UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF THERMOCHROMIC VO_2 NANOPARTICLES AND NANOTHERMOCHROMIC VO_2-PVP COMPOSITE COATING

HAMDI MUHYUDDIN D. BARRA

FS 2019 29

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By

HAMDI MUHYUDDIN D. BARRA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

April 2019

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To my wife Sharisse May

For the numerous times I appear to have given up,

you were there to lift my spirits up;

For every hump that seem to hold me back,

you never failed to put me back on track;

For each instance my self-esteem hits rock bottom,

your belief in me stayed rock solid.

For really… I thought this pursuit was improbable,

but not once have you doubted me...

For that and more, I thank you!

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
fulfillment of the requirement for the degree of Doctor of Philosophy

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By

HAMDI MUHYUDDIN D. BARRA

April 2019

Chair : Chen Soo Kien, PhD
Faculty : Science

Vanadium dioxide (VO_2) is a promising smart window material because of its thermochromic ability as it transitions from IR-transparent semiconductor to IR-reflectant metal at a critical temperature of 68 °C. However, the practical application of VO_2 is hindered by some restrictions including low hysteresis or transition strength, high phase transition temperature for near room-temperature applications, low visible transmittance and weak solar modulation ability. Thus, this research was conducted to address these problems. Nanostructured VO_2 was prepared by hydrothermal treatment of V_2O_5-$H_2C_2O_4$-H_2O solution. Various experimental conditions were employed to examine their effects on the resultant nanopowder. X-ray diffraction (XRD) scans of the samples showed that varying synthetic conditions resulted in the selective formation of the metastable B-phase of VO_2 from highly pure to polycrystalline that contained the metastable A-phase of VO_2 as well as other V-O based compounds such as V_6O_{13} and V_4O_7. In particular, the sample prepared with a molar ratio of 1:4, fill ratio of 0.63, and hydrothermally synthesized at 180 ºC in 24 hours exhibited narrow and high-intensity peaks belonging exclusively to VO_2 (B) indicating high purity and good crystallinity. In addition, field-emission scanning electron microcopy (FESEM) images of the samples revealed the formation of nanorods and nanobelts. Further, the thermochromic and thermodynamically stable M-phase of VO_2 was achieved by heating VO_2 (B) nanopowder under nitrogen atmosphere. Correspondingly, high purity VO_2 (B) resulted into high purity VO_2 (M) with improved crystallinity. Also, FESEM images revealed that the VO_2 (B) nanobelts and nanorods transformed into spherical, oblate, and plate-like shapes after annealing. Meanwhile, differential scanning calorimetry (DSC) measurements showed that VO_2 (M) samples exhibited a phase transition temperature of about 66 °C. Subsequently, samples with high purity, good crystallinity and smaller grain size displayed excellent thermochromic properties as indicated by the low hysteresis and high enthalpy. Specifically, it was found that the sample with the best thermochromic characteristics was annealed at a temperature of 650 °C in 2 hours. On the other hand, the addition of tungsten (W) in the synthesis of VO_2 resulted in the reduction of the phase transition temperature to as low as 31.64 °C . Moreover, an accompanying increase in the luminous transmittance, solar transmittance and thermal conductivity at room temperature were observed. Additionally, a discernible increase in the thermal

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conductivity across the phase transition temperature occurred indicating a transition from semiconducting to metallic state. Finally, VO_2-PVP composite coating was prepared by dispersing highly pure VO_2 nanoparticles onto a glass substrate with polyvinylpyrrolidone as polymeric host matrix. Surface analysis of the sample verified the effective dispersion of nanoparticles onto the substrate. More importantly, the luminous transmittance of the composite samples improved to as high as 86.75%. Indeed, in this work, the phase transition temperature, luminous transmittance, and solar transmittance were simultaneously enhanced which indicate great potential for smart window applications.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN NANOPARTIKEL VO_2 TERMOKROMIK DAN SALUTAN KOMPOSIT VO_2-PVP NANOTERMOKROMIK

Oleh

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Vanadium dioksida (VO_2) merupakan bahan tingkap pintar yang berpotensi kerana kemampuan termokromiknya yang beralih daripada semikonduktor lutsinar IR kepada bahan pemantul IR pada suhu kritikal 68 ºC. Walau bagaimanapun, aplikasi praktikal VO_2 terhalang oleh beberapa kekangan termasuk histeresis atau kekuatan peralihan yang rendah, suhu peralihan fasa yang tinggi untuk aplikasi menghampiri suhu bilik, transmisi terlihatkan yang rendah, dan kemampuan modulasi suria yang rendah. Justeru, kajian ini dilaksanakan bagi menangani permasalahan ini. Nanostruktrur VO_2 disediakan melalui rawatan hidroterma larutan V_2O_5-$H_2C_2O_4$-H_2O. Pelbagai keadaan eksperimen telah digunakan untuk mengkaji kesannya terhadap nanoserbuk yang terhasil. Imbasan pembelauan sinar-x ke atas sampel menunjukkan kepelbagaian keadaan sintetik menyebabkan pembentukan memilih fasa-B metastabil VO_2 daripada yang berketulenan tinggi kepada polihablur yang mengandungi fasa-A metastabil VO_2 dan juga sebatian berasaskan V-O seperti V_6O_{13} dan V_4O_7. Secara khususnya, sampel yang disediakan dengan nisbah molar 1:4, nisbah isi 0.63 dan disintesis secara hidroterma pada 180 ºC selama 24 jam menunjukkan puncak yang sempit dengan keamatan tinggi dimiliki secara eksklusif oleh VO_2 (B) membuktikan bahawa ia berketulenan tinggi dengan kehabluran yang baik. Tambahan lagi, imej sampel daripada mikroskop elektron imbasan pancaran medan (FESEM) mendedahkan pembentukan nanorod dan nanojalur. Selain itu, fasa-M VO_2 yang stabil secara termokromik dan termodinamik diperolehi melalui pemanasan nanoserbuk VO_2 (B) di bawah atmosfera nitrogen. Dengan demikian, VO_2 (B) berketulenan tinggi bertukar kepada VO_2 (M) dengan kehabluran yang lebih baik. Juga, imej FESEM mendedahkan nanojalur dan nanorod VO_2 (B) menjelma kepada bentuk sfera, oblik dan bentuk bak plat selepas proses penyepuhlindapan. Di samping itu, pengukuran kalorimetri imbasan pembeza (DSC) menunjukkan sampel VO_2 (M) mempunyai suhu peralihan fasa sekitar 66 ºC. Justeru itu, sampel dengan ketulenan tinggi, kehabluran yang baik dan saiz butiran yang lebih kecil memaparkan sifat termokromik yang unggul seperti ditunjukkan oleh histeresis yang rendah dan entalpi yang tinggi. Secara khususnya, didapati bahawa sampel dengan ciri termokromik terbaik adalah yang telah disepuh-lindapkan pada suhu 650 °C selama 2 jam. Sebaliknya, penambahan tungsten (W) dalam sintesis VO_2 menyebabkan penurunan suhu peralihan fasa kepada 31.64 ºC. Peningkatan transmisi bergerlap, transmisi suria dan kekonduksian terma pada suhu bilik telah diperhatikan. Tambahan pula, peningkatan jelas dalam

