GRAPHENE BASED THIN FILMS FOR PHOTOCATALYTIC AND OPTOELECTRONICS APPLICATIONS

ASIM JILANI

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School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

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Dedicated to the memory of my late mother, who always prayed for success in my life. You are gone but your belief in me has made this journey possible. My beloved father, for his encouragement to meet the challenges of my life.

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ABSTRACT

The composite materials of metals, metal oxides or polymers with different forms of graphene like pristine graphene (GN), graphene oxide (GO) and reduced graphene oxide (rGO) have attracted tremendous attention worldwide due to their potential applications in various fields such as optical, photochemical, electrical, electrochemical, and environmental applications. However, besides the importance of this noble material in energy and environmental sector, there are still few reports on the fabrication of GO and rGO thin films through the combination of chemical and physical routes, which are spin coating and direct current radio frequency sputtering. The detailed characterization analysis and further investigation on the applications of GO and rGO thin based films fabricated by aforementioned methodology has poorly been reported. Therefore, this study focused on the synthesis of GO, rGO and their composites with zinc oxide (ZnO), copper (Cu), nickel oxide (NiO) by the combination of spin coating, low temperature thermal annealing and direct current radio frequency (DC/RF) sputtering technique for wastewater treatment and optoelectronics applications. The 2-chlorophenol (CPs) was selected as a model pollutant due to its high cytotoxic, mutagenic carcinogenic properties threating the living beings. Initially, GO was synthesized by modified Hummers' method and afterwards, spin coating technique was used to deposit the GO thin films on glass substrate. The thin films deposited at different GO concentrations (1.6, 3.2, and 4.8 mg/mL) were qualitatively analyzed and further optimized having unique structural, optical, chemical states for further applications in environment and optics. The band gap of thin films was dependent on GO concentration which were 2.98, 2.86, and 2.71 eV for 1.6, 3.2 and 4.8 mg/mL of GO, respectively. The refractive indices were in the range of 1.35 to 1.58 depending on the GO concentration. The optimized GO thin films were further reduced to rGO by low temperature reduction. The reduction was done at different temperatures from room temperature to 300 °C. The band gap decreased from 4.10 to 2.41 eV with the formation of conjugated sp2 network. The increase in sp2 network from 36.57 to 68.71 % while the decrement of sp3 from 32.06 to 18.56% in rGO thin films also evidently proved the restoration of GN like properties in it. The optimized rGO thin films were further used to fabricate their composites with ZnO through DC/RF. The degradation efficiency (2-CP) increased from 44 to 74%. Further, GO/rGO nano composites thin films with NiO and Cu were synthesized to obtain their uniform thin films by controlling the deposition parameters of direct current radio frequency sputtering technique. The sp^2 hybridization in rGO caused more dielectric loss as compared to GO because of its conductive path ways in Cu-ZnO. GO and rGO did not affect the preferred structural orientation of Cu-ZnO, and NiO. Sp^2 network of GO/rGO also assisted their desirability for 2-CP which ultimately led to their degradation. The efficiency Cu-ZnO/rGO was 75% while in case of NiO composites it was found to be from 46 to 77 % depending on the NiO particle size. In summary, the physical and chemical properties of GO and rGO were improved in their thin film composites with ZnO, NiO and Cu which enhanced their capability as photo-catalyst which could be highly useful for building next generation devices in the field of optoelectronics and waste-water treatment.

