UNIVERSITI TEKNIKAL MALAYSIA MELAKA

ELECTRICAL AND OPTICAL PROPERTIES OF PHOSPHORENE / GRAPHENE ADDED POLYVINYLIDENE FLUORIDE NANOCOMPOSITES

MARZIANA BINTI HARUN

MASTER OF MANUFACTURING ENGINEERING
(INDUSTRIAL ENGINEERING)

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Faculty of Industrial and Manufacturing Technology and Engineering

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MARZIANA BINTI HARUN

A master project submitted
in partial fulfillment of the requirements for the degree of
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DECLARATION

I declare that this master project entitled “Electrical and Optical Properties of Phosphorene / Graphene added Polyvinylidene Fluoride Nanocomposites” is the result of my own research except as cited in the references. The master project has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :..

Name :..

Date :..

APPROVAL

I hereby declare that I have read this master project and in my opinion this master project is sufficient in terms of scope and quality as a partial fulfillment of Master of Manufacturing Engineering (Industrial Engineering)

Signature : ....

Supervisor Name : ....

Date : ....

DEDICATION

Grateful to Allah SWT for the "Nikmat" and "Rahmat" given in this life. Dear my loved mother and father, I express my heartfelt gratitude for your unwavering support and motivation in urging me to persevere in pursuing this academic endeavor. Dear Dr. Mohd Shahadan Bin Mohd Suan, I would like to express my sincere gratitude for your consistent assistance in conducting experiments and sharing priceless insights. To my comrades engaged in the same struggle to pursue this academic endeavor, I express my heartfelt gratitude for consistently providing words of motivation and backing. Appreciation is extended to each and every one of you.

ABSTRACT

Phosphorene/graphene-incorporated polyaniline nanocomposites have been synthesised by mechano-sonic techniques. Phosphorene, a fascinating two-dimensional substance with a puckered-layer structure, was invented to increase the energy storage capacity and preserve the electrical conductivity of graphene by infiltrating it between the layers of graphene. The nanocomposites acquired semiconductor characteristics as a result of the incorporation of the additives, which created an energy band gap in phosphorene. This study examines the impact of incorporating phosphorene into nanocomposites, with polyaniline acting as the matrix, on the electrical conductivity and optical band gap. The ratio of phosphorene to graphene in the mixture ranged from 0.2:1 to 1:1. The 2D nanomaterials were blended together using a high-energy planetary ball mill operating at a speed of 450 revolutions per minute for a duration of one hour. Afterwards, the powder that was prepared earlier was separated into layers using a centrifugal rotating machine in n-methyl-2-pyrrolidone. The separated layers were then mixed with polyaniline using an ultrasonic bath. Phosphorene and graphene were detected in each sample using XRD and Raman analysis. The FESEM microstructure images clearly showed two different layers, which were recognised as graphene and phosphorene profiles using EDX. The examination using UV-vis spectroscopy showed that the nanomaterials, when suspended in n-methyl-2-pyrrolidone, have an energy bandgap ranging from 1.38 eV to 2.28 eV. FESEM measurements revealed that the microstructure exhibited increased density, while the inter-grain boundaries displayed a smoother texture. These changes resulted in a reduction in graphene segregation and the creation of pathways for electrons.

Sifat Electrik dan Optik Nanokomposit Polyvinylidene Fluoride yang ditambah Phosphorene / Graphene

ABSTRAK

Polyaniline nanocomposite yang digabungkan dengan phosphorene/graphene telah disintesis dengan teknik mekano-sonik. Phosphorene, bahan dua dimensi yang menarik dengan struktur lapisan berkerut, dicipta untuk meningkatkan kapasiti penyimpanan tenaga dan memelihara kekonduksian elektrik graphene dengan menyusupkannya di antara lapisan graphene. Nanocomposite memperoleh ciri semikonduktor hasil daripada penggabungan bahan tambahan, yang mewujudkan jurang jalur tenaga dalam phosphorene. Kajian ini mengkaji kesan menggabungkan phosphorene ke dalam nanokomposite, dengan polyaniline bertindak sebagai matriks, terhadap kekonduksian elektrik dan jurang jalur optik. Nisbah phosphorene kepada graphene dalam campuran adalah antara 0.2:1 hingga 1:1. Bahan nano 2D telah diadun bersama menggunakan high-energy planetary ball mill yang beroperasi pada kelajuan 450 pusingan seminit untuk tempoh satu jam. Selepas itu, serbuk yang telah disediakan tadi diasingkan ke dalam lapisan menggunakan mesin berputar empar dalam n-metil-2-pirolidon. Lapisan yang dipisahkan kemudiannya dicampur dengan polianilin menggunakan mandi ultrasonik. phosphorene dan graphene dikesan dalam setiap sampel menggunakan analisis XRD dan Raman. Imej mikrostruktur FESEM jelas menunjukkan dua lapisan berbeza, yang diiktiraf sebagai profil graphene dan phosphorene menggunakan EDX. Pemeriksaan menggunakan spektroskopi UV-vis menunjukkan bahawa bahan nano, apabila digantung dalam n-metil-2-pirolidon, mempunyai jurang jalur tenaga antara 1.38 eV hingga 2.28 eV. Pengukuran FESEM mendedahkan bahawa struktur mikro menunjukkan peningkatan ketumpatan, manakala sempadan antara butiran menunjukkan tekstur yang lebih licin. Perubahan ini mengakibatkan pengurangan pengasingan graphene dan penciptaan laluan untuk elektron.