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kekonduksian terma merentasi suhu peralihan fasa telah berlaku dan ini menunjukkan peralihan daripada keadaan semikonduktor kepada logam. Akhirnya, salutan komposit VO_2-PVP telah disediakan dengan menyerakkan nanopartikel VO_2 berketulenan tinggi di atas substrat kaca dengan polivinilpirolidon (PVP) bertindak sebagai matriks perumah polimer. Analisis permukaan sampel yang mengesahkan penyerakan nanopartikel di atas substrat secara kerkesan. Yang terpenting, transmisi bergerlap sampel komposit meningkat sehingga 86.75%. Sesungguhnya, dalam kerja ini, suhu peralihan fasa, transmisi bergerlap dan transmisi suria telah dipertingkatkan serentak menunjukkan potensi besar untuk aplikasi pintar tingkap.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

%R	Percent Reflectance
%T	Percent Transmittance
A	Absorption
α	Thermal Diffusivity
C_p	Heat Capacity
ΔH	Enthalpy / Heat of Transition
ΔT_{sol}	Solar Modulation Ability
D	Crystallite Size
E_F	Fermi Energy
E_G	Energy Band Gap
f	Fill Ratio
η_T	Near-Infrared Switching Efficiency
h	Hysteresis
θ	Angle of Incidence
κ	Thermal Conductivity
λ	Wavelength
m	Mass
ρ	Mass Density
R	Reflectance
R_{lum}	Luminous Reflectance
S_a	Roughness Mean Height
S_q	Root Mean Square Height
τ	Temperature
τ_c	Phase Transition Temperature
τ_{cool}	Phase Transition Temperature during Cooling
τ_{heat}	Phase Transition Temperature during Heating
τ_{onset}	Onset Temperature
T	Transmittance
T_{lum}	Luminous Transmittance
T_{NIR}	Near-Infrared Transmittance
T_{sol}	Solar Transmittance
φ_{lum}	Luminous Efficiency of the Human Eye
φ_{sol}	Solar Irradiance Spectrum for Air Mass 1.5
wt%	Weight Percent

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AACVD	Aerosol Assisted Chemical Vapor Deposition
AFM	Atomic Force Microscopy
APCVD	Atmospheric Pressure Chemical Vapor Deposition
AR	Anti-Reflective
CVD	Chemical Vapor Deposition
DSC	Differential Scanning Calorimetry
EACVD	Electron-Field Assisted Chemical Vapor Deposition
EBE	Electron Beam Evaporation
EC	Electrochromic
EDX	Energy Dispersive X-Ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full-Width at Half Maximum
GC	Gasochromic
GHG	Greenhouse Gases
HiPIMS	High Power Impulse Magnetron Sputtering
HT	Hydrothermal Synthesis
HTP	High-Temperature Phase
HVAC	Heating, Ventilation and Air Conditioning
IR	Infrared
LFA	Laser Flash Analysis
LTP	Low-Temperature Phase
MIT	Metal-to-Insulator Transition
MS	Magnetron Sputtering
MST	Metal-To-Semiconductor Transition
NIR	Near-Infrared
PC	Photochromic
PLD	Pulsed Laser Deposition
PVD	Physical Vapor Deposition
TC	Thermochromic
TGA	Thermogravimetric Analyzer
TMO	Transition-Metal Oxides
UV	Ultraviolet
XRD	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

The aim of this chapter is to introduce the subject matter studied by this thesis. The sections are organized into the: background of the research; energy consumption in buildings; defining windows and smart windows; thermochromic material; performance evaluation of thermochromic windows; vanadium dioxide (VO_2); (1.7) VO_2 nanoparticles; problem statements and motivation; research objectives; scope of the study; and thesis structure.

1.1 Background of the Research

Global climate change is a worldwide phenomenon that impacts every living organism on Earth. Among its devastating effects include the increasing temperature around the globe, extreme heat waves, prolonged droughts, frequent wildfires, rising sea levels, intense tropical storms, and changing precipitation (Karl and Trenberth, 2003; Peng et al., 2011; Mendelsohn et al., 2012). Hence, this problem has attracted many scientists and researchers to put forward feasible answers to minimize its ill effects. Emphasis is particularly placed on energy saving methods to reduce fossil fuel need and consequently minimize greenhouse gases (GHG) emissions, mainly carbon dioxide (CO_2) which is one of the main culprits of the problem (Attari et al., 2010; Davis and Caldeira, 2010; Thomas et al., 2004).

Accordingly, energy conservation can be achieved by improving one or more of its components, namely: generation; storage; distribution; and efficiency. In the area of generation, renewable resources have been investigated as a potential replacement to nonrenewable fossil fuel source (Edenhofer, 2011; Ellabban et al., 2014). Likewise, researches are being done on the fabrication of new batteries and production of smart power systems for their potential as energy-conserving storage and distribution systems, respectively (Li et al., 2017; Garcia et al., 2018). Meanwhile, the fourth factor entails improving how energy is used and finding ways to maximize its utility. In this context, efficiency implies minimizing energy usage while maximizing its output (Baatz et al., 2018). Hence, enhancement of energy efficiency can be achieved in a number of ways.