ABSTRAK

Bahan-bahan komposit logam, logam oksida atau polimer dengan pelbagai bentuk grafin seperti grafin asli (GN), grafin oksida (GO) dan grafin oksida terturun (rGO) telah menarik perhatian seluruh dunia kerana potensi aplikasinya dalam pelbagai bidang seperti optik, fotokimia, elektrik, elektrokimia, dan aplikasi alam sekitar. Walau bagaimanapun, di samping pentingnya bahan yang baik ini dalam sektor tenaga dan alam sekitar, terdapat hanya beberapa laporan mengenai fabrikasi filem GO dan rGO yang nipis melalui gabungan laluan kimia dan fizikal, iaitu salutan berputar dan semburan arus terus frekuensi radio. Analisis perincian terperinci dan siasatan lanjut mengenai aplikasi filem GO dan rGO nipis yang dibuat oleh metodologi yang disebutkan di atas tidak dilaporkan. Oleh itu, kajian ini menumpukan kepada sintesis GO, rGO dan kompositnya dengan zink oksida (ZnO), tembaga (Cu), nikel oksida (NiO) dengan kombinasi berputar, penyempuh-lindapan haba suhu rendah dan teknik semburan arus terus frekuensi radio (DC/RF) untuk rawatan air sisa dan aplikasi optoelektronik. 2-klorofenol (CPs) dipilih sebagai bahan pencemar model kerana ia mempunyai sifat sitotoksik tinggi dan sifat karsinogen mutagen yang mengancam makhluk hidup. Pada mulanya, GO telah disintesis oleh kaedah Hummers yang diubahsuai dan kemudian, teknik salutan berputar digunakan untuk mendepositkan filem-filem nipis GO pada substrat kaca. Filem nipis yang didepositkan pada kepekatan GO berbeza (1.6, 3.2 dan 4.8 mg / mL) dianalisis secara kualitatif dan dioptimumkan lagi untuk mempunyai keadaan struktur, optik, dan kimia yang unik untuk aplikasi selanjutnya dalam alam sekitar dan optik. Jurang tenaga filem nipis bergantung kepada kepekatan GO yang masing-masing adalah 2.98, 2.86, dan 2.71 eV untuk 1.6, 3.2, dan 4.8 mg / mL GO. Indeks biasan berada dalam julat 1.35 hingga 1.58 bergantung kepada kepekatan GO. Filem GO nipis yang dioptimumkan diturunkan lagi kepada rGO oleh penurunan suhu rendah. Penurun dilakukan pada suhu yang berbeza dari suhu bilik hingga 300 ° C. Jurang tenaga menurun dari 4.10 ke 2.41 eV dengan pembentukan rangkaian susunan sp^2. Peningkatan rangkaian sp^2 dari 36.57 hingga 68.71% manakala penurunan sp^3 dari 32.06 hingga 18.56% dalam filem-filem nipis rGO juga membuktikan pemulihan sifat-sifat GN di dalamnya. Filem nipis rGO yang dioptimumkan digunakan untuk membuat komposit dengan ZnO melalui DC/RF. Kecekapan degradasi (2-CP) meningkat daripada 44 kepada 74%. Selanjutnya, GO / rGO filem tipis nano komposit dengan NiO dan Cu disintesis untuk mendapatkan filem tipis yang seragam dengan mengawal parameter pemendapan Teknik semburan arus terus frekuensi radio. Hibridisasi sp^2 dalam rGO menyebabkan kehilangan dielektrik yang lebih banyak berbanding dengan GO kerana cara laluan konduktifnya dalam Cu-ZnO. Selanjutnya, GO dan rGO tidak mempengaruhi orientasi struktur Cu-ZnO, dan NiO. Rangkaian GO/rGO juga membantu kegunaan mereka untuk 2-CP yang akhirnya membawa kepada perosotan mereka. Kecepkapan Cu-ZnO/rGO kecekapan adalah 75% manakala dalam komposit NiO didapati dari 46 hingga 77% bergantung kepada saiz zarah NiO. Ringkasnya, sifat fizikal dan kimia GO dan rGO bertambah baik dalam komposit filem nipis mereka dengan ZnO, NiO dan Cu yang meningkatkan keupayaan mereka sebagai pemangkin foto yang sangat berguna untuk membina peranti generasi akan datang dalam bidang optoelektronik dan sisa- rawatan air.

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LIST OF ABBREVIATIONS

2-CP	-	2-Chlorophenol
AFM	-	Atomic Force Microscopy
At %	-	Atomic Percenrage
CNT	-	Carbon Nanotube
CVD	-	Chemical Vapor Deposition
DC/RF	-	Direct Current Radio Frequency
EDX	-	Energy Dispersive X-ray spectrometer
FESEM	-	Field Emission Scanning Electron Microscopy
FLG	-	Few Layered Graphene
GBC	-	Graphene Based Compsoites
GN	-	Graphene
GO	-	Graphene Oxide
GO/GN	-	Graphene Oxide/Graphene
LPE	-	Liquid Phase Exfoliation
MB	-	Methylene Blue
PVA	-	Polyvinyl Alcohol
rGO	-	Reduced Graphene Oxide
SiC	-	Silicon Carbide
SLG	-	Single Layered Graphene
UV–Vis	-	Ultraviolet–Visible Spectroscopy
XPS	-	X-ray Photoelectron spectroscopy

