SYNTHESIS AND CHARACTERIZATION OF NANO-SIZED ALUMINIUM OXIDE AND ITS APPLICATION IN THE FABRICATION OF POLYANILINE-ALUMINA NANOFIBERS

by

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Special Dedication

In loving memory of my grandmother.

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LIST OF SYMBOLS

η	Eta
θ	Theta
χ	Chi
κ	Kappa
α	Alpha
δ	Delta
β	Beta
γ	Gamma
°C	Degree Celsius
σ	Standard deviation
Al_2O_3	Aluminium oxides / Alumina
AlOOH	Boehmite / Pseudoboehmite
H_2O	Water

LIST OF ABBREVIATION

nm	nanometer
UV	ultraviolet
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
FESEM	Field-Emission scanning electron microscopy
UV-Vis	UV-Visible spectroscopy
XRD	Powder X-ray diffraction
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
PANI	Polyaniline
CHN	Carbon, hydrogen and nitrogen elemental analysis

LIST OF PUBLICATIONS & SEMINARS

1.	**Poster Presentation** Malaysian Chemical Congress 2000 (MCC 2000) Hotel Casuarina Park Royal, Ipoh.	October 2000
2.	**Oral Presentation** Regional Conference for Young Chemists University Science Malaysia Conference Hall, University Science Malaysia.	April 2000
3.	**Master Conversion Seminar** School of Chemical Sciences University Science Malaysia.	July 2000
4.	Novel Insight to Sol-Gel Processed Alumina Nanofibers.	In preparation
5.	Facile Synthesis of Novel PANI-Al_2O_3 Nanofibers.	In Preparation

SINTESIS DAN PENCIRIAN ZARAH-NANO OKSIDA ALUMINA SERTA KEGUNAANNYA UNTUK PEMBENTUKAN POLIANILIN-ALUMINA GENTIAN-NANO

ABSTRAK

Alumina zarah-nano berbentuk gentian bernisbah aspek tinggi dengan saiz diameter 2 nm dan panjang 70 nm telah berjaya disediakan dalam kuantiti yang banyak pertama kali melalui proses sol-gel. Dalam proses penyediaan, kesan seperti masa untuk hidrolisis, suhu, pH, nisbah bahan-bahan tindak balas dan jenis alkohol yang digunakan bagi pembentukan alumina gentian-nano telah dibincangkan. Kajian morfologi telah dijalankan melalui TEM. Kesan perubahan suhu pengkalsinan terhadap perubahan fasa Al_2O_3 juga dinyatakan. Berdasarkan penyiasatan dengan menggunakan teknik XRD, sampel sebelum pengkalsinan merupakan pseudoboehmit yang berfasa amorfus, yang kemudian bertukar menjadi α-Al_2O_3 semasa pengkalsinan pada suhu 1050 °C selama 5 jam. Luas permukaan BET, isipadu liang dan diameter liang yang ditentukan oleh eksperimen penjerapan dan pendejerapan nitrogen untuk alumina yang telah dikalsinkan didapati merupakan fungsi perubahan suhu pengkalsinan. Luas permukaan bernilai 335 m^2/g telah diperolehi untuk sampel yang dikalsinkan pada suhu 540 °C. Pencirian juga dilakukan dengan spektroskopi FTIR dan ^{27}Al MAS NMR. Sifat terma untuk alumina gentian-nano telah diuji dengan kaedah TGA and DSC.

Anilin telah dipolimerkan dengan kehadiran alumina gentian-nano di dalam larutan akueus berasid dengan menggunakan kuantiti agen pengoksidaan yang secukupnya. PANI-Al_2O_3 komposit-nano yang mempunyai struktur gentian telah berjaya dihasilkan dan diameter gentian didapati dalam julat 30-70 nm. Sintesis PANI-Al_2O_3 gentian-nano telah dijalankan dengan teliti dengan memanipulasi pembolehubah seperti jumlah alumina gentian-nano yang ditambah, jenis and jumlah agen pengoksidaan yang digunakan serta jenis dan kepekatan asid. Komposit-nano telah dapat disediakan dengan menggunakan pelbagai jenis agen pengoksidaan dan asid. Keadaan optimum untuk menghasilkan PANI-Al_2O_3 gentian-nano juga dinyatakan. Nanokomposit yang terhasil dikaji dengan menggunakan kaedah pencirian seperti spektroskopi FTIR and UV-Vis, TEM, FESEM, EDX, CHN, XRD, TGA, DSC dan penyukatan kekonduksian elektrik dengan kaedah proba empat titik. Kekonduksian untuk nano-gentian didapati dalam lingkungan 10^{-6}-10^{-1} S cm^{-1}. Mekanisme pembentukan PANI-Al_2O_3 nanokomposit juga dibincangkan.

