

## Keynote Paper 2:

# NANOTECHNOLOGY IN MALAYSIA: A NEW PARADIGM

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### ABSTRACT

*Nanotechnology is defined as the science of material and systems with structures and components which display improved novel physical, chemical and biological properties; phenomenon that exist in the nano size scale (1-100nm). A nanometer (nm) is one billionth of a meter. Nanotechnology not only enables further technical and scientific advancement of existing technologies, rather creates new technology and imposes drastic impact on industries, economy and society in the coming decades. This means that investment in nanotechnologies is imperative for a developing nation like Malaysia in order to remain competitive and ensure a future growth industry in its own right. The National Nanotechnology Initiatives of Malaysia (NNIM) was officially launched by the Deputy Prime Minister YAB Datuk Sri Najib Tun Razak on 19 September 2006. The functions, strategies and future plans of NNIM will be presented. Malaysia has spent more than RM160 million on various areas of nanotechnology related research projects. The established research areas, research path and business opportunities in various areas of nanotechnology in Malaysia is proposed.*

### ABSTRAK

*Nanoteknologi ditakrifkan sebagai sains yang berkaitan bahan dan system yang mempunyai komponen dan struktur yang mempamerkan ciri-ciri baru yang dipertingkatkan dari segi fizikal, kimia dan biologi; fenomena yang wujud dalam skala bersaiz nano. Satu nanometer adalah bersamaan satu per billion meter. Nanoteknologi bukan sahaja membolehkan kemajuan saintifik dan teknikal teknologi sediaada, malah mewujudkan teknologi baru dan memberi impak yang drastik ke atas industri, ekonomi dan masyarakat dalam dekad akan datang. Ini bermakna pelaburan dalam teknologi nano adalah satu kemestian untuk negara membangun seperti Malaysia jika ingin terus bersaing dan memastikan pertumbuhan industri dimasa hadapan berada pada landasan yang betul. **National Nanotechnology Initiatives of Malaysia (NNIM)** telah dilancarkan secara rasmi oleh Timbalan Perdana Menteri YAB Datuk Sri Najib Tun Razak pada 19 September 2006. Fungsi, strategi dan perancangan masa depan NNIM akan dibentangkan. Malaysia telah membelanjakan lebih dari RM160 milion bagi projek penyelidikan berkaitan pelbagai bidang nanoteknologi. Bidang penyelidikan yang telah dipastikan, haluan penyelidikan dan peluang-peluang perniagaan dalam pelbagai bidang nanoteknologi dicadangkan.*

### INTRODUCTION

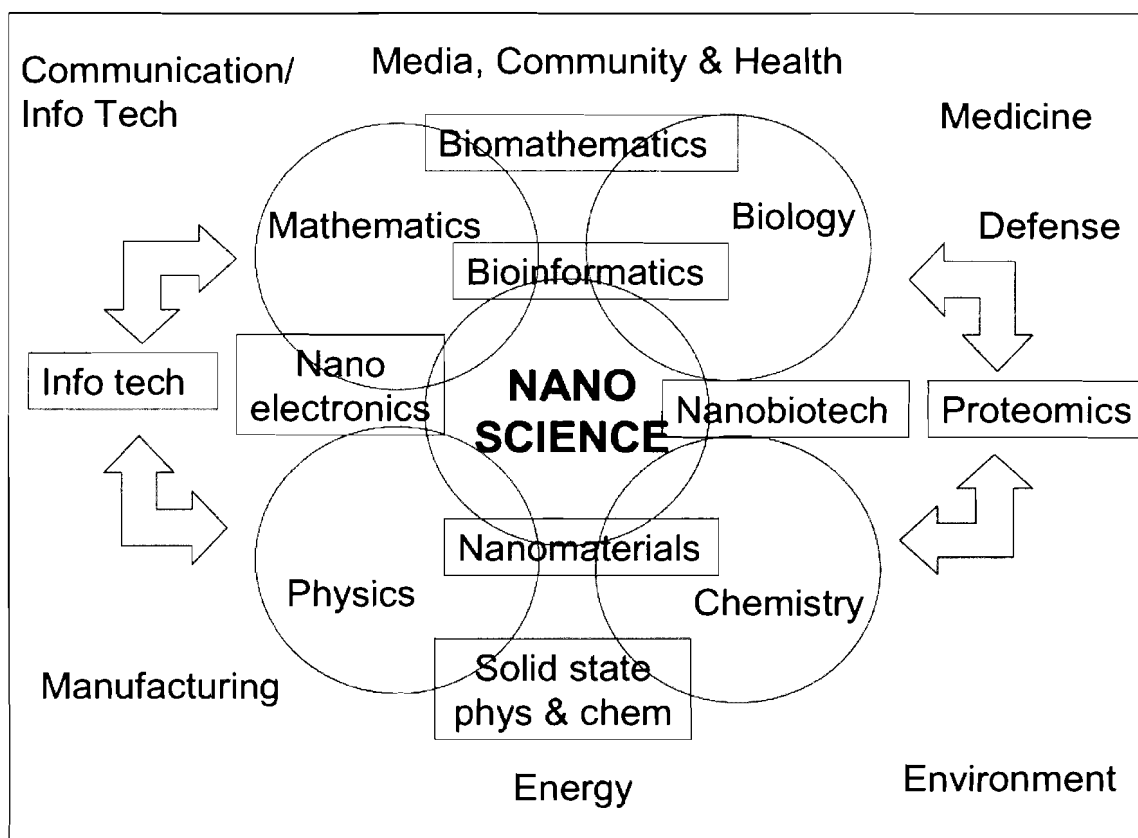
Nanotechnology is a basic science and emerging technologies; recognised having big potential to bring benefits to many areas of research and attracting rapidly increasing investments from government and from industry in many parts of the world. Nanotechnology is defined as “the science of materials and systems with structures and components which display improved novel physical, chemical and biological properties; phenomena that exist in the nano size scale (1-100nm)”.

