Faculty of Manufacturing Engineering

SYNTHESIS AND CHARACTERIZATIONS OF PHOSPHORENE ADDED GRAPHENE PREPARED VIA SOLID STATE REACTIONS

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SYNTHESIS AND CHARACTERIZATIONS OF PHOSPHORENE ADDED GRAPHENE PREPARED VIA SOLID STATE REACTIONS

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DECLARATION

I hereby, declared this report entitled “Synthesis and Characterizations of Phosphorene Added Graphene Prepared Via Solid State Reactions” is the result of my own research except as cited in references.

Signature :

Name : SOONG MENG KEONG

Date : 9/2/2022

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in term of scope and quality for the award of Master of Manufacturing Engineering (Industrial Engineering).

Signature :

Supervisor Name : DR MOHD SHAHADAN BIN MOHD SUAN

Date : 9/2/2022

DEDICATION

This report is dedicated to my beloved parents,

who educated me and enable me to reach this level.

To my honoured supervisor,

Dr. Mohd Shahadan Bin Mohd Suan

for her advices, support and patience during completion of this project

and to all staffs & technicians,

for their advices and cooperation to complete this project.

Thank You So Much & Love You All Forever

ABSTRACT

Graphene-based hybrid materials have been extensively used in widely range application such as electronic mobility, energy storage, electrochemical application and sensing device. Many of energy storage system of devices involved of graphene reinforce metal or polymer matrix composites for enhance electrical conductivity, energy storage performance and the energy capacity storage. Graphene been chosen as potential material due to its unusual electrical and mechanical properties such as large surface is for better movement of electrical charge and discharge, tensile strength are high and excellent electric conductive materials. The phosphorene used to overcome graphene theoretical value of the low energy capacity due to the graphene powder aggregation. Phosphorene, exfoliation of single layer black phosphorus possessed similar atoms with graphene where its stable in electrical conductivity and is most stable allotrope of the phosphorene with van der-Waals heterostructures are compatibles with graphene to perform a strong bonding of structure. In this research, solid state reaction is used for stability of both materials, graphene and phosphorene hybrid as well as to avoid the restacking graphene layer to cause large surface energy affected the ions storage capacity. Apart from that the method advantage low energy consumption and avoid chemical reaction process. The research will prepare phosphorene/graphene concentration ratio that is 02:1, 0.4:1, 0.6:1, 0.8:1, and 1:1 in solid state reaction method. The samples will be characterized of it structural properties by using XRD, FTIR and SEM while the investigation on energy storage performance include its electrical conductivity will be conducted by using four-point probe equipment correlation with correction factor formula.

ABSTRAK

Bahan hibrid berasaskan graphene telah digunakan secara meluas dalam pelbagai aplikasi seperti mobiliti elektronik, penyimpanan tenaga, aplikasi elektrokimia dan peranti penderiaan. Banyak sistem storan tenaga peranti yang terlibat dengan graphene mengukuhkan logam atau komposit matriks polimer untuk meningkatkan kekonduksian elektrik, prestasi penyimpanan tenaga dan storan kapasiti tenaga. Graphene telah dipilih sebagai bahan berpotensi kerana sifat elektrik dan mekanikal yang luar biasa seperti permukaan yang besar adalah untuk pergerakan cas dan nyahcas elektrik yang lebih baik, kekuatan tegangan adalah bahan konduktif elektrik yang tinggi dan sangat baik. Phosphorene digunakan untuk mengatasi nilai teori graphene kapasiti tenaga yang rendah disebabkan oleh pengagregatan serbuk graphene. Phosphorene, pengelupasan satu lapisan phosphorus hitam mempunyai atom serupa dengan graphene di mana ia stabil dalam kekonduksian elektrik dan alotrop phosphorene paling stabil dengan heterostruktur van der-Waals adalah serasi dengan graphene untuk melakukan ikatan struktur yang kuat. Dalam penyelidikan ini, tindak balas keadaan pepejal digunakan untuk kestabilan kedua-dua bahan, graphene dan phosphorene hybrid serta untuk mengelakkan lapisan graphene yang menyusun semula untuk menyebabkan tenaga permukaan yang besar menjejaskan kapasiti penyimpanan ion. Selain daripada itu kaedah ini memanfaatkan penggunaan tenaga yang rendah dan mengelakkan proses tindak balas kimia. Penyelidikan akan menyediakan nisbah kepekatan phosphorene/graphene iaitu 02:1, 0.4:1, 0.6:1, 0.8:1, dan 1:1 dalam kaedah tindak balas keadaan pepejal. Sampel akan dicirikan sifat strukturnya dengan menggunakan XRD, FTIR dan SEM manakala penyiasatan ke atas prestasi penyimpanan tenaga termasuk kekonduksian elektriknya akan dijalankan dengan menggunakan korelasi peralatan kuar empat mata dengan formula faktor pembetulan.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Revolution and development in industries with continuously improve technology and getting more and more involvement of automation and machines interact with human works, most materials such as in good conductive in electricity always been attractive and main focus by many researchers and developers due to its properties and characteristic which beneficial to variety applications. Energy storage development have been extensively studies and approached due to its ability for those tool, machines and equipment which support in high voltage devices, fast charging capabilities and wireless functionality devices. In today's world due to increase in demand for clean energy storage, hybrid vehicle and electronic devices raise attention on graphene-based material which provide good power density, resistance of temperature are high and long cycle life. In past of decades, graphene 2-dimensional (2D) material become most representative material that have been focused by many researchers due to its potential for applications of sensing, electrical, energy storage and catalysis. Graphene-based materials review on electrochemical energy storage such as lithium-ion and supercapacitor opportunities and challenges (Lv, W et al.,2016). Composites of graphene based able to combine the advantages of its graphene component with the electrochemical materials in order to obtain superior performance of the electrochemical applications (Wang, et al., 2019). A study on flexible energy storage in nanostructured graphene-based material pivotal advantages in modern electronic applications. Among of 2D materials, the nanostructured of the graphene-based exhibit good flexibility due to the possess of good mechanical strength when graphene fibers 1-dimensional, 2D graphene films and