SYNTHESIS AND CHARACTERIZATIONS OF NANO-SIZED ALUMINIUM OXIDE AND ITS APPLICATION IN THE FABRICATION OF POLYANILINE-ALUMINA NANOFIBERS

ABSTRACT

Fibrillar alumina nanoparticles of high aspect ratio with diameter of around 2 nm and length of about 70 nm have been successfully fabricated in bulk quantities for the first time *via* sol-gel process. In the course of preparation, the influences of the hydrolysis period, aging temperature, pH, the reactant molecular ratio and the type of solvent on the formation of alumina nanofibers were illustrated. Morphological studies were performed by TEM. The effects of various calcination temperatures on the phase transformation of Al_2O_3 were also demonstrated. The as-prepared sample gave amorphous phase assigned as pseudoboehmite, which was entirely converted into α-Al_2O_3 by calcination at 1050 °C for 5 h as verified by XRD patterns. The BET surface area, pore volume and the pore diameter of calcined alumina determined by nitrogen adsorption-desorption experiments were a function of the calcination temperature. Specific surface areas as high as 335 m^2/g were exhibited by the calcined solids at 540 °C. Molecular characterizations were also perfomed by FTIR and ^{27}Al MAS NMR spectroscopy. Thermal behavior of alumina nanofibers was investigated by TGA and DSC.

Aniline was polymerized in the presence of alumina nanofibers in aqueous acidic media using sufficient amount of oxidant. Conducting PANI-Al_2O_3 nanocomposites with fibrillar morphology were obtained and the typical diameter of these PANI-Al_2O_3 nanofibers is in the range 30-70 nm. Synthesis of PANI-Al_2O_3 nanofibers was achieved by careful control of experimental parameters such as the loading amount of alumina nanofibers, the type and loading amount of oxidants, as well as the type and concentration of acids. The nanocomposites were synthesized using a number of different oxidizing agents and different protonic acids. Optimum reaction conditions to yield PANI-Al_2O_3 nanofibers were outlined. The nanocomposites thus obtained were studied by characterization techniques such as FTIR and UV-Vis spectroscopy, TEM, FESEM, EDX, CHN, XRD, TGA, DSC and conductivity measurements by a four-point probe method. The conductivity of the nanofibers was in the range 10^{-6} - 10^{-1} S cm^{-1}. The mechanism of the formation of PANI-Al_2O_3 was proposed.

CHAPTER ONE
INTRODUCTION

1.1 Research Background

Over the past decade, nanomaterials have been the subject of enormous interest.[1] These materials, notable for their extremely small feature size, have the potential applications for wide-ranging industries, from extraordinary tiny electronic devices, including miniature batteries, to biomedical uses, and as packaging films, superabsorbants, components of armor, as well as parts of automobiles.[2,3] As a result of recent improvement in technologies to see and manipulate these materials, considerable efforts have recently been devoted to the design and fabrication of nanomaterials and nanostructures for the insatiable demand of miniaturization of devices.[4] Inorganic nanowires, nanotubes and nanofibers constitute an important class of one-dimensional materials which have been investigated extensively during the past few years.[5] The elongated structure of these high aspect ratio particles often result in inherent chemical, electrical, magnetic, and optical anisotropy that can be exploited for interactions with cells and biomolecules in fundamentally new ways.[6-8] Thus, one-dimensional nanostructures of Al_2O_3 and PANI are gaining renewed interest in recent years due to their high surface area and intrinsically high surface reactivity.[9,10]

1.2 Problem Statement

The problem statements to be justified are as follows:

(a) In particular, aluminium oxides (Al_2O_3) are of great interest because of their widespread utilities in catalysis as catalyst and catalyst support, adsorption and nanocomposite fabrication, depending on its purity and crystallinity.[11] Al_2O_3 are conventionally prepared by sol-gel method.[12] However, most of the previously reported sol-gel processed Al_2O_3 comprised mainly particles with grain size and reports on the formation of nanofibers are relatively sparse.

(b) Since the discovery in 1977 of the metallic properties of molecularly doped polyacetylene,[13] there has been rapid growth in the field of electronically conducting polymers.[14] Among the various conducting polymers, the polyaniline (PANI) family of conjugated polymers is of much interest worldwide because of its unique conduction mechanism and good environmental stability in the presence of oxygen and water.[15] One-dimensional PANI nanostructures including nanorods, wires, and fibers[16-18] have been chemically synthesized using templates, surfactants, carbon nanotubes and interfacial polymerization. Various nanocomposites[19,20] of PANI on nanosized SiO_2, SnO_2, MnO_2, ZrO_2 and V_2O_5 have been successfully fabricated. However, to the best of knowledge, no systematic studies have been reported on the use of alumina nanofibers to generate polyaniline having bulk nanofiber morphology.

