Faculty of Resource Science and Technology

Deposition and Characterization of Nanoparticles MnO_2 Thin Films on Aluminium Coated Plastic Substrate for Electrochemical Applications.

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A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science (Hons.)

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Declaration

I, the undersigned, declare that this work in this thesis was carried out in the accordance with the regulation of University Malaysia Sarawak. It is original and is the result of my work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted at this or any other university or academic institution for any other degree or qualification.

Caryn Tan Hui Chuin

Program of Resource Chemistry

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List of Abbreviations

MnO_2	Manganese Dioxide
$KMnO_4$	Potassium Permanganate
$Na_2S_2O_3$	Sodium Thiosulfate
NaOH	Sodium Hydroxide
$MnSO_4$	Manganese Sulfate
AAS	Atomic Absorption Spectrometer
BET	Brunauer-Emmett-Tellr
EDX	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Studies
EPD	Electrophoretic Deposition
ESD	Electrostatic Spray Deposition
ESs	Electrochemical Superconductors
FTIR	Fourier Transform Infrared
HRTEM	High Resolution Transmission Electron Microscopy
ITO	Indium Tin Oxide
SC	Specific Capacitance
SEM	Scanning Electron Microscope
SWCNT	Single Walled Carbon Nanotube
TEM	Transmission Electron Microscope
XRD	X-ray Diffraction

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Deposition and characterization of nanoparticles MnO_2 thin films on aluminium coated plastic substrate for electrochemical applications.

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Abstract

Manganese dioxide, (MnO_2) nanoparticles have been well-known to be deposited as thin-film materials because of its superior optical, electrical, catalytic, electrochemical properties and magnetic. Researchers had used many instruments in order to characterize physical properties of MnO_2 nanoparticles and deposited thin films. In this project, UV Visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Atomic Absorption Spectrometer (AAS) and Energy Dispersive X-ray Spectroscopy (EDX) were used to characterize MnO_2 nanoparticles and deposited thin films. Stable MnO_2 colloidal suspension will be synthesized by 2 techniques. The deposition of MnO_2 thin film on aluminium coated plastic substrate were conducted by electrophoretic deposition method by using a Scribner cell. Deposition parameters such as different voltage and time were used to investigate the thickness of manganese dioxide deposited on the substrate. The electrochemical properties of deposited MnO_2 films were studied.

Keywords: Manganese dioxide nanoparticles, aluminium coated plastic substrate, electrophoretic, electrochemical properties study

Abstrak

Nanopartikel mangan dioksida, (MnO_2) terkenal untuk dimendapkan sebagai bahan filem nipis adalah kerana dengan sifatnya yang unggul optik, pemangkin, elektrik, elektrokimia yang unggul dan magnet. Penyelidik telah menggunakan pelbagai jenis alatan untuk mencirikan sifat fizikal nanopartikel MnO_2 serta dimendapkan ke atas filem nipis. Dalam projek ini, UV spektroskopi Nyata, Fourier Transform Infrared Spektroskopi, Mikroskop Imbasan Elektron, Penghantaran Elektron Mikroskop, Penyerapan Spektrometer Atom, dan Tenaga Serakan X-ray Spektroskopi digunakan untuk mencirikan nanopartikel MnO_2 serta dimendapkan ke atas filem nipis. MnO_2 stabil dalam penggantungan koloid disintesis dengan 2 teknik. Pemendapan MnO_2 ke atas filem nipis aluminium disalut pada substrat plastik dijalankan dengan kaedah pemendapan elektroforetik dengan menggunakan sel Scribner. Parameter pemendapan seperti voltan dan masa yang berbeza digunakkan untuk menyiasat ketebalan mangan dioksida yang telah dimendapkan pada substrat. Sifat elektrokimia pemendapan MnO_2 akan dikaji.

Kata Kunci: nanopartikel mangan dioksida, aluminium bersalut substrat plastik, elektroforetik, kajian sifat elektrokimia.