3-dimensional graphene foam aligned and stack together in axial fiber direction (Guo et al.,2017). For energy storage, generally thermal energy is high when it operates using sensible heat and storing latent principles which affect low thermal conductivity. Therefore, in order to enhance the thermal energy storage efficiency, graphene composites work with energy storage materials (Azadmanjiri et al., 2018).

Arise interest on phosphorus, it possessed super conductivity when it come with critical temperature of 4 to 10K which presumably when it's in rhombohedral forms with high pressure cubic. However, the black phosphorus has a difficulty to controlling quality of materials and due to its diminutive bandgap of 0.3eV resulted less popular and discovery of graphene exfoliation development together with others thin-layer process to lead back the interest of black phosphorus which observed of it element is most stable allotrope than white and red phosphorus under normal condition of pressure and temperature (Carvalho et al., 2016). When black phosphorus in high temperature where intrinsic semiconductor form can obtain 0.33eV bandgap. From starting 21st century, black phosphorus material has been conducted by researcher to recognize as precursor due to its advantages for 2D materials, phosphorene, which has special properties and structure. Many investigations were conducted on potential application by using phosphorene after predict mechanical stability, optoelectronic and band gap variation (Ren et al., 2017). To define phosphorene, orthorhombic structure of phosphorene along with puckering characteristic, set aside from most of 2-dimensional material like graphene to from abnormal mechanical properties such as Poisson's ratio with negative value. There are also investigation of application phosphorene/black phosphorus towards devices storage and its energy conversion show the anisotropy structure play important roles in such as photovoltaic cells, lithium batteries and supercapacitors due to its large spacing of the layer phosphorene and its easy surface reaction (Pang et al., 2017).

Thus, in this research will be investigate the effect of the phosphorene concentration on the energy storage behaviour of phosphorene/graphene powder by using solid state reaction method. The characterizations by using XRD, FTIR and SEM on structural properties of phosphorene/graphene powder while the conductivity performance will be investigating via 4-point probe.

