

## Silica Aerogels' Nanostructure Studied using Small Angle Neutron Scattering Technique

(Struktur Nano Aerogel Silika dikaji Menggunakan Teknik Serakan Sudut Kecil Neutron)

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### ABSTRACT

*Small angle neutron scattering (SANS) technique has been widely employed in probing the microstructure of amorphous materials in the nanometer range. In aerogels system, the size range of 1 – 100 nm is of particular interest since the structural units, such as the pores and particles, often fall in this range. In a typical scattering experiment, scattered neutron intensity is measured as a function of the scattering angle. Various plots of intensity  $I(Q)$  and scattering vector,  $Q$ , can provide information about fractal dimensions, and particle and cluster sizes. In this study, SANS facilities, at Nuklear Malaysia (NM) and Badan Tenaga Atom Nasional (BATAN), Indonesia were used to analyse particle and cluster size of silica aerogels and titanium containing silica aerogels. Results from NM showed that silica aerogels have surface fractal dimension while titanium containing silica aerogels have mass fractal dimension. On the other hand, results from BATAN showed that both silica aerogels and titanium containing silica aerogels have mass fractal dimension. The particle size for silica aerogels and titanium containing silica aerogels samples obtained by NM were  $11.18 \pm 0.03$  and  $9.19 \pm 0.06$  nm, respectively while the respective values obtained from BATAN measurements were  $11.78 \pm 0.06$  and  $10.57 \pm 0.07$  nm.*

*Keywords: aerogels; particle size; small angle neutron scattering (SANS)*

### ABSTRAK

*Teknik serakan neutron sudut kecil (SANS) digunakan dengan meluas bagi mengkaji mikrostruktur bahan amorfus pada julat nanometer. Dalam sistem aerogel, julat saiz 1 – 100 nm diminati kerana unit struktur seperti liang dan zarah berada dalam julat sebegini. Dalam eksperimen serakan, keamatan neutron terserak diukur sebagai fungsi sudut serakan. Berbagai plot keamatan  $I(Q)$  dan vektor serakan,  $Q$  boleh memberikan maklumat mengenai dimensi fraktal, serta saiz zarah dan klusternya. Dalam kajian ini, kemudahan SANS di Nuklear Malaysia (NM) dan di Badan Tenaga Atom Nasional (BATAN), Indonesia digunakan bagi menganalisis saiz zarah dan kluster aerogel silika dan titanium mengandungi aerogel silika. Keputusan daripada NM menunjukkan aerogel silika mempunyai dimensi fraktal permukaan sementara titanium mengandungi aerogel silika mempunyai dimensi fraktal jisim. Sebaliknya keputusan dari BATAN menunjukkan kedua-dua sampel mempunyai dimensi fraktal jisim. Saiz zarah bagi aerogel silika dan titanium mengandungi aerogel silika dari NM ialah  $11.18 \pm 0.03$  and  $9.19 \pm 0.06$  nm sementara dari BATAN adalah  $11.78 \pm 0.06$  and  $10.57 \pm 0.07$  nm.*

*Kata kunci: aerogel; saiz zarah; serakan neutron kecil sudut (SANS)*

### INTRODUCTION

Small angle neutron scattering is a non-destructive technique for investigating the nanostructure of porous materials, in general, and of aerogels in particular. For gels in solution, which are polydisperse systems with microgels floating around the gel network, the scattering experiments give only an apparent fractal dimension which is related to the real fractal dimension of the gel network and to the exponent of the polydispersity. In the case of silica aerogels this problem does not exist because here all the scattering is caused by a coherent network, the cluster. For this reason silica aerogels can be good candidates to observe fractality in solids with scattering experiments (Woignier et al. 1990).

