Low Temperature Synthesis of Graphene as an Alternative Transparent Electrode for Large Area Organic Photovoltaics

by

Alaa Yousif Ali

BSc (Physics); MSc (Physics)

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Statement of originality

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision. The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

Alaa Yousif Ali
July 2020

Acknowledgment of authorship

I hereby certify that the work embodied in this thesis contains published paper/s/scholarly work of which I am a joint author. I have included as part of the thesis a written declaration endorsed in writing by my supervisor, attesting to my contribution to the joint publication/s/scholarly work.

By signing below, I confirm that **Alaa Yousif Ali** contributed to the papers/ publications entitled "Matrix assisted low temperature growth of graphene" by:

- Fabrication and characterisation of CVD graphene at low temperature growth.
- Preparation and optimisation of graphene films with different growth conditions.
- Conduct different characterisation measurements for the quality of graphene films.

Paul dastoor

December 2019

“For the soul of my father and brother ‘Muthanna’, to my mother, family and my wife ‘Zubaidah’ ”

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List of publications

1. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Xiaojing Zhou and Paul Dastoor," Growth of multi-layered graphene using organic solvent-PMMA film as the carbon source under low temperature conditions", World Academy of Science, Engineering and Technology International Journal of Chemical and Materials Engineering Vol: 13, No: 2, 2019.
2. Raid A. Ismaila, Abdul-Majeed E. Al-Samaraib, **Alaa Y. Ali**, "Preparation and characteristics study of CdS/macroporous silicon/c-Si double heterojunction photodetector by spray pyrolysis technique", Optik, Elsevier 168 (2018).
3. Kasman Sulaiman, **Alaa Y. Ali**, Daniel Elkington, Krishna Feron, Kenrick F. Anderson, Warwick Belcher, Paul Dastoor, Xiaojing Zhou "Matrix assisted low temperature growth of graphene", Carbon, 2016. http://www.sciencedirect.com/science/article/pii/S0008622316304468
4. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor, Xiaojing Zhou. "Low Temperature CVD-Grown Graphene as Transparent Electrode for Organic Photovoltaics", draft paper, pending.
5. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor, Xiaojing Zhoua."Low temperature CVD growth of graphene via organic solvent retention in polymer matrices", draft paper, pending.
6. M. N. Thameel, M. F. Al-Mudhaffer, K. Feron, R. Feron, N. Holmes, **Alaa Y. Ali**, L. Tegg, H. Heim, S. Oosterhout, N. Cooling, B. Vaughn, A. Fahy, M. Bar, X. Zhou, W. Belcher, J. Holdsworth, P. Dastoor and M. J. Griffith, "Directing Energy Transfer Pathways Through Control of Nanoscale Structure in Ternary Blended Organic Electronic Nanoparticles," pending, 2019.

Conference presentations

1. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Xiaojing Zhou and Paul Dastoor," CVD Graphene at Low Temperature Growth as Alternative Transparency Electrode for Organic Photovoltaics", participated as poster in the Gordon Godfrey Workshop on "Spins, Topology and Strong Electron Correlations", The workshop was held from the 25th -29th November, 2019 at the University of New South Wales, Sydney, Australia.
2. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Xiaojing Zhou and Paul Dastoor," Growth of multi-layered graphene using organic solvent-PMMA film as the carbon source under low temperature conditions", the oral and technical presentation, recognition and appreciation of research contributions to ICGCS 2019 : 21st International Conference on Graphene Chemistry and Structures, the mentioned paper has been selected as the best paper at ICGCS 2019 : International Conference on Graphene Chemistry and Structures, ISTANBUL, TURKEY, FEBRUARY 14-15, 2019.
3. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Xiaojing Zhou and Paul Dastoor " CVD growth of graphene using solvent residing in a PMMA matrix as the carbon source at low temperature condition", Poster presentation at the 4thInternational Conference on Two-Dimensional Materials and Technologies (ICON-2DMAT) held in Melbourne, 12 December 2018.
4. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Xiaojing Zhou and Paul Dastoor" Low temperature CVD growth of graphene via organic solvent retention in polymer matrices", Poster presentation at the 3rd International Conference on Emerging Advanced Nanomaterials held in Newcastle Exhibition & Conference Centre, Newcastle, Australia, 30thOctober - 2nd November 2018
5. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor and Xiaojing Zhou. "Low Temperature of CVD-Grown Graphene as Transparent Electrode for Organic Photovoltaics", abstract has been submitted, poster. The International Conference on Nanoscience and Nanotechnology 2018, University of Wollongong, NSW, Australia.
6. **Alaa Y. Ali**, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor and Xiaojing Zhou. "Low Temperature Synthesis of Graphene as an Alternative Transparent Electrode for Large Area Organic Photovoltaics", Participated THREE MINUTE THESIS presentation, Faculty of Science, University of Newcastle, Australia, 2017.

