Facile synthesis of 3D printed tailor-shape electrode ABS-GnP for electrochemical sensing

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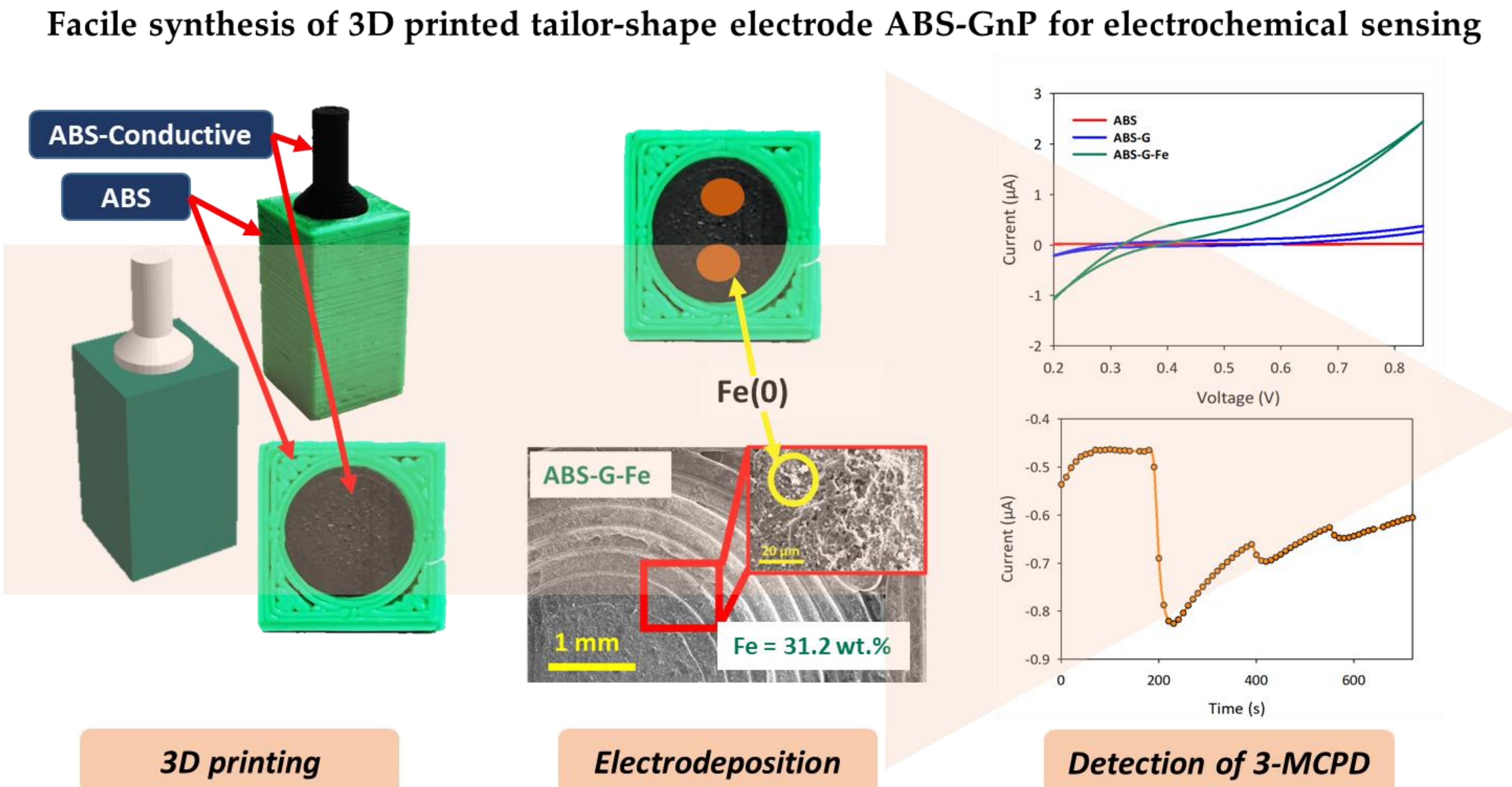
Graphical Abstract



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Abstract: Additive manufacturing (AM) makes enormous advancements in technology and materials development, thus requires attention in developing functionalized printed materials. AM can assist in manufacturing complex designed tailored-shaped electrodes efficiently for electrochemical sensing in the food industry. Herein, we used commercial fused deposition modelling (FDM) filament, acrylonitrile butadiene styrene (ABS) for FDM 3D printing of self-designed electrode with minimal time and cost compared to commercial electrodes. Surface functionalization on the 3D printed ABS electrode was done using GnP to enhance the electrical conductivity. Scanning electron microscopy confirms the homogenized surface coating of GnP that provides electron flow behaviour for the 3D printed electrode. The electrochemically functionalized 3D printed electrode was tested against standard 3-monochloropropane-1,2-diol (3-MCPD) with known concentrations and characterized using cyclic voltammetry and differential pulse voltammetry methods. Results showed a basis for promising application to detect and quantify 3-MCPD, a food contaminant known for its potential of being carcinogenic. Fabrication of functionalized 3D printed polymer electrodes paves way for the development of complete 3D-printable electrochemical systems.