LIST OF SYMBOLS

λ	-	Wavelength
C_o	-	Initial concentration
C_t	-	Concentration at specific time
D	-	Grain size
E_d	-	Dispersion energy
hv	-	Planks constant
n	-	Refractive index
Ra	-	Average roughness
$Rqms$	-	Roughness root mean square
$\tan\delta$	-	Dielectric loss
β	-	Full width half maximum
δ	-	Lattice strain
ε_1	-	Real part of dielectric constant
ε_2	-	Imaginary part of dielectric constant
σ_{opt}	-	Optical conductivity

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

With the first discovery by Novoselov et al. in 2004, graphene (GN) has attracted a tremendous attention worldwide due to its potential applications in various fields such as electrical, electrochemical, supercapacitor, photocatalytic, optical and biomedicine. GN comprises of sp2-hybridized, single layered, two dimensional carbon atoms arranged in an array of hexagonal honeycomb lattice. Its planer orbitals are energetically stable comprising the localized sigma bonds arranged at three adjacent carbon atoms in this lattice. This structure of GN is responsible for its high surface area, and good electrical conductivity other than some of its exceptional properties like breaking and tensile strength (Young modules) having respectively the benchmark values of ~$42Nm^{-1}$ and 1.0 TPa (Huang et al., 2011). Furthermore, the large surface area (2,630 m^2g^{-1}), electronic transportation i.e. high intrinsic mobility of (200 000 cm 2 v^{-1} s^{-1}), thermal conductivity (~5000 Wm^{-1} K^{-1}) and extra ordinary mechanical properties makes it a prominent material for its applications in aforementioned fields (Lee et al., 2008, Li et al., 2009). On top of that, there have been a dire in developing the new and easy ways to synthesize this material. It is thus synthesized by various techniques such as chemical vapor deposition (CVD) (Reina et al., 2009, Li et al., 2009), exfoliation process(Lotya et al., 2009, Liu et al., 2008), and direct growth from carbon source(Sun et al., 2010, Ruan et al., 2011). The synthesis methodology is directly related to the quality of the final GN product and thus, can be customized as per the need of application. For example, the reduced-GO possesses a lot of defects due to reduction of functional groups, but the genereated oxygen vacancies can also be help in engineering its band gaps (Pan et al., 2014). Likewise, the GN prepared via CVD possess lesser defects and show better electron conduction due to high planar structure and is thus suitable for building the electrical devices (Muñoz and Gómez-Aleixandre, 2013).

Graphene oxide (GO) has been preferred a good adsorbent in comparison to graphene (GN) as the ratio of oxygen in GO is comparatively high compared to the pristine GN which makes them more attractive and efficient materials with enhanced adsorption properties. Adding to this, the specific adsoroption properties and mesoporosity of GO or GN are being improved by making its composites by functionalization with different metal/metal oxides like ZnO. However, the efficiency of GO/GN to absorb the pollutants also depends on the pH, oxygen functional groups and the nature of the organic matter under analsyis (Zhao et al., 2011, Sitko et al., 2013). The adsorption process of these materials have been explored via three different mechanismss namely physical interaction occurring due to connection of adsorbant with π-π stacking of the GO/GN composites material, surface complication interaction because of the molecular ion of the GO/GN and the foreign material (Upadhyay et al., 2014). Other than its exploration as adsorbant, the graphene based materials (GBM) can also be used to establish the stable photocatalyst semiconductor materials (Liu et al., 2014, Chang et al., 2015). For this, these GBM are being explored to engineer the band gap of metal/metal oxides etc., which is of great boom to develop photocatalysis under visible light to aid environmental remedation.

Organic dyes or pigments such as 2-chlorophenol (2-CP) or its derivatives respectively released from the textile/leather and petroleum industry are the major examples to contaminate the streaming water. The high usage of these non-biodegradable textile dyes is releasing a tons of waste effluents into water bodies. Most of the dyes are water soluble and conventional and municipal aerobic treatments have been proven to be ineffective in their removal (Ajmal et al., 2014). These organic pollutants are discharged into water borne bodies which causes huge environmental concern. Recently, heterogeneous photocatalysis has proved to be one of the easiest and efficient way to combat these issues. Addition to photolysis, the catalyst engages these environmental pollutants through physico-chemical interaction process, which is delevloped by chemically engineering the surface chemistry of catalyst for selective and efficient adsorption (Dąbrowski, 2001).