1.0 Introduction

The research regarding to manganese dioxide, (MnO_2) nanoparticles which in the form of nanoparticulate thin-film materials gained a lot of attention due to their superior optical, electrical, catalytic as well as magnetic and electrochemical properties (Pang *et al.* 2012). There are numerous potential applications once the MnO_2 nanoparticles synthesized in a variety of fields such as piezoelectric crystals, pharmaceutical industries, sensors, fuel cell electrode and catalysis (Kumar *et al.* 2013). According to Pang *et al.* (2012), MnO_2 has been identified as electrode material in either primary or secondary batteries due to its favorable electrochemical properties, low cost and environmental friendly.

MnO_2 nanoparticles had it sizes which is extremely small, then resultant nanostructures will be characterized by transmission electron microscopy (TEM), nitrogen adsorption, and X-Ray diffraction (XRD) which are reported by Zhu *et al.* (2005). MnO_2 nanoparticles of different crystal morphologies and crystallographic types had been synthesized by the facile hydrothermal route and electrochemically investigated as the electro cathode active materials of primary and rechargeable batteries. The as-synthesized samples were characterized by scanning electron microscope (SEM), and the high resolution as well as energy filtered transmission electron microscopy (HRTEM) (Cheng *et al.* 2006).

There are a lot of methods to prepare or synthesize MnO_2 nanoparticles. One of the methods are the conventional co-precipitation method which had been widely used because it is cheap and affordable (Kumar *et al.* 2013). Co-precipitate method is transferring the impurities down by a precipitate under certain condition together with deposited substrate. The other

method to synthesize MnO_2 nanoparticles is by mixing aqueous solutions of $KMnO_4$ and $MnSO_4$ at controlled temperature, pressure and pH of solution mixture (Xiao *et al.* 1998).

In order to deposit MnO_2 nanoparticles on aluminium coated plastic film, electrophoretic deposition (EPD) is one of the best methods (Cao, 2004). This EPD method is chosen because it is rapid, cheap and requires simple set up. EPD can potentially be used in manipulating and controlling the deposition of a range of nanoparticles (Boccaccini *et al.* 2010). According to Palmer *et al.* (2009), EPD is increasingly popular in the manufacturing of engineered materials because of its low cost, flexibility, and efficiency. EPD has many applications and specifically in nanotechnology and material science. It is also known as e-coating or electrophoretic coating because the substrate is being coated with oppositely charged particles to form a thin layer (Riddel, 2014). Nanoparticles suspended in a solvent and move in desired direction by an applied electric field and deposited on an electrode surface (Tassel and Randall, 2006).

Aluminium coated plastic film is rarely reported to be used as a supporting substrate for depositing MnO_2 thin film (Fujino *et al.* 2005) as there are many types of supporting substrates which have been widely used for depositing MnO_2 thin film including nickel (Pang *et al.* 2013), iron (Varma *et al.* 1974), silver (Hu *et al.* 2013), and graphite carbon (Perez *et al.* 2011). For this research, aluminium coated plastic film will be used as the substrate for the deposition of MnO_2 nanoparticles on the thin film.

1.1 Research Questions

Aluminium coated plastic substrate is not being widely used in the research field. If aluminium coated plastic film is used throughout the experiment, will MnO_2 nanoparticles form uniform film on the aluminium substrate by electrophoretic deposition? What will be the physical properties thin film on the aluminium substrate?

1.2 Objectives

1. To synthesize MnO_2 nanoparticles in the form of colloidal suspension and to determine the physical properties of MnO_2 nanoparticles.

2. To deposit manganese dioxide on aluminium coated plastic thin films of different thickness and to investigate the chemical composition of manganese thin film.

2.0 Literature Review

2.1 Synthesis of Manganese Dioxide Nanoparticles

Manganese dioxide nanoparticles are synthesized in a solution phase (Jaganyi *et al.* 2013). 0.0158 g of $KMnO_4$ was dissolved in 75 ml of ultra-pure water and the solution mixture was stirred for at least 2 hours. Then 0.0931 g of sodium thiosulphate was dissolved in 25 ml of ultra-pure water and was then added to permanganate solution at room temperature. The colour of solution changed rapidly from purple to yellow-brown and finally turned into dark brown which indicates the formation of manganese dioxide nanoparticles. The suspension of manganese dioxide was greatly transparent and very stable over a period of few months.