The structure of silica aerogels has been the subject of numerous investigations, mainly because of the possible fractal aspects (Fricke & Reichenauer 1987; Lours et al. 1987; Rousset et al. 1990; Vacher et al. 1988; Woignier et al. 1990). Small angle neutron scattering seems to show that such heterogeneous materials are fractal in the limited length domain. Aerogels are made of a disordered, array of connected fractal clusters which result from the aggregation of primary particles (Fricke & Reichenauer, 1987). The fractal nature of intra-cluster particle correlation is revealed by a power law behaviour  $QD$ , where  $D$  is the fractal dimension. The power law region is observed in double logarithmic plot of intensity  $I(Q)$  versus scattering vector  $Q$ .

In the 1990s, the bulk structure of silica aerogels has been extensively studied mainly by scattering techniques (neutrons, X-rays, light) (Marliere et al. 2001). It has been shown that small silica particles aggregate to constitute a fractal network. Its fractal dimension is strongly dependent on the synthesis conditions such as pH of gelifying solutions and also supercritical drying media and heat treatment (Tajiri & Igarashi 1998). These typical lengths range from 1 to 100 nm. At these scales, aerogels are described as self-similar (fractal) materials, the structure of which is characterised by different parameters such as the fractal dimension and the particle size.

Small angle neutron scattering is a powerful tool to characterise porosity (Schaefer et al. 1994). The purpose of the study was to demonstrate how far one can go in characterising porosity using classical methods based on Porod's law. They have pointed out that surface area is the key parameter used to characterise porosity and the specific surface area is determined from small angle data using Porod's approximation.

In this study, SANS facilities available at NM and BATAN were used to study the nanostructure of silica aerogels with the aim of testing the reliability and usefulness of SANS for probing nanostructures as well as to compare the results for fractal dimension and particle size obtained from both facilities.

#### THEORETICAL FRAMEWORK OF SANS

Small angle neutron scattering is based on particle radiation. Neutron beams interact with the nuclei of atoms via strong nuclear forces call nuclear scattering. The type of neutron scattering depends on the incident wave frequency, the scattered wave frequency and the change of energy. Coherently elastic scattering of neutrons measures the correlation between scatterings centers and therefore very useful for the study and confirmation of polymers.

A collimated beam of neutrons will exhibit a distribution of wavelengths. The beam can be monochromated by the use of a crystal with planes separated by  $d$ ; the Bragg equation can be written as;

$$\lambda = 2d \sin \theta \quad (1)$$

where  $\theta$  is the angle between the neutron beam and the planes of the crystal. A band of wavelength is selected by the crystal monochromator determined by the angular divergence of the neutron beam.

The momentum transfer,  $Q$  is the modulus of the resultant between the incident,  $k_i$  and scattered  $k_s$ , wave vectors which is given by:

$$|Q| = |k_s - k_i| = \frac{4\pi}{\lambda} \sin \theta \quad (2)$$

Substituting equation (2) into Bragg's Law of diffraction yields a very useful expression

$$d = \frac{2\pi}{Q} \quad (3)$$

Equations (1) and (2) are central to SANS experiments because through their combined use it is possible to configure an instrument and to rapidly "size" the scattering bodies in a sample from the position of any diffraction peak in  $Q$ -space.

The neutron scattering density,  $\rho$ , of a molecule of  $i$  atoms may be readily calculated from the simple expression:

$$\rho = \sum_i b_i \frac{DN_A}{M_w} \quad (4)$$

where  $D$  is the bulk density of the scattering body and  $M_w$  is its molecular weight. The contrast is simply the difference in  $\rho$  values between that part of the sample of interest,  $\rho_p$  and the surrounding medium,  $\rho_m$ , all squared; i.e.,  $(\Delta\rho)^2 = (\rho_p - \rho_m)^2$ . The scattering energy is distributed over the surface of a sphere of surface area  $4\pi r^2$ , the minimum value of which is  $4\pi b_0^2$ . The quantity  $b_0$  is known as the neutron scattering length.

