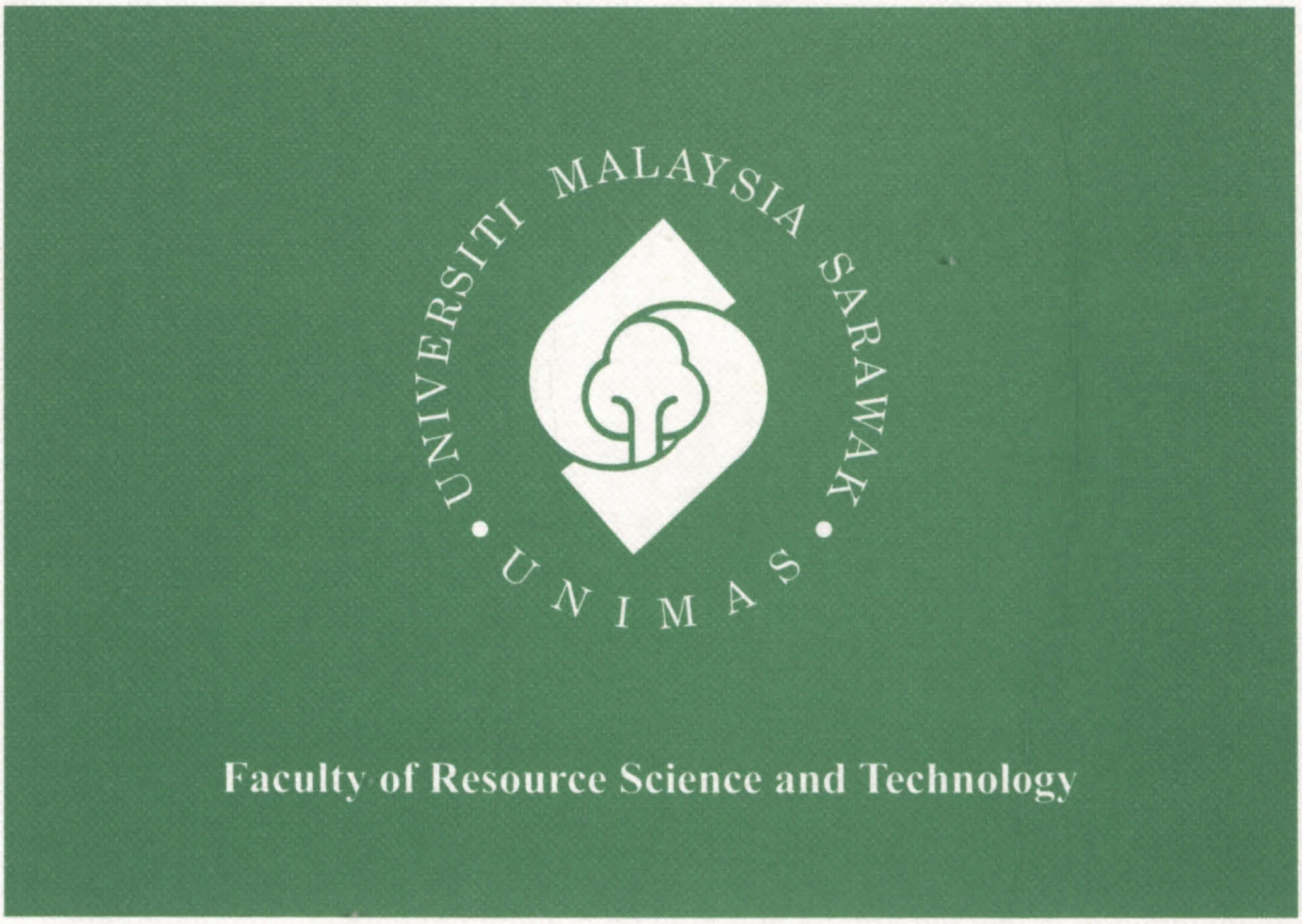

SYNTHESIS AND CHARACTERIZATION OF SELF-ASSEMBLED MANGANESE DIOXIDE NANOSTRUCTURES AND THIN-FILM MATERIALS

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ABSTRACT

Manganese dioxide (MnO_2) nanostructures in the forms of thin film and powder had been prepared by two different preparative approaches. There were sol-gel and hydrothermal approaches. In the sol-gel synthesis approach, stable colloidal suspensions of MnO_2 were prepared by chemical reduction of permanganate salt. Nanostructured MnO_2 thin films were prepared by a self-assembly horizontal submersion process which involved spontaneous assembly of MnO_2 nanoparticles in stable colloidal suspension. The films were subsequently deposited directly onto the supporting substrate (stainless steel foils or Ni-coated PET films) under controlled conditions. The effects of deposition parameters and conditions on the microstructure of deposited thin films were investigated. Material characterization by various techniques indicated that self-assembled MnO_2 thin films were nanoparticulate and highly porous in nature and their surface morphological characteristics and microstructure were significantly influenced by the deposition conditions. Electrochemical characterization showed that these self-assembled MnO_2 thin films exhibited excellent capacitive behavior, high cycling reversibility and stability within an appropriate potential range in a mild Na_2SO_4 aqueous electrolyte. MnO_2 films deposited on Ni-coated PET films were observed to exhibit higher charge capacity compared to MnO_2 films deposited on stainless steel foils. In the hydrothermal synthesis approach, the effects of hydrothermal conditions such as aging temperature and duration on the formation of MnO_2 nanostructures were studied. The aging temperature and duration appeared to have predominant effect on the shape and morphology of MnO_2 nanoparticles and nanostructures formed. MnO_2 nanoparticles of spherical shape were

formed initially which subsequently self-assembled into MnO_2 nanostructures of sea urchin-like shape and nanorods after being aged for 24 h at 25 °C and 80 °C respectively. Phase transformation of δ–MnO_2 to α–MnO_2 was observed for nanostructured MnO_2 prepared at higher aging temperature. MnO_2 samples of higher degree of crystallinity were obtained at prolonged aging duration and higher aging temperature. However, MnO_2 nanostructures obtained at shorter aging duration were observed to exhibit higher charge capacity and specific capacitance.