1.3 Scope of the Study

The scope of this study will be focused on the preparation of Al_2O_3 nanofibers with high aspect ratio via sol-gel processing and PANI-Al_2O_3 nanofibers by chemical oxidative polymerization. One often used aluminium alkoxide, aluminium isopropoxide, as the precursor for the preparation of Al_2O_3 nanofibers in most contexts. The particle mean size and morphology were studied by varying the relative concentration of water to aluminium isopropoxide, the kind of solvent, hydrolysis period, aging temperature and pH. PANI-Al_2O_3 nanofibers can be obtained in acidic aqueous medium by polymerization of the aniline monomer in the presence of Al_2O_3 nanofibers and oxidant. Various parameters have been examined including the loading amount of Al_2O_3 nanofibers, the type and concentration of acids, and the type and loading amount of oxidants. The resultant nanofibers were then characterized by techniques such as TEM, SEM, FESEM, EDX, FTIR, XRD, TGA and DSC analysis.

1.4 Research Objectives

The objectives of this study are:

(a) To synthesize and characterize the Al_2O_3 nanofibers by sol-gel method.

(b) To synthesize and test the possibility for the use of Al_2O_3 nanofibers to generate fibril-like PANI-Al_2O_3 nanocomposites and to characterize the resulting products.

1.5 Outline of the Dissertation

This dissertation comprises of six chapters. Chapter 1 provides an overview of the study. The problem statements, research backgrounds and objectives are described. Chapter 2 presents a literature review on the related subjects and the development of the research. Chapter 3 outlines the research design, techniques, and methodology of this study. Chapter 4 discusses the effect on morphology and the formation of Al_2O_3 by tailoring the synthesis conditions. Chapter 5 illustrates the synthesis of PANI-Al_2O_3 nanofibers in various parameters. Finally, a conclusion and future research are addressed in Chapter 6.

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CHAPTER 2
LITERATURE REVIEW

2.1 NANOWORLD

Technology in the twenty first century requires the miniaturization of devices into nanometer sizes whilst their ultimate performance is dramatically enhanced.[1] This raises issues regarding to new materials for achieving specific functionality and selectivity.[2] Nanostructured materials,[3] a new branch of materials research, are attracting a great deal of attention because of their potential applications in areas such as electronics, optics, catalysis, ceramics, magnetic data storage and nanocomposites.[4,5] The unique properties and the improved performances of nanomaterials are determined by their sizes, surface structures and interparticle interactions.[6] The role played by particle size is comparable, in some cases, to the particle chemical composition, adding another flexible parameter for designing and controlling their behavior.[7]

Nanomaterials have been important in the materials field for quite a long time. Nanomaterials are not simply another step in miniaturization, but a different arena entirely. The nanoworld lie midway between the scale of atomic and quantum phenomena, and the scale of bulk materials.[8] At the nanomaterial level, some material properties are affected by the laws of atomic physics, rather than behaving as traditional bulk materials do.[9]

2.2 Nanomaterials

Nanomaterials can be metals, ceramics, polymeric materials or composite materials.[10] All materials are composed of grains, which in turn comprise many atoms. These grains can be visible or invisible to the naked eye, depending on their size. Conventional materials have grains varying in size anywhere from hundreds of microns to centimeters. Nanomaterials are commonly defined as materials with an average grain size less than 100 nm.[11] The unit of nanometer derives its prefix nano from a Greek word meaning dwarf or extremely small. One nanometer spans 3-5 atoms lined up in a row. By comparison, the diameter of a human hair is about 5 orders of magnitude larger than a nanoscale particle. Nanomaterials are bridging the gap between molecular level system design and single crystal based solid state devices as shown in Figure 2.1.[12]

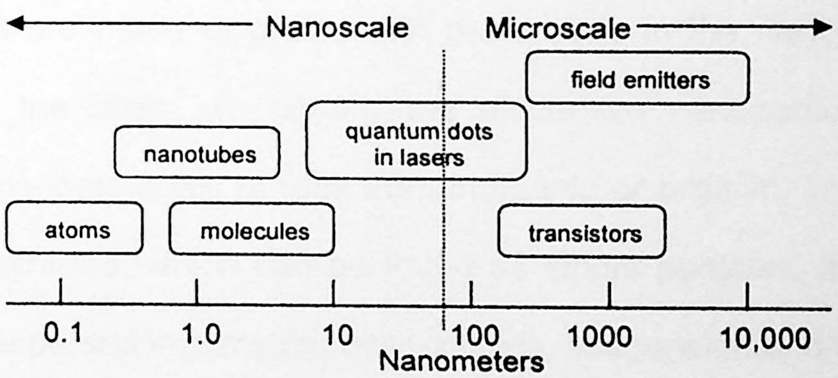


Figure 2.1 Functional device scales.[12]

In nanometer-size regime, the properties of materials, such as optical, electric, magnetic, and mechanical, can be tuned merely by varying their physical sizes, creating unique phenomena found in neither bulk nor molecular systems.[13] What makes these nanomaterials so different and so intriguing? Surfaces and interfaces are important in explaining nanomaterial behavior.[14] The two reasons for this change in behavior are the increased relative surface area which producing increased chemical reactivity and the increasing dominance of quantum effects with effects on the material's optical, magnetic or electrical properties.[15] As an example, size reduction of metals and semiconductors to the range of a few nanometers can lead to novel and peculiar properties.[16] Owing to their large active surface, metal nanoparticles exhibit interesting catalytic properties.[17]

