Evaluation of Average Wall Thickness of Organically Modified Mesoporous Silica

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Abstract: The small angle X-ray scattering of organically modified MSU-X silica prepared by co-condensation of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) show negative deviation from Debye's theory due to the existence of the organic interface layer. By exerting correction of the scattering negative deviation, Debye relation may be recovered, and the average wall thickness of the material may be evaluated.

Keywords: Organically modified mesoporous silica, average wall thickness, small angle X-ray scattering (SAXS).

Mesoporous silica has many scientific and industrial applications[1]. To improve the surface property, an effective method is to form organic layers on the surface of siliceous materials by co-condensation of tetraethoxysilane (TEOS) and organotriethoxysilane around self-assembled surfactant micelle templates[2]. Much attention has been focused on characterization of its pore structure by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), N_2 adsorption, small angle X-ray scattering (SAXS) *et al.*, but seldom concerning its average wall thickness[1-4]. This short communication introduced a flexible method to evaluate the average wall thickness of organically modified MSU-X mesoporous silica under examination by SAXS.

Organically modified MSU-X silica was prepared by co-condensation of TEOS and methyltriethoxysilane (MTES) using $(C_8H_{17}(C_6H_4)(EO)_{15}H$, Tx-15) as template under neutral condition. The synthesis was as follows: 1.04 g of Tx-15 was dissolved in 40 mL deionized water to form a clear solution, then the mixtures of TEOS, MTES, and 2 mL ethanol were added to the above surfactant solution at 25°C. After 30 min stirring, 0.032 g KF was added finally (the mole composition is 0.2 MTES: 0.8 TEOS: 0.08 Tx-15: 146 H_2O: 0.02 KF). The solution was transferred into an autoclave and heated at 100°C for 72 h. The resulting mixture was filtered, air-dried and the surfactant was extracted by Soxhlet method with ethanol for 48 h. Then the final solid was filtered, washed and dried at 100°C in air.

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Figure 1   HRTEM image of methyl-modified MSU-X wormlike mesostructure
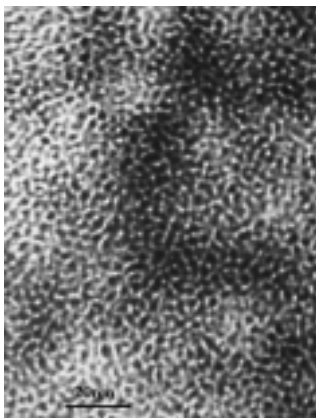
XRD, N_2 adsorption and HRTEM measurement (**Figure 1**) with HITACHI-9000 illustrated that the sample is of amorphous state and of mesoporous structure.

SAXS experiment was performed using synchrotron radiation as X-ray source with a long-slit collimation system at Beijing Synchrotron Radiation Laboratory.   Incident X-ray wavelength λ was 0.154 nm, and the scattering angle 2θ was approximately 0~3°, the scattering vector was denoted as q, where $q=4\pi\sin\theta/\lambda$.   The scattered X-ray intensity was recorded using imaging plate technology.   The background scattering and the absorption of the sample were corrected.   Data analysis was directly based on slit-smeared intensity.

In the SXAS of ideal two-phase system of mesoporous material, the average pore size l_p, the average wall thickness of the solid matrix l_s and the correlation distance a_c that is a measure of phase size[5] existed the following relation:

$$\frac{1}{a_c} = \frac{1}{l_p} + \frac{1}{l_s} \qquad\qquad (1)$$

Thus, once a_c and l_p have been determined, l_s could then be deduced from the formula (1).   In this paper, a_c and l_p were determined from Debye plot and Guinier plot, respectively.

An ideal two-phase system possesses sharply defined phase boundary. The electron density in each phase is different (such as the mesoporous pure silica without organic groups prepared by condensation of tetraethoxysilane under similar process to that of the sample here[6]), according to Debye's theory[7,8], the observed slit-smeared scattering intensity is given as,

$$J_{obs}(q)=A(1+a_c{}^2q^2)^{-3/2} \qquad\qquad (2a)$$

i.e.

$$J_{obs}(q)^{-2/3}=A^{-2/3}+A^{-2/3}a_c{}^2q^2 \qquad\qquad (2b)$$

where A is a constant.   Equation (2b) implies that plot of $J_{obs}(q)^{-2/3}$ *versus* q^2 is linear in the whole experimental scattering angle range with a positive slope.   Then, correlation distance a_c can be determined from the slope and intercept.