SINTESIS DAN PENCIRIAN PERKUMPULAN SENDIRI NANOSTRUKTUR MANGAN DIOKSIDA DAN BAHAN FILEM NIPIS

ABSTRAK

Nanostruktur mangan dioksida (MnO_2) dalam bentuk filem nipis dan serbuk telah disediakan dengan menggunakan dua kaedah penyediaan yang berbeza iaitu sol-gel dan hidroterma. Dengan kaedah sintesis sol-gel, bahan koloid MnO_2 yang stabil telah disediakan dengan penurunan kimia garam permanganat. Filem nipis nanostruktur MnO_2 disediakan dengan proses perkumpulan sendiri perendaman secara mendatar di mana ia melibatkan perkumpulan secara spontan nanopartikel MnO_2 dalam bahan koloid yang stabil dan mendap secara terus ke atas bahan penyokong (kepingan keluli atau filem PET diselaputi Ni) dalam keadaan terkawal. Kesan parameter dan keadaan pemendapan ke atas mendapan mikrostruktur filem nipis telah dikaji. Pencirian bahan dengan pelbagai teknik menunjukkan bahawa perkumpulan sendiri filem nipis MnO_2 adalah nanopartikel dan bersifat poros dan ciri-ciri morfologi permukaan dan mikrostruktur adalah nyata sekali dipengaruhi oleh keadaan pemendapan. Pencirian elektrokimia bagi perkumpulan sendiri filem nipis MnO_2 menunjukkan bahawa ia mempunyai sifat kapasitor yang baik, pusingan ulangan yang tinggi dan kestabilan ke atas lingkungan potensi yang bersesuaian dalam Na_2SO_4 elektrolit. MnO_2 filem yang dimendapkan ke atas filem PET diselaputi Ni telah diperhatikan mempunyai kapasiti caj yang lebih tinggi berbanding dengan MnO_2 filem yang dimendapkan ke atas kepingan keluli. Dengan kaedah hidroterma, kesan kaedah sintesis seperti suhu dan masa penuaan ke atas pembentukkan nanostruktur MnO_2

telah dikaji. Masa dan suhu penuaan diperhatikan mempunyai kesan pradominan ke atas bentuk dan morfologi bagi pembentukkan nanopartikel dan nanostruktur MnO_2. MnO_2 nanopartikel dalam bentuk sfera yang terbentuk pada mulanya telah melalui pembentukkan sendiri kepada MnO_2 nanostruktur dengan bentuk seperti landak laut dan nanorod selepas melalui proses penuaan selama 24 jam pada 25 °C dan 80 °C masing-masing. Penukaran fasa dari δ–MnO_2 kepada α–MnO_2 telah diperhatikan bagi MnO_2 nanostruktur yang disediakan pada suhu yang lebih tinggi. Kristaliniti yang tinggi telah diperoleh bagi MnO_2 sampel dengan memanjangkan masa penuaan dan juga pada suhu penuaan yang lebih tinggi. Walau bagaimanapun, MnO_2 nanostruktur yang diperolehi pada masa penuaan yang singkat telah diperhatikan mempunyai kapasiti caj dan kapasitan spesifik yang lebih tinggi.

