DETERMINATION OF SILICA AEROGELS NANOSTRUCTURE CHARACTERISTICS BY USING SMALL ANGLE NEUTRON SCATTERING TECHNIQUE

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To my beloved parents,
brothers and friends

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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 (1 to 100 nm). In this study, small angle neutron scattering was used to study the structure of the silica aerogels and titanium containing silica aerogels by using SANS facility at MINT, Malaysia and BATAN, Indonesia. Besides scattering method, imaging technique such as transmission and scanning electron microscopy (TEM and SEM) can be used to provide real-space structure. However, microscopy image may include artifacts and may not be truly representative of the sample. While SANS does not provide real space structure directly, the technique does probe the sample in its entirety. In this work, the aerogels physical properties such as particle size and fractal dimension as a function of pH were studied. In a typical scattering experiment, an incident neutron beam is bombarded to the sample and is elastically scattered. The scattered intensity is measured as a function of the scattering angle which occurs at small angle of less than 10^0. Reactor was used as our neutron source. The monochromated neutron beam has a wavelength of 0.5 Å. The sample which is in powder form is filled into a quartz cell with a 2 mm pathlength. A complete data set consists of three measurements; scattering measured from the sample, scattering from the empty sample holder and scattering from the dark counts due to complete absorber in sample position. The scattered neutrons were detected by a 128 X 128 array area sensitive, gas-filled proportional counter, which is known as Position Sensitive Detector (PSD). A personal computer which is linked to the PSD neutron counting system is used for data collection. SANS neutron counting system programs include the display of scattered neutron data in two and three dimensional isometric view. The resulting 2D scattering pattern is reduced to 1D profile for further analysis. Plots of $I(Q)$ vs Q were derived. Results show that as pH decreases fractal dimension decreases from 3.60 to 2.44. On the other hand, particle size increases from 9.87 nm to 11.26 nm with decreasing pH of the aerogels. Titanium containing silica aerogels has bigger fractal dimension and smaller particle size compared to silica aerogels.

ABSTRAK

Teknik penyerakan neutron sudut kecil telah banyak diaplikasikan dalam mengukur microstruktur bahan amorfus dalam julat nanometer (1 hingga 100 nm). Dalam kajian ini, serakan neutron sudut kecil digunakan untuk mengkaji struktur aerogels silika dan aerogels silica yang mengandungi titanium dengan menggunakan instrumen serakan neutron sudut kecil di MINT, Malaysia dan BATAN, Indonesia. Selain kaedah penyerakan, teknik pengimejan seperti mikroskopi transmisi elektron (TEM) dan mikroskopi pengimbasan elektron boleh digunakan untuk memperoleh struktur ruang nyata. Walaubagaimanapun, imej mikroskopi mungkin merangkumi artefak dan mungkin tidak dapat mewakili sampel sebenar itu sepenuhnya. Walaupun teknik penyerakan sudut kecil tidak memberi struktur ruang nyata secara langsung, ia dapat mengkaji sampel tersebut secara keseluruhan. Sifat fizik aerogels seperti saiz zarah dan dimensi fraktal dalam fungsi pH dikaji. Dalam eksperimen penyerakan, satu sinar neutron ditujukan kepada sampel and sinar neutron tersebut diserak secara kenyal. Keamatan serakan diukur sebagai fungsi kepada sudut serakan yang berlaku pada sudut kecil kurang daripada 10^0. Reaktor digunakan sebagai sumber neutron. Sinar neutron yang dimonokromatkan mempunyai panjang gelombang 0.5 Å Sampel dalam bentuk serbuk diisi ke dalam sel kuartz dengan ketebalan 2 mm. Satu set data yang lengkap terdiri daripada tiga set pengukuran iaitu serakan daripada sampel tersendiri, serakan daripada pemegang sampel yang kosong dan juga serakan daripada bilangan latar belakang disebabkan penyerap neutron yang terletak di kedudukan sampel. Neutron yang terserak dikesan oleh 128 X 128 jalur dan baris kawasan sensitif, pembilang perkadaran yang berisi gas, juga dikenali sebagai Pengesan Sensitif Kedudukan (PSD). Satu komputer disambung kepada sistem pembilangan neutron untuk pengumpulan data. Program sistem pembilangan neutron meliputi paparan data serakan neutron dalam pandangan isometri dua dan tiga dimensi. Data penyerakan dalam dua dimensi ditukar kepada satu dimensi untuk dianalisis. Hasil kajian menunjukkan bahawa apabila nilai pH menurun, dimensi fraktal juga berkurangan daripada 3.60 kepada 2.44. Saiz zarah meningkat daripada 9.87 nm kepada 11.26 nm apabila nilai pH menurun. Aerogels silika yang mengandungi titanium mempunyai dimensi fraktal yang lebih besar dan saiz zarah yang lebih kecil berbanding dengan aerogels silika.