1.2 Energy Consumption in Buildings

One of the areas where efficiency can be greatly improved is in built environments or buildings, since they use up significant amount of energy. In fact, buildings consume about 30-40% of the world's primary energy mainly for heating, ventilation and air conditioning (HVAC), lighting, and appliance usage (Granqvist et al., 2009). For instance, China and the USA – the world's first and second largest energy consumers– expend about 27.4% and 41% of energy in buildings, respectively (Wei and He, 2017; Kamalisarvestani et al., 2013). Also, in Europe, a continent consisting of highly industrialized countries, built environment accounted for 40 to 45% of their energy use (Agostino et al., 2017). Indeed, the high energy demands in buildings resulted in increased GHG emissions. As a matter of fact, in 2010, as much as 40%, 36% and 18% of CO_2 emissions in the USA, Europe, and China, respectively, were due to energy use in buildings (Kamalisarvestani et al., 2013; Nejat et al. 2015).

In addition, with the increasing global average temperature, energy demand for air conditioning is growing rapidly primarily to fulfill people's needs for thermal comfort. In the European Union, an increase of 17% in their energy usage per year is observed (Granqvist et al., 2009). An even more concerning scenario can be observed in hot humid countries, where an upsurge in air conditioning usage is inevitable. In fact, due to increased necessity, some countries spend one-third to one-half of their produced electricity for their energy needs in buildings (Yusoff and Mohamed, 2017). In Malaysia, for instance, the building sector uses up to 48% of the country's generated electricity (Hassan et al., 2014). Considering that 94% of Malaysia's energy source is fossil fuel, the energy consumption in buildings translate into as much as 40% of the country's GHG emissions (Zaid et al., 2015). Henceforth, considerable attention is needed to put forward energy saving strategies to lessen the energy demands in buildings and ultimately reduce CO_2 emissions.

Energy saving methods in buildings can be categorized into two: active and passive. Active strategies involve upgrading the qualities and increasing the energy efficiencies of HVAC and lighting systems (Li et al., 2017). On the other hand, the passive approach includes treating and enhancing building envelopes including walls, roofs, and windows (Seyfouri and Binions, 2017). In fact, substantial studies have been done on improving the properties of windows to reduce energy losses.

1.3 Defining Windows and Smart Windows

Windows or glazed areas are fundamental elements in buildings as they play dual roles of being a barrier as well as a connection between the indoors and outdoors. As a barrier, they provide us protection from the outside world; while, as a connection, they endow us visually with the beauty of the surrounding environment (Li et al., 2011). Moreover, they have become a very important feature in architectural design for practical and aesthetic reasons. Specifically, large areas of glazed windows give good indoor-outdoor contact as well as comfort (Saeli et al., 2013).

However, windows are also labeled as among the most inefficient components of buildings. Inasmuch as they allow heat to go in or out, more energy is required for the use of space cooling or heating to balance the increase or decrease in temperature (Kamalisarvestani et al. 2013). For instance, during summer or hot days, heat can easily pass through windows resulting in heat gain and temperature increase inside buildings. This prompts the use of air conditioning to give indoor comfort. Conventionally, curtains or blinds are implemented to block the intense heat from the sun. As a consequence, this necessitates the use of lighting which leads to more energy usage.

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Indeed, a promising avenue to reduce energy expenditure and losses in buildings is by fabricating energy-efficient windows with the ability to control the throughput of transmitted light, heat and solar energy, that is, developing smart windows. This may be done by coating spectrally selective materials on the surface of windows (Gao et al., 2012). By blocking unwanted and/or regulating solar radiation, HVAC and lighting use can be minimized, which in turn, translates into reductions in energy use and GHG emissions.

Smart windows can be achieved through chromogenic technologies, that is, materials whose optical characteristics can vary depending on an external stimulus (Granqvist et al., 2013). The most common type of chromogenic devices includes: electrochromic (EC); thermochromic (TC); photochromic (PC); and gasochromic (GC), which can be stimulated by applied electric field, change in temperature, irradiation of light (photons), and exposure to gas, respectively. Figure 1.1 shows a comparison between chromogenic-based fenestrations and conventional window glazing in terms of their energy requirements for cooling and electric lighting (Kamalisarvestani et al., 2013).

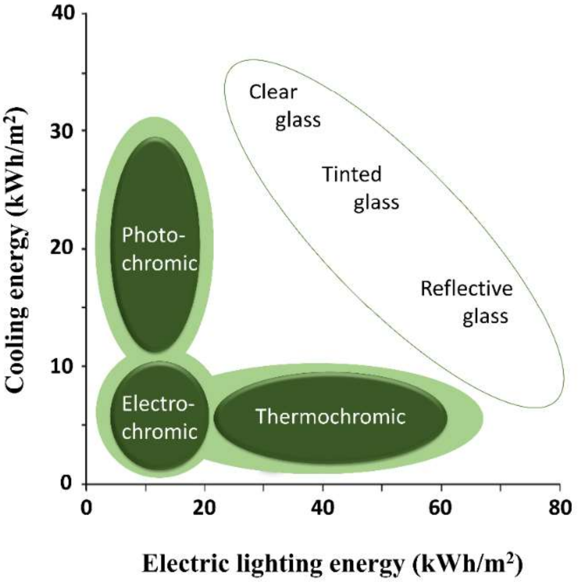

Figure 1.1: Glazing Materials and Their Electric Lighting Energy and Cooling Energy (Granqvist et al., 2013)

Accordingly, employing chromogenic materials lowers the cooling energy need as well as minimizes electric lighting. In addition, comparing the chromogenic materials would show that electrochromic (EC) and thermochromic (TC) provide the lowest cooling energy while EC requires lesser electric lighting than TC. However, electrochromic glazing is constrained by wiring and switching requirements as it depends on the application of electric field (Granqvist et al., 2009). Meanwhile, thermochromic has the advantage of regulating its optical property automatically based on temperature change alone (Gao et al., 2012). Moreover, TC window has uncomplicated structure and involve facile preparation, which makes it a promising material for smart window application (Seyfouri and Binions, 2017).