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LIST OF ABBREVIATIONS

AAM	-	Anode active material
BP	-	Black Phosphorene
C	-	Carbon
CVD	-	Chemical vapour deposition
EDX	-	Energy dispersive X-Ray spectroscopy
ev	-	Electron volt
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared spectroscopy
G	-	Graphene
LEDs	-	Light-emitting diodes
LIB	-	Lithium-ion batteries
LiPSON	-	Lithium phosphorous sulfuric oxynitride
Mg	-	Magnesium
$MgCI_2$	-	Magnesium chloride
MoS_2	-	Molybdenum disulfide
$NiCI_2$	-	Nickel (II) choloride
NiO	-	Nickel oxide
nm	-	Nanometer
NMP	-	N-Methyl-2-pyrrolidone
P	-	Phosphorene
PVDF	-	Polyvinylidene fluoride

S/cm	-	Siemens per centimeter
Wt%	-	Percentage by weight
XRD	-	X-ray diffraction
2D	-	Two dimensional
$4H_2O$	-	Four Molecules of water

LIST OF SYMBOLS

~	-	Approximately
^{o} C	-	Degree Celsius
>	-	Greater
λ	-	Lambda
%	-	Percentage
θ	-	Theta

CHAPTER 1

INTRODUCTION

1.1 Background

Renewably sourced energy storage impedes technological advancements in electronics, devices, and electric vehicles. Lithium-ion batteries, renowned for their efficiency and capacity, offer a potential alternative. Researchers are developing ever-changing anode materials with remarkable charging and discharging speeds, significant capacity, a wide operating voltage window, and strong cycling stability, all driven by the continuous search for better lithium-ion batteries. Commercial LIBs frequently use graphite as an anode material due to its outstanding cycling performance, high energy stability, and affordability. Despite its low capacity and weak Li adsorption strength in graphite, its applicability is limited, making it unsuitable for portable electronic equipment. To meet the growing demand for batteries with high energy density, researchers have dedicated many resources to the search for a new LIB anode other than graphite. Recently, researchers have thoroughly investigated black phosphorus, which has an extraordinarily high capacity, as an electrode material to replace graphite (Javadian, Atashzar, Gharibi, & Vafaee, 2019).

Graphene is a two-dimensional (2D) material utilized in lithium-ion energy storage systems. It is a carbon-based material that serves as an anode active material (AAM) (Yu et al., 2022) and functions as the negative electrode in lithium-ion energy storage applications. Besides graphene, Idumah (2023) also classifies phosphorene and silicene as 2D materials.

Among these 2D materials, graphene stands out due to its superior electrical conductivity, cost-effectiveness, and stable structure. These qualities make graphene a commonly employed material in lithium-ion energy storage applications (Yu et al., 2022). However, under actual conditions, graphene experiences a 50% reduction in energy storage capacity compared to theoretical conditions.

To achieve the maximum energy storage capacity, it is essential to separate the atomically flat layer of graphene. Consequently, researchers are exploring diverse approaches to enhance energy storage capacity for efficient energy storage and release. One such method involves the combination of graphene with other 2D materials. This study combines two types of 2D materials, phosphorene and graphene, using polyvinylidene fluoride nanocomposites. The ratio employed to blend these two materials ranges from 0.1:1 to 1:1.

Graphene and phosphorene work together as a separator because phosphorene acts as a separating agent for atoms. Notably, phosphorene shares the same atomic structure as graphene. Additionally, polyvinylidene fluoride nanocomposites form the foundation for the electrical and optical properties of both phosphorene and graphene.

