UNIVERSITI PUTRA MALAYSIA

PREPARATION OF 3D NANOSTRUCTURED POROUS GRAPHENE FRAMEWORK FOR OIL SORBENT APPLICATION

NURUL AQILAH POHAN BT TARMIZI POHAN

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PREPARATION OF 3D NANOSTRUCTURED POROUS GRAPHENE FRAMEWORK FOR OIL SORBENT APPLICATION

By

NURUL AQILAH POHAN BT TARMIZI POHAN

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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NURUL AQILAH POHAN BT TARMIZI POHAN

July 2021

Chairman : **Mohd Haniff Wahid, PhD**
Faculty : **Science**

The preparation of graphene in three-dimensional (3D) mode serves as an alternative to maintain its characteristically large surface area, which under normal circumstances, is diminished by the restacking of the individual graphene sheets. In addition, 3D graphene enables the surface area to be reserved and combined with void spaces, the potential as an oil absorbent material is anticipated.

In this study, 3D graphene oxide (3D GO) was prepared from the Pickering emulsion of GO in water/toluene mixture. The Pickering emulsion was first prepared by mixing toluene (9.35 M) and water in the presence of graphene oxide (2 mg mL^{-1}). The trapped solvents were then removed by freeze-drying thus forming porous structure. At PVA content 30%, 120 minutes of sonication and thermal reduction temperature of 150 °C for 30 minutes, the targeted surface area improvement was observed where the surface area of 3D GO obtained is 104 $m^2 g^{-1}$ compared to the surface area of GO in 2D form which is 36 $m^2 g^{-1}$. Oil absorption capacity obtained is 145 g g^{-1} which is on par with other graphene-based oil absorbent.

As confirmed by scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and Brunauer-Emmett-Teller (BET), the 3D GO displayed dual pore size distributions of macropores and mesopores where porosity value of 0.95 obtained from bulk density of 0.03 g mL^{-1} ratio to particle density of 0.60 g mL^{-1}. The reusability study meanwhile shows at capacity of 145 g g^{-1} to 55 g g^{-1} ten repetition sorption-desorption cycle, the 3D GO able to be reuse although downfall significantly.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN STRUKTUR NANO BERLIANG GRAFIN 3D SEBAGAI BAHAN PENJERAP MINYAK

Oleh

NURUL AQILAH POHAN BT TARMIZI POHAN

Julai 2021

Pengerusi : Mohd Haniff Wahid, PhD
Fakulti : Sains

Penghasilan grafin dalam mod tiga dimensi (3D) menjadi alternatif bagi mengekalkan ciri luas permukaan tinggi grafin, yang pada kebiasaannya terjejas akibat pencantuman semula lapisan helaian individu grafin. Tambahan pula, melalui penstrukturan grafin 3D membolehkan kawasan permukaan disimpan dan apabila digandingkan bersama ruang rongga yang lompong maka penggunaan sebagai bahan penjerap adalah dinantikan.

Dalam kajian ini, grafin oksida 3D (3D GO) telah disediakan daripada emulsi Pickering grafin oksida dalam larutan air/toluena. Penyediaan emulsi Pickering dimulakan dengan mencampurkan pelarut toluena (9.35 M) dan air dengan kehadiran grafin oksida (2 mg mL^{-1}). Pelarut yang terperangkap dikeluarkan menggunakan pengering beku yang menghasilkan pembentukan struktur berliang. Pada kandungan PVA 30%, 120 minit tempoh sonikasi dan suhu termal 150 °C untuk 30 minit, kawasan permukaan yang disasarkan telah diperhatikan dimana pada 3D GO adalah 104 m^2 g^{-1} manakala bagi kawasan permukaan GO dalan bentuk 2D adalah 36 m^2 g^{-1}. Kapasiti serapan minyak adalah 145 g g^{-1} setanding dengan bahan penjerap minya grafin yang lain.

Seperti yang dibuktiktikan melalui imej mikroskopi pengimbasan elektron (SEM), porosimetri merkuri (MIP) dan Brunauer-Emmett-Teller (BET), 3D GO memaparkan taburan saiz liang dwi-model iaitu makro dan meso dengan nilai keliangan 0.95 yang diperoleh melalui ketumpatan pukal 0.03 g mL^{-1} nisbah kepada ketumpatan zarah 0.60 g mL^{-1}. Manakala, kajian keupayaan penggunaan semula menunjukkan sebanyak 145 g g^{-1} sehingga 55 g g^{-1} sepuluh ulangan kitaran penyerapan-penyahjerapan, 3D GO boleh digunakan semula walaupun mengalami penurunan yang ketara.

