



Faculty of Resource Science and Technology

**PREPARATION AND CHARACTERIZATION OF ELECTRICALLY
CONDUCTIVE FILMS FROM AGAR-AGAR (CARRAGEENAN)**

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PREPARATION AND CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE
FILMS FROM AGAR-AGAR (CARRAGEENAN)

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Declaration

I hereby declare that this thesis is my original work except for quotations and citations which have been acknowledged.

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Table of Content

| | |
|---|-----|
| Acknowledgement..... | I |
| Declaration..... | II |
| Table of contents..... | III |
| List of abbreviations..... | V |
| List of tables and figures..... | VI |
| Abstract..... | 1 |
| Introduction..... | 2 |
| Literature review..... | 3 |
| Agar-agar or Carrageenan..... | 3 |
| Conducting Polymer..... | 4 |
| Characterization of agar-based thin films..... | 5 |
| Materials and methods..... | 7 |
| Sample preparation..... | 7 |
| Preparation of agar-based film..... | 8 |
| Preparation of copper sulphide suspension..... | 8 |
| Preparation of electrically conductive agar- based thin film..... | 8 |
| Effect of CuS coating..... | 8 |
| Characterization of electrically conductive agar-based thin film..... | 9 |
| Physical characterization..... | 9 |
| Chemical characterization..... | 10 |
| Results and Discussion..... | 11 |
| Agar-based thin film..... | 11 |
| Preparation of CuS/agar films..... | 11 |
| Characterization of CuS/agar films..... | 13 |
| Electrical conductivity..... | 13 |
| Scanning electron microscope (SEM)..... | 15 |
| Atomic Absorption Spectroscopy (AAS)..... | 19 |

| | |
|---|----|
| Chemical characterization..... | 21 |
| Fourier transform infrared spectroscopy (FTIR)..... | 21 |
| Conclusion..... | 23 |
| References..... | 24 |
| Appendices..... | 27 |

List of Abbreviation

| | |
|---|---|
| AAS | Atomic absorption spectroscopy |
| Cu | Copper |
| $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | Copper sulphate anhydride |
| CuS | Copper sulphide |
| EC | Ethylene carbonate |
| FTIR | Fourier transform infrared spectroscopy |
| KBr | Potassium bromide |
| $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ | Sodium thiosulphate anhydride |
| PEI | Poly(ethyleneimine) |
| PEG | Poly(ethylene glycol) |
| PET | Poly(ethylene terephthalate) |
| SEM | Scanning electron microscope |

List of Tables and Figures

- Figure 1 A flow chart which show an overview of methodology used for the preparation of electrically conductive agar-based films
- Figure 2 Agar-based films before and after drying 24 hours at 60°C in the oven
- Figure 3 CuS/agar films formed from CuS dispersion in a) pure water and b) ethanol
- Figure 4 Effect of CuS relative thickness on the conductivity of CuS/agar films
- Figure 5 SEM micrographs of a) pure agar-based film and b) CuS/agar film at 1,000x and 5,000x magnifications respectively.
- Figure 6 SEM micrographs of CuS/agar film, a) and b) 39.58 mg/L/cm² Cu concentration and c) and d) 67.05 mg/L/cm² Cu concentration in water dispersion at 5,000x and 10,000x magnifications respectively.
- Figure 7 SEM micrographs of CuS/agar film, a) and b) 30.43 mg/L/cm² Cu concentration and c) and d) 36.51 mg/L/cm² Cu concentration in ethanol dispersion at 5,000x and 10,000x magnifications respectively.
- Figure 8 Effect of CuS dispersion volume used on the Cu concentration bar graph
- Figure 9 FTIR Spectra for a) pure agar-based film, and b) CuS/agar film
- Figure 10 Effect of conductivity on mass of CuS per cm² of CuS/agar film
- Figure 11 Linear fit line obtained for Cu using AAS
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- Table 1 Effect of CuS relative thickness on the resistivity of CuS/agar films
- Table 2 Total mass of CuS per cm² of CuS/agar film for all samples
- Table 3 Concentration of Cu detected using AAS

**PREPARATION AND CHARACTERIZATION OF ELECTRICALLY
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AGAR-AGAR (CARRAGEENAN)**

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Abstract

In this study, commercially available agar-agar (carrageenan) was used to produce electrically conductive agar-based thin film. Agar strips as the starting material were gelatinized in water by heating, and glycerol was then added as a plasticizer to produce agar-based thin films. A thin layer of copper sulphide (CuS) was then deposited on the surface agar-based film to form electrically conductive films upon drying at 60°C in the oven for 24 hours.