2.3 Classification of Nanomaterials

Nanomaterials are classified into nanostructured materials and nanophase/nanoparticle materials.[14] The former refer to condensed bulk materials that are made of grains with grain sizes in the nanometer size range, while the latter are usually the dispersive nanoparticles.[18] The spectrum of nanomaterials ranges from inorganic or organic, crystalline or amorphous particles, which can be found as single particles, aggregates, powders or dispersed in a matrix, over colloids, suspension and emulsions, nanolayers and films, up to the class of fullerenes and their derivatives. Also supramolecular structures such as dendrimers, micelles or liposomes belong to the field of nanomaterials.[19]

Generally there are different approaches for a classification of nanomaterials, some of which are summarized in Figure 2.2.[20] Depending on their relative sizes in different spatial directions, materials can be divided into categories of different dimensionality ranging from three-dimensional (3D) to two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D). The above classification is introduced for materials with simple shapes such as slabs/sheets (2D), wires/tubes/rods (1D) and cubes/spheres (0D). With the rapid advance in nanotechnology, it is now possible to produce materials with a variety of shapes and asymmetry; this will add more degrees of freedom to the nanomaterials that can be used to alter their properties.

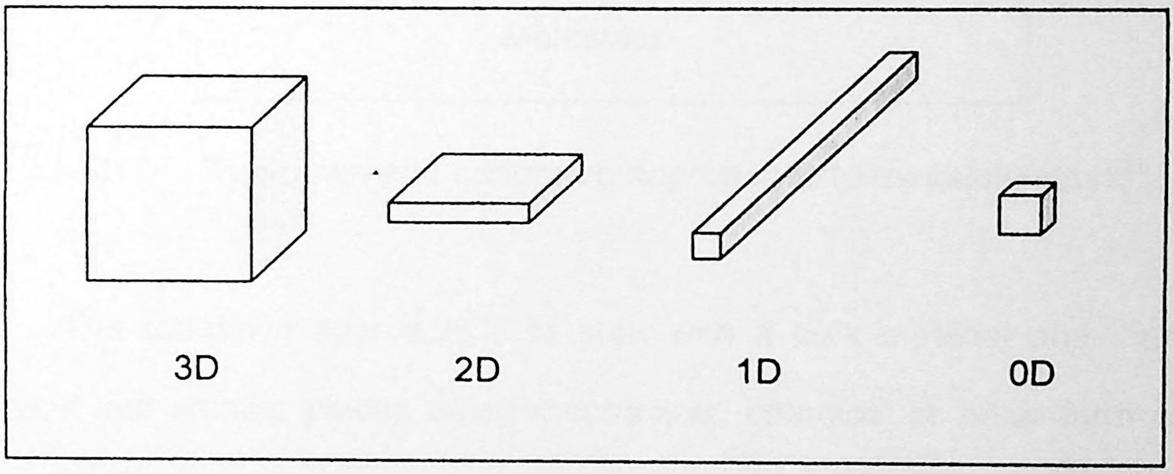


Figure 2.2 Schematic illustration of materials of different dimensionality ranging from 0D to 3D.[20]

2.4 Synthesis of Nanomaterials

The synthesis of nanomaterials can be accomplished through "bottom-up" or "top-down" methods,[21,22] as shown in the Figure 2.3.