Apart from their potential use in environmental sector, the high need for highly efficient energy storage devices in recent past has triggered the application of GBM in this area. GN/GO are considered promising high performance electrode materials, due to their high conductivity and thus can increase the performance such as the lithium-ion battery and supercapacitor, and make next generation devices, such as the lithium-sulfur battery, lithium-O_2 battery and sodium-ion battery. The electron mobility in GN at room temperature is ~15,000 cm^2/Vs, and the electrons in GN can cover large distances without being scattered, even at room temperature. It shows much lower resistivity than silver and the pore size in the GN does not effects its surface area, which make the GN ideal candidate for the supercapacitor applications as compared to other carbon material like carbon nano tube (CNT) (Tan and Lee, 2013). However, the aggregation of the GN may raise the van der Waals interactions among the GN layers, which could affect the supercapacitor application. The modification of the GN with metal/metal oxides, polymers etc as stated above can enhance the specific surface area and minimize the aggregation of GN layers (Kim et al., 2011). The functionalization of GN/GO thin films may also create defects in the lattice and is expected to give GO/GN composites with hitherto unreported properties.

The electronic transport properties and application of the GN may change with the number of GN layers, which can be calculated by the Raman spectroscopy or through the atomic force microscope (AFM). The increasing layers in the GN render the optical and electrical properties (Nourbakhsh et al., 2011, Miyazaki et al., 2010). The band gap engineering can easily be done in the few layered graphene (FLG) as compared to the single layered graphene (SLG) (Ohta et al., 2006, Tian et al., 2010). The stacking interactions within the layers present in the GN may also change the nature of GN because of its aggregation (van der Waal interaction). Thus, it is desirable to synthesize FLG for application point of view as large number of layers limits its application (Torres et al., 2014).

One of the easiest ways to tailor GN thin films with desired thickness is by using graphene oxide (GO) as the precursor. GO can be easily deposited into single or few layers, which can be later converted into GN by various techniques such as chemical, thermal etc. Thus, GO can be easily incorporated into polymers, metal oxides etc and later its conversion into GN can give GN composites with unique properties.

1.2 Problem Statement

Inspite of the interesting properties of GN and GO which makes it promising, these materials still have a long way to go before being ready for practical device applications. GN has been researched intensively, but it is far from replacing silicon in electronics such as chips etc (Chiappetta, 2014). Thus, several general problems are an issue of concern in order to make it truly viable for mass applications.

The synthesis method for the production of high quality GN sheets on larger scale must be developed. The synthesis methodology should involve less corrosive reagents (without acids or dilute acid solution). In corrosive environment, the honeycomb lattice of GN sheet may sustain damage, such as defects and functionalization by various groups, during the exfoliation process, which may further limit its application (Parveen et al., 2015). The number of layers in the GN is important for its electrical and optical properties as stacked layering may reduce its efficiency. Thus, an optimized methodology is needed for single and few layered GN synthesis. Optimized layering of GN sheets should be done in order to solve the switching problems in optical and electrical devices

Uniform few layered semitransparent film depositions need to be done for GN/GO composites with metal oxides, polymers, metals etc. One of the main problems in GN based composite films is the agglomeration of GN sheets inside the matrix for example in polymers (Atif et al., 2016). Thus, the selection of the right modification method for the tuning of van der Waal forces, π-π interlayer stacking of graphene layers, balancing of electrostatic intersection between the GN layers needs to be done (Hassan et al., 2009).

The use of corrosive chemicals may give highly defective GN, which hinders the electron mobility and thus affects the quality. Hence proper chemical-thermal or a combination of both methodologies should be optimized for obtaining highly ordered GN. The functionalization of GN and GO can increase its adsorbent capacity. Hence functionalization should be done with surfactants, polymers etc to impart additional functional groups and to improve the selectivity (Sohail et al., 2017). Band gap of GN is zero which also hinders its applications in photocatalysis and energy devices. Hence band gap engineering with metal oxides or polymer or a ternary system of GN/GO-metal oxides-polymers may be explored (Zhang et al., 2015c).. So, to obtain the maximum efficiency of the GN/GO and its derivatives, the above mentioned concerns should be minimized for advanced applications.