A nanometer (nm) is one billionth of a meter. For comparison, a single human hair is about 80,000nm wide.

People are interested at the nanoscale because it is at this scale that the properties of materials can be very different from those at a larger scale. Chemists have been making polymers, which are large molecules made up of nanoscale subunits.

The properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area when compared to the same mass of materials produced in a larger form. This can make materials more chemically active and affect their strength or electrical properties. Second, quantum effects can begin to dominate the behaviour of matter at the nanoscale particular at the lower end, affecting optical, electrical and magnetic behaviour of materials. Nanotechnology includes various fields of sciences which are related to each other as shown in Figure 1. The convergence of various disciplines towards nanotechnology is clearly shown with synergistic effort between the nanoscience and nanotechnology disciplines.

Nanotechnology is a field that incorporates a wide range of activities including manufacturing, synthesis and processing of functional nanostructures with designated properties, the chemistry of supramolecule and nanomolecule, self-assembly and replication techniques, sintering of nanostructured alloy, the application of quantum effect, template and chemical and biological sensor, modification of surfaces, membranes, thin films and measurements of nanostructures (Figure 2).



**Figure 1: The interdisciplinary field of sciences in Nanotechnology**

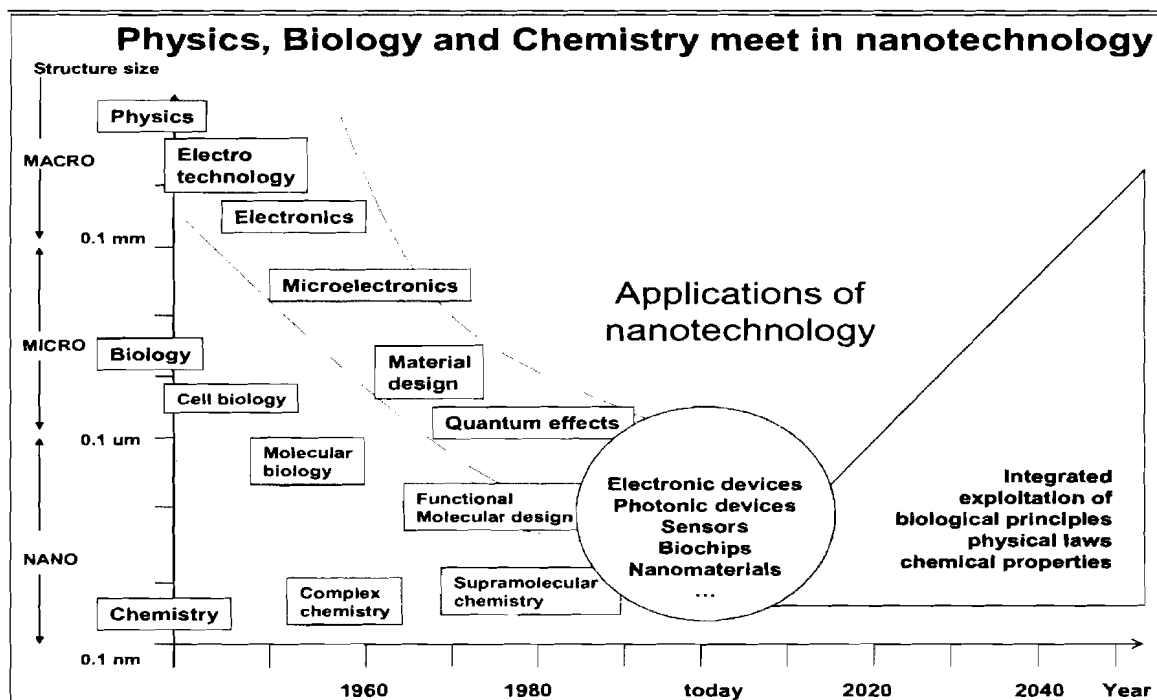


Figure 2: Research approach in Nanotechnology (Tegart, G, *Nanotechnology: The Technology for the 21<sup>st</sup> Century*, Vol II The Full Report, APEC Center for Technology Foresight (2002)).

## THE ECONOMICS OF NANOTECHNOLOGY

Virtually all industrialised countries have in development or have established a national strategy for nanotechnology. The focus varies from a general science-based strategy (for example the United States and France) to industry relevance-driven strategy (for example the European Community, Korea and Taiwan) from broad spectrum of areas (as in United States, Japan and Germany) to specific strengths. The level of investments in nanotechnology R&D has increased in most countries since 1997 (Table 1). A breakdown of other APEC economies is given in Table 2.

Table 1: Estimated government-sponsored R&D (from Roco, J. of Nanoparticle 2005) – (US million)

	1999	2000	2001	2002	2003	2004	2005
W Europe	179	200	Est.225	400	650	950	1050
Japan	157	245	550	753	800	900	950
USA	255	270	422	697	774	989	1081
Others	96	110	380	550	800	900	1000
TOTAL	687	825	1577	2400	3024	3739	4081

Research spending on nanotechnology, mainly within the USA is large and growing as part of a National Nanotechnology Initiative worth approximately USD1000 million in FY2005. The largest US spender on nanotechnology research is the National Science Foundation (USD338 million), followed by the Department Of Defense (mainly the Defense Advanced Research Projects Agency (DARPA)) which is spending around USD257 million in the area. The next biggest spender is the Department of Energy (USD210 million) with the National Institutes of Health spending USD142 million.