Keywords: additive manufacturing; fused deposition modelling; polymer; palm oil contaminant; cyclic voltammetry

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Problem Statement

REUTERS

June 5, 2020

European move to ban palm oil has become a heat argument among Malaysia palm oil stakeholders as Malaysia is the second largest palm oil exporter in the world. [1]

Effects

1.9 million tonnes palm oil cannot be exported

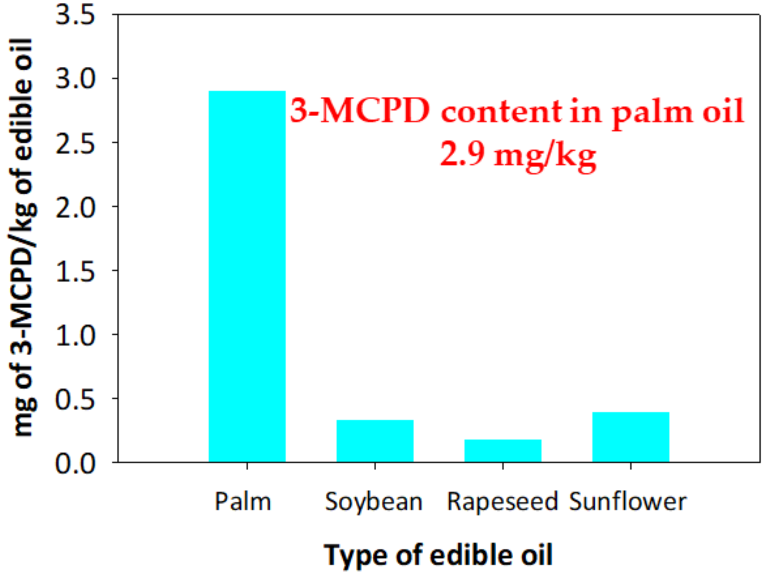
RM 10 billion revenue loss per year

Why ban palm oil?

3-MCPD (3-monochloropropane-1,2-diol) – food contaminant that is carcinogenic.

(Total dosage intake: 2 μg/kg body weight for EU and US)

Palm oil has comparatively higher 3-MCPD content at 2.9 mg/kg compared to other edible oils (e.g. soybean, rapeseed and sunflower oil). [2]



[1] https://www.reuters.com/article/malaysia-palmoil idUSL4N2DH2FM
[2] https://www.gea.com/en/articles/3-MCPD/3-MCPD-esters-in-palm-oil.jsp

Problem Statement

How palm oil has highest 3-MCPD content?

3-MCPD does not occur naturally in palm oil.

3-MCPD formed in palm oil during chemical reaction in the deodorization stage.

Chloride + lipids glycerol ➡ 3-MCPD

Why only deodorization process?

Chloride presence water at high temperature in contact with the palm oil will trigger the formation of 3-MCPD at the process.

3-MCPD monitoring steps at refining process?

Instrumental methods using GCMS which is not immediate, time consuming and expensive.

Palm oil refining process

Crude palm oil
↓
Filtration
↓
Degumming
↓
Deacidification
↓
Decolourization
↓
DEODORIZATION
↓
Fractionation
↓
RBD palm oil

Commercial potentials

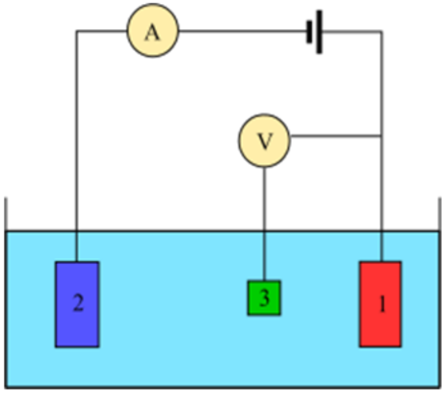
- ❑ A transducer that can be modified with any type of recognition element
- ❑ Simple and low-cost production of an electrochemical sensor

Introduction

Electroanalytical methods have been increasingly preferred to cater for various type of industries (eg. food, fuel and environmental sciences).

Advantages over instrumental methods:

- ✓ Sensitivity
- ✓ Portability
- ✓ Low-cost instrumentation
- ✓ High speed testing



Electroanalytical methods

Electroanalytical methods

- the species of interest in an analytical test–by quantification of current and/or potential within an electrochemical cell.