Sol-gel method also used to synthesize manganese dioxide nanoparticles by using fumaric acid as a reduction agent as reported by Jehng *et al*. (2014). The purpose of using fumaric acid as a reduction agent is to intercalate $FeCl_2$ precursor into MnO_2 structure.

Hydrogen-reduction technique had been used to synthesize MnO_2 nanoparticles within the self-ordered mesoporous carbon. MnO_2 nanoparticles was successfully synthesized inside the channel's pore of ordered mesopores carbon CMK-3 which was then confirm by using transmission electron microscope (TEM) that confirm the presence of MnO_2 nanoparticles. The content of MnO_2 nanoparticles inside the CMK-3 can be controlled by varying the time of reaction (Zhu *et al.* 2005).

Kumar *et al.* (2013) reported that MnO_2 nanoparticles were synthesized by co-precipitation technique. This techniques were co-precipitate the manganese salt under a fine controlled pH by using sodium hydroxide solution which yields the corresponding of manganese

oxide nanoparticles. Microemulsion-based method has been reported by Li *et al.* (2013) that it was useful to synthesize MnO_2 nanoparticles. This method enables the nanomaterial's to be synthesized with different types of shapes and sizes by change the various components that involved in the formation of microemulsion.

2.2 Characterization of Manganese Dioxide Nanoparticles

MnO_2 nanoparticles were characterized by using UV- visible spectrometer, Transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy. FTIR spectra of pure MnO_2 showed the occurrence of O-Mn-O vibrational mode at approximately 600 and 475 cm^{-1}. The absorption board with the wavelength range of 4000 and 3000 cm^{-1} showed both stretching collision between hydroxyl and H-O-H absorption. The chemical composition was obtain by EDX analysis and confirmed the presence of manganese and oxygen in the sample. In TEM analysis, the surface morphology of MnO_2 nanoparticles shows uniformly dispersed particles in spherical shape. The selected area of electron diffraction patterns revealed that MnO_2 nanoparticles were crystalline in nature. UV-visible absorption spectra are obtained a UV-spectrophotometer (UV-1800 Shimadzu) using a 10 mm quartz cell. Transmission electron microscopy (TEM) was carried out on a transmission electron microscope (TEM)(JEOL-2010) which was operated at an accelerating voltage of 80 kV. EDX spectrum was obtained from ISIS 300 (Oxford, Link) instrument. Fourier transforms infrared (FTIR) spectra of MnO_2 nanoparticles were recorded with a FTIR infrared spectrometer (Perkin Elmer BX) within the range of 4000-400 cm^{-1} (Jaganyi *et al.* 2013).

X-ray diffraction (XRD) patterns of MnO_2 nanoparticles were obtained by using an X-ray diffractometer (TW3040/60 Tanalygical Company, Holland) in which Cu-Kα (*λ=0.154 nm*)

was used as the radiation source (Li *et al*, 2013). While according to Kumar *et al.* (2013), the X-ray diffraction proves the presence of manganese oxide metal particles which was crystalline purely in nature. The mean size of manganese oxide nanoparticles was between 25.0 – 35.0 nm which correspond to 100 percent intensity peak and calculate using Scherrer equation. The surface morphologies of manganese dioxide nanoparticles were examined by scanning electron microscopy (SEM) (Hitachi S-4800) and transmission electron microscopy (TEM) (JEM-2100F). The surface area of manganese dioxide nanoparticles determined by using automated adsorption apparatus (Micromeritics ASAP 2020) based on the Brunauer-Emmett-Tellr (BET) equation (Li *et al.* 2013).

Scanning electron microscopy (SEM) had used to examine the morphologies of manganese oxides (Liu *et al*. 2006 and Huang *et al.* 2006). Huang *et al*. (2006) reported that scanning electron microscopy (SEM) (Hitachi-650) was used to observe and identify the surface morphology of manganese oxide electrodes. They investigated the surface morphology of manganese oxides that deposited at various potential energy. The surface morphology of manganese oxides changed with different potentials. The size of manganese oxide particles deposited became bigger and the thickness of manganese oxide films turned thicker at higher potential.