7. **Alaa Y. Ali**, presented in the inaugural postgraduate Art in MAPS exhibition held on the 23rd of May 2017, won second prize in the art night event, Newcastle University, Australia.
8. **Alaa Y. Ali**, John Holdsworth, Warwick Belcher, Paul Dastoor and Xiaojing Zhou, "Synthesis of Graphene Thin Films at the Low Temperature as an Alternative Transparent Electrode for Organic Photovoltaics", Smart Future Cities 2015 (SFC2015) Conference was held at the Newcastle City Hall on the 1-2 October 2015, Abstract has been submitted. I won the prize for having presented the best poster at the smart future cities 2015 conference, Newcastle, Australia.

Abstract

This thesis presents a systematic study of the fabrication and optimisation of graphene films as an alternative electrode for large area organic photovoltaics (OPVs). It is mainly focused on the growth of graphene layers at low temperatures (below 700 °C) using chemical vapour deposition (CVD) method. A routine procedure was developed to produce large-area graphene films of centimetre size.

Firstly, we demonstrated that we could fabricate multi-layers of graphene films utilising organic solvent residual in a polymer film matrix as the carbon source. The polymer matrix is poly (methyl methacrylate) (PMMA), which can be dissolved in a polar solvent, such as, chlorobenzene. When PMMA is dissolved in chlorobenzene and drop-cast as a film into a quartz slide, a small amount of chlorobenzene is trapped in the PMMA. When heating up the quartz slide to 180 °C, chlorobenzene molecules evaporate and land on copper foils, which is maintained at much high temperature in the growth zone in the CVD system. Copper (Cu) catalytically promotes chlorobenzene dissociation and formation of micron-sized graphene domains at the different growth temperature. After a parametric study, we found that at 75 sccm (standard cubic centimeters per minute) of H_2 flow during the growth while maintaining the Cu foil at 600 °C, produced the optimal graphene growth conditions.

We also compared PMMA dissolved in other organic solvents and as carbon sources at low-temperature growth ~450 °C for deposition of the graphene layers onto a Cu catalyst. An optimisation process was carried out to see the effects of other carbon sources on the quality of graphene films. The carbon sources studied were both aliphatic solvents (dichloromethane, chloroform, acetone) and aromatic solvents (p-xylene, toluene, o-xylene, chlorobenzene, dichlorobenzene), to probe the growth mechanism of graphene formation. However, none of the other solvents produced a better quality of graphene than chlorobenzene.

Lastly, graphene films were used to replace indium tin oxide (ITO) in the OPV device fabrication. The results showed that working devices were successfully made for both small and large areas OPVs.

Table of contents

List of abbreviations and symbols

a	Length
A	Absorbance of incident light
AFM	Atomic force microscopy
Ag	Sliver
Al	Aluminium
AM1.5	Air Mass 1.5: Reference Solar Spectrum for OPV characterisation
Ar	Argon gas
Au	Gold
$AuCl_3$	Gold chloride
BCP	Bathocuproine
BE	Binding energy
BHJ	Bulk Heterojunction
BN	Boron nitride
BSE	Backscattered electron
c	Light speed
C	Carbon
C (b/s,a/b)	Additional dimensionless correction factor
$C_{12}H_{22}O_{11}$	Sucrose
$C_{13}H_{10}$	Fluorene
C_2H_2	Acetylene
C_2H_4	Ethylene
C_5H_5N	Pyridine
C_{60}	Buckminsterfullerene
Ca	Calcium
CH_3OH	Methanol
CH_4	Methane
Cl	Chlorine
CNTs	Carbon nanotubes
Co	Cobalt
Cu	Copper
Cu_2O	Copper oxide
CuCl	Cuprous chloride