Objectives of this research

- create electrochemical analysis method for detection and monitoring of 3-MCPD in palm oil with integration of 3D printing technology

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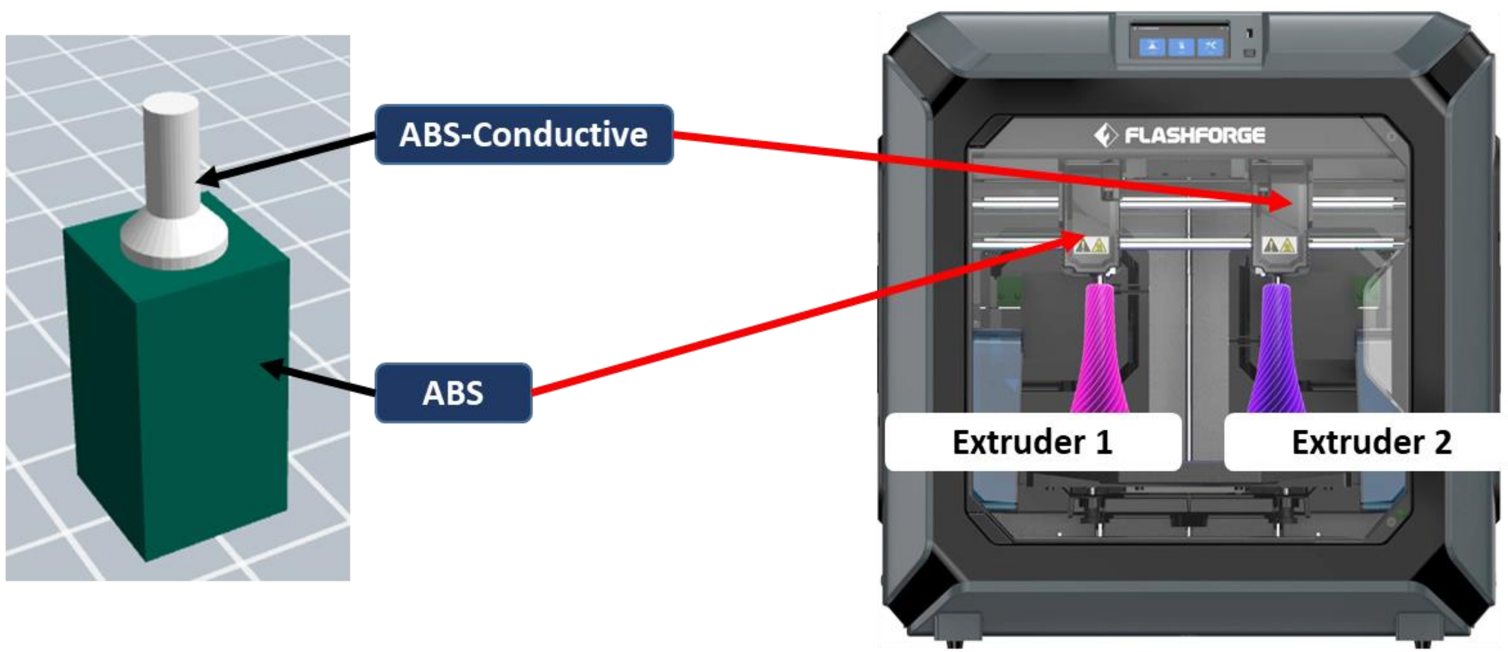
Introduction

<u>3D printing</u> – emerging technology in development of novel materials and devices for wide range of applications including <u>Electrochemistry and Analytical Chemistry</u> areas.

FDM Dual extrusion technology – provides the opportunity to reinforce and create a system with tailored design.

One extruder can print the nonconductive ABS material while the other extruder can print specific ABS conductive material for designated area electrochemical sensing.