**Table 2: Estimated nanotechnology R&D in some APEC economies (US million)**

	2001		2002		2004
China	35.6		35.6		200
Korea	54		142		300
Singapore	7.5		9		-
Chinese Taipei	10		22		110
Australia	15		40		100

Continental European research currently at USD175 million, is on the increase but does not match the level of US investment. Japan also has a substantial research programme funded by government to a level of about USD85 million. Within the UK the Research Councils are starting a number of initiatives in support of building expertise and knowledge in nanotechnology. The Engineering and Physical Sciences Research Council (EPSRC), and the Medical Research Council (MRC) are each already sponsoring a number of related grants together worth more than USD25 million and have both separately conducted 'theme day' conferences in the past year. Furthermore, they together with the Biotechnology and Biological Sciences Research Council (BBSRC) and Ministry of Defence (MINDEF) are considering sponsoring a small number of nanotechnology Interdisciplinary Research Collaborations worth a total of about USD5.2 million.

In Asia Pacific, almost all countries including Korea (July 2001), China (2002), Taiwan (September 2002), India (2003), Australia (2003), Singapore (2003) and Thailand (2003) have launched their National Nanotechnology Initiative. Asia countries have spent more that USD1.5 billion for nanotechnology development.

#### **NANOTECHNOLOGY INITIATIVE FOR MALAYSIA: "THE WAY FORWARD"**

Malaysia has for decades trained scientists capable of contributing to the national development in science and technology (S&T), where some pioneering work in nanotechnology were initiated since the Seventh Malaysia Plan (7MP) in 1995-1999. Current database indicates that there are about 150 local scientists directly involved in various areas of nanotechnology research.

In his 2006 Budget Speech, the Prime Minister YAB Datuk Sri Abdullah Ahmad Badawi among other words stated that: "To further strengthen and diversify the sources of economic growth, the Government will intensify its efforts to encourage the private sector to venture into new areas with high growth potential and competitive edge. These include modern methods for agriculture, biotechnology, nanotechnology, high-technology manufacturing as well as services, especially ICT, education and tourism". The inclusion of nanotechnology as a priority area under Intensified Research and Prioritised Areas (IRPA) for Eighth & Ninth Malaysia Plan is timely, and is poised to position the country in the long term to nurture a nanoscience research culture among researchers and develop world class nanotechnology laboratories in Malaysia. At the end of Eighth Malaysia Plan, Ministry of Science, Technology and Innovation (MOSTI) has awarded about RM160 million to nanotechnology related research projects. The budget is expected to increase significantly in the Ninth Malaysia Plan (2006-2010).

Under the current National Science and Technology Policy (NSTP), nanotechnology is included in the strategy of building competence for specialisation in key emerging technologies, and has been identified as a

key technology area to support the local industry. In order to move forward, the industry participation must be strengthened by encouraging the private sector to be directly involved in the development of nanotechnology. The government should encourage local industries, including GLCs to use local R&D products/processes. In addition, the gross expenditure on R&D (GERD) and number of scientists to population will be increased from 0.5% to 1.5% and 18 to 60 per 10,000 by year 2010. The underlying objective is to enhance commercialisation of local products and increase the critical mass in the focus areas.

The short term strategy of Malaysia is geared towards identifying researchers in various areas of nanotechnology with specific expertise; upgrading and equipping nanotechnology laboratories with state-of-the-art facilities; and to prepare a comprehensive human resource development programme for producing nanotechnologists.

The National Nanotechnology Initiatives of Malaysia (NNIM) was officially launched by the Deputy Prime Minister YAB Datuk Sri Najib Tun Razak on 19 September 2006 with the mission: Nanotechnology for sustainable national development of science, technology, industry and economy. The functions of NNIM are:

1. To integrate all existing local nanotechnology activities.
2. To coordinate and plan the R&D activities.
3. To prepare a platform for commercialisation and transfer of new technology to generate economic return for the general public.
4. To develop educational resources, skilled labour, expertise and nanotechnology infrastructure.
5. To provide facilities and nanotechnology research support services.

The strategies on NNIM focus on the improvement of Malaysian economic competitiveness to face global challenges, acceleration of scientific breakthrough on selective beneficial nanotechnologies and enhancement of societal and environmental contribution.

MOSTI is now entrusted to spearhead the planning and development of the NNIM. The following actions have been implemented by MOSTI:

1. Incorporation of nanotechnology as a national priority in the Ninth Malaysia Plan by the Cabinet.
2. Proposed establishment of National Nanotechnology Center (NNC).
3. Establishment of the Brain Gain Program for Nanotechnology under the Academy of Sciences Malaysia.
4. Study on Business Opportunity and R&D in Nanotechnology by MIGHT; commissioned by the Economic Planning Unit (EPU).

## **NANOACTIVITIES IN MALAYSIA**

The potential benefits of nanoscience and technology are pervasive, as illustrated in the burst of interest and effort worldwide in several fields outlined below: materials and manufacturing; nanoelectronics and computer technology; medicine and health; aeronautics and space exploration; environment and energy; biotechnology and agriculture; national security; and science and education.

There are many groups actively involved in nanotechnology R&D in Malaysia. The committed support from the government, seen in the increased R&D funding to MOSTI for nanotechnology R&D, enabled the growth of a significant number of research centres pursuing nanoscience and technology.

### **Materials and Molecular Design**

One of the major areas pursued by Malaysian scientists, in tandem with governmental funding through

research and educational sponsorship by MOSTI, is the molecular design of nanomaterials, chemical manipulation of nanostructured materials, metal composites, catalysts and chemical sensors.