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I certify that a Thesis Examination Committee has met on 22 July 2021 to conduct the final exanimation of Nurul Aqilah Pohan Bt Tarmizi Pohan on her thesis, entitled “Preparation of 3D Nanostructured Porous Graphene Framework for Oil Sorbent Application”, in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Shahrul Ainlianh Binti Alang Ahmad, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Suzana Binti Yusop, PhD
Professor, IR
HICoE Center for Biofuel & Biochemical Research
Universiti Teknologi Petronas
Malaysia
(External Examiner)

Zuriati Ahmad Zukarnain, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as partial fulfillment of the requirements for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Mohd Haniff bin Wahid, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zulkarnain bin Zainal, PhD
Professor, ChM
Faculty of Science
Universiti Putra Malaysia
(Member)

Nor Azowa binti Ibrahim, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

____

ZALILAH MOHD SHARIF, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 9 March 2022

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of the thesis were under our supervision;
- supervisory responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2012) are adhered to.

Signature: __________________________
Name of Chairman of Supervisory Committee: Mohd Haniff Wahid

Signature: __________________________
Name of Member of Supervisory Committee: Zulkarnain Zainal

Signature: __________________________
Name of Member of Supervisory Committee: Nor Azowa Ibrahim

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LIST OF ABBREVIATIONS

GO	Graphene oxide
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
PVA	Poly Vinyl Alcohol
MIP	Mercury Intrusion Porosimetry
BET	Brunauer-Emmett-Teller
r-GO	reduced graphene oxide
3D	Three-Dimensional
3D GO	Three-Dimensional Graphene Oxide
3D r-GO	Reduced Three-Dimensional Graphene Oxide
CVD	Chemical Vapour Deposition
GA	Graphene aerogel
wt %	weight percent
PU	Polyurethane
PDMS	Polydimethylsiloxane

CHAPTER 1

INTRODUCTION

1.1 Research background

The idea of constructing a 3D GO structure can be visualized as arrangement of the 2D graphene sheets in space to form a three-dimensional structure. This is particularly important for the preservation of the enormous surface area of graphene and the simultaneous incorporation of porosity into the system (Nardecchia et al., 2013). Therein, the empty spaces present within the sheets may act as pores that can be utilized for sorption purposes (Fig. 1.1) (Hiew et al., 2018). Thus far, the use of 3D graphene has already featured in several industries of electrochemical energy storage (Mao et al., 2015), bioelectronics devices (Qiu et al., 2017), gas storage (Dos Santos et al., 2017), sensors (Qiu et al., 2017), and catalysis (Fan et al., 2015).

The 3D GO configuration theoretically constitutes a multi-level, interconnected porous architecture comprised of micropores, mesopores and macropores. In this regard, both microporosity and mesoporosity renders graphene the high surface area property and acts as side branches for the larger pores to which facilitate oil retention, while macroporosity provides easy access of bulky molecules into the sorbent material (Nardecchia et al., 2013). Overall, in general, such hierarchical porous structures are desirable due to their immense potentials to enhance adsorption properties, catalysis performance, drug delivery and energy applications (Fig. 1.2) (Wu et al., 2021, Dutta et al., 2014).

Being abundant in nature, carbon-based material holds potential to be developed as functional materials for the future. This includes its possibility to be utilized for sorbent applications. To date, different types of carbon derived products have been studied and used as sorbent materials, namely, activated carbon, carbon nanotubes, soot, graphite, and graphene (Gupta et al., 2016).

Figure 1.1: Illustration diagram to construct 3D graphene from graphene layers. The construction of graphene in 3D mode can allow the full utilisation of surface area due to suppressed restacking of the sheets. (Image taken from Hiew et al., 2018)

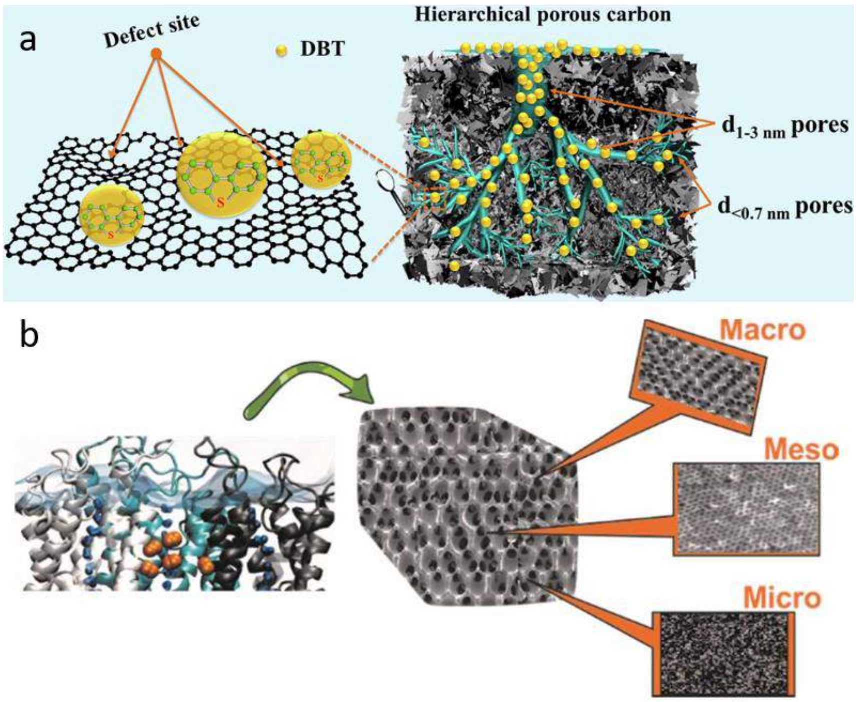

Figure 1.2: Schematic illustration of hierarchical porous carbon featuring in a) desulphurisation and b) energy applications. (Image taken from Wu et al., 2021 and Dutta et al., 2014)