1.2 Problem Statement

Graphene-based materials provided unique characteristics and functionalities such as mechanical properties of Young modulus approximately reach 1TPa Young's module as well as intrinsic strength reach approximately 130 GPa. Graphene has a high surface area allows high electron mobility under room temperature which advantages to energy storage application in industry 4.0. However, graphene theoretically can't serve the energy storage efficiently and effort to stack up graphene nanosheets due to the weak attraction of van der Waals between single layers of the graphene. As the result, the specific of surface area is reduced affected the electrode and electrolyte less ion exchange and interaction. Restacking of graphene sheet to sheet cause rapid loss of the transportation ion charge/discharge as well as serious aggregation occur in thin film of polymer. To prevent less energy storage efficiency and increase to maximum capacity of energy storage, layer of graphene to be separated and obtain good atomic distribution by using 2D monolayer material to interfacial with graphene layers. The chosen of the materials should have strong ion bond which won't lower energy storage capacity and similar atomic structure to provide good reaction with graphene in order become separator of graphene monolayers. Thus, phosphorene to be proposed and bulk of black phosphorus can be exfoliated to produced monolayer phosphorene with stable due to black phosphorus is most stable allotrope among white and red phosphorus under normal temperature and pressure. Currently, phosphorene anode performance able to overcome 2D materials issue properties and characteristic such as control surface/interface electronic structure and segregation of atomic layers. The improvement of electrochemical performance associate phosphorene which comparable properties with allotrope of carbon material like graphene in term of in term of ultrahigh surface are, excellent conductivity in electrical and high carrier mobility as well as show quantum confinement effect able to surmount the large volumetric change and poor electroconductibility. Although phosphorene has wide range interesting properties lead to potential application but instability black phosphorus against air is a concern and degradation of black phosphorus pristine under reaction with aqueous oxygen affect material change properties in physical and chemical. Thereby, ball mill synthesis method on black phosphorus avoided high temperature need in the process sealed in stainless

steel crucible which produced very fine powder (less than or equal 10microns of the particles size) and this culminates into production with good stability of evenly dispersed solid.

1.3 Objective

1) To synthesize a series of phosphorene/graphene powder via solid state reaction.
2) To characterize structural properties of phosphorene/graphene powder by using XRD and SEM.
3) Identifies the chemical bonds of the phosphorene/graphene powder compositions by using FTIR Spectroscopy determine through spectrum data.
4) Investigate electrical conductivity of phosphorene/graphene powder through four-point probe equipment and correlation with correction factor formula.

1.4 Scopes of the Research

The research of phosphorene concentration on the energy storage behaviour of phosphorene/graphene powder focused on the characterization of structural properties, measure the conductivity and the chemical bonds for the energy storage application in lithium ion. Red phosphorus turns black phosphorus synthesized via mechanical ball mill method and the synthesis of phosphorene/graphene powder using solid state reaction method due to this method provided stability for both materials involved. Phosphorene/graphene concentration parameter using different ratio 1.2:1, 0.6:1, 0.8:1, and 1:1. The result and investigation on the effect phosphorene/graphene powder of its structural properties via XRD technique using Bruker D8-advanced machine and microstructure of the powder samples were observed by using Carl Zeiss evo 50 SEM machine as well as FTIR spectroscopy to examined the presence of the unknown materials and bonds between phosphorene and graphene. Each of the phosphorene/graphene powder samples has been pelletized using manual hydraulic press in order conduct four-point probe experiment to investigate conductivity for implementation of lithium ion energy storage.

1.5 Significant of Research

The completion of the research of effect phosphorene concentration on energy storage behaviour of phosphorene/graphene powder will be giving benefits and contribute to electrochemical application due to mobility and wireless automation machine electrical technology dependent on energy storage technology usage with generation on batteries in high voltage especially. Somehow, phosphorene effect on the conductivity properties of graphene powder will be further investigate.

CHAPTER 2

LITERATURE REVIEW

This chapter is to review the related research and studies from previous papers in order to gain information and findings regarding to this title project which is the effect of the phosphorene concentration on the energy storage behaviour of phosphorene/graphene powder. The raw materials, synthesis method and characterization method of the studies and review will be discussed.

2.1 Graphene properties

Graphene, two-dimensional material known as advanced carbon nanomaterial type as the network packed of atom come with hexagonal lattice and solitary layer arrangement of carbon atoms structure as shown in Figure 2.1. The contribution of the mechanical properties and it characteristic yield 42N/m of its strength and ultimate tensile strength reach to 130Gpa with approximately 25% of mechanical strain which consider high compared to steels of it 400Mpa tensile strength in theoretical value. The crystal of graphene from microscopic level preserved very stable and heat conduction is very good. The main reason of the energy storage application used of graphene due to it high surface area which allow to the electron activities flow in ion exchange for charge and discharge (Olabi et al.,2021). Stack of layer graphene sheets would only 1mm equal of it thickness while the layer spacing only 0.335nm as shown in Figure 2.2. The building of the carbon allotrope block of it honey crystal lattice or honeycomb network wrapped zero-dimension fullerenes form, carbon nanotubes 1D-dimensional and 3D-dimensional when it stacked together to form graphite. The extraordinary features and its properties, the high electronic mobility of intrinsic carrier (200k