### **Nanoelectronics**

This area of nanotechnology is the main driver of the field. It is embedded into the current production strategy of the industry and is a major single source of innovation. It is thus important for Malaysia to pursue some research activities with international visibility. Examples of projects in electronics and communications include MEMS and microsensors/organic electronics and advanced optical crystal for electro-optic applications.

### **Life Sciences / Medicine and Health**

Living systems are governed by molecular static and dynamical properties at nanometer scales, where the disciplines of chemistry, physics, biology, and computer simulation all now converge. There is one area of development in life-sciences with Malaysia's active participation: the design and synthesis of biologically functional nanostructures by genetically modified living systems.

## **ENHANCEMENT OF NANOTECHNOLOGY RESEARCH ACTIVITIES**

By end of Eighth Malaysian Plan, Malaysia has spent more than RM160 million on various areas of nanotechnology related research projects. Currently, nanotechnology research is conducted by separate research groups in various local public universities and government research institutions. Major areas pursued by Malaysian scientists are molecular manipulation and generation of nanomaterials, nanoelectronics and living systems. One area of life-sciences in which local nanoscientists are active in is the design and synthesis of biologically functional nanostructures by genetically modified living systems. Research in nanotechnology is governed by molecular static and dynamical properties at nanometer scales, where the disciplines of chemistry, physics, biology and computer simulation all now converge. Therefore, the implementation and management of research in nanotechnology needs to be coordinated, organised and interdisciplinary. To be an effective technology watcher and obtain key information from the international research community in particular, the government needs to sponsor some nanotechnology research on topics of recognised significance.

A study on Business Opportunity and R&D in Nanotechnology in Malaysia; conducted recently, concluded that the areas of research in Nanotechnology need to be focused, enhanced and sustained. Based on the availability of resources, needs, infrastructure and technical strength, it is proposed that nanotechnology research in Malaysia, in the long term, should focus on the following areas:

1. Solar Cells - Photovoltaic and Dye-sensitized.
2. Lithium ion batteries.
3. Plant Vaccines.
4. Nano Biodevices - lectin chips/ glycol chips and environment management using DNA chip analysis.
5. Nano Biosensors – nanoagricultural diagnostics with nanomaterials.
6. Drug Delivery Systems - liposome technology and nano-encapsulation for food and drug delivery.

## **CONCLUSION**

Looking to the near-term future, it is necessary for Malaysia to introduce and create awareness among the public by organising a programme in nanotechnology. A conference on nanotechnology will hopefully demonstrate and explain the worldwide investment in nanotechnology research is already large and is set to grow stimulated by potentially vast civil markets for products.

To be an effective technology watcher and obtain key information from the international research community

## INTRODUCTION

Some clay minerals like zeolite are known to exhibit excellent sorptive and ion exchange properties. Zeolites are microporous crystalline solids with well-defined structures. Generally, they contain silicon, aluminium and oxygen in their framework, while cations, water and/or other molecules within their pores. Many zeolites occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses.

Because of their unique porous properties, zeolites are used in a variety of applications with a global market. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification) and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. Zeolites are often referred as molecular sieves.

As rice husk is normally discarded as waste material, its disposal is considered to be hazardous to the environment and public health. Research studies conducted by Universiti Teknologi Malaysia (UTM) have shown that various types of zeolite can be synthesised from rice husk ash (RHA) which contains approximately 20% amorphous silica in the rice husk. The synthetic zeolite produced from the RHA is found to possess superior properties in terms of its excellent ion exchange capacity and robust structural stability when compared to natural zeolite.

Hydrous tin (IV) oxide ( $\text{SnO}_2$ ) gels, commonly referred to as ortho-stannic acid (or  $\alpha$ -stannic acid) and meta-stannic acid ( $\beta$ -stannic acid), are known to exhibit excellent ion exchange properties. Unlike conventional organic ion exchange resins, hydrous  $\text{SnO}_2$  is stable relatively at high temperature and resistant to strong acid and nuclear reaction. These features allow  $\text{SnO}_2$ -based materials to be used for the separation of radionuclides, which find extensive use in analytical and diagnostic medical techniques and potential for application such as in water treatment at elevated temperatures and chemical processing of solution containing nuclear waste (Cusack., 2006).

The high affinity of  $\text{SnO}_2$  for transition metal ions generally, allows its use for removal of trace levels transition metal contaminants from solution of salts of alkali metals and alkaline earth metals. In this research, the concept of combining the ion exchange properties of hydrous  $\text{SnO}_2$  species with active support material, including zeolites and clays, for developed new system in ion exchanged system (Cusack., 2006)

The main feature of tin (II) compounds is the ease of their oxidation to tin (IV) materials. In solution, tin (II) species rapidly oxidise on exposure to air and even solid tin (II) salts are slowly oxidised by atmospheric oxygen. Tin chemicals generally find widespread use as reagents in preparative organic and inorganic chemistry, and tin (II) salts use as reducing agents in a wide range of industrial application. Tin (IV) oxide is amphoteric and dissolves in an aqueous solution of acids to form tin (IV) salts and in aqueous caustic alkalis to form hydroxystannates (IV). Unlike their tin (II) analogues, inorganic tin (IV) colloids have been widely studied and commercial tin (IV) oxide sols are being marketed as passivation agents for removal of trace metal in the petrochemical industry, precursors for forming thin (IV) oxide layers on glass and other substrate, binders in ceramic and catalytic application, fire-retardant additives for polymeric substrates and replenishing additives to alkaline electrolytic tin and tin alloy plating baths (Tin Sol) (Cusack., 2006).

## EXPERIMENTAL

In this project, three stages of experimental work were conducted. It started with synthesis of Zeolite X (NaX) by using RHA as silica source, after that, impregnation of tin species on NaX ( $\text{SnNaX}$ ) and lastly, ion-exchange study on the NaX and  $\text{SnNaX}$ .