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1.4 Thermochromic Material

Etymologically, the name thermochromic is derived from the Greek words' *thermos* and *chroma* which mean hot and color, respectively (Merriam-Webster, 2019). As the name suggests, thermochromic or TC materials are substances that change color due to variations in temperature. Examples of such are liquid crystals, leuco dyes and almost all inorganic compounds (Kiri et al., 2010). These materials can gradually alter color over a range of temperatures (continuous thermochromism) or abruptly change its structural phase at a certain critical temperature (discontinuous thermochromism) (Mott, 1974). Furthermore, the phase change can be reversible or irreversible, and be first- or second-order in nature (Mott, 1974).

The mechanism of how a TC material functions is illustrated in Figure 1.2. As seen in the diagram, the material has two different states relative to a phase transition temperature, τ_c. At the cold state or below transition temperature, it exists as a semiconductor with a monoclinic structure.

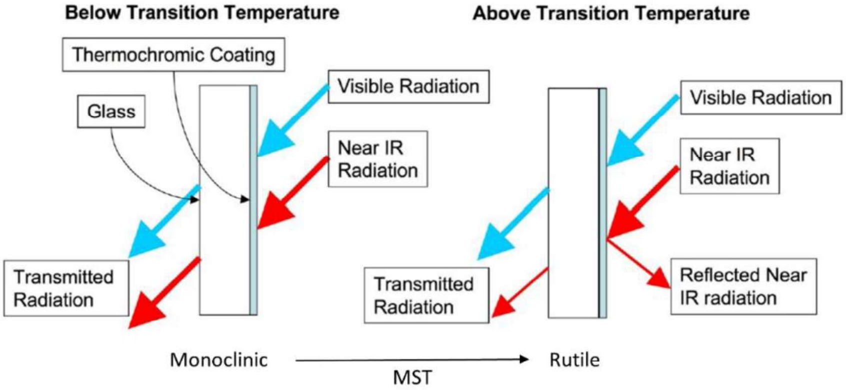

Figure 1.2: Schematic of Thermochromic Behavior (Saeli et al., 2013)

While at the hot state, above τ_c, it is in a metallic state with a rutile structure (Saeli et al., 2013). The process whereby this material changes phase is termed metal-to-semiconductor transition (MST) (Morin, 1959; Goodenough, 1971). As the material undergoes a shift in phase, its optical properties also change. Specifically, when the material is monoclinic, it is transparent to infrared (IR) radiation; whereas, when it is in rutile form, it becomes reflective of IR radiation (Goodenough, 1971). However, the transmission of visible radiation does not change in both states. Hence, TC material has great potential in the fabrication of smart windows.

Among the inorganic compounds that exhibit thermochromism are transition-metal oxides (TMO). In 1959, Morin discovered a certain behavior on the lower oxides of titanium and vanadium. By thoroughly studying the electrical properties of these oxides in varying temperatures, he found that these materials undergo transitions from a semiconducting state at low temperatures to a metallic state upon reaching a critical temperature (Morin, 1959). A number of studies were then carried out as a follow-

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through to Morin's findings (Kachi et al., 1973). Also, only TiO as well as V_3O_5 and V_7O_{13} in the family of titanium and vanadium oxides do not shift in phase as they are metallic throughout (Morin, 1959). Interestingly, the τ_c of vanadium dioxide (VO_2), which is ~341 K (68 °C), is closest to room temperature compared with other compounds (Goodenough, 1971). Hence, VO_2 is widely considered for near room-temperature applications such as in thermal sensors, optical and electrical switching devices, optical filters, and smart windows (Chen et al., 2011, Liang et al., 2016, Mjejri et al., 2014; Velichko et al., 2015).

1.5 Performance Evaluation of Thermochromic Windows

The performance of TC windows in buildings is characterized by their ability to let visible light pass through and block IR and ultraviolet (UV) radiations. By letting visible rays in, natural day-lighting and better see-through property can be achieved. Meanwhile, blocking IR and UV rays, which carry majority of solar energy and heat, would minimize solar heat gain and reduce heat loss inside buildings (Kamalisarvestani et al., 2013). Hence, TC windows can be evaluated using the following parameters: visible or luminous transmittance (T_{lum}), luminous reflectance, (R_{lum}), near-infrared (NIR) radiation transmittance (T_{NIR}), NIR switching efficiency (η_T), solar transmittance (T_{sol}) and solar modulation ability (ΔT_{sol}) (Zhao et al., 2014). Specifically, T_{lum} is defined as the percentage of visible radiation that propagates through a material; whereas, R_{lum} is the percentage of light that bounces off. Similarly, T_{NIR} and T_{sol} are the amounts of radiations that pass through a material in the NIR and solar range, respectively. Hence, it is necessary to employ a spectrophotometer that is capable of measuring transmitted and reflected radiations in the UV, visible, and NIR regions. Figure 1.3 shows a typical spectrum of transmittance and reflectance of a VO_2 sample.

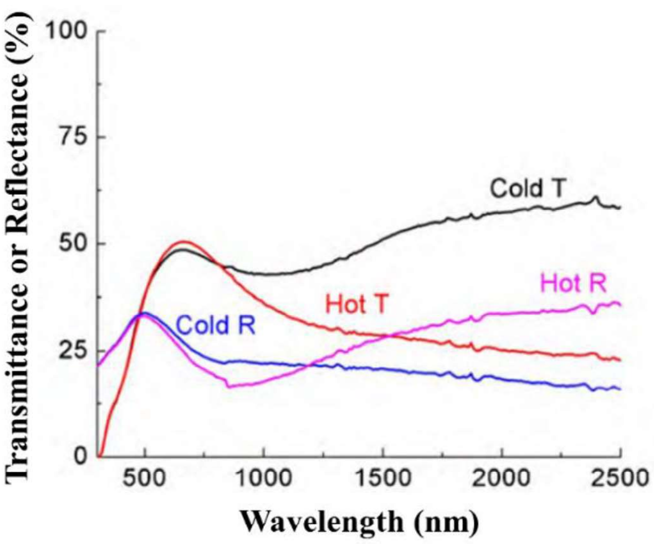

Figure 1.3: Transmittance and Reflectance of a VO_2 Sample (Saeli et al., 2010)