1.1.1 Background research of graphene-based material

Graphene is a chemically inert carbon allotrope with a theoretical surface area of 2630 m^2/g, making it a promising candidate for absorbent material development. It was first isolated by A.K. Geim and K.S. Novoselov in 2004 via the mechanical exfoliation ("Scotch-tape" method) of bulk graphite (Novoselov et al., 2004). Since then, concentrated efforts were made in synthesis and modification of graphene and its derivative and towards exploring its various potential applications (Alkhouzaam et al., 2020, Yu et al., 2020, Marcano et al., 2018). Nevertheless, the utilisation of graphene is bound to the isolation of its monoatomic layers in which the Van der Waals interaction promotes restacking, hence limiting its large surface area characteristic (Gupta et al., 2015).

Several works have been reported on the preparation of 3D graphene using different techniques of which can be classified into template-based and template-free method. Examples of template-based 3D graphene preparation techniques are such as polymer framework carbonization (Patil et al., 2016), chemical vapour deposition (CVD) (Sha et al., 2016) and template-assisted hydrothermal (Yin et al., 2014). These techniques, however, are associated with high production costs and involves template-removal step at the end of the process (Hiew et al., 2018). Alternatively, soft template or template-free method could possibly lower the production cost through alleviation from the use of hard substrate. This includes the use of Pickering-emulsion technique where foams are utilised as template to form hollow structures.

Application of Pickering emulsion technique in different product manufacturing industries and research has started to gain popularity owing to its hard template-free design (Low et al., 2020) and offering more control towards manipulation of the 3D microstructure (Chen et al., 2014). One of the pioneering works of developing 3D graphene using this method was carried out by Chen et al. (2014) by introducing amphiphilic graphene oxide sheets to the water/toluene system followed by sonication to establish a long-lasting Pickering emulsion. After the removal of the trapped solvent a 3D hollow graphene oxide structure was obtained (Chen et al., 2014). The resultant 3D graphene featured as light-brown coloured foam-like material which is highly porous.

1.2 Research problems and motivation

Several intervention approaches were identified to retain the large surface area characteristic of graphene. One of the most effective and practical to date is by introducing oxygen-rich functional groups on the surface of graphene which increases its interlayer spacing and helps stabilizes graphene in aqueous and common organic solvents (Rajaura et al., 2016). Even though certain appealing characteristics of graphene such as high mechanical strength and excellent electrical conductivity were altered as a result of oxidation, graphene can still be reduced back to recover its properties (De Silva et al., 2017). Meanwhile, very recently another alternative approach to preserve the large surface area characteristic of graphene was introduced, namely, formation of 3D graphene (Hiew et al., 2018). By constructing graphene in three-dimensional mode, the restacking of graphene sheets is suppressed, hence enabling the utilization of graphene's large surface area (Hiew et al., 2018).

1.3 Significance and impacts of the research

In this study, the method of preparing 3D graphene adopts the method used by Chen et al. (2014) but with additional modifications. Since the 3D graphene developed in this study carries the prospect for absorbent application, the microstructural and surface properties of the sample have been given focus. The Pickering emulsion approach was chosen to allow the control of desired microstructures, phase composition and surface chemical properties. This approach lowers the production cost through alleviation from the use of hard substrate and the foams are utilised as template to form hollow structures. On top of Chen's developed method, we have incorporated thermal treatment step to recover the hydrophobic property of graphene, as well as studying the effects of different preparation conditions, namely, the addition of cross-linking agent i.e., PVA at different content, sonication time, and thermal reduction temperature. Sonication plays an important role in forming smaller size of oil droplets which contributes to the stabilisation of the Pickering emulsion formed. The sonication was performed at fixed frequency of 40 kHz at different time duration to determine the appropriate processing time. Furthermore, the 3D r-GO's sorption capacity and regeneration ability against different types of oils and organic solvents were also reported herein.

1.4 Objectives

The objectives of this work are as follows:

1. To develop, characterize and identified optimum parameter of the 3D r-GO foams which encompasses the aspects of surface area, porosity, morphology and response towards oil absorption capacity.
2. To evaluate the versatility of 3D r-GO foams as sorbent material over diverse types of organic solvents and oils.
3. To assess an ability of 3D r-GO for regeneration as absorbent material and collect the extracted used engine oil.

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