### SYNTHESIS OF ZEOLITE X

A batch formula ( $4.54 \text{ Na}_2\text{O} : 3.44 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 180 \text{ H}_2\text{O}$ ) by Shinde et. al. (2004) was selected for producing NaX. Chemical reagents used are Sodium Hydroxide and Sodium Aluminates and Silica content in RHA. Synthesized NaX powder was analyzed by XRD. XRD powder diffraction pattern of the sample was recorded on a JEOL X-Ray Diffractometer JDX-3500 with a  $\text{Cu-K}\alpha$  radiation source.

Two separate aqueous mixtures were prepared namely silicate and aluminate with a total weight of 100g. Silicate mixture was prepared by mixing together appropriate proportions of NaOH, RHA and  $\text{H}_2\text{O}$ . The mixture was stirred until all solids dissolved. It was then heated in the oil bath at  $95^\circ\text{C}$  for 2 hours.

Simultaneously, aluminate mixture was prepared by mixing appropriate proportions of NaOH, NaAlO<sub>2</sub> and H<sub>2</sub>O. The mixture was then heated on a hotplate at 45°C for 1 hour.

Both aqueous mixtures of silicate and aluminate were then mixed and stirred well for about 1 to 2 hours. The mixture was then aging for 24 hours at room temperature to achieve its homogeneity. After that, the solution was put in the oven for about 6 to 8 hours at temperature of 100°C. The sample was then cooled to room temperature for about 30 minutes. Immediately after that, the precipitate was filtered and washed with distilled water. The solid sample was then dried overnight in an oven before analysed for physical properties.

## IMPREGNATION

Stannum dichloride (SnCl<sub>2</sub>·H<sub>2</sub>O) was used as tin source. Prior to impregnation, stannum dichloride solution was prepared with six concentrations of 0.3 M, 0.4 M, 0.5M, 0.6 M, 0.7M and 1.0M respectively.

The impregnation was prepared with proportion of 3.0 ml of SnCl<sub>2</sub> to 1.0 g of NaX. Subsequently, 1g weight of NaX was added respectively into six concentrations of stannum dichloride solutions. The respective mixtures were immediately stirred for 30 minutes for homogenizing without heating and subsequently dried in the oven at 100°C overnight. The samples were then calcined for 10 hours at a temperature of 500°C for removing organic materials. The dried samples were then analysed for physical properties. The impregnation methodology was adopted from Xu et. al. (2005).

## ION EXCHANGE

Copper (Cu<sup>2+</sup>) and lead (Pb<sup>2+</sup>) solutions were used in ion exchange experiments. The ion exchange experiment was performed on both samples, NaX and SnNaXl. As for Cu metal ion, 1000 ml solution of CuSO<sub>4</sub>·5H<sub>2</sub>O was prepared with copper concentration of 1000 ppm. Similarly, the same procedure applies for Pb metal ion. The source of Pb was obtained from Pb (NO<sub>3</sub>)<sub>2</sub>.

Subsequently, 100ml of each metal solution was added with 0.4 g NaX. The mixture was then stirred for 2 hours. About 10ml of sample was collected at time intervals of 5, 10, 20, 30, 40, 50 and 60 minutes. The collected samples were then centrifuged and the supernatant tested for remaining metal ion by using AAS.

## CHARACTERISATION

The chemical composition of RHA was analysed with Shimadzu X-Ray Fluorescent Spectrometer 1700 (XRF). The X-ray power diffraction (XRD) patterns of the samples were collected using JEOL X-Ray diffractometer JDX -3500 with CuKα radiation in the range of 5–60° (2θ) with a rate of 8° (2θ)/min. The morphology of the samples was observed with a Field Emission Scanning Electron Microscope (FESEM), Supra 35 VP Leo Gemini instrument. The chemical components of the samples were analysed with energy disperse X-ray (EDX) which attached to FESEM.

The specific surface area and the pore volume of the samples were measured from the adsorption and desorption isotherms of N<sub>2</sub> at 77 K using a Quantachrome Corporation NOVA 1000 (BET) instrument. The samples tested were dehydrated at 573 K for 6 h before determination.

Cation exchange capacity (CEC) of the zeolite was also measured to determine the ability of zeolite in ion exchange process. The unit measurement of CEC is milliequivalent per 100 gram (meq/100g).

## RESULT AND DISCUSSION

### XRF IDENTIFICATION

RHA was used as silica source in the synthesis of NaX. The results of XRF analysis on RHA are shown in Table 1. XRF result (Table 1) shows that amount of SiO<sub>2</sub> in RHA only about 94%. Composition of SiO<sub>2</sub> is crucial for the formulation in order to obtain high quality zeolite.