$cm^2V^{-1}s^{-1}$) is necessary for energy storage capacity and the performance as well as it thermal conductivity is very high which 5000W m^{-1} K^{-1} 10 times compared to copper in theoretical value. Most of the restore structure and conductive properties of graphene used in oxidation exfoliation method due to the low-cost and production in large-scale benefits on converted graphene or chemically graphene derived. Chemical reagent organic or inorganic used for graphene hybrid used in different synthesized method generally mixed with polymeric or metallic matrix by using ball milling or shear mixing known as physical process method. Even though the mechanically reinforced of graphene alter properties of the matrix in some of specific field such as lightweight and electrically conductive material but composites are rather limited mostly due to poor interfacial adhesion or contact of interfacial.

The electronic properties of graphene are one of the most useful properties due to zero overlap semimetal and yield high conductivity of electrical. Commonly for carbon atoms have 6 total electrons, divided 4 at outer which allow for chemical bonding on single atom and 2 for inner shell but for graphene there is 3 carbon atoms which connected to each atom on 2D-dimentional plane giving free movement of 1 electron in 3rd dimension for electronic conductive reaction.

Table 2.1: Graphene's electrical and mechanical properties (Hyun Kim et al.,2013)

Graphene properties	Description
Thermal conductivity	5000W m^{-1} K^{-1}
Level of transparency	97.4%
Young's modulus	1 Tpa
Bandgap	0
Electrical charge carrier mobility	200K cm^2/V. s
Tensile strength	1100 Gigapascals
Specific surface area	2630m^2/g

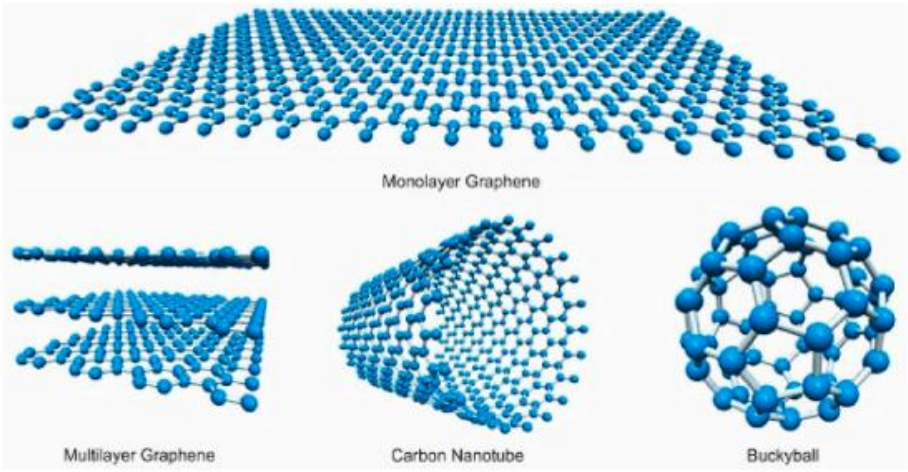

Figure 2.1: Different allotrope of graphene (Olabi et al.,2021)

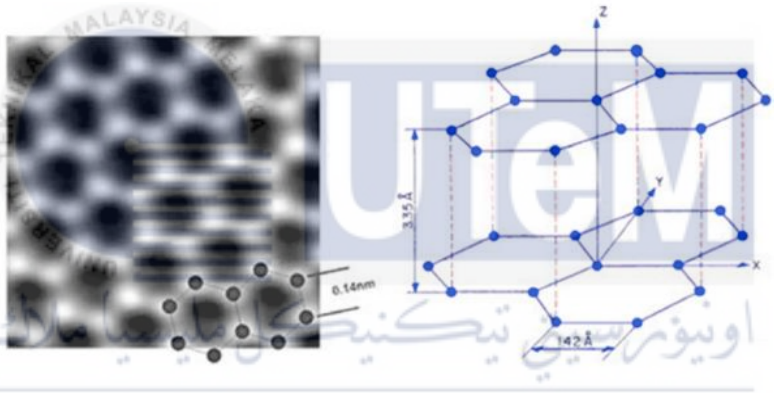

Figure 2.2: Layer spacing of graphene sheets (Olabi et al.,2021)

2.2 Graphene applications

Since graphene is a thinnest material in world and it is a disruptive technology, it very promising in most application used especially electronic and electrochemical filed due to its extremely high surface area to volume ratio. This led to supercapacitor storage and graphene-based batteries enable to increase its performances. Coating, sensors and electronic devices efficiently used and perform faster such as DNA sequencing, drug delivery and solar panel usage as well as good thermal conductivity enable graphene involve in long lasting LED light application in examples, where graphene is a solution material for heat spreading and thermal foils for mobiles devices.