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To deduce this seemingly complex data, the optical properties can be expressed numerically as follows (Zhao et al., 2014):

$$T_{lum} = \frac{\int \varphi_{lum}(\lambda)T(\lambda)d\lambda}{\int \varphi_{lum}(\lambda)d\lambda} \tag{1.1}$$

$$R_{lum} = \frac{\int \varphi_{lum}(\lambda)R(\lambda)d\lambda}{\int \varphi_{lum}(\lambda)d\lambda} \tag{1.2}$$

$$T_{NIR} = \frac{\int \varphi_{sol}(\lambda)T(\lambda)d\lambda}{\int \varphi_{sol}(\lambda)d\lambda} \tag{1.3}$$

$$T_{sol} = \frac{\int \varphi_{sol}(\lambda)T(\lambda)d\lambda}{\int \varphi_{sol}(\lambda)d\lambda} \tag{1.4}$$

where φ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes (Sharpe et al., 2005), φ_{sol} is the solar irradiance spectrum for air mass 1.5, which was taken from the American Society for Testing and Materials (ASTM, 2013), T is transmittance, R is reflectance, and λ is wavelength, which ranges from 390 to 780 nm for T_{lum} and R_{lum}, from 780 to 2500 nm for T_{NIR}, and from 280 to 2500 nm for $T_{sol.}$ Indeed, these wavelength-integrated properties provide an easier way to characterize and describe smart window materials. Furthermore, η_T and ΔT_{sol} are derived from equations (1.3) and (1.4). Mathematically, η_T and ΔT_{sol} can be expressed as follows,

$$\eta_T = \Delta T_{\lambda_{max}} = T_{\lambda_{max},cold} - T_{\lambda_{max},hot} \tag{1.5}$$

$$\Delta T_{sol} = T_{sol,cold} - T_{sol,hot} \tag{1.6}$$

where, λ_{max} is the maximum wavelength in the NIR region, and the subscripts' *hot* and *cold* denote that the values are respectively taken above and below τ_c. As equation (1.5) suggests, η_T describes the maximum change in transmittance before and after τ_c, which is usually taken at the wavelength of 2500 nm in the NIR region. Meanwhile, ΔT_{sol} refers to the overall switching efficiency of the material, that is, the difference in transmitted solar radiation above and below the critical temperature. Indeed, η_T and ΔT_{sol} are the benchmarks in determining how energy efficient a material is.

1.6 Vanadium Dioxide

VO_2 is a layered binary compound that exists in many polymorphic phases, namely, VO_2 (A), VO_2 (B), VO_2 (C), VO_2 (D), VO_2 (M) and VO_2 (R) (Leroux et al., 1998; Cao et al., 2008; Liu et al., 2013). Of these phases, only VO_2 (M) and VO_2 (R) are thermodynamically stable and exhibit thermochromic ability (Dai et al., 2011). Accordingly, monoclinic VO_2 (M) undergoes a first-order reversible phase transition to rutile tetragonal VO_2 (R) at 68 °C (Goodenough, 1971). More significantly, this shift in phase is accompanied by changes in the optical properties of the material (Alie et al., 2014; Seyfouri et al., 2017; Venta et al., 2013), that is, below τ_c, it is IR transparent; whereas, above τ_c, it becomes IR reflectant. Figure 1.4 shows the molecular crystalline structure and band diagram of VO_2 in both phases.

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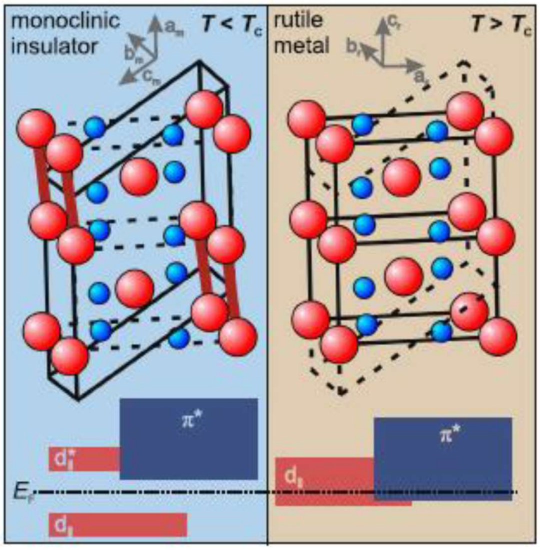

Figure 1.4: Crystallographic Structures with Band Diagrams of Monoclinic and Rutile States of VO_2 (Wegkamp and Stahler, 2015)

As seen, its shift in phase is due to the molecular rearrangement from monoclinic to rutile structure. At a temperature below τ_c, vanadium ions dimerize which causes localization of the outer-shell vanadium electrons as seen in its band structure. When the temperature rises above τ_c, a rapid surge in electrical conductivity occurs and the lattice relaxes to a rutile structure.

1.7 VO_2 Nanoparticles

During the early stages of its discovery, VO_2 was synthesized in bulk form via chemical transport reaction (Kachi et al., 1973). However, further studies on bulk VO_2 showed that it breaks after a few cycles of phase change due to structural distortions (Gao et al., 2012). Due to this limitation, researches have shifted to the syntheses of thin films and nanoparticles, which have been found to have greater endurance towards structural deformity. In fact, these forms of VO_2 can withstand distortions for more than 10^8 cycles of phase transition (Guzman et al., 1996; Livage, 1996; Beteille et al., 1998), which make them more suitable for a smart glazing system.

Furthermore, due to the limitations of thin-film VO_2, particularly its low T_{lum}, weak ΔT_{sol}, undesirable film color, and long processing time, a significant number of studies have focused on the synthesis of VO_2 in nanostructure form (Zhang et al., 2012). This is mainly acquired by using hydrothermal synthesis (HT), wherein an enclosed autoclave containing water-based solution is heated at a relatively low temperature inside an electric oven for a certain duration of time (Ji et al., 2011). Moreover, experimental conditions in the hydrothermal method result in unique structures and morphology. The various nanostructures of VO_2 are pictured in Figure 1.5. Hence, this method affords

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easier procedural steps and structure control at a lower temperature compared to solid-state reactions that rely on high temperature processing (Alie et al., 2014). This is important in VO_2 synthesis because empirical results showed that the morphology and structure of VO_2 can directly affect its thermochromic and functional properties (Son et al., 2010; Dai et al., 2011; Li et al., 2018).