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List of Abbreviations

AAS	atomic adsorption spectroscopy
BET	Brunauer-Emmet-Teller analysis
CV	cyclic voltammograms
CPV	cumulative pore volume
1D	one dimension
DC	direct current
EDX	energy dispersive X-ray microanalysis
EMD	electrolytic manganese dioxide
EPD	electrophoretic deposition
ESD	electrostatic spray deposition
FESEM	Field emission scanning electron microscopy
FTIR	Fourier Transformed Infrared Spectrometer
h	hour
IUPAC	International union of pure and applied chemistry
$KMnO_4$	potassium permanganate
Min	minute
MnO_2	manganese dioxide
$MnSO_4$	manganous sulphate
$Na_2S_2O_3$	sodium thiosulphate
Ni-coated PET	nickel-coated poly(ethylene terephthalate)
PCD	pulse current electrodeposition
SAM_s	self-assembled monolayers
SCE	saturated calomel electrode
SCR	selective catalytic reduction
SEM	scanning electron microscopy
TEM	transmission electron microscopy
Vs	versus
XRD	X-ray diffractometry

List of Symbols

>	more than
<	less than
%	percentage
α	alpha
β	beta
γ	gamma
δ	delta
mΩ	milliohm
A	ampere
mA	milliampere (10^{-3})
μA	microampere (10^{-6})
mA/cm^2	milliampere per centimeter square
$\mu A/cm^2$	microampere per centimeter square
Å	Armstrong (10^{-10})
C	coulomb
mC	millicoulomb (10^{-3})
mC/cm^2	millicoulomb per centimeter square
°C	degree Celsius or Centigrade
cm^2	centimeter square
cm^3	centimeter cube
cm^3/g	centimeter cube per gram
F	farad
mF	millifarad (10^{-3})
mF/cm^2	millifarad per centimeter square
F/g	farad per gram
hr	hour
g	gram
mg	milligram (10^{-3})
mg/cm^2	milligram per centimeter square
g/mol	gram per mole
mol/L	mole per liter
L	liter
mL	milliliter (10^{-3})
m	meter
μm	micrometer (10^{-6})
nm	nanometer (10^{-9})
m^2	meter square
m^2/g	meter square per gram
M	molar
pH	negative logarithm of the hydrogen ion concentration
Qa/Qc	anodic/cathodic charge ratio
s	second
V	voltage
kV	kilovolt (10^3)

mV	millivoltage (10^{-3})
mV/s	milivoltage per second
wt	weight
wt %	weight percentage

CHAPTER 1

INTRODUCTION

1.1 Background

The unique properties and potential applications of nanostructured materials have attracted much research attention in various fields of chemistry and physics. Nanostructures are assemblies of bonded atoms that have dimensions within the range of 1 and 100 nanometers (nm). According to Iqbal and Zahoor (2007), the energy levels of semiconductors in the nanosize regime become more separated from each other and their effective band-gaps increase as the particle sizes decrease. These unique properties have resulted in various potential applications in areas such as microelectronics, photovoltaics, imaging and display technologies, sensing devices and thin-film coatings.

Increasing demands for light weight and compact electrical power sources had led to the development of portable charge-storage systems with increasing power density. Batteries and conventional capacitors are not suitable for these applications because of their heavy weight, low power and energy density, low reversibility and short cycle life. Electrochemical capacitors which possess higher power density and longer cycle life than batteries, as well as higher energy density than conventional capacitors are therefore highly desirable to ensure the fabrication of energy storage systems which are highly portable and versatile (Chang *et al.*, 2008a; Huang *et al.*, 2006; Reddy and Reddy, 2003).

Double-layer electrochemical capacitors store energy at the electrode-electrolyte interface without the involvement of irreversible electrochemical reactions as in the case of batteries (Shinomiya *et al.*, 2006). Electrochemical capacitors are applicable in electronic devices, such as power electronics, hybrid electric vehicles, as well as in space flight technology (Zolfaghari *et al.*, 2007).

Materials research have been focusing on the development of electrode materials, such as activated carbon which possesses high specific surface area, conducting polymers with several oxidation states or structures and transition metal oxides (Huang *et al.*, 2006; Shinomiya *et al.*, 2006). However, these materials have their own advantages and limitations that need to be taken into consideration in their utilization as electrode materials of electrochemical devices. Most research works on supercapacitors that are based on pseudocapacitance have focused on transition metal oxide materials. Hydrous metal oxides have been found to possess significant energy storage capacities and represent promising electrode materials for applications in electrochemical capacitors (Grupioni *et al.*, 2002). Among these metal oxides materials, hydrous ruthenium dioxide (RuO_2) has been found to be the most promising with a specific capacitance value of 720 F/g reported at a scan rate of 2 mV/s in an aqueous acidic electrolyte (sulfuric acid) within a potential window of 1.4 V (Zheng, 1999). However, it has several disadvantages such as being expensive, toxic and requires the use of strong acidic electrolyte such as sulfuric acid. These disadvantages have limited the practical applications of RuO_2 and have prompted research interest on other transition metal oxides (Xue *et al.*, 2007; Djurfors *et al.*, 2006; Huang *et al.*, 2006).