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LIST OF SYMBOLS

A	-	area
b	-	barns
b	-	scattering length
b_c	-	coherent part of scattering length
b_{ic}	-	incoherent part of scattering length
b_i	-	scattering length of *i*th atom
b_o	-	average scattering length
d	-	sample thickness
d_c	-	correlation length / average chord
D	-	fractal dimension
D_b	-	bulk density of scattering body
D_m	-	mass fractal dimension
D_s	-	surface fractal dimension
E_i	-	incident energy
E_s	-	final energy
$F(r)$	-	autocorrelation function
F(Q)	-	form factor of single particle
$g(r)$	-	pair correlation function
I	-	beam intensity
$I(Q)$	-	scattering intensity
$I(\theta)$	-	scattering intensity, in function of scattering angle
J_1	-	first order spherical Bessel function
k_i	-	incident wave vector
k_s	-	scattered wave vector
$M(r)$	-	distribution of mass

M_w	-	molecular weight
n	-	number of particle
n_i	-	reflecting index
N	-	number density of target nuclei
$P(Q)$	-	form factor
$P(r)$	-	Patterson function
Q	-	scattering vector / momentum transfer
r	-	average radius
r	-	position of nucleus
R_c	-	cluster radius
R_g	-	radius of gyration
R_p	-	particle radius
S	-	surface area
$S(Q)$	-	structure factor
t	-	counting time
T_s	-	sample transmission
z	-	atomic number
Å	-	Angstrom
nm	-	nanometre
μm	-	micrometer
mm	-	milimetre
cm	-	centimetre
m	-	metre
^0C	-	centigrade degree
keV	-	kilo electron volt
Σ	-	macroscopic cross section
Σ_t	-	total cross section per unit sample volume
Σ_c	-	coherent cross section per unit sample volume
Σ_i	-	incoherent cross section per unit sample volume
Σ_a	-	absorption cross section per unit sample volume

σ	-	scattering cross section
σ_s	-	standard deviation
v_o	-	incident wave frequency
v	-	scattered wave frequency
θ	-	scattering angle
λ	-	wavelength
λ_i	-	incident wavelength
λ_s	-	final wavelength
ρ	-	scattering length density
$(\Delta\rho)^2$	-	contrast term
ρ_{m}	-	scattering length density of surrounding medium
ρ_{p}	-	scattering length density of sample
$\rho(r)$	-	density of subvolume
ϕ	-	neutron flux
Ω	-	solid angle
ε	-	detector efficiency
φ	-	tilting angle
Δx	-	thickness
$d\sigma/d\Omega$	-	differential cross section

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CHAPTER 1

INTRODUCTION

Small angle scattering (SAS) is the collective name given to techniques of small angle neutron (SANS), X-Ray (SAXS) and light (SALS) scattering. Small angle scattering, by definition, differs from other scattering or diffraction techniques in that it uses information derived from the scattered beam at small angles (Hu *et al*., 2002). For typical SAS measurements, the scattering angles are in the range of 0.01^0 to 10^0. A general feature of scattering is the reciprocity behaviour: large structural entities show up at small scattering angles, and vice versa (Emmerlling and Fricke, 1992). At larger scattering angles, distances in the length range of chemical bonds on the scale of angstroms are probed.

Small angle neutron or X-Ray scattering is the technique of choice for probing structural features that occur on length scales between approximately 10Å and 1000 Å. The size range spans a vast range of science, from proteins and viruses (biology and medical sciences) to emulsions and microemulsions (polymer and material science) to phase separation and fractal growth (physics, geology and metallurgy). It can be easily used to study liquid, amorphous and crystalline samples. Information about the size, shape or distribution of inhomogenities can be extracted from the scattering data (Li, 2000).