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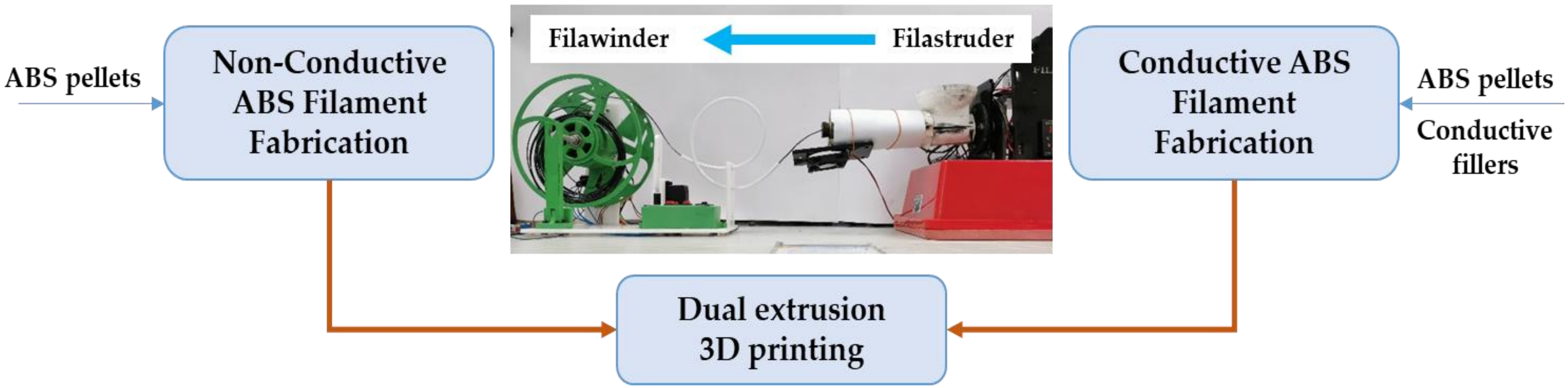
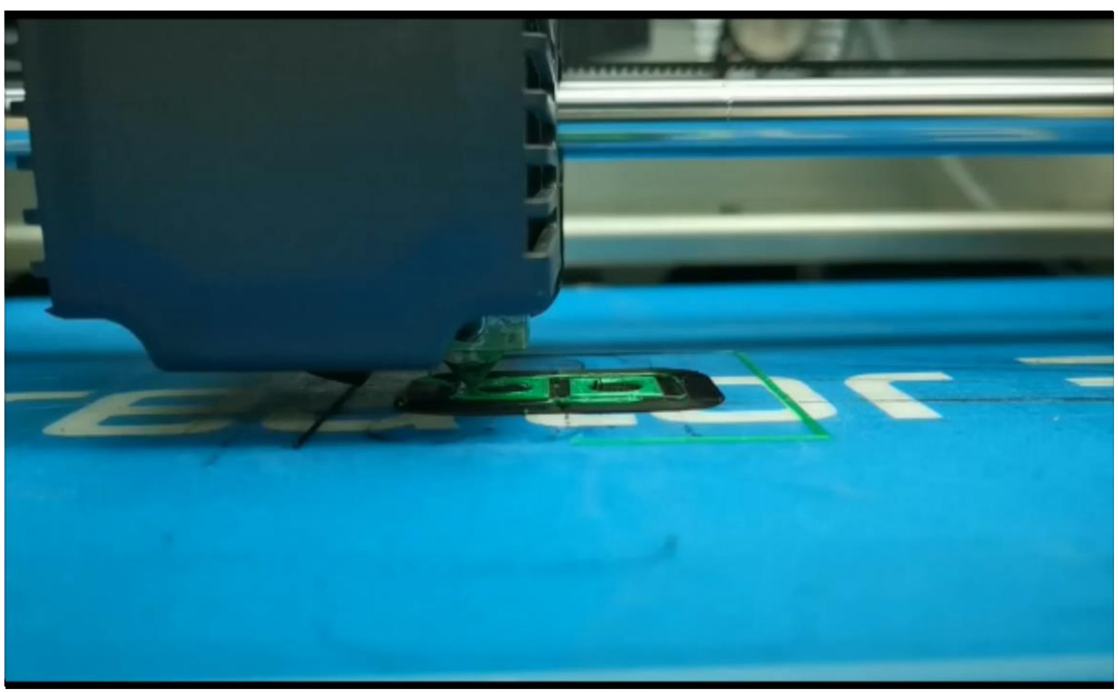
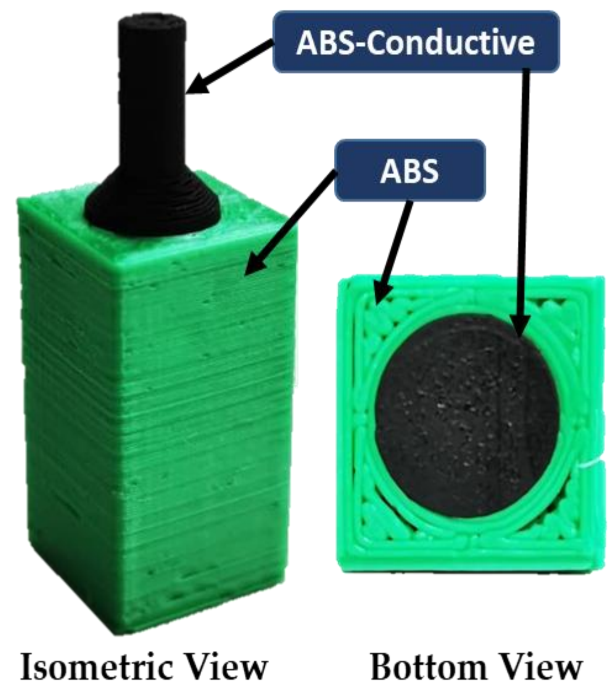
Research Methodology