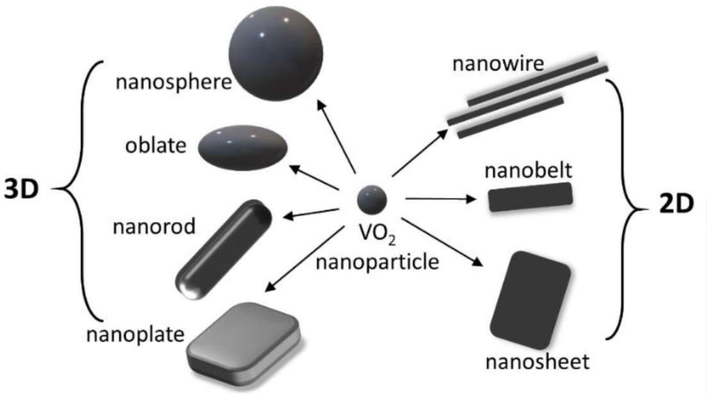

Figure 1.5: Different Nanostructures of VO_2 in 2D and 3D

Moreover, VO_2 nanopowder can be prepared using different precursors such as organic alkoxides (e.g. vanadium triisoproxy oxide, $VO(C_3H_7O)_3$), inorganic salts (e.g. divanadium pentoxide or V_2O_5), and vanadium oxyacetylacetone ($VO(AcAc)_2$). Of these substances, V_2O_5 stands out for practical considerations because it is inexpensive and easily obtainable (Dachuan et al., 1996). Moreover, comparative studies show that the use of V_2O_5 resulted in better thermochromic behavior (Hanlon et al., 2002). Thus, many researches have utilized this compound as a VO_2 precursor. To reduce the oxidation state of V_2O_5 from 5+ to the preferred 4+ (the oxidation state of VO_2), reduction agent, such as oxalic acid ($H_2C_2O_4$), is needed (Xu et al., 2014).

1.8 Problem Statements and Motivation

The potential of VO_2 as a smart window material is so promising that many novel techniques have emerged over the years for its synthesis (Nag and Haglund, 2008; Wang et al., 2016). But while the technologies involved in preparing VO_2 have developed in recent years, its real-world application is still hampered by some limitations, particularly in its fabrication as well as its intrinsic properties.

Regarding the production of VO_2, the set of technologies used in its synthesis still has some issues that need resolutions. For instance, while physical vapor deposition (PVD) techniques, such as pulsed laser deposition (PLD) and sputtering system, provide better control of synthetic conditions and high purity samples, they are constrained by high cost, long processing time, and poor growth rate (Maaza et al., 2000; Chae et al., 2003; Kiri et al., 2010). Coupled with these is its inability for large scale application (Nag and Haglund, 2008). Meanwhile, though the chemical vapor deposition (CVD) processes

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offer commercial scalability and fast growth rate, they also require non-cost-effective equipment and high energy need (Osmolovskaya et al., 2014). On the other hand, solution-based methods such as sol-gel technique and hydrothermal synthesis (HT) have been found to be great alternative routes in the preparation of VO_2 because they are cost-effective, easy to use, require low processing temperature and capable of large area applications (Velichko et al., 2014). Nevertheless, these methods suffer from low precision control of process parameters and lower purity (Kamalisarvestani et al., 2013). Hence, modifications are necessary to enhance and take away the shortcomings of the aforesaid techniques.

For practical reasons, the drawbacks of solution-based methods can be remedied *easily* compared to the PVDs and CVDs. This can be done by meticulously finding the optimum synthetic conditions in the growth of high purity VO_2. Hence, several studies have dealt with the many experimental parameters involved in the synthesis of VO_2 using solution-based processes. For instance, in the hydrothermal preparation of VO_2, synthetic conditions such as the type of V precursor, molar ratio of precursors, fill ratio, operating temperature, duration of process, and annealing conditions were found to affect the purity as well as the crystal structure and morphology of the resulting VO_2 (Wang et al., 2016).

In the work of Alie et al. (2014), the effects of molar ratio (ratio of V_2O_5 and $H_2C_2O_4$), operating temperature, and precursor concentration were investigated. They found that lower molar ratio (1:2), synthesis temperature (160 to 240 °C), and concentration (2.5 mg/mL) resulted in the non-thermochromic VO_2 (B). While at a temperature of 260 °C, molar ratio of 1:3, and concentration of 12.5 mg/mL, they were able to successfully synthesize the thermochromic VO_2 (M), albeit with some impurities. On the other hand, Popuri et al. (2013) described the effect of varying molar ratios when they used the ratios of 1:1.5 and 1:4.5 at 250 °C in 24 h, which resulted to VO_2 (A) and VO_2 (M), respectively. However, the hysteresis width – a measure of the strength of a material's thermochromic behavior – of their samples was high, which implies a weak transition performance.

Meanwhile, another thermodynamic variable, pressure, which plays a vital role during the hydrothermal treatment, is scarcely studied. This is mainly due to the difficulty of configuring an in-situ pressure gauge during the process. Nonetheless, a study conducted by Ji et al. (2011) showed a means to do away with this constraint by using *synthesis pressure* or fill ratio (f), that is, the ratio between the volume of the solution and the volume of the autoclave used. Indeed, they have demonstrated that there is direct proportionality between fill ratio and pressure, in that, increasing the volume of a solution relative to the volume of the autoclave causes an elevation in pressure. This is evident from their results, wherein, at a lower fill ratio ($f = 0.4$), with a synthesis temperature of 270 °C and holding time of 24 h, they obtained the metastable VO_2 (A); whereas, when f was increased to 0.6, they acquired the thermodynamically stable VO_2 (M).

While the works mentioned above used temperatures ranging from 250 to 270 °C to obtain the thermochromic VO_2 (M), other studies on hydrothermal preparation of VO_2 involved lower temperatures (160 – 230 °C), which usually resulted in the metastable

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VO_2 (B) or VO_2 (A) (Valmalette and Gavarri, 1998; Zhang et al., 2006; Xu et al., 2014; Zhang et al., 2016). However, these phases can be converted to VO_2 (M) via heat treatment under vacuum or Ar atmosphere. Empirical studies have shown that the annealing temperature and time highly influence the crystallinity, morphology, and grain size distribution of VO_2 (Qi and Niu, 2012; Zhang et al., 2012; Popuri et al., 2013). Furthermore, the acquired VO_2 (M) has higher purity compared to one-step hydrothermal processed samples (Alie et al., 2014; Li et al., 2017).