SANS data are often presented on an absolute macroscopic cross section scale independent on instrumental conditions and on sample volume. The scattered intensity for given  $(\lambda, \theta)$  is given by;

$$I(\lambda, \theta) = I_0(\lambda, \theta) \Delta\Omega \eta(\lambda) T V_p \frac{d\sigma}{d\Omega}(Q) \quad (5)$$

$$\frac{d\sigma}{d\Omega}(Q) = N_p V_p^2 (\Delta\rho)^2 P(Q) S(Q) \quad (6)$$

where  $I_0$  is the incident flux,  $\eta$  is the detector efficiency,  $T$  is the sample transmission,  $N_p$  is the number concentration of scattering bodies,  $V_p$  is the volume of scattering body,  $(\Delta\rho)^2$  is the square of the difference in neutron scattering length density,  $P(Q)$  is the form factor,  $S(Q)$  is the structure factor and  $Q$  is the modulus of scattering vector

Form factor,  $P(Q)$  is a function that describe how  $d\sigma/d\Omega$  is modulated by interference effects between radiation scattered by different parts of the same scattering body. It can be calculated for different shape. On the other hand, the structure factor  $S(Q)$  is a function that describe how  $d\sigma/d\Omega$  is modulated by interference effects between radiation scattered by different scattering bodies which depends on the degree of local order in the sample.

#### EXPERIMENTAL METHODS

##### SAMPLE PREPARATION

The first step in any SANS experiment is to define the structural feature of interest and then decide if the feature is accessible with the SANS technique, which is applicable for length scale of 10 Å to 5000 Å. Secondly, since the scattering intensity is proportional to the (scattering contrast) squared therefore there must be a scattering contrast between the sample and the medium surrounding the sample. In this work, the silica aerogels samples were provided by the Zeolite Group of Universiti Teknologi

Malaysia. The sample cell used was quartz cell of width 18 mm and 2 mm path length.

#### COLLECTION OF DATA

Number of counts recorded by the detector with the sample in place can come from three sources, neutrons scattered by the sample itself, neutrons scattered from something other than the sample, neutrons that reach the detector without passing through the sample and electronic noise in the detector itself. Thus in order to separate these three contributions, three types of measurements were performed; scattering measured with the sample in place, scattering measured with the empty sample holder in place and the dark counts measured with cadmium absorber placed at the sample position.

In addition to these three scattering measurements, the transmission (the fraction of the incident beam intensity that passes through the sample without being scattered or absorbed) of the sample and the sample cell must also be measured in order to correctly subtract the contributions to the background and to calibrate the scattering on an absolute cross section scale.

#### DATA ACQUISITION PROTOCOL

Data reduction consists of correcting the measured scattering from the sample for the sources of background. The background-corrected neutron counts,  $I_{cor}(Q)$ , recorded in a detector pixel in a time interval  $t$  are related to absolute cross section,  $d\Sigma(Q)/d\Omega$ , through the expression

$$I_{cor}(Q) = \phi A \Delta \Omega \epsilon t D T \left( \frac{d\Sigma(Q)}{d\Omega} \right) \quad (7)$$

$\phi$  is the neutron flux at the sample,  $A$  is the area of the beam incident on the sample,  $D$  is sample thickness,  $T$  is the transmission of the sample and its container,  $\Delta\Omega$  is the solid angle subtended by one pixel of the detector,  $\epsilon$  is the detector efficiency and  $t$  is the counting time

The sample scattered pattern was corrected for backgrounds according to the following relationship.

$$I_{cor} = (I_{sam} - I_{bgd}) - \left( \frac{T_{sample+cell}}{T_{cell}} \right) (I_{emp} - I_{bgd}). \quad (8)$$

Finally, the corrected data was multiplied by the detector sensitivity matrix to account for the pixel to pixel variation in detector efficiency.