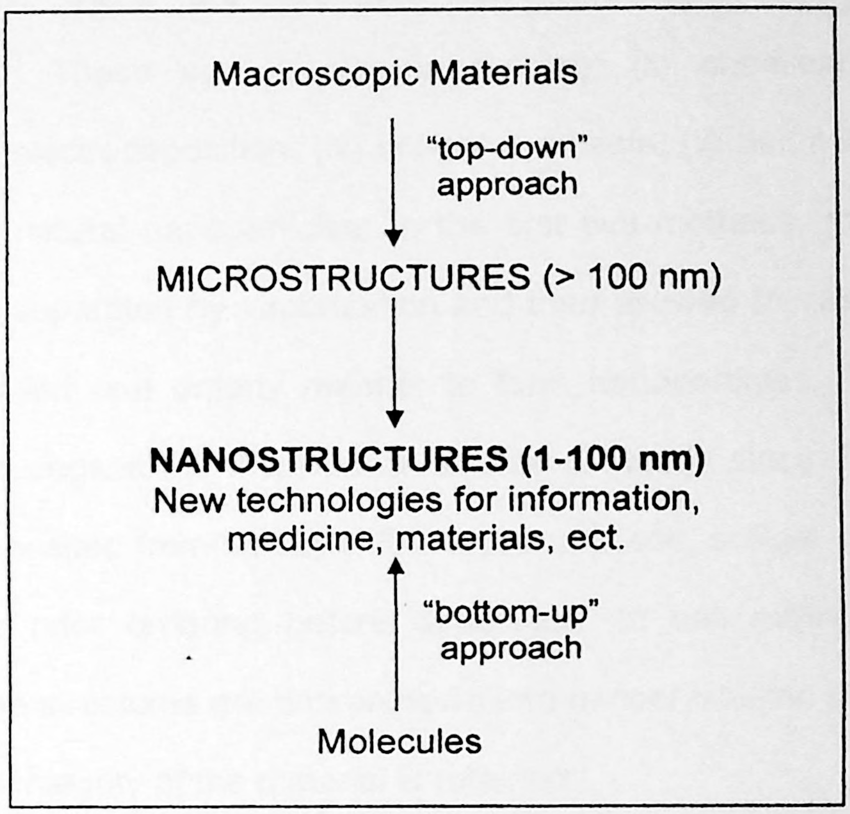


Figure 2.3 Top-down and bottom-up approaches to miniaturization.[23]

The top-down approach is to start with a bulk material and then break it into smaller pieces using mechanical, chemical or other form of energy. Examples of this approach include lithographic techniques (e.g. UV, electron or ion-beam, scanning probe, optical near field),[24,25] film deposition and growth,[26] laser-beam processing[27] and mechanical techniques[28] (e.g. machining, grinding and polishing). The bottom-up approach is to synthesize the material from atomic or molecular species via chemical reactions, allowing for the precursor particles to grow in size, for example by chemical synthesis,[29] laser-induced assembly,[30] selfassembly[31] and colloidal aggregation.[32] Both approaches can be done in either gas, liquid, supercritical fluids, solid states, or in vacuum.

Generally, there are six well known methods to produce nanomaterials.[33] These are (i) plasma arching, (ii) chemical vapour deposition, (iii) electrodeposition, (iv) sol-gel synthesis, (v) ball milling and (vi) the use of natural nanoparticles. In the first two methods, molecules and atoms are separated by vaporization and then allowed to deposit in a carefully controlled and orderly manner to form nanoparticles. The third method, electrodeposition, involves a similar process, since individual species are deposited from solution. The fourth process, sol-gel synthesis, involves some prior ordering before deposition. In ball milling, known macrocrystalline structures are broken down into nanocrystalline structures, but the original integrity of the material is retained.

The synthesis of such materials through low temperature chemical routes allows a better control of their microstructure. Among the different processes involving low temperature, sol-gel processes are a way of making highly dispersed materials through the growth of metal oxo-polymers in a solvent.[34] These soft chemistry processes are based on hydrolysis-condensation reactions of molecular precursors such as metal alkoxides $M(OR)_4$ (M = Si, Ti, Al...).

2.5 Characterization of Nanomaterials

Nanotechnology, by definition, is the willful manipulation of matter at the atomic level to create better and entirely new materials, devices, and systems.[35] Development of nanotechnology has been spurred by refinement of tools to see the nanoworld, such as more sophisticated electron microscope[36] and scanning probe microscopy.[37] The hunt for new applications of nanostructured systems is now a major area of research in material science and technology.[38] To exploit the full potential that nanosystems offer, it is important that novel methods of manipulation and fabrication be developed, in addition to extending current techniques of sample characterization to smaller sizes.[39] Success in devising and assembling systems on the scale of nanometers will require a deeper understanding of the basic processes and phenomena involved.[40] Hence, one of the current key objectives is to adapt and develop a range of techniques that can characterize the structural, electronic, magnetic and optical properties of nanostructured systems. Table 2.1 gives an overview of the available methods.[41] Some of these techniques are briefly discussed below.

Table 2.1 The most common characterization techniques in the study of nanomaterials.[41]

Acronym	Full name and most important information
AFM/SFM	Atomic force microscopy (scanning force microscopy) • Nanometer-scale morphology of surfaces • Not limited to conducting systems
EXAFS	Extended X-ray absorption fine structures • Atomic scale structure information • Only applicable in reflection or fluorescence modes
IR	Infrared spectroscopy • Adsorbed species on surface
STM	Scanning Tunelling Spectroscopy • Atomic scale morphology of conducting surfaces • Diameter of particles
TEM	Transmission electron microscopy • Morphology of particles • Structure of particles by electron diffraction • Sintering studies
UV-Vis	UV-Visible sectrocopy • Particle size • Degree of cluster aggregation
XRD	Powder X-ray diffraction • Identification of nanocrystalline phases • Crystal size and distribution
XPS	X-ray photoelectron spectroscopy • Elemental surface composition • Oxidation states • Layer thickness

2.6 Applications of Nanomaterials

The integration of materials at the nanoscale has the potential to revolutionize many fields of science and technology. Since nanomaterials possess unique, beneficial chemical, physical, and mechanical properties, they can be used for a wide variety of applications.[42,43] These applications include, but are not limited to, the following:[44]

2.6.1 Next-generation computer chips

The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors and capacitors, are reduced in size.[44] By achieving a significant reduction in their size, the microprocessor which contain nanomaterials, can run much faster, thereby enabling computations at far greater speeds. However, there are several technological impediments to these advancement, including lack of ultrafine precursors to manufacture these components and poor reliability. Nanomaterials help the industry break these barriers down by providing the manufacturers with with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity and longer-lasting, durable interconnections between various components in the microprocessors.