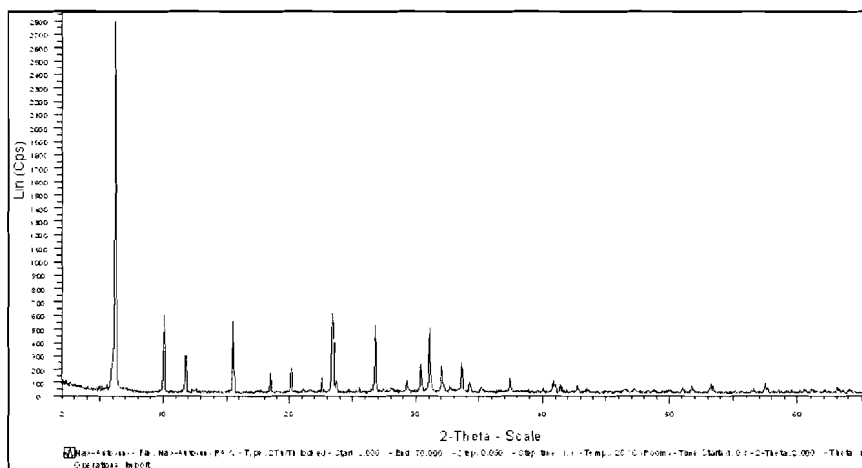
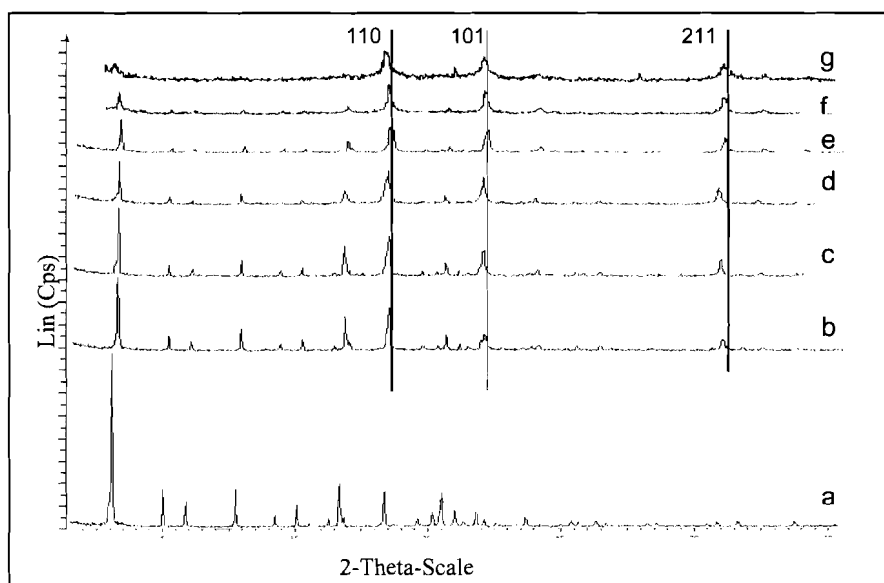


**Table 1: Chemical composition of RHA**

Chemical composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	LOI
Percent %	93.99	1.69	0.77	0.20	0.02	1.27	0.30	0.34	1.42

**XRD IDENTIFICATION**

Prior to further test works, synthesized NaX and SnNaX powders were sent for XRD analysis to examine the crystallinity of zeolite crystal. The XRD pattern of the NaX is shown in Figure 1 whilst the XRD patterns of the SnNaX with various concentrations are shown in Figure 2. The XRD patterns of the NaX sample displays a high count persecond (CPS) value of more than 2400 and none of amorphous phase are visible.

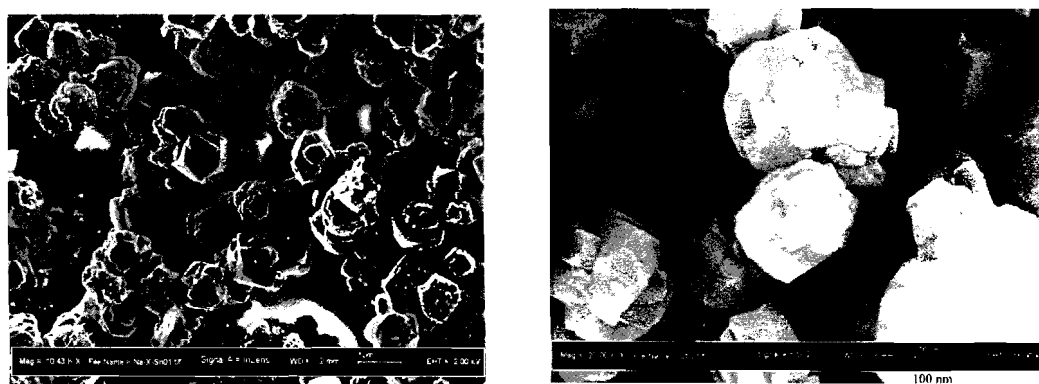
**Figure 1: The XRD pattern of Zeolite X**

**Figure 2: The XRD patterns of: (a) NaX, (b) SnNaX-0.3M, (c) SnNaY-0.4M, (d) SnNaY-0.5, (e) SnNaY-0.6M, (f) SnNaY-0.7M, and (g) SnNaY-1.0M. (The perpendicular lines indicate the characteristic peaks of SnO<sub>2</sub>.)**

In Figure 2, there are three broad peaks, indexed to the diffraction of 110, 101 and 211 of the tetragonal lattice of  $\text{SnO}_2$  ( $a = b = 0.474$  nm,  $c = 0.319$  nm, and JCPDS file No. 21-1250) exhibit, respectively, at 0.335 nm, 0.264 nm and 0.177 nm/d in the XRD pattern of SnNaX-0.3M, SnNaX-0.4M, SnNaX-0.5M, SnNaX-0.6M, SnNaX-0.7M and SnNaX-1.0M implying that  $\text{SnO}_2$  nano-particles have formed on NaX zeolite (Xu et al., 2005). However, the diffraction intensity of NaX, especially at  $6^\circ$ , characteristic peaks in the XRD pattern of SnNaX-1.0M is weaker than that of XRD patterns of SnNaX-0.3M, SnNaX-0.4M, SnNaX-0.5M, SnNaX-0.6M, SnNaX-0.7M. This implies that the high molarity of a  $\text{SnCl}_2$  used in impregnation the crystallinity of zeolite will be decreased. Decreasing crystallinity of the sample is proven by micrographs images from FESEM as shown in Figure 3.