Key words: agar-based thin film, carrageenan, plasticizer, coating

Abstrak

Dalam kajian ini, agar-agar (carrageenan) komersial yang mudah didapati telah digunakan bagi menghasilkan filem yang nipis berasaskan agar-agar. Agar-agar telah digunakan sebagai bahan pemula dan dipanaskan bersama gliserol pemplastik untuk menghasilkan filem nipis berasaskan agar-agar. Lapisan kuprum sulfide (CuS) telah digunakan sebagai bahan salutan untuk menghasilkan filem berasaskan agar-agar yang dapat mengalirkan arus elektrik selepas pengeringan pada suhu 60°C di dalam ketuhar selama 24 jam.

Kata kunci: filem nipis berasaskan agar-agar, carrageenan, pemplastik, salutan.

1.0 Introduction

1.1 Background

Film or thin film is derived from word 'thin' which means less than about one micron (10,000 Angstroms, 1000nm). A 'film' is a layer of material on a supporting substrate and if there is no supporting substrate, it is known as a foil. Film has its special properties that make it different from bulk materials.

Agar-agar or carrageenan is a type of hydrocolloid. Hydrocolloid can be defined as heterogeneous group of long chain polymers (polysaccharides and proteins) characterized by their property of forming viscous dispersions and/or gels when dispersed in water. The presence of a large number of hydroxyl (-OH) groups markedly increase their affinity for binding water molecules rendering them hydrophilic compounds. Furthermore they produce a dispersion, which is intermediate between a true solution and a suspension, and exhibit the properties of a colloid. Considering these two properties, they are aptly termed as 'hydrophilic colloids' or 'hydrocolloids' (Dipjyoti *et al.*, 2010).

In this study, agar-agar or carrageenan was used as the main precursor material for the preparation of electrically conductive thin films. This study focused on the addition and optimization of a copper sulphide layer in order to form a uniform and electrically conductive agar-based thin film.

1.2 Objectives

The objectives of this study are:

- To prepare electrically conductive agar-based films from carrageenan (agar-agar)
- To characterize and optimize the electrical conductivity of agar-based films.

2.0 Literature Review

2.1 Agar-agar or carrageenan

Agar-Agar, also simply called agar, was the first phycocolloid used as a food additive in our civilisation having been employed in the Far East over 300 years ago. Phycocolloids are those gelling products extracted from marine algae that are utilized in several ways solely because of their colloidal properties. The most important ones are agar, alginates and carrageenans that are produced in industrial quantities and presented in the form of clear colored powders. In the Orient 'natural agars' in the old forms of strips and squares are still being used at home to prepare traditional dishes. Agar, carrageenan, and alginate are polysaccharides derived from algae. They are hydrocolloidal sources, with many applications in the food, pharmaceutical, cosmetic and biotechnology industries, as gelling agents, thickeners or stabilizing and emulsifying agents. Agar and carrageenan constitute two well defined families of polysaccharide which are derived from different genera in the Rodophyta, collectively known as agarophytes and carragenophytes (Yaphe, 1984). The basic structure of agar is a regularly alternating sequence of 3-linked- β -D-galactopyranose and 4-linked 3, 6-anhydro- α -L-galactopyranose. Carrageenan is a linear polysaccharide with a repeating structure of alternating 1, 3-linked β -D galactopyranose and 1, 4-linked α -D galactopyranose units. The 3-linked units occur as the 2-and 4-sulfate or unsulfated, while the 4-linked units occur as the 2-sulfate, 2, 6-disulfate, the 3, 6 anhydrid and the 3, 6 anhydrid 2-sulfate (Norman Stanley, 1987). Agar, similarly to starch is a heterogeneous mixture of two polysaccharides: agarpectin and agarose. Although both polymers share the same galactose-based backbone, agarpectin is heavily modified with acidic side-groups, such as sulfate and pyruvate; agarose has a neutral charge (Ellen Raphael, 2010). Agar has an ability to form reversible gels (Stephen *et al.*, 1995; Lyons *et al.*, 2009; Philips

et al., 2000). Agar is unique among gelling agents in that gelation occurs at temperatures below the gel's melting point (Nussinovitch, 1997). Nonetheless, the thermal sensitivity of both chitosan and agar, individually, limits their application in extreme processing environments (Nazarudin *et al.*, 2011). Agar swells in cold water but is not soluble. The agar dissolves in boiling water to become an aqueous solution, and forms a gel when it is cooled. It is widely accepted that agarose molecules take a random coil conformation in aqueous solution at higher temperatures while they form double helices at lower temperatures, and the aggregation of helices leads to the gel formation. A quickly soluble agar is commercially available (Katsuyoshi, 2003).