3D printed electrode fabrication flowchart

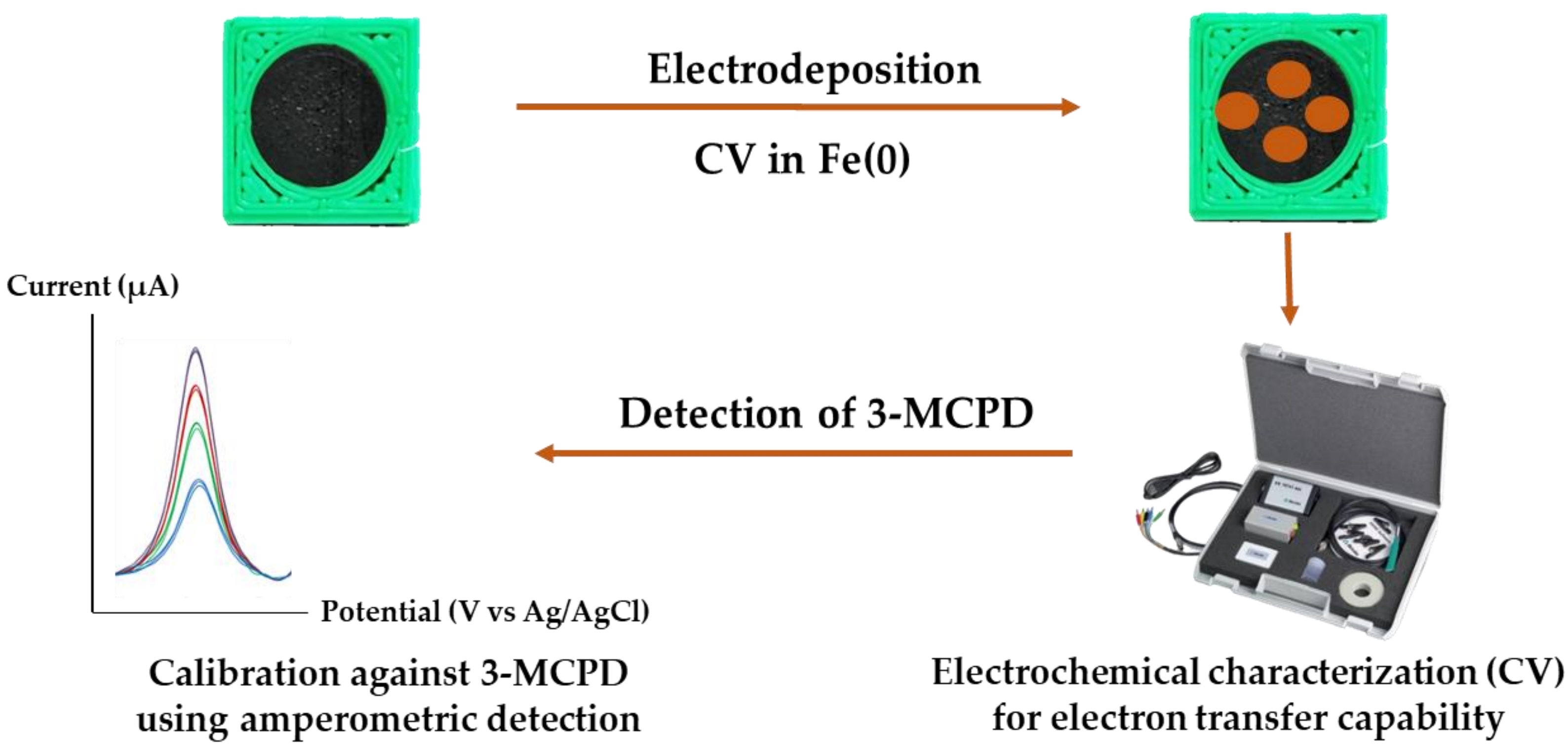


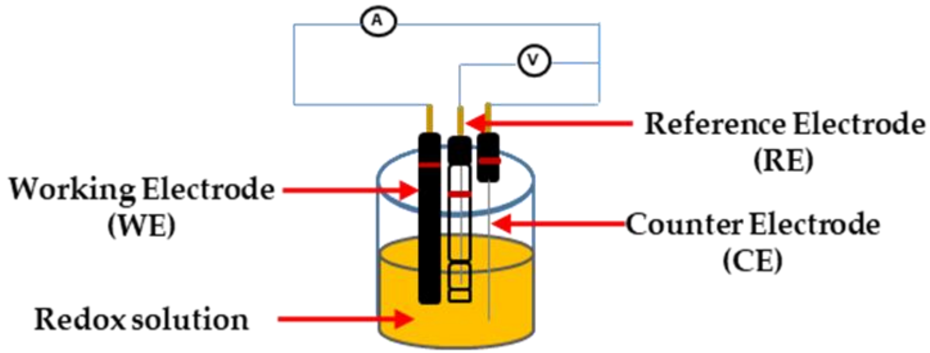




Research Methodology

Electrochemical sensing of 3-MCPD





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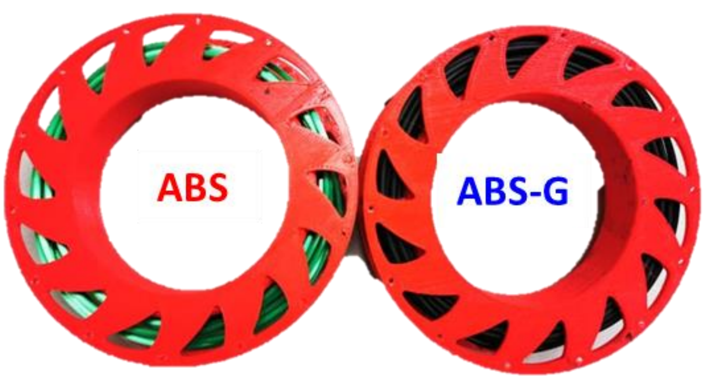
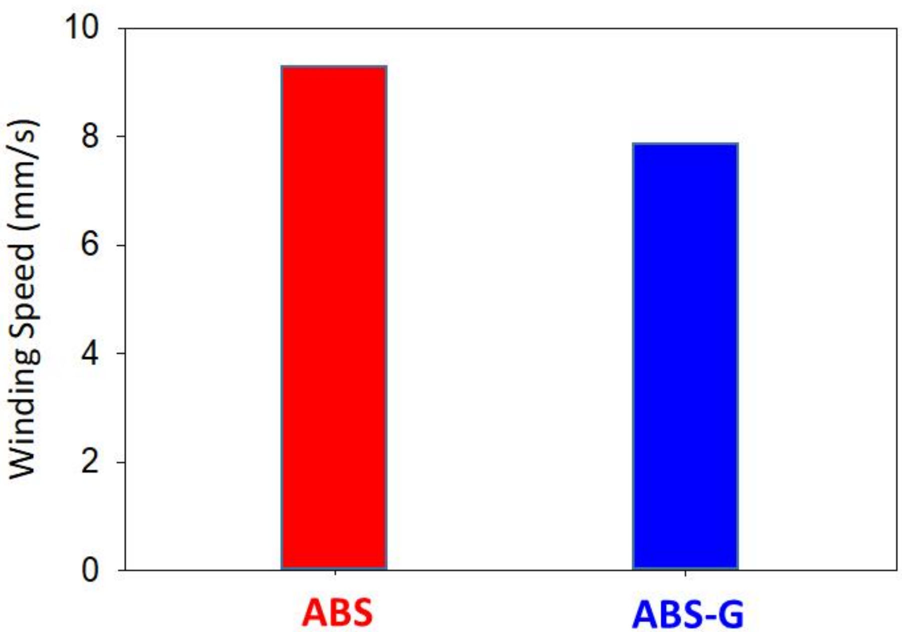
Results and Discussions

Physical Compatibility of Conductive Fillers

Extrusion of Composite Filament

1. Incorporation of graphene in the ABS pellets has increased the shear rate of the material
2. The flowability of the composite gets reduced and melt viscosity for the ABS conductive composite.