An important question is, why use neutron as opposed to X-Ray? The most fundamental difference between neutron and electromagnetic radiation is the mechanism by which the incident radiation interacts with matter. Neutrons have no charge, thus, unlike electrons, they have no electrostatic interaction. Likewise their electric dipole moment is either zero or too small to be measured by the most sensitive modern techniques and this cause almost no polarization of the electron clouds. On the other hand, X-Rays have a very strong electric field associated with them which may ionize the atoms they pass through. Electrons interact electrostatically with the electrons in materials (Li, 2000). X-Ray is scattered by the electrons surrounding atomic nuclei, but neutrons are scattered by the nucleus itself. Table 1.1 summarises the properties of the interaction of X-Rays and neutrons with matters.

The strength of the neutron-nucleus interaction varies randomly with atomic number and is independent of momentum transfer Q. Even isotopes of the same element will have different neutron scattering cross section, σ (Hammouda, 1995). The interaction of neutrons with matter is weak and the absorption of neutrons by most materials is corresponding small. Neutron radiation is therefore very penetrating for most elements (Kostorz and Lovesey, 1979). Thus, neutrons can be used to probe the bulk properties of samples with pathlengths of several centimetres. Neutrons can penetrate a number of materials such as silicon, quartz and sapphire with little attenuation. These materials can act as both substrates for samples and windows for cells.

The wavelength of thermal neutrons is appropriate to reveal the atomic arrangement in the sample (Kostorz and Lovesey, 1979). The uniqueness of some of the information obtained from small angle neutron scattering may offset the relatively high cost of such experiments.

Table 1.1: The properties of the interaction of X-Rays and neutrons with matters.

Radiation type	**Interacts with**	**Interaction force**	**Penetrate depth**
X-Rays	Electrons	Electromagnetic	Slight deep
Neutrons	Atomic nuclei	Nuclear force	Very deep

1.1 Research Background

The major strength of the SANS technique is that it can be used as a probe on a host of materials, which cover a wide range of research disciplines. Materials that are routinely characterized using SANS technique include alloys and ceramics, biological materials, colloidal materials, complex fluids, polymers, surfaces and interfaces and flux lattices in superconductors and so on.

Small angle neutron scattering has been widely employed in modern materials science. It is a powerful tool for probing the microstructure of amorphous materials in the nanometre range. In this study, small angle neutron scattering has been utilized to study the structure of silica aerogels. As mentioned before, for typical SAS measurements, the structural information that can be obtained is in the range of 10Å to 1000Å. In aerogels systems, this size range of 1 to 100nm is of particular interest since the structural units, such as the pores and the particles, often fall in this range. Therefore, small angle neutron scattering is suitable for the characterization of the microstructure of the aerogels materials (Hu, 2002).

Many people assume that aerogels are recent products of modern technology. In reality, the first aerogels were prepared in 1931 by Steven. S. Kistler. Kistler's aerogels were very similar to silica aerogels prepared today. They were transparent, low density, and highly porous materials that stimulated considerable academic interest. Aerogels had been largely forgotten when, in the late 1970s, the French government approached Stanislaus Teichner at Universite Claud Bernard, Lyon seeking a method for storing oxygen and rocket fuels in porous materials. In subsequent years, Teichner's group, and others extended this approach to prepare aerogels of a wide variety of metal oxide aerogels (Hunt and Ayers,1995).

Aerogels are highly porous solid materials with unusually low densities and high specific surface areas. They usually are prepared by the supercritical drying of highly cross-linked inorganic of organic gels. The most commonly studied aerogels contain only silica, but studies also have been carried out on silica-based gels that contain organic compounds. To incorporate organic modifiers effectively, the silica component of the gel must be prepared under carefully controlled conditions so that it leads to microstructure that can interact with these modifiers. The microstructure of the silica component of the aerogels and the sol gel from which it is made is sensitive to preparation conditions such as pH, and the ratio of the silica precursor to the solvent in the sol gel processing, and other factors. The microstructure can be controlled in the gelation, aging, and drying process (Wang *et al.*, 1991) as well as by isothermal sintering (Emmerling and Fricke, 1992). The interaction between the silica network and its modifiers also may affect the resulting aerogels structure.

The microstructure of aerogels strongly depends on the preparation conditions and the choice of precursors. Therefore, each aerogel has its own structural characteristics. The gathering of information on the structure of aerogels requires methods which cover the length scale from the lower nanometer range (structure of the primary particles) to the micrometer range (linking of the particles, etc). No single method can provide the complete information.