Dai *et al.* (2006) reported that the surface morphology of manganese oxide by using scanning electron microscope (Hitachi S-4700). They reported that the structure of manganese oxide films were prepared by electrostatic spray deposition (ESD) were rough and had porous with many cracks. The cracked surfaces were related to huge volume difference which occurred during the drying process. Thus, they reported that the specific capacitance (SC) was seriously

affected by the surface morphology of the electrode material because the electrode was facile to penetrate into the porous and cracked manganese oxide thin film.

2.3 Deposition of Manganese Dioxide Nanoparticles

Electrodeposited nano manganese oxide films were examined by using X-ray diffraction analysis (XRD) and were identified to exist in different phases (MnO, MnO_2 and Mn_3O_4). The electrochemical experiments were carried out using potentionist CHI 410a (CH Instruments, USA. A conventional three-electrode system which contains a bare or nano manganese oxide layer electrochemical deposited ITO glass as working electrode, Ag/AgCl (saturated KCl) as a reference electrode and a platinium wire as the counter electrode were used. Electrochemical impedance studies (EIS) were performed using impedance analyzer ZAHNER (Germany) (Thiagarajan *et al.* 2011).

Shen *et al.* (2012) reported that MnO_2 nanoparticles were deposited in single walled carbon nanotube (SWCNT) films by a facile and scalable asymmetric in-situ deposition method. With the addition of $KMnO_4$ solution which had been infiltrated, a thin layer of MnO_2 nanoparticles was then deposited on SWCNT surface. The intact layer of SWCNT layer served as a current collector. The result showed that the electrochemical performance of SWCNT with MnO_2 composite electrodes depended on the porosity film in SWCNT, concentration of the $KMnO_4$ solution used, pH, deposition temperature and time. They had optimized two electrode electrochemical capacitors together with the addition of 1 M of $Na_2S_2O_3$ in water as electrolyte and had shown a brilliant performance with specific capacitance of 529.8 Fg^{-1}, energy density of 73.6 Wh kg^{-1}, power density of 14.6 kW kg^{-1}, excellent capacitance retention (99.9%) after 2000 charge and discharge cycles and the highest reported frequency responses (1318 Hz). The

superior performance flexible electrochemical capacitors have broad applications in portable electronics and electrical vehicles.

Electrophoretic deposition (EPD) for the deposition of manganese oxide nanoparticles that prepared by a chemical precipitation method used before as reported by Wei *et al.* (2007). Then, manganese oxide nanoparticles for EPD were synthesized by the reduction of $KMnO_4$ with ethanol. EPD was carried out from the 1 g/L suspension of manganese oxide nanoparticles in ethanol at constant voltages of 50-100 V. Nanostructured porous manganese oxide films for electrochemical superconductor were prepared by EPD and cathode deposition.

Su *et al*. (2012) also reported that electrophoretic deposition (EPD) is one of an important technique to composite film for electronic and other applications. EPD is attractive for fabrication of MnO_2 - CNT composite for application in electrochemical superconductors (ESs). They had found that adsorbed anionic and cationic polyelectrolytes provide an efficiency in charging of CNT in suspension and allowed the formation of anodic and cathode deposition by EPD. Electrophoretic deposits were obtained on stainless steel substrates (50 x 50 mm) from MnO_2 suspension, containing 0 – 1 gL^{-1} MWCNT and 0 – 10 gL^{-1} in ethanol. The deposition was performing in a constant potential energy within 10 – 70 V and the deposition time was varied in the range of 0 – 10 minutes.

Electrophoretic method has a great importance for the fabrication of ceramic superconductors and fuel cells (Ata *et al.* 2012). Electrophoretic depositions were obtained on stainless steel substrates from 4 gL^{-1} MnO_2 suspension in ethanol. The deposition process was conducted at a constant potential energy of 20 V and the distance between the substrate and platinum counter electrode was 15 mm. The deposition time was within 0 – 8 minutes.