The Debye plot I ($J_{obs}(q)^{-2/3}$ *versus* q^2) of methyl-modified mesoporous silica in **Figure 2** deduced from the original measured data is not linear but presents a upward concave curve, it is obvious that the scattering shows a negative deviation from Debye's theory suggesting that the sample is of non-ideal two-phase structure.   This is because the electron density does not change abruptly, but changes gradually over a certain range between two phases (solid skeleton and pore) of the sample.   This range is called an interface layer that is composed of organic groups (*i.e.* methyl) as FT-IR experiment has detected[2].   It is the interface layer that causes a depletion of the scattering (especially the high-angle scattering) of pores and results in the negative deviation from Debye's theory.   The observed slit-smeared scattering intensity $J_{obs}(q)$ can be expressed by extending Debye equation (2) as follows[9]

$$J_{obs}(q)=A(1+a_c^2q^2)^{-3/2}\exp(-\sigma^2q^2) \qquad (3)$$

where $\exp(-\sigma^2q^2)$ is the fourier transform of the auto-correlation of the Gaussian smoothing function for the sigmoidal–gradient model and represents the negative deviation due to the diffuse interface; σ is the standard deviation of the Gaussian smoothing function, *i.e.* a parameter in relation to the thickness of the interface layer.

Equation (3) may be transformed into a tractable form.

$$\exp(-2/3\sigma^2q^2)J_{obs}(q)^{-2/3}=A^{-2/3}+A^{-2/3}a_c^2q^2 \qquad (4)$$

By introducing appropriate value of σ, the plot of $\exp(-2/3\sigma^2q^2)J_{obs}(q)^{-2/3}$ *versus* q^2 should be (or statistically be) linear.   Therefore, Debye's equation may be recovered by exerting correction of the negative deviation due to the existence of the interface layer using the following equation,

$$J(q)^{-2/3}=\exp(-2/3\sigma^2q^2)J_{obs}(q)^{-2/3} \qquad (5a)$$

or

$$J(q)=\exp(\sigma^2q^2)J_{obs}(q) \qquad (5b)$$

where $J(q)$ is the negative deviation corrected scattering intensity which agrees with Debye's theory and can be used to study the microstructure of the system under examination. Then, correlation distance a_c can be determined from the slope and intercept of the plot of $J(q)^{-2/3}$ *versus* q^2 (see the linear plot II in **Figure 2a**).   The result is that a_c equals to 0.84 nm.

Figure 2   SAXS plots of methyl-modified MSU-X silica **a** Debye plot and **b** Guinier plot
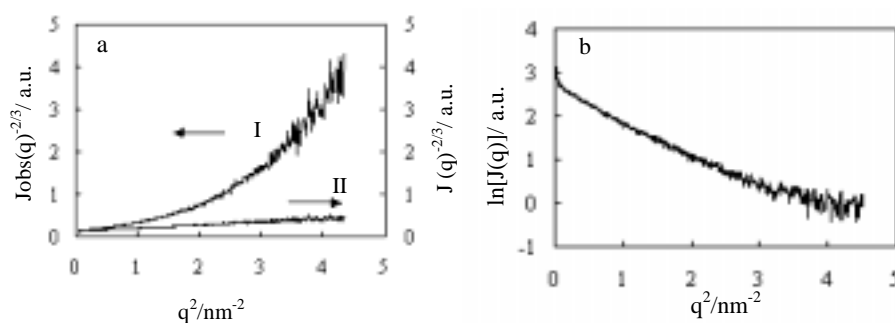
Guinier plot in **Figure 2b** of the methyl-modified mesoporous silica derived from the negative deviation corrected scattering intensity is continuous and strongly concave shows that the pores in the sample are polydispersive[6]. The relation between the scattering intensity $J(q)$ and the pore size distribution $V_i(D)\sim D_i$ is as follows[10]:

$$J(q) = \sum_{i=1}^{n} CV_i D_i^3 \exp(-\frac{3}{20}D_i^2 q^2) \qquad (2)$$

where C is a constant, $V_i(D)$ is the fraction of the volume of the pores with diameter D_i to the total volume of all pores in the sample. By using the Shull-Roess method[11], the pore size distribution $V_i(D)\sim D_i$ is deduced from Equation (2) and **Figure 2a.** The average pore diameter lp can then be determined as:

$$l_p = \sum_{i=1}^{n} D_i V_i \qquad (3)$$

The result is that l_p equals to 2.21 nm.

Having obtained a_c and l_p, the average wall thickness of silica skeleton l_s in the sample could then be determined with equation (1), and the result of l_s equals to 1.35 nm. It is difficult to evaluate the wall thickness for the wormlike mesoporous silica from HRTEM experiment in **Figure 1**.

Unlike other techniques such as N_2 adsorption and HRTEM, SAXS can be used to study the microstructure of both wet and dry porous materials whether the pores are open or closed. Comparatively speaking, measurement of the average wall thickness of mesoporous material by SAXS probably represents the value close to the absolute limit.

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