Nonetheless, there are still some gaps in the aforementioned researches. For instance, the work of Ji et al. (2011) was limited to $f = 0.4, 0.5, 0.6$. Prior to this study, different groups that synthesized VO_2 used differing f such as 0.32 (Alie et al., 2014), 0.33 (Zhang et al., 2012), 0.4 (Xu et al., 2014), 0.7 (Zhang et al., 2016), and 0.72 (Popuri et al., 2014). Also, in the work of Alie et al. (2014), they only used molar concentrations of 2.5 and 12.5 mg/mL and molar ratios of 1:1, 1:3 and 1:6; while, the work of Popuri et al., employed molar ratios of 1:1.5 and 1:4.5 (2013). As such, the first part of this thesis dealt with expanding the synthetic conditions in the hydrothermal synthesis of VO_2 to better understand their effects and relationships. In particular, parameters such as synthesis temperature, fill ratio, molar ratio, precursor concentration, and process duration were examined to determine the best results. Moreover, because the experiments were carried out at a lower synthesis temperature of 180 °C, due primarily to apparatus limitations, annealing was carried out. As a follow-through to previous works, nitrogen gas (N_2) was employed. More importantly, the evolution of VO_2 (B) to VO_2 (M) was analyzed and the annealing conditions were examined to get the optimal results.

But while high purity VO_2 can be successfully synthesized via the hydrothermal method at carefully chosen experimental parameters, its intrinsic properties still present three major challenges (Li et al., 2010). Firstly, the τ_c of VO_2, which is ~68 °C, is too high for usage in buildings. Ideally, VO_2-based windows should reflect heat-carrying IR rays at room temperature (~25 °C) to achieve people's thermal comfort. Secondly, it suffers from low visible transmittance, that is, its T_{lum} of 40% is quite below the acceptable value of 65% (Saeli et al., 2013). Thirdly, its solar modulation ability (ΔT_{sol}) is very weak at less than 10% (Li et al., 2010). For windows to be considered energy efficient, the required ΔT_{sol} must be 15% or more (Wang et al., 2016).

An effective way to lower the phase transition temperature of VO_2 is doping. Accordingly, the atomic radii of a dopant must be larger than the V^{4+} ion to create V^{5+} defects in the lattice resulting to a reduction of τ_c (Kiri et al., 2011). This is evident in the use of tungsten (W) and molybdenum (Mo) which can reduce the τ_c of VO_2 to as low as 23 °C and 24 °C (Hanlon et al., 2013), respectively. However, these dopants do not have a significant effect on the material's T_{lum} and ΔT_{sol} (Wang et al., 2016)

Among the solutions being done to improve the optical properties of VO_2 is layering with anti-reflective (AR) compounds. Systems such as two-layer VO_2-SiO_2 (Zhao et al., 2014), three-layer $TiO_2/VO_2/TiO_2$ with self-cleaning ability (Zheng et al., 2015), and five-layer $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ (Mlyuka et al., 2009) have been reported with improved visible transparency and solar modulation characteristic. Nonetheless, because

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there is a need to stack multiple layers of films, this process can be time and energy consuming.

A facile and innovative way to improve T_{lum} and ΔT_{sol} is by using a VO_2 composite coating (Li et al. 2010); whereby, VO_2 nanoparticles are embedded onto a substrate with a polymeric host matrix (Alfred-Duplan et al. 1994 and Valmalette and Gavarri, 1994). Polymers such as polyethylene (PE), polyurethane (PU), polyvinylphenol, and polyvinyl alcohol (PVA) have been used in previous researches (Alfred-Duplan et al., 1994; Valmalette and Gavarri, 1994; Dai et al., 2013; Madida et al., 2014).

Moreover, simulation studies by Li et al. (2010) showed that T_{lum} and ΔT_{sol} depend on the shape and size of the nanoparticles. Accordingly, T_{lum} of 75% and 65 % at the semiconducting and metallic states, respectively, and ΔT_{sol} as high as 16.6% were calculated for spherical nanostructures. Indeed, these values were higher compared to thin film samples.

Hence, the second part of this thesis dealt with addressing the three aforementioned challenges by doping VO_2 with W, as well as preparing VO_2-based nanocomposite film that was derived from hydrothermally prepared VO_2. In addition, the use polyvinylpyrrolidone or povidone (PVP) as polymeric host matrix was examined. Furthermore, phase, morphology, topography, and optical property analyses were carried out to investigate the properties of the acquired composite samples.

1.9 Research Objectives

The preceding sections demonstrated the need to further investigate the various factors that affect the synthesis of highly pure nanostructured VO_2 with excellent thermochromic behaviors. It is also essential to find a means to enhance the attributes of VO_2 for practical applications. Therefore, this research work sought to achieve the following objectives:

I. Study the effects of fill ratio, precursors ratio, molar concentration, synthesis temperature and holding time on the structural and morphological properties of hydrothermally prepared VO_2.
Hypothesis 1a: Increase in temperature will result in higher peak intensities
Hypothesis 1b: Increase in fill ratio will lead to increase in peak intensities and particles with lesser grain size
Hypothesis 1c: Increasing V precursor/reductant molar ratio will result in more nano-sized particles
Hypothesis 1d: Increase in treatment time will result in more sharp peaks and larger grain size

II. Examine the conversion of VO_2 polymorphs from B-phase to M-phase via annealing under nitrogen atmosphere, and to examine the annealed sample’s structural, morphological, thermochromic, and optical properties.