3. The winding speed has to be adjusted lower to compensate for obtaining filament diameter close to desired 1.75 mm.



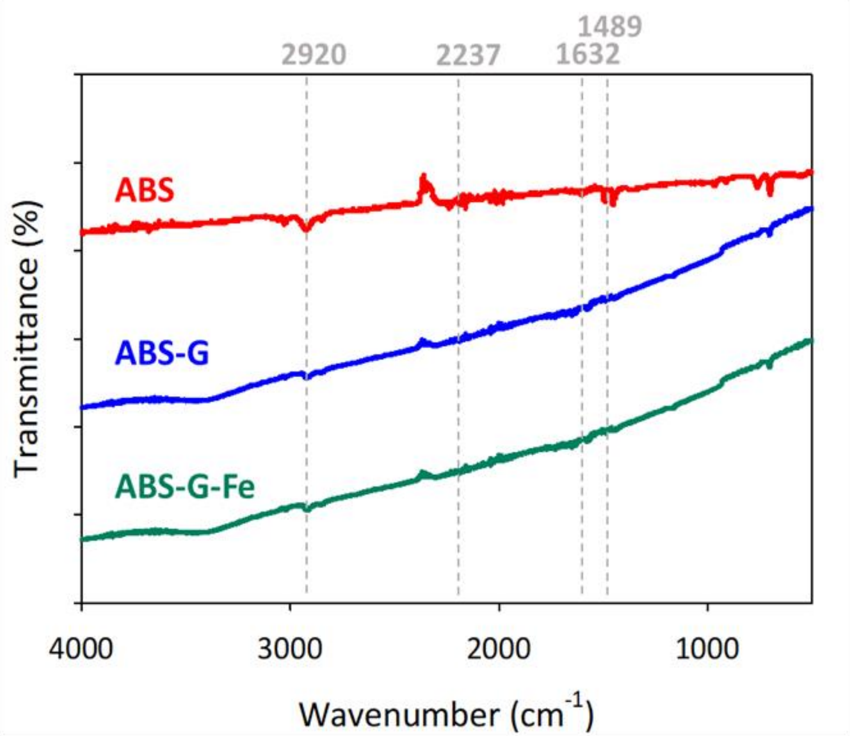


Results and Discussions

Chemical Characterization of 3D printed composite

FTIR

1. Aromatic and aliphatic stretching of –CH in ABS can be observe at wavelength of 3000 – 3200 cm^{-1} and 2920 cm^{-1}.
2. C=C bonds at 1632 and styrene unit at 1489 cm^{-1}
3. Incorporation of fillers such as graphene and surface functionalisation of Fe^{2+} did not alter the chemical structure of ABS.