The demand for charge-storage devices fabricated from nanoparticulate thin-film materials is expected to rise continuously. Besides, many research efforts are made to develop novel electrode materials which are environmental friendly, low toxicity, abundant and cheap for the fabrication of charge-storage devices of high power and energy density. Manganese dioxide (MnO_2) was selected in this study because it has always been a promising material for electrochemical technological development. MnO_2 has been widely used as electrode material in batteries due to its low cost, low toxicity, environmentally benign and abundant in nature (Reddy and Reddy, 2003; Huang *et al.*, 2006). MnO_2 has good electronic conductivity, possesses relatively high charge capacity and specific capacitance. It is also capable of providing several redox reactions involving different oxidation states of Mn metal centers (Grupioni *et al.*, 2002). Numerous research works on the suitability of MnO_2 thin films for battery applications have widely been published, however only few papers dealt with its application in electrochemical capacitors.

MnO_2 have received considerable attentions since Pang *et al.* (2000) reported on a specific capacitance value of 720 F/g at 50 mV/s for ultra-thin MnO_2 films prepared by the sol-gel process. These films have been shown to be highly porous, relatively conductive and possess high specific surface area. MnO_2 are the potential low cost electrode materials for the fabrication of supercapacitors with high power density suitable for use in household device applications if optimized conditions for enhancing their electrochemical properties are achieved (Shinomiya *et al.*, 2006). Although the capacitive

behaviors of MnO_2 prepared by various methods have been found to be rather different, a clear relationship between the microstructure and the specific capacitance of the MnO_2 prepared by various methods has not been established. In this study, the effects of synthesis conditions on the microstructure and electrochemical properties of deposited MnO_2 thin films were investigated.

Different synthetic conditions would result in MnO_2 of different physical and chemical properties such as crystallinity, specific surface areas, conductivity, magnetic and electrochemical properties. However, the ability to prepare MnO_2 nanoparticles of desired size distribution remains a challenge as the characteristic of the particles formed are very sensitive to the synthesis parameters. To date, many chemical routes for the preparation of MnO_2 thin films have been developed such as the sol-gel process (Pang *et al.*, 2000), chemical co-precipitation (Lee and Kim, 2001), chemical oxidation (Patrice *et al.*, 2001) and electrochemical deposition (Hu and Tsou, 2002). Studies have shown that the self-assembly process is emerging as an effective technique in chemical synthesis and capable of generating nanostructures within the dimension range of 1 to 100 nm (Whitesides *et al.*, 1991). Alessandri *et al.* (2005) reported that self-assembly through spontaneous organization via non-covalent interactions is a very promising route for the synthesis of materials with tailored mesostructure and enhanced performances for the fabrication of functional devices. In this study, two different self-assembly synthetic approaches were used for the preparation of MnO_2 nanostructures in the form of both thin film and powder. Sol-gel and hydrothermal approaches were used to prepare MnO_2 sol and powder. The sol-gel process has several advantages as this method provides

homogeneous mixing of reactant at molecular level. As such, this method can be used to control shape, morphology, and particle size of resulting products (Reddy and Reddy, 2004a). While, hydrothermal method offers a potentially low temperature, low cost and environmental friendly process to prepare materials of different nanoarchitectures (Zhang *et al.*, 2003).

1.2 Objectives of Study

The objectives of this study include:

a. To prepare MnO_2 nanostructures and thin films using different self-assembly approaches.
b. To characterize the physical, chemical and electrochemical properties of self-assembled MnO_2 nanostructures and thin films.
c. To elucidate the effect of synthesis parameters and deposition conditions on the microstructure of MnO_2 thin films deposited directly on suitable supporting substrates.

1.3 Scope of Study

The scope of this study entails the preparation of nanostructured MnO_2 thin films using two different self-assembly approach. Chapter 1 describes the background and justification of this study. Chapter 2 provides an introduction of nanostructured materials,

electrochemical capacitor, as well as an overview of the recent development in the synthesis methods of MnO_2 colloidal suspension and thin films and their applications. Chapter 3 describes the newly developed horizontal submersion method in preparing MnO_2 thin films deposited on nickel-coated poly(ethylene terephthalate) films (Ni-coated PET films) and stainless steel foils. The effect of synthesis conditions on the microstructure and electrochemical properties of deposited MnO_2 thin films were investigated. Chapter 4 describes on the synthesis and characterization of nanostructured MnO_2 powder by a facile self-assembly hydrothermal approach under mild conditions. Effects of synthesis parameters on the microstructured evolution of MnO_2 nanostructures were investigated. Attempts were made to elucidate the microstructure-property relationship of MnO_2 thin films formed from various MnO_2 nanostructures synthesized.