2.6.2 Low-cost flat-panel display

Flat-panel displays represent a huge market in the laptop computers industry.[44] By using nanomaterials, the resolution of these display devices can be greatly enhanced, and the manufacturing costs can be significantly reduced. Also, the flat-panel displays constructed out of nanomaterials possess much higher brightness and contrast than the conventional ones owing to their enhanced electrical and magnetic properties.

2.6.3 Elimination of pollutants

Nanocrystalline materials possess extremely large grain boundaries relative to their grain size.[45] Hence, nanomaterials are very active in terms of their chemical, physical and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

2.6.4 High Energy Density Batteries

Conventional and rechargeable batteries are used in almost all applications that requires electric power.[44] These applications include automobiles, laptop computers, electric vehicles, next-generation electric vehicles to reduce environmental pollution, cellular phones, toys and watches. The energy densities and storage capacity of these batteries is quite low and requires frequent charging. Nanomaterials are candidates for separator plates in batteries and hold considerably more energy than conventional ones. Furthermore, they are envisioned to require far less frequent recharging and to last much longer because of their large surface area and enhanced physical, chemical and mechanical properties.

2.7 Sol-Gel Chemistry and Technology

2.7.1 Introduction to Sol-Gel

A process that has, in the past years, gained much notoriety in the glass and ceramic fields is the sol-gel reaction.[46] This chemistry produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors. Although first discovered in the late 1800s and extensively studied since the early 1930s, a renewed interest surfaced in the early 1970s when monolithic inorganic gels were formed at low temperatures and converted to glasses without a high temperature melting process.[47] These sol-gel produced glasses and ceramics are derived from the various material shapes generated in the gel state such as monoliths, films, fibers and monosized powders.[48] The specific applications include optics, protective and porous films, optical coatings, window insulators, dielectric and electronic coatings, high temperature superconductors, reinforcement fibers, fillers and catalysts.[49,50]

The sol-gel process can be described as the creation of an oxide network by progressive polycondensation reactions of molecular precursors in a liquid medium, or as a process to form materials via a sol, gelation of the sol and finally removal of the solvent.[51] This method is considered as a "chimie douce" or soft chemical approach to the synthesis of metastable (amorphous) oxide materials. The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).[34] However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process.[34]

A sol is a stable suspension of colloidal solid particles or polymers in a liquid.[52] The particles can be amorphous or crystalline. A gel consists of a porous, three-dimensionally continuous solid network surrounding and supporting a continuous liquid phase as wet gel.[51] In "colloidal" gels, the network is made by agglomeration of dense colloidal particles, whereas in "polymeric" gels the particles have a polymeric sub-structure made by aggregation of sub-colloidal chemical units.[53] In general, the sol particles can be connected by covalent bonds, Van der Waals forces, or hydrogen bonds. Gels can also be formed by entanglement of polymer chains. In most sol-gel systems used for materials synthesis, gelation is due to the formation of covalent bonds and irreversible. Gel formation can be reversible when other bonds are involved in gelation.

2.7.2 Forming Nanostructured Materials Using the Sol-gel Process

Figure 2.4 presents a scheme of the different processing routes leading from the sol to a variety of materials.[54] Powders can be obtained by spray-drying of a sol. Gel fibers can be drawn directly from a sol, or thin films can be prepared by standard coating technologies such as dip- or spin-coating, spraying, etc. Here, gelation occurs during the preparation of the film or fiber due to rapid evaporation of the solvent.