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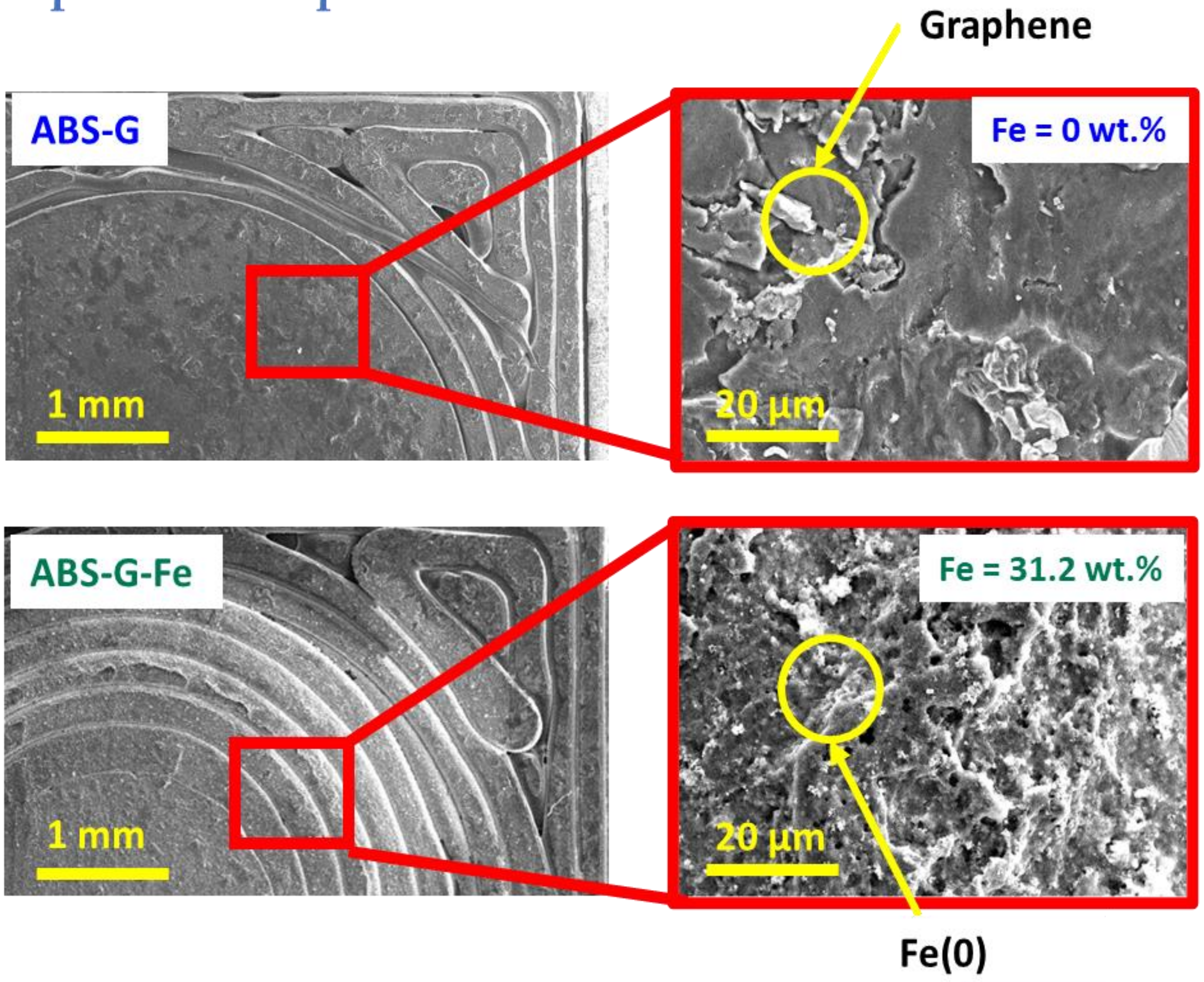
Results and Discussions

Chemical Characterization of 3D printed composite
SEM-EDX

1. There were significant increment in Fe from 0 to 31.2 wt.% showing effective electrodeposition of Fe(0) on the 3D printed ABS-G electrode.