2.2.1 Graphene hybrid in use of batteries

In graphene hybrid with Li ion batteries such as core shell-by shell design, the graphene shell of it outer layer performs better elasticity and higher conductivity of electronic than carbon coating amorphous which generally used in most energy storage application. The involved hybrid builds graphene in electrical device not only accommodated the volume capacity change but also increase active material both alloying and conversion reaction process provide better electrical contact with material particles. The unique structure of the core-shell graphene hybrid hindered the aggregation and movement reaction in nano matrix scale between Sn and Li_2O effectively, agglomeration of Sn prevented and maintained better contact. As conclusion, the hybrid material of SnO_2-SiC/G successfully perform high reversible capacity of 810mAhg^{-1} and capacity retention as much as 83% in scope of 150 charge/discharge cycles at the rate of 0.1g^{-1} between 1.5 to 0.01 Voltage (Li et al.,2018). There is study using graphene wrapped Ge nanowires where the graphene shells by using CVD process to put on the surface of Ge nanowires without using any metal catalyst resulted in high capacity of the energy storage (1059mA h g^{-1} and 200 cycle of its cycle life as well as 90% of the capacity retention (Kim et al.,2013). Graphene hybrid with metal sulfides such as MoS_2, SnS_2 and WS_2 shown great potential in application of lithium ion batteries which used as alternative anode materials. Metal sulfides alone not in satisfaction state for the electrochemical application used due to the low conductivity of the electron affected to cycle stability and the performance rate. Therefore, graphene hybrid metal sulfide design approached to overcome and optimize the electrochemical performance with synergetic interaction between both materials. The graphene incorporation enhancement of the whole conductivity metal-sulfides with graphene hybrid resulted in high specific capacity of 1100 mA h g^{-1} and rate of capability and cycling stability are excellent performances at current density of 100 mA g^{-1} as shown figure 2.3 (Xiong et al.,2016).

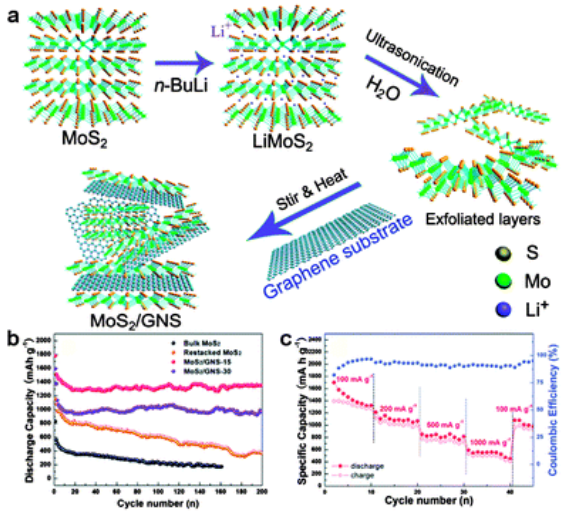

Figure 2.3: rate of cycling stability and capacity performance (Xiong et al.,2016)

2.2.2 Graphene hybrid in use of supercapacitors

Several studies and research on supercapacitor conducted using advancement of graphene materials where the recorded of the capacitance reached between 100 to 200F/g considered higher value compared to high surface area activated carbons materials. The activities and efforts to enhancement of more room and larger surface area to allow more capacity storage by restacking the graphene in order to prevent wastage of surface area total usage. Investigation of phenomena hybrid graphene capable on improvement electrode surface area and improve the network conductivity lead ionic transport in electrolyte is being created in large macropore channels. Mostly, graphene used as electrode while the hybrid electrode integrates of metal oxides or conducting polymer in order to avoid low energy density. On the best thickness graphene relationship with electrode volume fraction and volume density, the electrode design thickness of 400 micrometers compared to 800 micrometers, lower thickness perform higher volumetric energy density than supercapacitor with whole device lead acid battery and much higher compared to Li ion and Nickel-metal hydride battery due to hybrid graphene electrode attribute the high operation of voltage and extraction capacitance from the thickness is much higher as shown in figure 2.4 (Li et al.,2016).