#### RESULTS AND DISCUSSION

The characteristics of the scattering pattern of SANS can be related to the different structural feature on the respective length scale. Power law scaling for example depict the characteristic of fractals. Therefore, a relationship which yields a straight line on log-log coordinates can identify an object as fractal. When the scattering intensity  $I(Q)$  follows the Power law;

$$I(Q) \sim Q^{-z} \quad (9)$$

it suggests the micro-structure as having a fractal nature. The characteristics of the fractal can be determined from the value of  $z$  such that;

$$\begin{aligned} 1 \leq z \leq 3 & \quad \text{mass fractal} \\ 3 \leq z \leq 4 & \quad \text{surface fractal} \end{aligned}$$

Figures 1 and 2 show the double logarithmic plot of intensity  $I(Q)$  versus momentum transfer,  $Q$  performed using SANS facility at NM for silica aerogels and titanium containing silica aerogels respectively. As shown, silica aerogels has fractal dimension of 3.69, corresponding to surface fractal. The roughness of a surface is represented by a fractal dimension of less than 4. The result suggests that the surface of the silica aerogels particle is rough since a smooth surface will have a surface fractal dimension of 4. On the other hand, titanium containing silica aerogels has a fractal dimension of 2.66 suggesting that it has a mass fluctuation.

Figures 3 and 4, plots of  $I(Q)$  vs  $Q$ , obtained using SANS at BATAN. As can be seen from the slope of the graphs, the values of  $z$  are less than 3, suggesting that both the samples have mass fractal dimension. Silica aerogels has smaller fractal dimension as compared to titanium

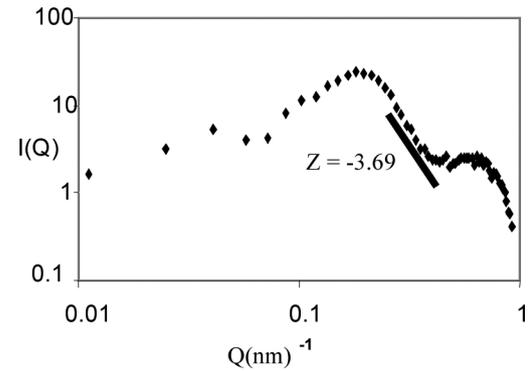


FIGURE 1. Double logarithmic plot of intensity  $I(Q)$  versus momentum transfer,  $Q$  for silica aerogels (NM)

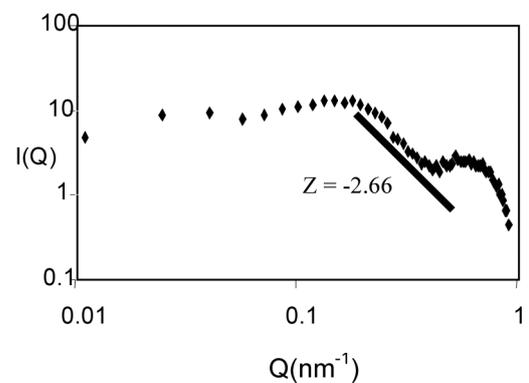


FIGURE 2. Double logarithmic plot of intensity  $I(Q)$  versus momentum transfer,  $Q$  for Titanium containing silica aerogels (NM)

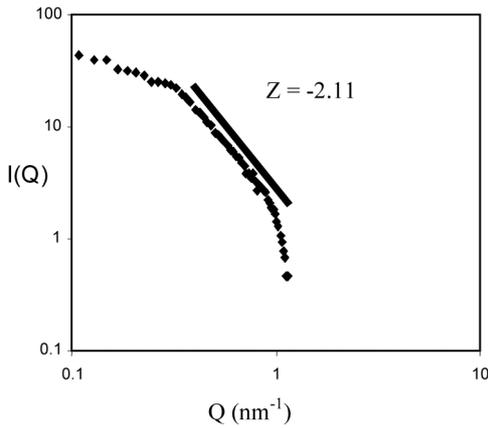


FIGURE 3. Double logarithmic plot of intensity  $I(Q)$  versus momentum transfer,  $Q$  for silica aerogels (BATAN)