2.2 Conducting Polymer

Conductive polymers have been extensively explored during last several decades because of their excellent electronic, physical properties and chemical stability which are due to their unique π -conjugated system and switchable conductivity between metal and insulator (Monika, 2010). Electric current will be produced when the electrons are moving along the polymer chains. Several examples of conjugated conducting polymers are polyacetylene, polypyrrole, polyaniline and polythiophene (Harun *et al.*, 2007).

An effective means for increasing the ionic conductivity of polymer electrolytes consists in plasticizing the polymer electrolyte with organic molecules such as ethylene carbonate (EC), poly(ethylene glycol) (PEG), and glycerol, which have high electric constant and low vapor pressure. These plasticizer help in improving the electrical conductivity of polymer electrolyte by increasing the amorphous phase content, dissociating ion aggregates and lowering the glass transition temperature (T_g) (Raphael *et al.*, 2010).

Among the transition metal sulfides that are widely studied include copper sulfides. Copper sulfides exist in various stoichiometries such as CuS and Cu₂S at room temperature. Green copper sulfide or covellite, CuS is of particular interest to the industry as it exhibits a metal-like electrical conductivity. Copper sulfides are also widely applied in thin films and composite materials for their unique properties such as opto-electronic, high capacitance, catalytic, gas sensing, etc (Boey *et al.*, 2007).

The electrically conductive films have been developed by Yamamoto, Tanaka, Kubota and Osakada (1993) by depositing copper sulfide on the surface of the films. A PET film (1 cm X 2 cm) was immersed for 48h at room temperature in a methanol solution (1 %) of PEI in a 300-mL beaker and dried in the air for 2-3 h. The PEI-treated film was connected with a wire and dipped in an aqueous solution (100 mL) of CuSO₄·5H₂O (0.10M) and Na₂S₂O₃ (0.10M) in a beaker. The reaction mixture was heated at 70°C by an oil bath with magnetic stirring. Color of the solution changed from yellow green to yellow brown, then dark brown, and finally to black in the initial 0.5 h. A small amount of black solid was deposited, and the film was colored yellow. Heating the reaction mixture for additional 1.5 h caused complete deposition of a black solid to give almost colorless solution. The film color was turned into green. The film was rinsed with water several times, dipped in water under ultrasonification for 0.5 h and dried in the air. The resulting Cu_xS-PET film shows surface resistivity of 55 Ω /square (Yamamoto *et al.*, 1993).

2.3 Characterization of agar-based thin films

Fourier transform infrared spectroscopy (FTIR) is used to confirm the functional groups present in the samples (Nazarudin *et al.*, 2011). FTIR spectrum of agar shows an absorption band at about 3342 cm⁻¹ which is associated with O-H stretching (Tako *et al.*,

1999; Armisen *et al.*, 1987). The band at around 1635 cm^{-1} is due to the stretching of the conjugated bond formed by (amide I) (C=O) groups (Cristiaen *et al.*, 1983). The peak at 1367 cm^{-1} is belonging to C-C bending and the bands at 1041 cm^{-1} are corresponded with the C-O stretching (Chirapart *et al.*, 1995).

3.0 Materials and Methods

3.1 Sample Preparation

Agar strips was purchased from the local store and used without any purification. Agar strips could be stored in room temperature and remain its originality. Figure 1 shows the flow chart of an overview of methodology used in this study.