Besides small angle neutron scattering, imaging methods such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) also have such a capability to resolve inhomogenities of this lengths scale (nm to μm) (Santos *et al.* 1987, Rousset *et al.* 1990, Foret *et al.* 1992, Jarzebski *et al.* 2001, Hu *et al.* 2001, Yamauchi *et al.* 2004). They provide images in real space, for instance pictures of individual grains in a nanocystalline material. SANS on the other hand provides information averaged over all grains of different sizes with high statistical accuracy.

1.2 Research Problem

Small angle neutron scattering technique has been widely employed in probing the microstructure of amorphous material in nanometre range. However, it is not so popular in use due to neutron is expensive to produce. According to statistics, there are total of 32 SANS facility at all around the world (Hammouda, 1995).

SANS facility at MINT is the one and only SANS facility in Malaysia. The construction of SANS facility was completed by the end of 1994 and many tests were carried out from 1995 to 1996. Analyzing real samples have been pursuited from 1997 onwards.

Before this, several surfactant based colloidal samples have been irradiated in the SANS facility (REACTOR TRIGA PUSPATI). However, in this present work, silica aerogels and titanium containing silica aerogels produced from rice husk ash (RHA) were being used as samples. Based on literature review, small angle neutron scattering is very suitable to characterize the structure of silica aerogels since the structural units such as particle size and pore size is in the nanometre range.

The structure of the aerogels depends strongly on the preparation condition and composition during the synthesis of aerogels. In this study, the particle size, fractal dimension and also the surface area of silica aerogels in conjunction of different pH is being verified. The fractal dimension and particle size for silica aerogels and titanium containing silica aerogels are compared to each other.

1.3 Research Objectives

- To verify the performance of small angle neutron scattering (SANS) facility at Malaysian Institute of Nuclear Technology Research (MINT).
- To demonstrate the suitability of SANS in probing microstructures.
- To develop a new SANS data reduction program written in FORTRAN language.
- To measure the fractal dimension and particle size of silica aerogels and titanium containing silica aerogels.
- To study the effect of pH on the variation of particle size and fractal dimension.

1.4 Scope of Studies

In order to verify the performance of SANS facility at MINT, several preliminary experiments have been done. However, the preliminary results show that the neutron beam which comes out from the reactor is off-centred. Hence, calibration of the facility was done. However, results obtained after the calibration was not convincing.

To overcome this problem, some powder samples were sent to Badan Tenaga Nuklir Nasional (BATAN), Indonesia to be irradiated. The results obtained from SANS facility at MINT were compared to results obtained at BATAN, Indonesia. At MINT the sample to detector distance (STD) was fixed to 4m and the Q-range fall between 0.1 nm^{-1} and 0.9 nm^{-1} (See section 3.2.1 for definition of Q). While for the SANS facility at BATAN the sample to detector distance varies from 1.5m to 4m to 13m. The corresponding Q range is between (0.06 - 3) nm^{-1}.

The silica aerogels was not synthesized personally. Instead, it was obtained from the Zeolite and Porous Material Research Group (ZPMG) of Department of Chemistry at Universiti Teknologi Malaysia (UTM). The aerogels was known as Maerogel and it was produced from rice husk ash (RHA).

Data correction and data reduction from two-dimensional scattering pattern to one-dimensional profile was performed by a new program developed. The program was written in FORTRAN language by J. Suzuki of Japan Atomic Energy Research Institute (JAERI). The program was modified in order to suit to our computer system and input data file. By using the program, scattering vector *Q* and corrected intensity *I(Q)* was calculated.

One of the objectives of this study is to characterize the structure of silica aerogels and titanium containing silica aerogels as a function of pH. The particle size and fractal dimension of silica aerogels was determined. Guinier law and power law and were applied for the characterization of the structure of the silica aerogels and titanium containing silica aerogels.

1.5 Organization of Thesis

This thesis details the work, results and analysis from the study of silica aerogels and titanium containing silica aerogels. The introduction describes the SANS method broadly and indicates why SANS was used to study silica aerogels. Following the introduction chapter, literature review on SANS studies will be reported in Chapter 2. Some fundamental aspects of small angle neutron scattering will be presented in Chapter 3. Chapter 4 covers a brief review of silica aerogels and the SANS facility at MINT, experimental details, data acquisition and also data reduction. Chapter 5 is a presentation of analysis and discussion of silica aerogels' microstructure. Finally, the conclusion of the work and a list of suggestions for further work are presented in Chapter 6.

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