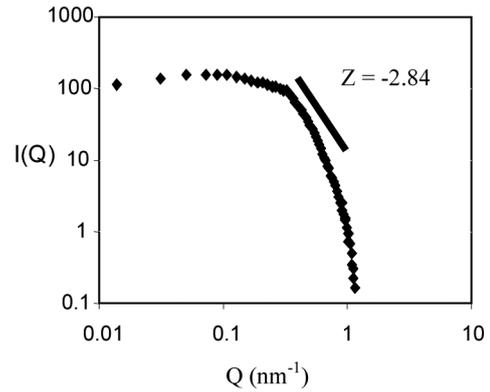


FIGURE 4. Double logarithmic plot of intensity  $I(Q)$  versus momentum transfer,  $Q$  for titanium containing silica aerogels (BATAN)

containing silica aerogels. The magnitude of fractal dimension is related to the openness of the structure. The more open the structure becomes, the smaller the fractal dimension becomes. Hence, titanium containing silica aerogels is denser than silica aerogels.

The region at low scattering vector,  $Q$  has  $R_g \leq 1$ , where  $R_g$  is the radius of gyration, or also known as the Guinier region.  $R_g$  is the root mean square of the distance from all the neutrons in a scattering entity to its centre of mass. According to the Guinier approximation (Hammouda 1995), the scattering intensity at low  $Q$  is related to  $R_g$  by the following expression:

$$\ln(I(Q)) = \ln(I(0)) - Q^2 R_g^2 / 3 \tag{10}$$

Therefore, a plot of  $\ln(I(Q))$  vs.  $Q^2$  would give a straight line with negative slope for a proper  $Q$  range, and from the slope,  $R_g$  can be calculated.  $R_g$  is related to particle size,  $R_o$ , and for a sphere,

$$R_g^2 = (3/5)R_o^2 \tag{11}$$

Data obtained using SANS at NM could fairly provide good information on the Guinier region, probably caused by the scattering angle which is not small enough since the sample to detector distance (STD) was only 4 meters.

In order to obtain a proper Guinier region, samples were sent to BATAN for analysis. The STD of the SAN facility can be varied from 1.5 meter to 4 meter and up to 13 meter. To obtain the information of fractal dimension, where power law lies in the intermediate  $Q$ -region, 4-meter-data was used. However, for the Guinier region which falls in the low- $Q$  region, 13 meter STD was used.

Plots of  $\ln(I(Q))$  versus  $Q^2$  for silica aerogels and titanium containing silica aerogels show a linear relationship in low region, indicating that a Guinier analysis of the data is appropriate for the extraction of radius of gyration. Guinier plot in Figure 5 for silica aerogels and Figure 6 for titanium containing silica aerogels have two linear regions.

Tables 1 and 2 show the summary of the analysis used to calculate the particle radius from both the facilities. The particle sizes obtained from both SANS are comparable to each other. The particle radius of gyration can be extracted

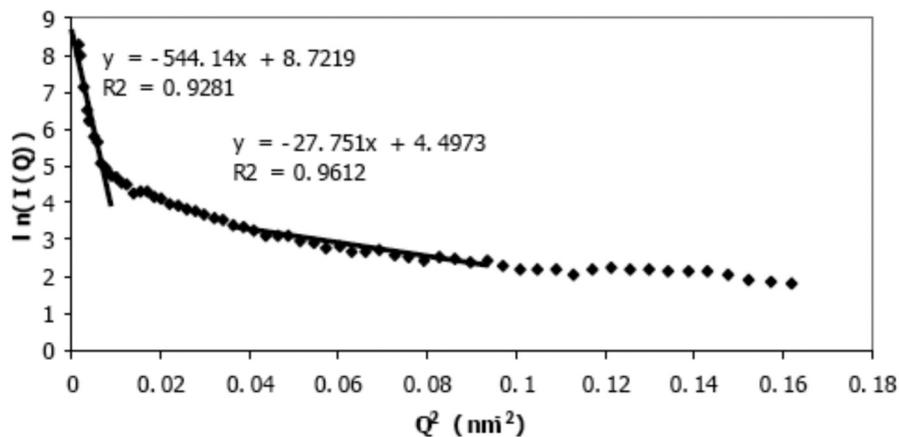


FIGURE 5. Guinier plot for silica aerogels (BATAN)