The overview of electrophoretic process involved two step processes which the first step is the migration of particles towards the electrode via electrophoresis and the second step is the deposition of the particle surface (Timothy, 2009). The schematic diagram of electrophoretic process can be seen in Figure 1.

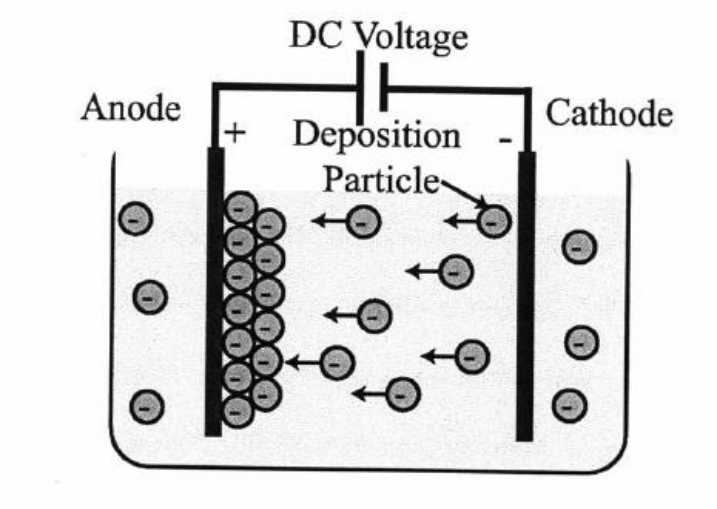

Figure 1: Schematic diagram of electrophoretic process.

According to Corni *et al.* (2008), electrophoretic deposition had covered many applications such as coatings and thin film, porous materials, functionally graded materials, composites, and nanostructures surfaces. Thus, for this proposed research, electrophoretic deposition technique is chosen because it has many advantages. It has the opportunity to tune the local ordering of particles or microstructure within deposit. EPD can control over the quantity of material deposited and extremely rapid as most cast can be prepared in minutes rather than hours.

3.0 Materials and Methods.

3.1 Synthesis of Manganese Dioxide Colloidal Suspension

The synthesis of manganese dioxide colloidal suspensions was prepared based on methods reported by Perez-Benito *et al.* (1996) and Sostaric *et al.* (1995).

a) *3.1.1 Synthesis Method 1*

MnO_2 colloidal suspension was prepared based on method reported by Perez-Benito *et al.* (1996). An aqueous solution of 2.5 mL of $KMnO_4$ with the concentration of 1.00×10^{-1} mol dm^{-3} was mixed with 5 mL of $Na_2S_2O_3$ with the concentration of 1.88×10^{-2} mol dm^{-3} in a 500 mL volumetric flask. The mixed solutions were evenly mixed by stirring gently for approximately 2 hours. The solution was then transferred into 3500 MW dialyzed tubes and dialyzed against 2L of ultrapure water for 4 days. The water was changed every day and during the water changing, the pH was tested to avoid as well as monitor the considerable pH change. The temperature was maintained constant throughout the experiment. The synthesis of manganese dioxide colloidal suspension was illustrated in Figure 2.