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Hypothesis 2a: Annealing under N_2 atmosphere will result in the conversion of VO_2 from B-phase to highly pure M-phase with large grain size
Hypothesis 2b: Decrease in grain size will result in decrease in phase transition temperature
Hypothesis 2c: High purity will result in enhanced hysteresis and enthalpy

III. Investigate the influence of W-doping on the structural, thermochromic, thermophysical, and optical properties of VO_2.
Hypothesis 3a: Doping with tungsten will result in an increase in lattice strain
Hypothesis 3b: Increase in doping concentration will lead to a decrease in phase transition temperature

IV. Synthesize VO_2–PVP composite film and analyze its structure, topography, and optical properties.
Hypothesis 4: Dispersed VO_2 nanoparticles on the surface of a glass substrate will increase its luminous and solar transmittances

1.10 Scope of the Study

In lieu of the aforementioned objectives, this research work encompassed the following:

I. Hydrothermal treatment with differing synthetic conditions were carried out using V_2O_5 and oxalic acid as V precursor and reducing agent, respectively. In particular, experimental runs with differing fill ratio, molar ratio, molar concentration, process temperature and duration were conducted to find a set of parameters that should result in highly pure and well crystallined VO_2 (B) nanoparticles.

II. Annealing runs with varying temperatures and times were done to evaluate their effects on the formation of VO_2 (M) and find the optimal conditions on the synthesis of highly pure thermochromic VO_2. Further, analysis of the phase structure and morphology as well as the resulting thermochromic and optical properties were conducted to find correlations.

III. In the intent of improving the attributes of VO_2, analysis on the enhancements of doping VO_2 with W is performed. Subsequently, influences of the dopant on the phase, structure, thermochromic, optical, and thermophysical properties of VO_2 were explored.

IV. In an effort to advance the practical application of VO_2 as smart window material, VO_2-based composite coating was prepared and evaluated on its resulting attributes.

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1.11 Thesis Structure

This thesis is comprised of six themed chapters. The first chapter gives an introduction of the research work including a brief background, motivation, and objectives of the study. In addition, basic terminologies and related matters such as smart windows, thermochromism, and performance evaluation of thermochromic materials are presented. Chapter 2 discusses the theoretical foundations and conceptual models relevant to the study. The third chapter presents a review and integration of empirical information on the research variables investigated by this study. Chapter 4 describes the methodology employed in the research, including sample preparations and characterizations. The findings derived from the experimental runs carried out in this work is discussed in Chapter 5 under four subsections, namely: (a) results of the hydrothermal synthesis of VO_2 at different experimental parameters; (b) elucidation of the effects of annealing conditions to the conversion of VO_2 (B) to VO_2 (M) under N_2 flow; (c) explanation of the influence of tungsten as dopant on the properties of VO_2; and (d) analysis of the prepared VO_2-PVP nanocomposite film. Finally, the sixth chapter reflects on the conclusions and recommendations for future research.

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BIODATA OF STUDENT

Hamdi Muhyuddin Didaagun Barra was born and raised in Marawi City, Philippines. He completed his primary and secondary levels of education at the Dansalan College Foundation, Inc. in Marawi City. In 2005, he then earned the degree of Bachelor of Science in Physics through the full academic scholarship granted by the Mindanao State University (MSU) Marawi Campus. He was a consistent honor student from the first grade until the undergraduate level wherein he graduated *cum laude*. He was also a finalist to the Ten Outstanding Young Muslims (TOYM) award in the Philippines. Due to his love for physics, he pursued Master of Science in Physics at the University of the Philippines Diliman through the scholarship grants accorded by the Philippine Council for Advanced Science and Technology Research and Development (PCASTRD, DOST) and the Advance Personnel Development Program Scholarship (APDP) of MSU. He is presently a PhD candidate in the field of Materials Science at the Universiti Putra Malaysia (UPM). For his doctoral studies, he became a recipient of the Malaysia International Scholarship (MIS) granted by the Ministry of Higher Education.

Mr. Barra has been involved in various research projects since his undergraduate years. He has presented some research outputs in various national and international conferences. In 2018, he won the Best Paper Award for the science category as well as the Grand Award at the International STEAM Research Congress held in the Philippines. He has also published some research articles in peer-reviewed journals. Needless to say, he still considers himself a novice researcher and still in the process of honing his research skills. Furthermore, Mr. Barra has a passion for teaching and has worked as a lecturer at MSU for six years.

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Journal Articles

Barra, H. M.; Chen, S. K.; Tamchek, N.; Talib, Z. A. A Facile Preparation of VO_2-PVP Nanocomposite Coating for Smart Window Application with Improved Visible Transmittance. *Innovative Technology and Management Journal* **2018,** *1,* 1. (ISSN: 2546-1117)

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International Conference

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PENGESAHAN STATUS UNTUK TESIS/LAPORAN PROJEK DAN HAKCIPTA

SESI AKADEMIK : _______________

TAJUK TESIS/LAPORAN PROJEK :

ASPEK BAHASA DAN FALSAFAH DALAM MUKUN MELAYU SARAWAK

NAMA PELAJAR : HAMSIAH BT JUKI

Saya mengaku bahawa hakcipta dan harta intelek tesis/laporan projek ini adalah milik Universiti Putra Malaysia dan bersetuju disimpan di Perpustakaan UPM dengan syarat-syarat berikut :

1. Tesis/laporan projek adalah hak milik Universiti Putra Malaysia.
2. Perpustakaan Universiti Putra Malaysia mempunyai hak untuk membuat salinan untuk tujuan akademik sahaja.
3. Perpustakaan Universiti Putra Malaysia dibenarkan untuk membuat salinan tesis/laporan projek ini sebagai bahan pertukaran Institusi Pengajian Tinggi.

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☐ **SULIT** (mengandungi maklumat di bawah Akta Rahsia Rasmi 1972)

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☐ **AKSES TERBUKA** Saya bersetuju tesis/laporan projek ini dibenarkan Diakses oleh umum dalam bentuk bercetak atau atas talian.

Tesis ini akan dibuat permohonan :

☐ **PATEN** *Embargo* ____________ hingga ____________
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Pengesahan oleh:

(Tandatangan Pelajar)	(Tandatangan Pengerusi Jawatankuasa Penyeliaan)
No Kad Pengenalan / No Pasport.:	Nama:
Tarikh :	Tarikh :

[Nota : Sekiranya tesis/laporan projek ini SULIT atau TERHAD, sila sertakan surat dari organisasi/institusi tersebut yang dinyatakan tempoh masa dan sebab bahan adalah sulit atau terhad.]