To comprehend the electrical and optical characteristics, the nanocomposites are characterized using a four-point probe and UV-visible spectroscopy. Techniques such as Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) achieve structural confirmation of the presence of phosphorene and graphene (Naeem et al., 2020).

Phosphorene and graphene must undergo ball-milling to blend the two materials into smaller sizes and achieve a homogeneous mixture. (Yu et al., 2022).

1.2 Problem Statement

Currently, lithium-ion energy storage applications frequently use graphene due to its high energy carrier capacity, excellent thermal properties, significant surface reactivity, and exceptional electrical conductivity. Because of these qualities, graphene is often used to store energy in lithium-ion applications. Its theoretical value suggests that it can store a lot of energy in capacitors, which makes them better at both charging and discharging.

However, practical applications involving 2D graphene-based materials with PVDF electrodes reveal an approximate 50% deficiency in energy storage capacity. To address this limitation and prevent such capacity inadequacies, this study explores the combination of graphene with another material from the same class. We specifically investigate the synergistic pairing of graphene and phosphorene. We choose phosphorene not only for its proposed role as a separator, but also for its identical atomic structure to graphene (Idumah, 2023).

1.3 Objective

In this research, there are three objectives that have been identified as follows:

i) To formulate and synthesis Phosphorene and Graphene added PVDF nanocomposite by using mechano-sonically technique.

ii) To investigate the effects of phosphorene to graphene ratio (P:G) to the electrical and optical properties of the nanocomposite.

iii) To correlate the relations between the electrical and optical properties of the nanocomposite to their morphological structure.

1.4 Scope of Research

High-energy planetary ball milling completely converts the red phosphorus into black phosphorus. Next, we mix a variety of ratios of graphene and black phosphorus with toluene. Ultrasonic baths disperse or exfoliate the materials for 4 hours. Control the concentration of phosphorene and graphene using a specific ratio, and the preparation involves a mechano-sonic process to assess and investigate the electrical and optical properties.

The phosphorene and graphene ratio ranges from 0.2:1 to 1.0:1. The first objective of this research is to formulate and synthesize a controlled concentration of a mixture of black phosphorus or a few layers of phosphorene and graphene using mechano-sonic techniques.

After mixing with an ultrasonic bath, thin films of black phosphorus and graphene nanocomposites receive PVDF solutions. The second objective is to synthesize and analyze these mixtures' morphology.

Used FESEM (Field Emission Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray Spectroscopy) equipment to synthesize and analyze PVDFs added to the graphene and black phosphorus mixture. Before beginning this analysis, add black phosphorus and graphene to a PVDF solution. After mixing, place the solution on a petri dish and dry it in an oven at 100 °C for 8 hours. Once the solution forms a thin film, it can perform analysis.

Furthermore, use Fourier transform infrared spectroscopy (FTIR) to identify the materials present in the samples. FTIR can discern the presence of organic, polymeric, and inorganic materials. Field emission scanning electron microscopy (FESEM) provides microstructural images of the materials.

This study uses a four-point probe and UV-visible spectroscopy to determine electrical and optical characteristics. The four-point probe measures resistivity within the material, while UV-visible spectroscopy gauges the extent of light absorption through the material.

CHAPTER 2

LITERATURE REVIEW

2.1 Two-dimensional (2D)

Two-dimensional (2D) materials fall within the category of nanomaterials (Huang, et al., 2020) and consist of single layers of atoms or molecules. One defining characteristic of 2D materials is their high surface-to-volume ratio, (Kumbhakar, et al., 2023) contributing to distinctive properties and applications. Additionally, these materials exhibit excellent electrical conductivity. 2D materials exhibit lightweight and flexible characteristics that render them well-suited for diverse applications. Additionally, these materials are recognized for their exceptional strength, establishing them as robust elements in material science.

2D materials possess distinctive characteristics, including high electrical conductivity, strength, and flexibility, making them well-suited for diverse applications in fields such as electronics, healthcare, and renewable energy. Commonly employed types of 2D materials include graphene, silicene, phosphorene, transition metal oxides, and many others (Idumah, 2023). Each of these materials exhibits unique properties that contribute to its specific functionality.

Two-dimensional (2D) materials encompass six key properties, including electrical, optical, mechanical, chemical, structural, and thermal characteristics (Si & Niu, 2020). Regarding electrical properties, these materials primarily exhibit traits in the electric field, involving conductivity, electronic band structure, and resistance to electrical elements. In