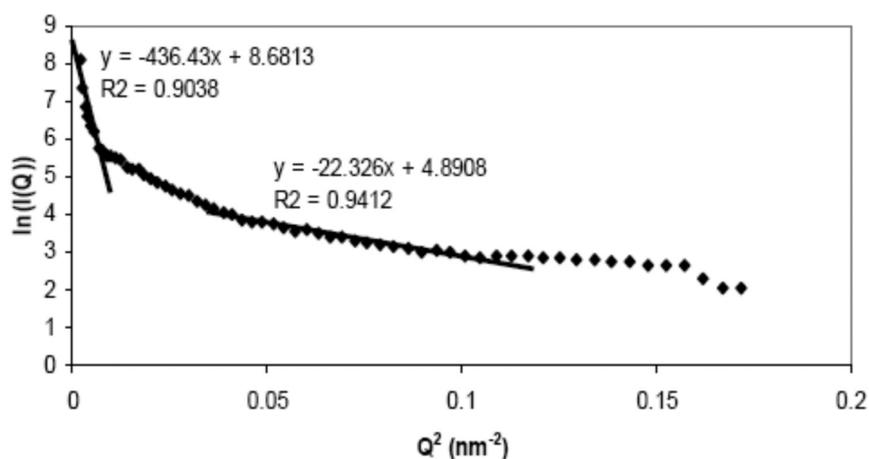


FIGURE 6. Guinier plot for titanium containing silica aerogels (BATAN)

from slope at higher  $Q$  region and the parameters are shown in Table 2 while the cluster radius of gyration can be extracted from slope at lower region and the parameters are shown in Table 3.

The results of NM show that silica aerogels has a particle radius of 11.18 nm while titanium containing silica aerogels has a particle radius of 9.19 nm. This suggest that silica aerogels has larger particle radius as compared to titanium containing silica aerogels.

The results of BATAN show that the particle radius for silica aerogels is 11.78 nm while titanium containing silica aerogels has a particle radius of 10.57 nm. These values are consistent and in good agreement with the values obtained from NM.

Table 3 shows the parameters obtained from the Guinier plots. The longer STD of the SANS enabled the measurements to be made for low  $Q$  values. The measured cluster radius for silica aerogels and titanium containing silica aerogels were 52 nm and 47 nm, respectively.

TABLE 1. Particle radius for silica aerogels and titanium containing silica aerogels obtained from SANS at NM

Sample	Slope of Guinier plot	Radius of gyration, $R_g$ (nm)	Particle Radius, $R_p$ (nm)
Silica Aerogels	24.983	$8.66 \pm 0.03$	$11.18 \pm 0.03$
Titanium containing Silica Aerogels	16.883	$7.12 \pm 0.06$	$9.19 \pm 0.06$

TABLE 2. Particle radius for silica aerogels and titanium containing silica aerogels obtained from SANS at BATAN

Sample	Slope of Guinier plot	Radius of gyration, $R_g$ (nm)	Particle Radius, $R_p$ (nm)
Silica Aerogels	27.75	$9.12 \pm 0.06$	$11.78 \pm 0.06$
Titanium containing Silica Aerogels	22.33	$8.18 \pm 0.07$	$10.57 \pm 0.07$

TABLE 3. Cluster radius for silica aerogels and titanium containing silica aerogels obtained from SANS at BATAN

Sample	Slope of Guinier plot	Radius of gyration, $R_g$ (nm)	Cluster Radius, $R_p$ (nm)
Silica Aerogels	544	$40 \pm 1$	$52 \pm 1$
Titanium containing Silica Aerogels	436	$36 \pm 1$	$47 \pm 1$

## CONCLUSION

The SANS results of NM, although with STD of only 4 meters, was able to provide reasonably good measurements on the fractal dimensions and particle sizes. The particle size obtained for both samples are in agreement with the results of BATAN. However, the results for fractal dimension of silica aerogels differ. While the results of NM predict the possibility of mass fractal, the BATAN's data suggest silica aerogel to have surface fractal. In conclusion, the study have shown that SANS can be a reliable tool for the study of nanostructure especially for aerogels.

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