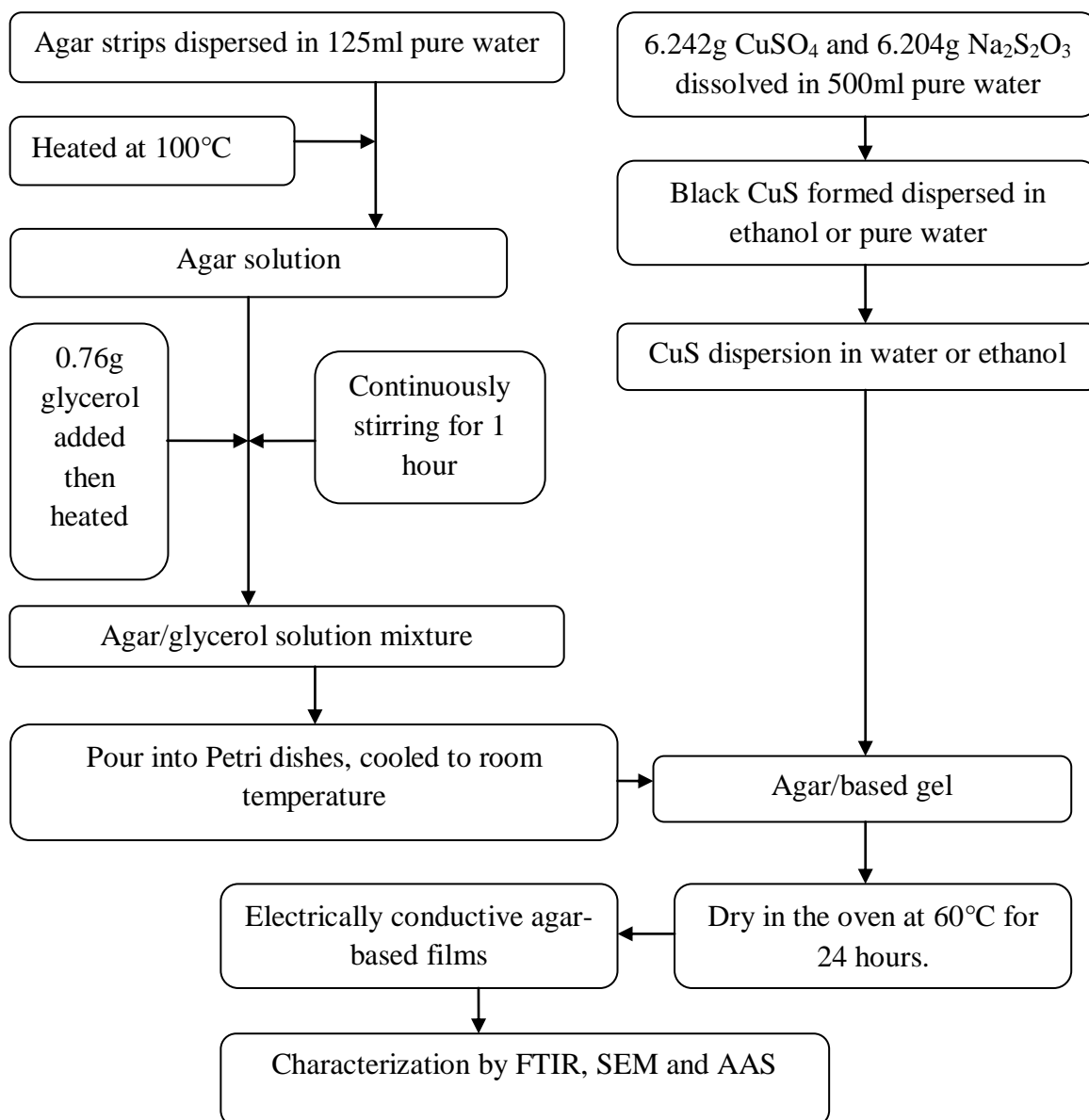


Figure 1: A flow chart which show an overview of methodology used for the preparation of electrically conductive agar-based films

3.2 Preparation of Agar-based Film

3.842g of agar strips was dispersed in 125ml of ultra pure water and heated for an hour at 100°C. The mixture was allowed to cool down for few minutes before 0.76g of glycerol was added into the mixture. The solution mixture was then continuously stirred for an hour until all components have dissolved completely. The resulting solution mixture was poured into separate Petri dishes and allowed to cool down to room temperature.

3.3 Preparation of Copper Sulphide Suspension

6.242g of copper sulphate (CuSO_4) (0.1M) and 6.204g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) (0.1M) were dissolved in 500ml of ultra pure water in a volumetric flask. The solution was then heated at 70°C for about an hour until black suspended solid was formed. The black suspended solid was filtered using filter paper and dispersed into ethanol and pure water. The resulting solutions were sonicated for 20 minutes.