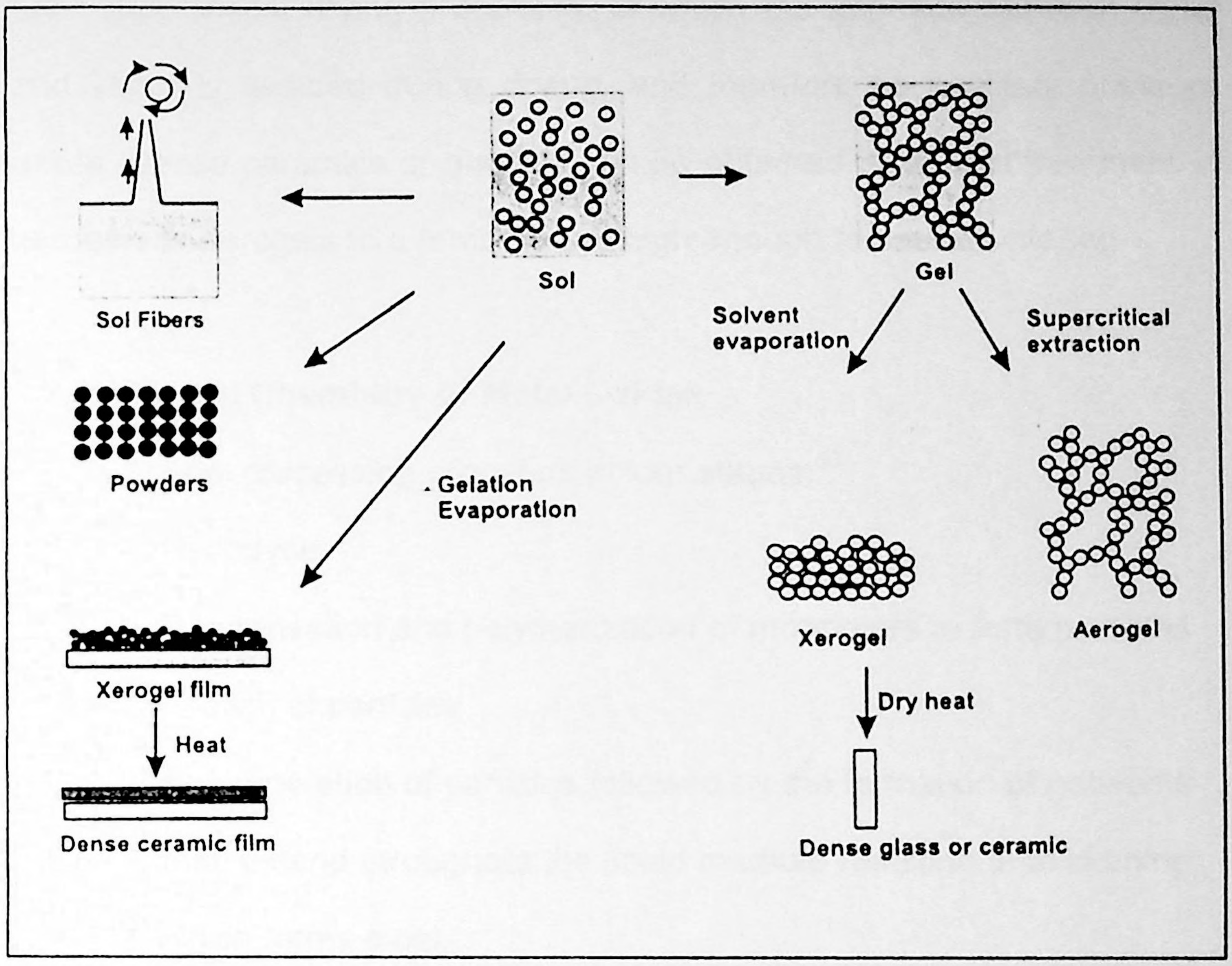


Figure 2.4 Sol-gel processing options.[54]

Gelation can also occur after a sol is cast into a mold, in which case it is possible to make monolithic objects of a desired shape. Drying by evaporation of the pore liquid gives rise to capillary forces that causes shrinkage of the gel network. The resulting dried gel is called a xerogel. Compared to the original wet gel its volume is often reduced by a factor of 5 to 10. Due to the drying stress, the monolithic gel body is often destroyed and powders are obtained. When the wet gel is dried in a way that the pore and network structure of the gel is maintained even after drying, the resulting dried gel is called an "aerogel".[55] Aerogels are usually obtained after supercritical drying processes, in which the interface between liquid and vapor is avoided during drying, and therefore no capillary pressure exists. Dense ceramics or glasses can be obtained after heat treatment of xerogels or aerogels to a temperature high enough to cause sintering.

2.7.3 Sol-gel Chemistry of Metal Oxides

Sol-gel processing proceeds in four stages:[56]

1. Hydrolysis
2. Condensation and polymerization of monomers to form particles
3. Growth of particles
4. Agglomeration of particles followed by the formation of networks that extend throughout the liquid medium resulting in thickening, which forms a gel.