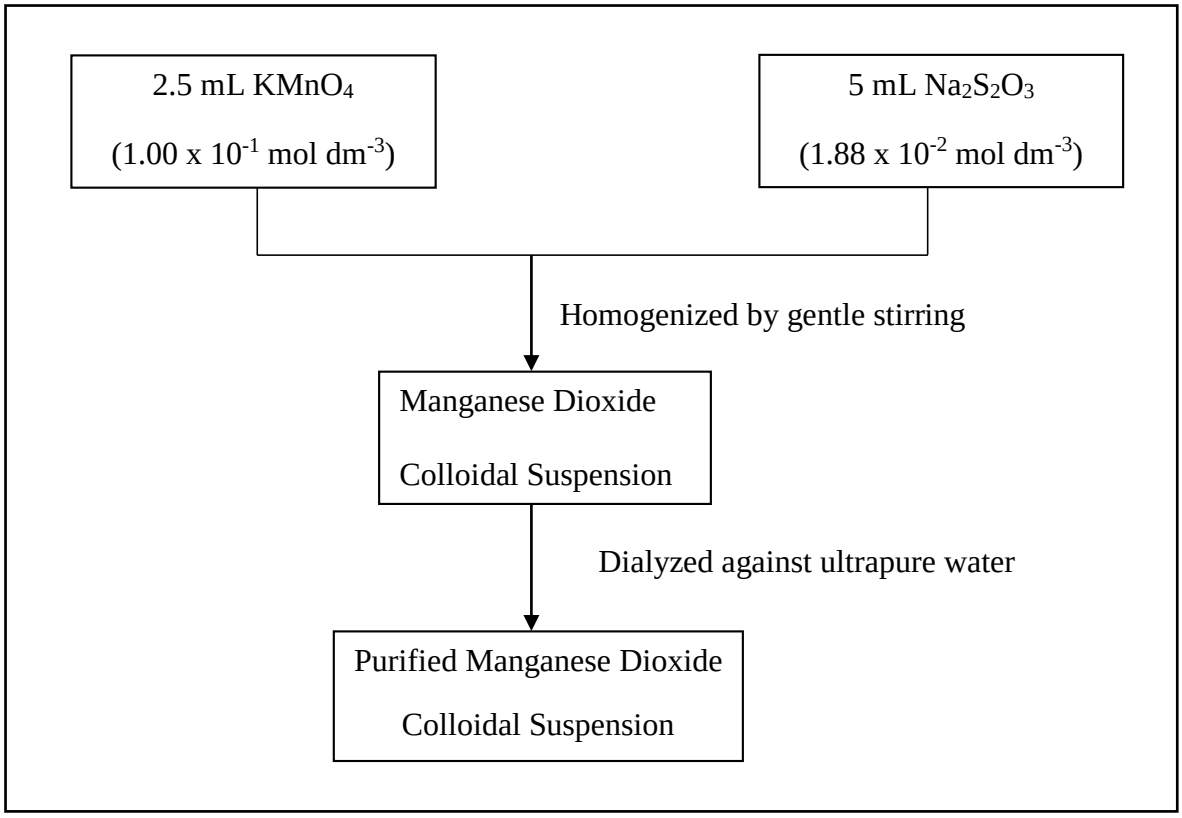

Figure 2**:** Synthesis of manganese dioxide colloidal suspension based on the method reported by Perez-Benito *et al*. (1996).

b) *3.1.2 Synthesis Method 2*

Another method of synthesis of manganese dioxide colloidal suspension was based on the method reported by Sostaric *et al.* (1995). $KMnO_4$ added into NaOH solution to produce 500 mL of 8.00 x 10^{-5} mol dm^{-3} MnO^{4-} at the pH within the range of 10 – 11. 0.8 mL of $MnSO_4$ solution with the concentration of 7.50 x 10^{-3} mol dm^{-3} added rapidly by using a micropipette to the permanganate solution stirred vigorously in the volumetric flask. The colloidal suspension formed was then placed into dialyzed tubes (3500 MW), and dialyzed against 2 L ultrapure water. The ultrapure water was changed every day for 4 days. The synthesis procedure of manganese dioxide colloidal suspension was illustrated in Figure 3.