3.4 Preparation of Electrically Conductive Agar-based Films

A measured amount of copper sulphide suspension was poured onto the agar gel and allowed to dry in an oven at 60°C for 24 hours.

3.5 Effect of CuS coating

The black CuS precipitate was dispersed in either ethanol or ultra pure water to form suspensions. Different volumes of CuS suspension used for coating onto the agar-based films were 10ml, 15ml, 20ml and 30ml. These films were allowed to dry in an oven for 24 hours at 60°C.

3.6 Characterization of Electrically Conductive Agar-based Film

3.6.1 Physical Characterization

a) Conductivity measurement

The conductivity of each agar-based film was measured by using a multimeter at a fixed distance of 1cm the two electrodes.

b) Surface morphology

The surface morphology of all electrically conductive agar-based films was observed using a Scanning Electron Microscope (SEM) JEOL-JSM-6390LA with the magnification of 5000x and 10000x. The samples were coated for few minutes using an Auto Fine Coater JEOL JFC-1600. By using SEM, the micrographs were also obtained from agar-based films with different amount of CuS coating.

c) Concentration of CuS

The total amount of CuS absorbed by a film was determined using Atomic Absorption Spectroscopy (AAS) Thermo Scientific iCE 3500. Each film was cut into 1cm X 1cm per piece. To obtain mean CuS concentration for each film, triplicate samples of each film were dissolved separately into 10ml of 65% of nitric acid in the beakers. These samples were heated in order to dissolve all materials completely. A watch glass was put over the beaker to avoid evaporation. Once dissolved, the solution was added slowly into approximately 30ml of ultra pure water and filtered using a filter paper number 47 before being transferred into 100ml volumetric flask. The beaker was rinsed for several times with small amount of pure water to ensure that all the material was transferred. The sample solution was diluted to the mark with ultra pure water. Further dilution was done after the solution was observed to be too concentrated for AAS measurement. The dilution was

done by pipetting 10ml from each flask and diluted to the mark with ultrapure water in a 100ml volumetric flask.

3.6.2 Chemical Characterization

The chemical structure and composition of electrically conductive agar-based films were determined using Fourier Transform Infrared Spectroscopy (FTIR) within the range of 400cm^{-1} to 4000cm^{-1} . The samples were mixed with KBr to form pellet for infrared measurements.

4.0 Results and Discussion

4.1 Agar-based film

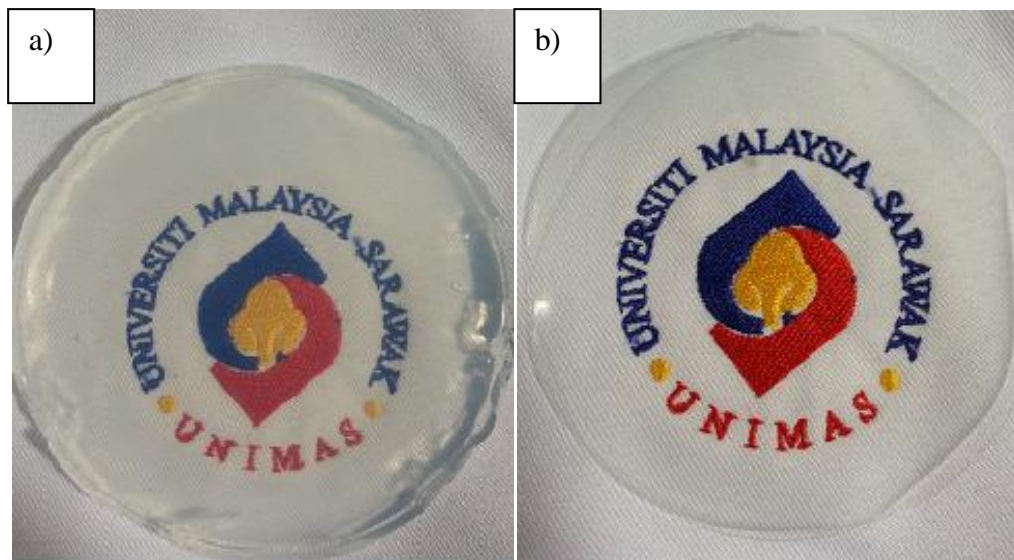


Figure 2: Agar-based films a) before and b) after drying 24 hours at 60 °C in the oven.