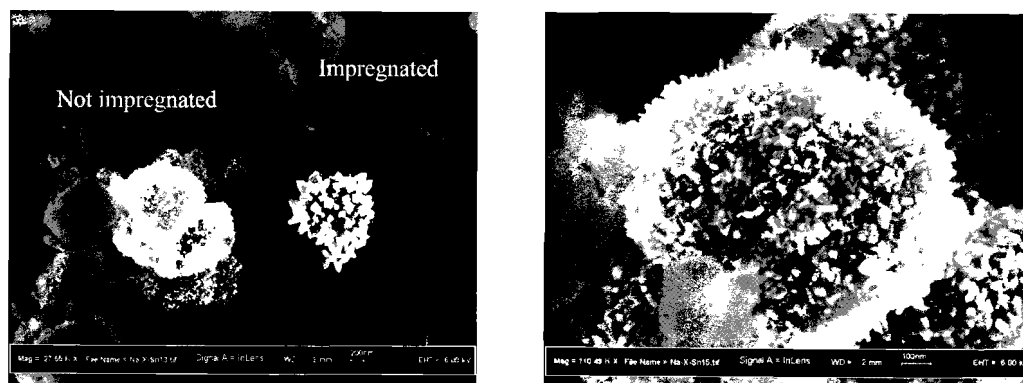
## MORPHOLOGY

Images in Figures 3, 4, 5 and 6 were taken with Field Emission Scanning Electron Microscope (FESEM). The FESEM images show that the surface morphology of NaX and impregnated tin species NaX. Figure 3 revealed that NaX having uniform particle and shape. The surface area of NaX also having perfect formed crystal and well distributed sizes. The particles also exhibit flat planes with crystal material features.



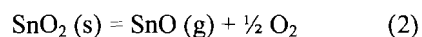
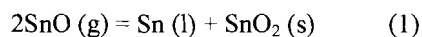
**Figure 3: FESEM images of Zeolite X**

Figure 4 shows the image of tin impregnated NaX with concentration of 0.7M. Two clear images of the NaX particles show impregnated and non-impregnated with tin species can be distinctly observed. The  $\text{SnO}_2$  nano-particles are formed on the outer surface of NaX crystallites. The  $\text{SnO}_2$  nano-particles are in a form of arrays of nano-single-crystal-rods grown on the outer surface of NaX crystals. The presence of elements such as Sn, Si, Al and Na were traced by Electron Dispersive X-ray (EDX). Figures 5 and 6 show that Sn was not detected on the NaX crystals, it means that  $\text{SnO}_2$  was not formed.



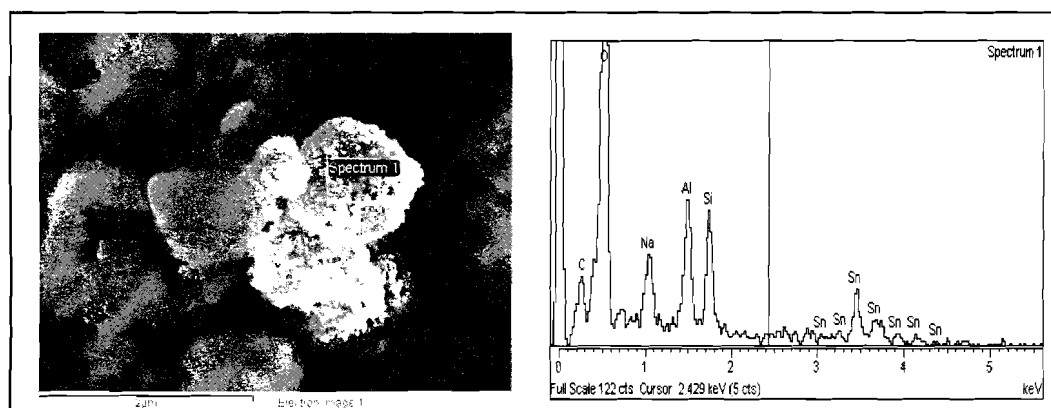
**Figure 4: FESEM images of Impregnated tin species in Zeolite X**

Theoretically partly ionic bonds between cation and the Si-O-Al-O surface of zeolite lead to inability to form monolayers of SnO<sub>2</sub> on the zeolite. In this situation the formation of SnO<sub>2</sub> nano-particles on the zeolite surface involved a process of heterogeneous nucleation and growth (HGN). The surface of zeolite plays a role in the heterogeneous nucleus, which greatly increases the possibility of forming SnO<sub>2</sub> nano-particles on the zeolite surface. This indicates that SnO<sub>2</sub> crystallise with high nucleation rate and low growth rate at calcinations temperature of 350°C. On raising the calcinations temperature, the nucleation rate obviously decreases and the growth rate increases, resulting in forming solo and bigger nano-crystallites. Therefore, the nano-particles of the oxide with various temperatures of calcinations were on the surface of the zeolite. When heating in moist at 95°C, tin (II) chloride hydrolyzes to form mixture of SnO and SnO<sub>2</sub>. On further heating, the following chemical reactions occur at temperatures above 300°C.