CuPc	Copper phthalocyanine
CVD	Chemical vapour deposition
d	Width
DCB	Dichlorobenzene
DI	Deionised water
DSSCs	Dye-sensitized solar cells
e	Electron charge
E_D	Energy denoted
ED	Electron diffraction
EDS	Energy dispersive X-ray spectroscopy
E_F	Fermi energy
EQE	External quantum efficiency
ETL	Electron transporting layer
eV	Electron volt
Fe	Iron
$Fe\ (NO_3)_3$	Iron nitrate
FET	Field effect transistors
FF	Filling factor
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
G	Graphene
G(s,t)	Proportionality constant depending upon the geometry of sample
GNRs	Graphene nanoribbons
GO	Graphene oxide
h	Planck's constant
H_2	Hydrogen gas
HCl	Hydrochloric acid
HOMO	Highest occupied molecular orbital
HOPG	Highly ordered pyrolytic graphite
HTL	Hole transporting layer
I	Electrical current
IH	Hydrogen iodine
IPA	Isopropanol

IPCE	Incident photon to current efficiency
IQE	Internal quantum efficiency
Ir	Iridium
I_{SC}	Short circuit current
ITO	Indium Tin Oxide
J_{sc}	Short-circuit photocurrent density
J-V	Current density-Voltage
LCD	Liquid crystal displays
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
MEH-PPV	Poly (2-methoxy-5-(2'-ethyl-hexyloxy)- 1,4-phenylene vinylene)
MLG	Multilayers of graphene
MoO_3	Molybdenum trioxide
MoS_2	Molybdenum di-sulphide
MWCNT	Multiwall carbon nanotube
N	Number of Layers
n	Integer
n GL	Number of layers of graphene
N_2	Nitrogen gas
$NaBH_4$	Sodium borohydride
NEXAFS	Near-edge X-ray absorption fine structure
Ni	Nickel
O_2	Oxygen
OLEDs	Organic light emitting diodes
OPV	Organic photovoltaic
P3HT	Poly(3-hexylthiophene)
PBASE	Pyrene buanoic acid succidymidylester
PC	Bisphenol A carbonate
PCBM	Phenyl-C61-butyric acid methyl ester
PCE	Power convention efficiency
Pd	Palladium
PDMS	Polydimethylsiloxane
PEDOT-PSS	Poly(3,4-ethylenedioxithiophene):poly(styrenesulfonate)

PET	Polyethylene terephthalate
PI	Polyimide
P_{max}	Maximum Power Point of I-V Curve
PMMA	Poly(methyl methacrylate)
Pt	Platinum
PV	Photovoltaic
QDSSC	Quantum dot sensitized solar cell
R	Reflectance of light
R_s	Series resistance
Rsh	Shunt resistance
R_{sheet}	Sheet resistance
Ru	Ruthenium
s	Distance between two neighbouring tungsten pins
SAED	Single area electron diffraction
sccm	Standard cubic centimeter per minute
SE	Secondary electron
SEM	Scanning electron microscopy
SG	Single layer of graphene
Si	Silicon
Si_3N_4	Silicon nitride
SiC	Silicon carbide
SiO_2	Silicon dioxide
SNW	Sliver nanowire
STXM	Scanning Transmission X-ray Microscopy
SWCNT	Single-wall carbon nanotube
T	Optical transmittance
T_{500nm}	Transmission of light at wavelength of 500nm
TCNQ	Tetracyanoquinodimethane
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
$T_{Annealing}$	Temperature annealing
T_{growth}	Temperature growth

T_{source}	Temperature source
UPS	UV photoelectron spectroscopy
UV-vis	Ultraviolet-visible
V	Voltage
V_{oc}	Open-circuit voltage
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction
ZnO	Zinc oxide
η	Solar cell power conversion efficiency
η_c	Carrier collection efficiency
η_e	Energy conversion efficiency
λ	Wavelength
ρ	Sheet resistivity
σ	Conductivity
2D	Two dimensional
3D	Three dimensional

List of figures

List of tables