As shown in the Figure 2, agar solution formed as agar gel upon cooling to room temperature exactly like the agar that was used as food stuff. Upon further drying a clear, flexible and transparent film with good uniformity was formed.

4.2 Preparation of CuS/agar films

In order to optimize the electrical conductivity of agar-based films, different concentrations of CuS dispersions in ethanol and pure water were used. It was observed that CuS could be dispersed well in pure water but not in ethanol. Figure 2 shows comparison of CuS/agar films formed from the CuS suspensions in pure water and ethanol.

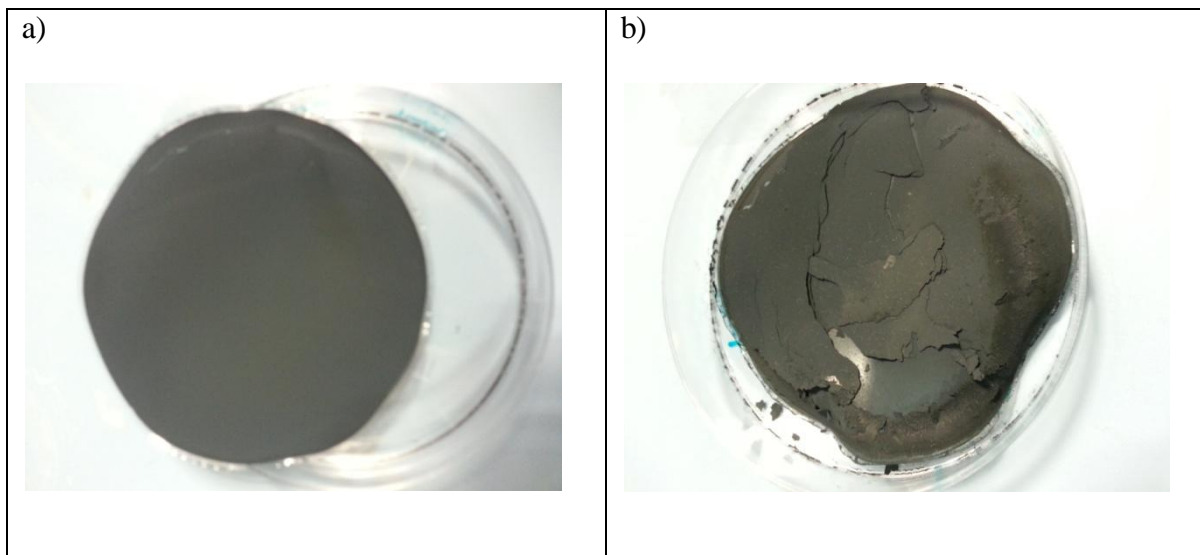


Figure 3: CuS/agar films formed from CuS dispersion in a) pure water and b) ethanol

Upon drying in the oven, CuS particles dispersed in water were observed to have embedded well within the films. In contrast CuS dispersion in ethanol led to the deposition of coating which was brittle and easily detached from the film. Besides, the CuS layer was observed to be non-uniform with cracks.

4.2 Characterization of CuS/agar films

4.2.1 Electrical Conductivity

Table 1 shows the effect of CuS relative thickness on the resistivity of CuS/agar films.

Table 1: Effect of CuS relative thickness on the resistivity of CuS/agar films

| Volume of CuS coating, ml | Relative thickness of CuS coating, ml/cm ² | Films resistivity, Ω /cm | |
|---------------------------|---|---------------------------------|--------------------------|
| | | CuS dispersion (water) | CuS dispersion (ethanol) |
| 10 | 0.17 | 5 | 5 |
| 15 | 0.26 | 5 | 5 |
| 20 | 0.34 | 8 | 5 |
| 30 | 0.52 | 6 | 10 |

The resistivity of CuS/agar films was measured using an ordinary multimeter with separation of electrodes being fixed at 1cm.

$$\text{Resistivity} = 1/\text{Conductivity} \quad (1)$$

The resistivity of films is inversely proportional to its conductivity as shown in equation (1) above. As such, the lower the resistivity, the higher the conductivity. The volume of 10ml to 15ml of CuS dispersion (1:2 to 1:3 v/w %) with relative thickness 0.17 ml/cm² and 0.26 ml/cm² respectively was observed to form conductive CuS/agar film with lowest resistivity of 5 Ω /cm. However, a volume ratio 1:1 of CuS dispersion and agar solution was observed to be unsuitable due to the observed high resistivity of CuS/agar films formed. As observed in this study, it was necessary for the CuS dispersion to be poured slowly to

ensure homogeneous mixing of black suspended solid particles within the agar gel in order to form films with high conductivity.