2. The electrodeposited Fe(0) will help in increasing the selectivity of the printed electrode for detection of 3-MCPD.



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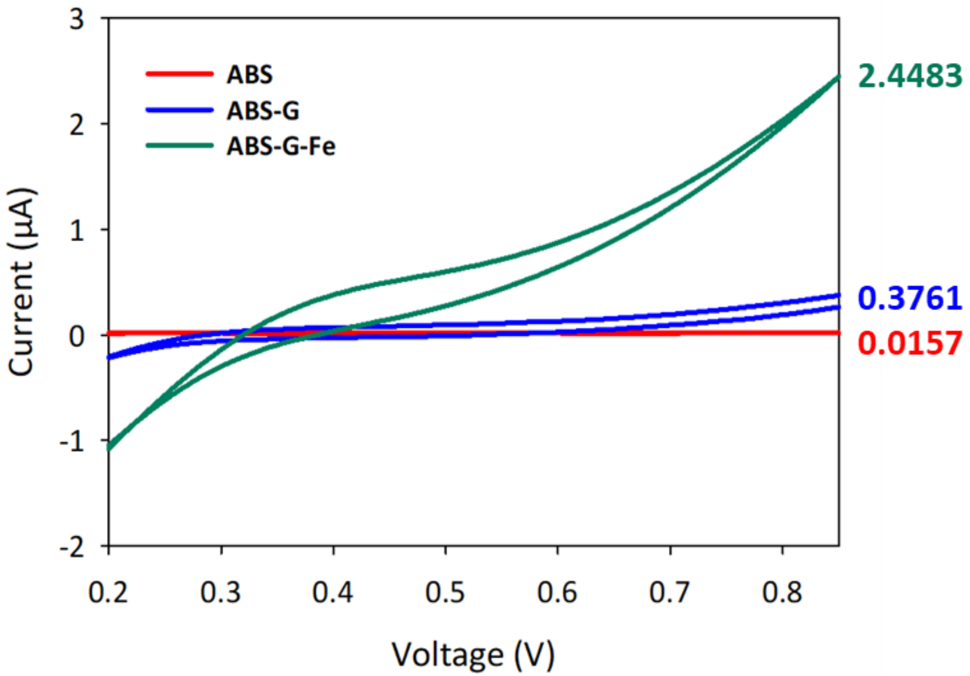
Results and Discussions

Electrochemical analysis of 3D printed electrode

Cyclic Voltammetry (CV)

1. Voltammograms of ABS shows negligible oxidation and reduction reaction indicating the non conductive behaviour of ABS in $Fe(CN)_6$ redox solution.
2. Extrusion of ABS with graphene enhanced the conductivity of the ABS-G composite shown by the increment in redox current.
3. Electrodeposition of Fe(0) shows the desirable oxidation and reduction curves for the 3D-printed electrode with electron flow behaviour.



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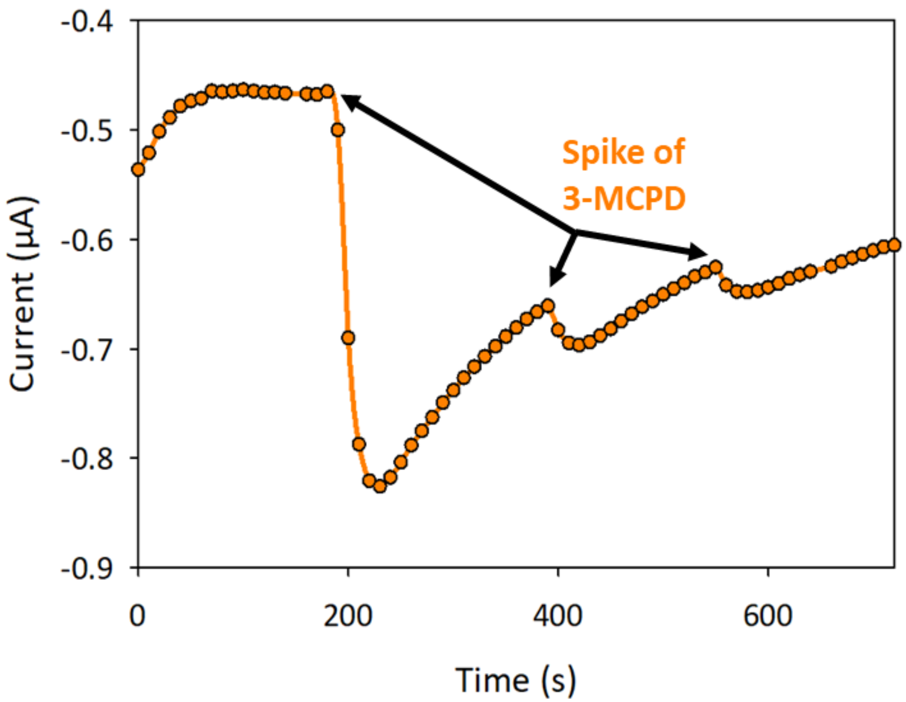
Results and Discussions

Electrochemical analysis of 3-MCPD

Amperometric Detection

1. Calibration was performed using amperometric detection in DI water with sequential addition of 3-MCPD in specific interval.
2. Results showed sudden change in current upon addition of 3-MCPD. Bubbles were also observed at the tip of the electrode. This shows electrochemical reaction as constant voltage was applied throughout the experiment.
3. Therefore, the modified transducer showed promising application towards 3-MCPD detection in water environment.



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Conclusions and Future Works

1. 3D printing technology could be utilised in electrochemical sensing applications by incorporation of conductive fillers/nanomaterials in commercially available polymers.

2. Further functionalisation by electrodeposition on 3D printing materials could enhance the redox capability of the tailor designed 3D printed products.

3. The functionalised 3D printed transducer showed promising application towards 3-MCPD detection and paving way towards rapid and cheap electrochemical sensing of contaminants in palm oil.

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Acknowledgments

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