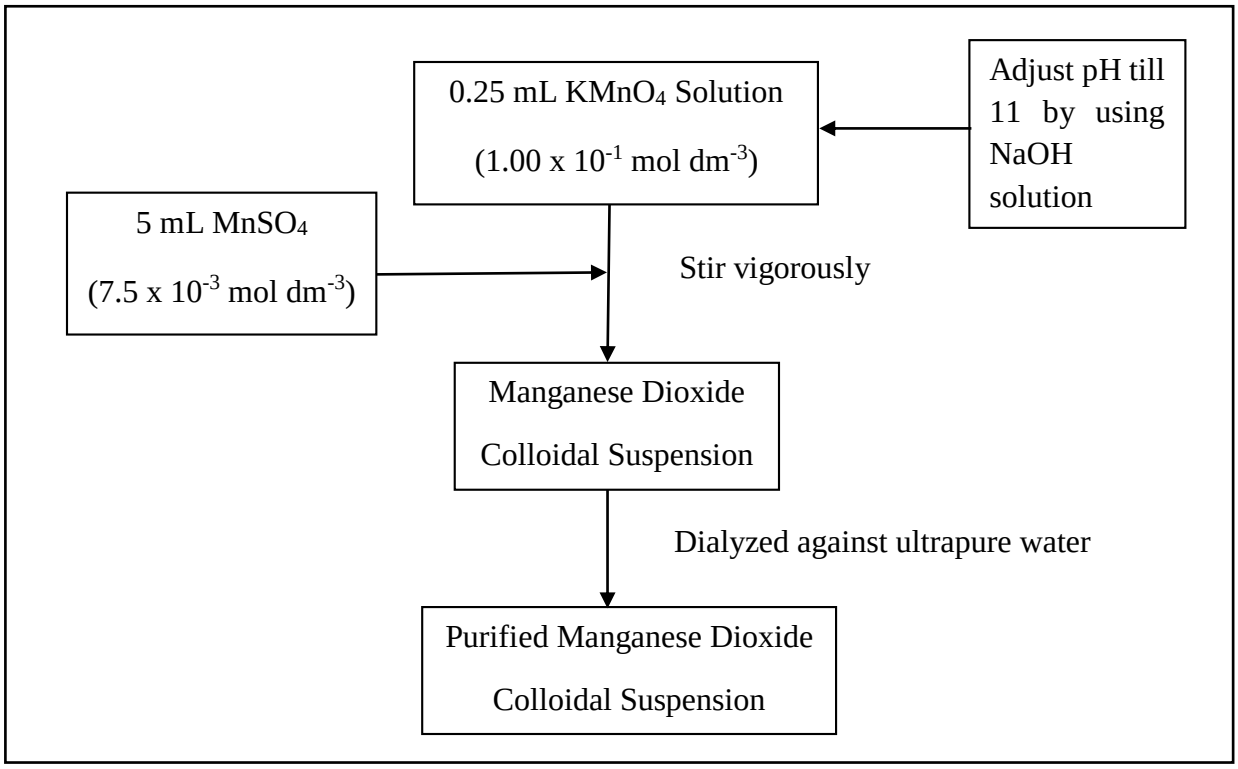

Figure 3**:** Synthesis of manganese dioxide colloidal suspension based on the method reported by Sostaric *et al.* (1995).

3.2 Characterization of Manganese Dioxide Nanoparticles

The properties of manganese dioxide nanoparticles had been characterized by using UV Visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), and Atomic Absorption Spectrometer (AAS).

3.2.1 UV Visible Spectroscopy

Ultraviolet spectrometer (Jasco V- 630) was used to investigate the aggregation and stability of all manganese dioxide colloidal suspension within the wavelength range of 200 – 1000 cm^{-1}.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) (NICOLET iS10) operated in the wavelength range of 500 - 4000 cm^{-1} was used to ascertain the purity and nature of manganese dioxide nanoparticles.

3.2.3 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) (JEOL Model JSM-6390 LA) was used to determine the surface morphology and the size distribution of manganese dioxide nanoparticles. All the manganese dioxide nanoparticles were drop on aluminium plate and then pre-coated.

3.2.4 Atomic Absorption Spectrometer (AAS)

The concentrations of manganese colloidal suspensions were determined by using Atomic Absorption Spectrometer (AAS) (Thermo Scientific iCE 3500). 10 mL of manganese colloidal suspensions were mixed with 3 mL of 10% nitric acid (HNO_3) and 3 mL of 10% hydrogen peroxide (H_2O_2). The solution mixture was then diluted with 100 mL of ultrapure water and the standard solution was prepared in 1 ppm, 2 ppm, and 3 ppm. The samples were analyzed to determine the average concentration of manganese as well as the manganese dioxide colloidal suspension.

3.2.5 Energy Dispersive X-ray Spectroscopy (EDX)

The chemical composition of manganese colloidal suspension will be identified by Energy Dispersive X-ray Spectroscopy (EDX) (JEOL Model JSM-6390 LA). The electron beam voltage was set for 10 kV during the EDX imaging. The instrument was exactly the same as SEM but EDX uses liquid nitrogen.