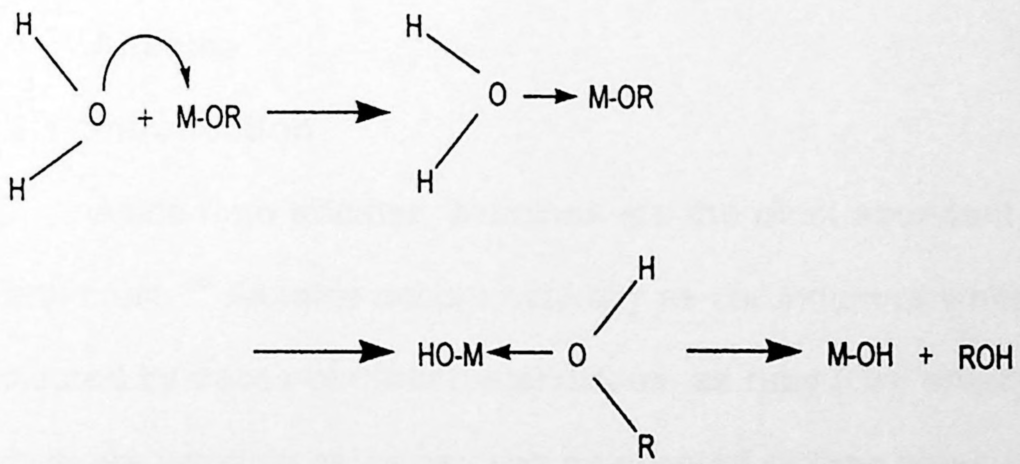
All four of the above processes are affected by the initial reaction conditions. Thus the characteristics and properties of a particular sol-gel network are related to the parameters which influence hydrolysis and condensation and whose deliberate variations are used for material design, such as:

1. the kind of precursor(s)
2. the kind of solvent
3. the temperature
4. the pH
5. the relative concentration of the components in the precursor mixtures.

By controlling these factors, it is possible to vary the structure and properties of the sol-gel derived inorganic network over wide ranges.

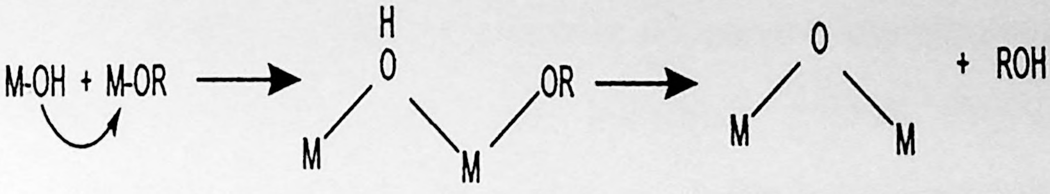
Among the different network-forming precursors, metal alkoxides have clearly become the most important ones, although metal carboxylates are also used.[57] The sol-gel route involving metal alkoxides $M(OR)_n$, where M is Al, Si, Ti, V, Cr, Mo, W, *etc.*, and OR is an alkoxy functionality, may be considered as a two-step inorganic polymerization. Hydrolysis of metal alkoxides occurs by an addition and elimination mechanism.[58] Both olation (equation 2.1) and oxolation (equation 2.2) are possible. Olation is a condensation process in which a hydroxyl bridge is formed, while oxolation is a condensation process in which an oxo bridge is formed.

Initiation occurs via hydrolysis of alkoxy ligands to yield an alcohol (ROH) and, as new reactants, hydroxylated metal centers (M-OH).



Equation 2.1

Three-dimensional propagation then occurs as the hydroxylated species condense to form oxypolymers. Polycondensation involves an oxolation reaction which creates oxygen bridges and expels XOH species as follows:



Equation 2.2

Oxolation with elimination of an alcohol is also called alcoxolation (equation 2.2).

2.7.4 The advantages of the sol-gel approach over traditional methods of preparation

Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, purity, optical transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperatures, as opposed to the much higher melting temperatures required in the production of conventional inorganic glass.[59]

2.8 Alumina

2.8.1 Introduction

Aside from silicates, aluminas are the most abundant mineral of the Earth crust. [60] Alumina occurs naturally as corundum or white sapphire and, coloured by traces of other metal oxides, as ruby (Cr), amethyst (Mn), etc., which are valuable as gemstones on account of their beauty and hardness. The most common ore is bauxite, which is aluminium oxide, Al_2O_3, mixed with oxides of silicon, iron and other elements and varying small percentages of clay and other silicates.[61]

2.8.2 Forms and Types of Aluminas

Alumina is frequently used in the generic identification of any of the several crystalline forms of aluminium oxides (Al_2O_3), aluminium trihydroxides [$Al(OH)_3$], and aluminium oxide hydroxides [$AlO(OH)$].[62] The properties of these forms are influenced both chemically and physically by the properties of the precursor hydroxide forms and subsequent processing steps. Subsequent thermal treatment of these hydroxides leads to crystalline phase transitions and the loss of hydroxide groups and protons (H^+), which are liberated as water leaving Al_2O_3 alumina forms.

Five structures of hydroxide (trihydroxides and oxyhydroxides) exist in nature. Industrially, three can be synthesized: gibbsite, boehmite and bayerite. Two loosely structured forms are also manufactured: amorphous gel and pseudoboehmite gel. There are numerous ways of synthesizing hydrates, going from the gibbsite obtained through Bayer process or precipitated amorphous gel.

2.8.3 Thermal development of aluminas

2.8.3.1 Transition aluminas

The transition aluminas represent a group of technically important materials used in a wide variety of applications. They are obtained by thermal dehydration of aluminium hydroxides, leaving a highly porous structure of aluminium oxide. The hydroxide and the dehydration processes largely determine the structure and the texture of the oxide and a large effort has been put into studies of this materials.[63]