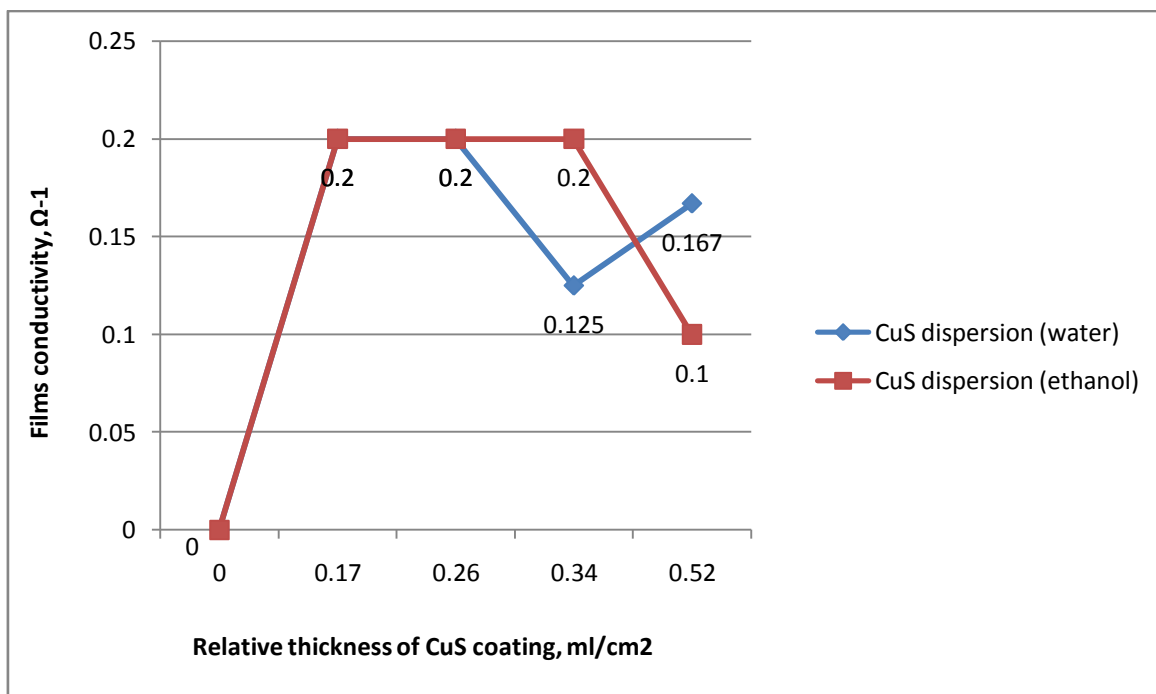


Figure 4: Effect of CuS relative thickness on the conductivity of CuS/agar films

4.2.2 Scanning Electron Microscope (SEM)

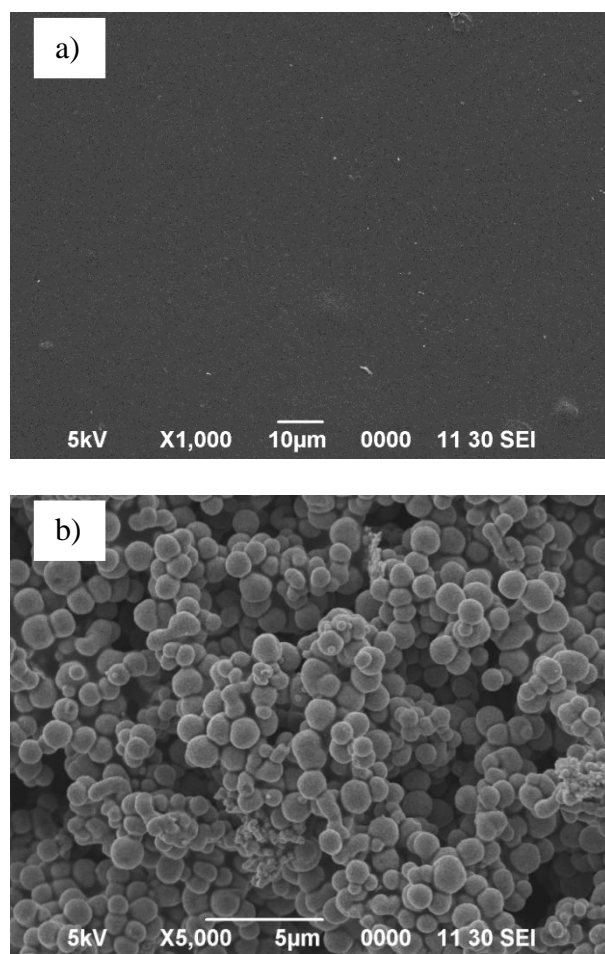


Figure 5: SEM micrographs of a) pure agar-based film and b) CuS/agar film at 1,000x and 5,000x magnifications respectively.