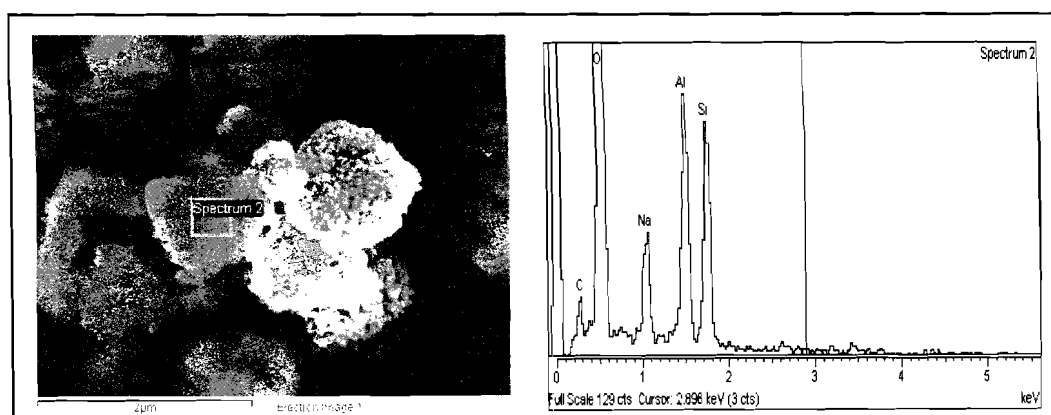


Chemical reaction (2) is reversible. Sn (l) plays an important role in the growth of SnO<sub>2</sub> nano-rods on the external surface of the zeolite. On cooling, Sn liquid in the zeolite moves out to the surface of the zeolite when in contact with oxygen resulting in the HGN and growth of SnO<sub>2</sub> crystallites (Xu et al., 2005).

EDX analysis shown in Figure 5 and Figure 6 proved that tin species have actually being formed on active surface of NaX crystals.



**Figure 5: EDX analysis of spectrum 1 displaying tin element on Zeolite X particles**



**Figure 6: EDX analysis of spectrum 2 displaying no tin element on Zeolite X particle**

## SURFACE AREA ANALYSIS

NaX and SnNaX samples were measured for their respective surface area using BET. BET surface area measurement was done by Quantachrome Autosorb Automated Gas Sorption System. Detailed BET results are shown in Table 2. Results on NaX alone show high value of surface area compared to SnNaX. This situation was due to active sites of zeolite may have been blocked by nano-size of  $\text{SnO}_2$  crystals, which resulting in reducing its surface area. Result also shows that higher molarity reduces the surface area substantially.

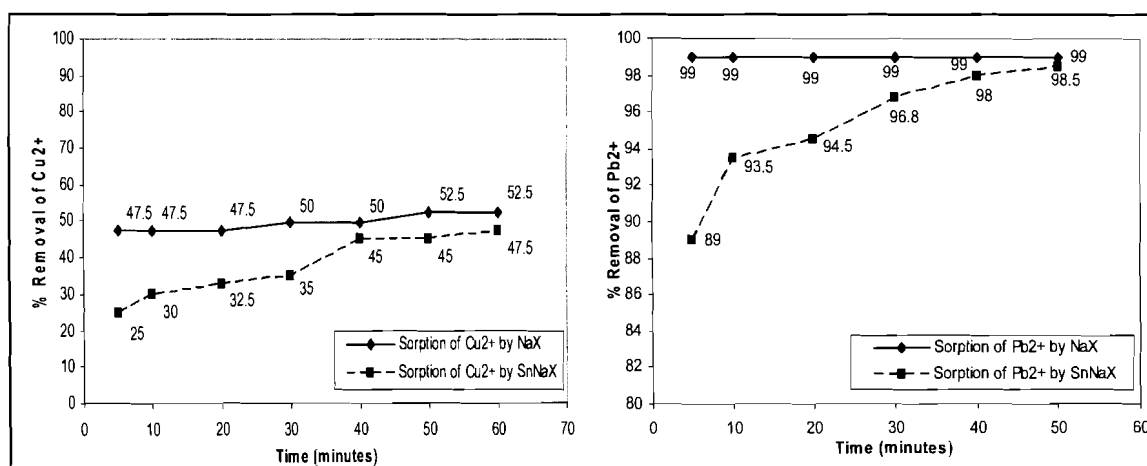
**Table 2: Surface area of Sn for NaX, SnNaX-0.3M and SnNaX-0.6M**

Sample	BET Surface Area (m <sup>2</sup> /g)
NaX	888
SnNaX-0.3M	511
SnNaX-0.6M	392

## ION EXCHANGE ANALYSIS

In this series testwork  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  cations were measured using Atomic Absorption Spectroscopy (AAS). Those cations are generally found in effluent such as from semiconductor factory. The results of analysis on those cations are shown in Figure 7.

Removal Cu at 60 minutes for NaX was 52.5%, while for SnNaX was 47.5%. However removal of Pb was achieved at 99% even from 5 minutes time for NaX compared to 98.5% at 60 minutes for SnNaX. Ten minutes period of time was sufficient to exchange  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from the solution. In contrast, SnNaX needs longer time to adsorb heavy metal cations until equilibrium system achieved. The results show that NaX alone can be removed both cations from solution better than SnNaX. From BET results the surface area of NaX has higher surface area than SnNaX. It is concluded that Na from NaX structure is more reactive compared to  $\text{SnO}_2$ .



**Figure 7: Removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by using NaX and SnNaX**

Cation exchanged capacity (CEC) was also measured for NaX and SnNaX. The results of CEC analysis on NaX and SnNaX are shown in Table 3. The test was adopted by Kjeldahl ammonia distillation of  $\text{NH}_4^+$  solution (Kitsopoulos., 1999).

**Table 3: CEC analysis**

Sample	CEC (meq/100g)
NaX	206.0
SnNaX-0.6M	140.0

Results show that CEC value of NaX is higher than SnNaX. This result implies that NaX can exchange cations 60 miliequivalent per 100g more than impregnated NaX from the prepared cationic solution.

## CONCLUSION

Impregnating tin species on zeolite mineral and experiments of ion exchange research with various parameters were also successfully conducted. The following conclusions are drawn from research work done on ion-exchange:

- 1) Zeolite X (NaX) was higher affinity for copper and lead removal compared with Zeolite X coated with tin (SnNaX).
- 2)  $\text{SnO}_2$  can absorb some heavy metal cations especially transition metal ions from effluent.

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