive to pores with even larger size. The pores with radius less than 10 nm will escape

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from the detection by this method. Some other methods might be more useful for the study of pore structure in mesoporous materials.

Positron annihilation spectroscopy has emerged as a powerful probe for the pore structure [16–21]. In many materials, positron will capture one electron to form a metastable hydrogen-like particle called positronium (Ps) atom. According to the spins of the positron and electron, the Ps atom exists in two states: the triplet spin state ortho-positronium (o-Ps) ( $s=1$ ,  $m_s = -1, 0, +1$ ) and the singlet spin state para-positronium (p-Ps) ( $s=0$ ,  $m_s=0$ ). The formation probability of o-Ps is about three times of that of p-Ps. In vacuum, the o-Ps has a long lifetime of 142 ns, and it converts to  $3\gamma$  rays through self-annihilation. The p-Ps has a relatively shorter self-annihilation lifetime of 125 ps by emitting  $2\gamma$  rays.

In porous materials, the annihilation of o-Ps depends on the structure of the pore [22]. When o-Ps is trapped in the pore, it will pick one electron from the wall of the pore and then annihilates into  $2\gamma$  rays, which is called pick-off annihilation. For pores with diameter smaller than 1 nm, the pick-off annihilation lifetime of o-Ps will be reduced to about 1–20 ns, which is closely related to the pore size. The positronium formation probability, which is reflected by the o-Ps intensity, is in accordance with the porosity. So, the formation and annihilation of positronium, especially the o-Ps, could be utilized to study the pore structure. This probe can detect micropores and mesopores, and can detect both closed pores and open pores, which shows advantage over other methods such as the gas adsorption method [14].

In this paper, we prepared a series of porous silica under acidic condition [23–25]. The effect of synthesis temperature on the pore structure was studied by positron annihilation measurements together with SAXS, HRTEM, SEM and  $N_2$  adsorption–desorption measurement.

## 2. Experiment

Mesoporous silica was prepared using amphiphilic triblock copolymer Pluronic P123 ( $M_w = 5800$ , EO<sub>20</sub>–PO<sub>70</sub>–EO<sub>20</sub>, Sigma Aldrich) as the structure agent and tetraethyl orthosilicate (TEOS, C<sub>8</sub>H<sub>20</sub>O<sub>4</sub>Si) as the silica source [24]. The 37 wt% HCl aqueous solution is diluted to 2 mol/L with distilled water for further use. P123 was first dissolved in a mixture of distilled water and HCl solution, then it was stirred under constant agitation at room temperature for 30 min until P123 is completely dissolved. After that, H<sub>2</sub>SO<sub>4</sub> and sucrose were added to the mixture and was stirred for another 30 min. Finally, the silica source TEOS was added to the mixture and was stirred until the solution was distributed homogeneously. The mole ratio of P123:TEOS:HCl:H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O:sucrose is 1:48.3:649:40:6357:7.2. The mixture was stirred for 72 h at 323 K and then conveyed into the Teflon-lined autoclave under static conditions at the given synthesis temperature (80 °C, 100 °C, 130 °C, 150 °C, 180 °C). The final silica/P123/sucrose gel was filtered, washed with distilled water (and ethanol) and dried at 373 K for 24 h. At the last, the final silica powder was obtained after calcination at 823 K for 6 h in the open air. The synthesized mesoporous silica powders were further hand milled in agate mortar for 2 h and then pressed under a static pressure of 6 MPa for 5 min to pellets with 1.5 mm thickness and a diameter of 15 mm. These pellets were dried over night at 100 °C in the autoclave for other measurements.

SAXS measurements were carried out using an X-ray diffractometer (X'Pert Pro, PANalytical, Netherlands) with Cu K $\alpha$  radiation operated at 40 kV and 40 mA. The incident X-ray wavelength  $\lambda$  was 1.5406 Å and the scanning angle  $2\theta$  was from 0.6123 to 10° with the step of 0.001°.  $N_2$  adsorption–desorption measurements were performed at 77 K by using a Micromeritics ASAP

2020 gas-sorption analyzer. The sample was degassed in a vacuum at 180 °C for the desorption process. Pore size distribution and average pore size were estimated from adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method [26]. At the same time the specific surface area was calculated from the Brunauer–Emmett–Teller (BET) method [27] over the relative pressure  $P/P_0$  range of 0.05–0.25. Scanning electron microscope (SEM) (XL 30 (Philips), Amsterdam, Netherlands) and high resolution transmission electron microscopy (HRTEM) (JEOL JEM-2010FEF (UHR), Tokyo, Japan) images with acceleration voltage at 200 kV were taken to study the pore morphology and pore ordering.

Positron lifetime measurements were performed at room temperature using a conventional fast–fast coincidence lifetime spectrometer with a time resolution of 280 ps in full width at half maximum (FWHM). A 10  $\mu$ Ci <sup>22</sup>NaCl source was sandwiched between two pellet samples and the sample–source–sample sandwich was placed into a vacuum chamber with air pressure lower than  $1 \times 10^{-5}$  torr. The lower level of the energy window on the discriminator for the stop signal (0.511 MeV annihilation  $\gamma$ -ray) was set to as low as possible in order to collect the  $3\gamma$  annihilation signal of o-Ps. In our experiment, we have tried to measure the positron lifetime spectrum using a time range of 500 ns for the TAC. The resolved long lived lifetime values ( $\tau_3$  and  $\tau_4$ ) and their intensities are almost the same for the two different time ranges. But time range of TAC of 500 ns leads to the larger uncertainties for the short lifetime components. So in our later measurements we just used the 200 ns range. The total channel number is 4096 and the time scale is 50.3 ps/channel. For each sample, two lifetime spectra were collected with a total count of  $1.5 \times 10^6$  for each spectrum. The counting rate is about 26 count per second. Doppler broadening spectra of the positron annihilation radiation were measured simultaneously using a high purity Ge (HP-Ge) detector which was placed perpendicular to the direction of positron lifetime measurements. The energy resolution of the HP-Ge detector is about 1.2 keV in full width at half maximum at 511 keV. The *S* and *W* parameters are calculated from the spectrum, which represent the ratio of low-energy ( $|E_L| \leq 0.68$  keV) region and high-energy region ( $2.8$  keV  $\leq |E_L| \leq 5.73$  keV) to the total region of 511 keV annihilation peak, respectively. The total count of each Doppler broadening spectrum is more than  $1 \times 10^7$ .

## 3. Results and discussion

### 3.1. SAXS measurement

In order to verify the pore ordering of the synthesized silica, SAXS measurements were performed for the samples synthesized at various temperatures. The measured SAXS patterns are shown in Fig. 1. For most of the samples, the diffraction peaks are nearly the same. There are three main diffraction peaks at around 0.98, 1.64, and 1.85°. They are indexed as the (100), (110), and (200) diffraction peaks, which reflect the hexagonal space group (*P6mm*). This indicates that the porous silica has long-range ordering. In other words, our synthesized silica has ordered structure.

It can be seen from Fig. 1 that the positions of the three diffraction peaks have some shifts at different synthesis temperatures. More importantly, the intensities of these peaks have significant change with increasing synthesis temperature. Actually for the sample synthesized at 130 °C, all the three peaks (100), (110), and (200) become weaker, which indicates that the pore ordering is somewhat deteriorated at this temperature. However, for the sample synthesized at 150 °C, the pores show high ordering again. When the synthesis temperature increases to 180 °C, only the peak at 0.98° shows weak signal, and the other two peaks disappear completely. This suggests that pore ordering is

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