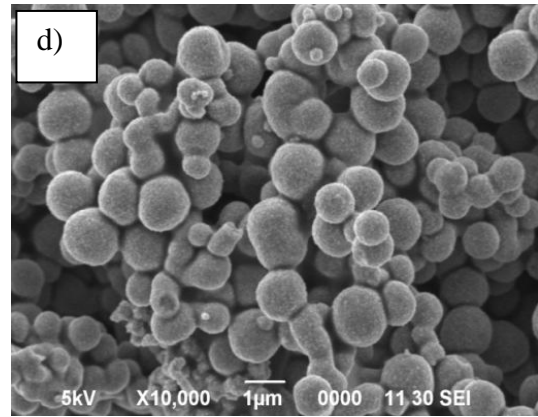
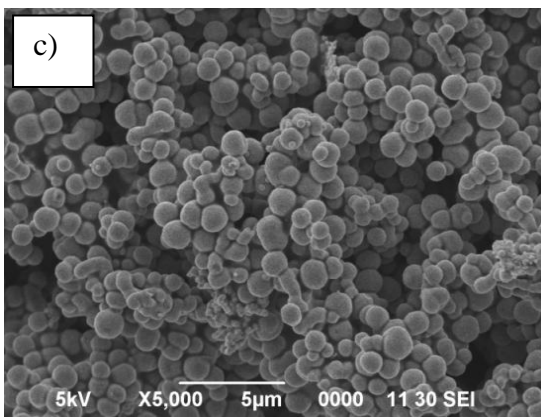
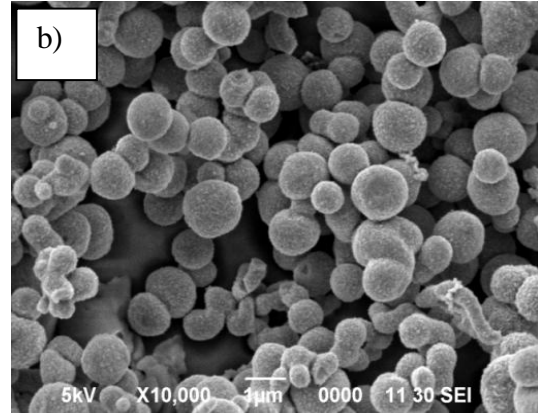
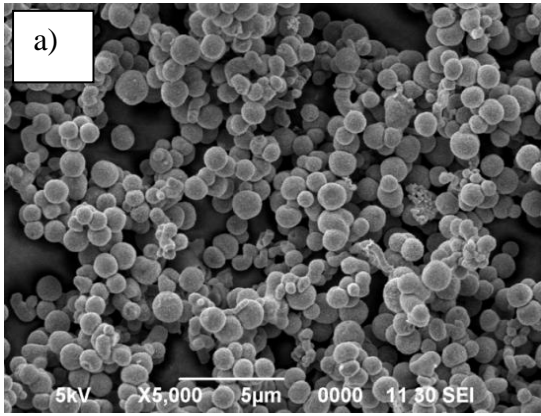


Figure 6: SEM micrographs of CuS/agar film, a) and b) 39.58 mg/L/cm^2 Cu concentration and c) and d) 67.05 mg/L/cm^2 Cu concentration in water dispersion at 5,000x and 10,000x magnifications respectively.