In the viewpoint of synthesizing noble materials for the advanced applications and safeguarding the environmental challenges, we have designed this research project which involves the fabrication of exciting next generation carbon based materials such as GN and GO. The materials will be fabricated into different morphological, chemical functionalization and further their composites with ZnO, Cu and NiO. The wide band gap of ZnO ((3.37 eV) leads to good optical, electronic and catalytic properties Similarly, NiO is also a promising candidate for decades due to its interesting electronic structure, wide band gap (3.6-4.0 eV), low resistivity and catalytic activity for optoelectronics and environmental applications. Moreover, doping of metallic Cu can further enhance the properties of ZnO and NiO. However, the doping of Cu should be optimized otherwise it can decay the basic properties of ZnO and NiO. The prepared samples will be studied for photocatalytic activities of 2-chlorophenol, apart from the characterization on the energy applications. The prepared samples will have hugely potential to enlighten a better tomorrow for the human beings

1.3 Objective of the Study

The major goal of this research is to produce high performance rGO/metal@metal oxide (ZnO, CuO and NiO) composite with via DC/RF sputtering for the application in photocatalytic degradation of pollutants and optoelectronics. Therefore, four specific objectives are outlined as follows;

i. To synthesize GO thin film from graphite via modified Hummer method and spin coating technique, and investigate the effect of GO concentration on their physico-chemical properties.
ii. To convert GO thin film to reduced GO (rGO) thin film at temperature varied from $25^{o}C$ to $300^{o}C$ and to modify the band-gap of GO/rGO by compositing it with ZnO for better performance in photocatalysis and optoelectronics.
iii. To further enhance the photocatalytic and optoelectronics properties of the GO/rGO-ZnO composite thin film by incorporating Cu through direct current radio frequency (DC/RF) sputtering method.
iv. To examine the effect of deposition time of NiO as alternative additive onto GO thin film on photocatalytic and optoelectronics properties.

1.4 Scope of the Study

The following scopes have been identified to achieve the above discussed objectives.

1. Selection of facile synthesis method for GO
   i. Determining the suitable concentration of sulfuric acid, phosphoric acid and the ratio of graphite and potassium permanganate.
   ii. To find the suitable reaction time (2 to 30 h) for complete oxidation of graphite into high quality GO.
   iii. Synthesising GO thin films by using spin coater and further the selection of its rotation speed (1000 to 4000 rpm), deposition time (10

to 60 sec) and GO concentration to obtain high quality uniform GO thin films.

iv. Characterizing the deposited thins films for their structural (X-ray diffraction spectroscopy), surface (atomic force micrscopy and felid emission scanning electron microscope), qualitative (Raman spectroscopy) and chemical state (X-ray photoelectron spectroscopy) analysis.

v. Calculating the band gap, optical absorption and dielectric constants through UV data.

2. Reduction of GO to rGO with less defective and high conductivity sheets

   i. Identifying the impact of reduction temperature (range from room temperature to 300^{o}) on structural, surface composition, surface morphology and functional groups of rGO.

   ii. Calculating the band gap of rGO at reduction temperature range from room temperature to 300^{o}.

   iii. Selection of highly conductive, uniform and less defective rGO for its composites fabrication with ZnO through DC/RF sputtering system for photocatalytic and optoelectronics (such as light transmittance and absorption, band gap and dielectric constants) applications.

3. Synthesis of GO/rGO nano composites thin films with metal/metal oxides (ZnO, and Cu) through spin coating and DC/RF sputtering technique.

   i. Selection of deposition parameters of DC/RF sputtering technique such as thickness (few nanometers), deposition time (up to 1200 seconds) and doping rate (change in atomic weight percentage) to obtain uniform nano composites thin films.

   ii. To find ratio of GO/rGO with ZnO (35 %) and Cu (4.5 %) in nano composites thin films.

   iii. Investigation of the effect of ZnO and Cu concentration over the GO/rGO thin films at different parameters of DC/RF sputtering.

   iv. Comparative study (degradation of 2-chlorophenol) of pure GO/rGO thin films in comparison to Cu-ZnO nano composites thin films.

4. Synthesis of GO-NiO composites for photocatalytic (degradation of 2-chlorophenol) and optoelectronics applications
   i. Obtaining the UV-spectroscopy (Wavelength 190 to 900 nm) data for prepared graphene based composites
   ii. Calculating the optical constants (band gap, transmittance, absorbance, intenal heat effect dielectric loss) through UV- obtained data
   iii. Environmental application of prepared nanocomposites thin films through photodegradation.
   iv. Investigating the relation between structural, surface, band gap, chemical state, photocatalytic degradation of organic pollutants
   v. Proposing the tentative mechanism of photocatalytic degradation of organic pollutants
   vi. Comparsion for ZnO, Cu and NiO nanocomposites thin films for the degradation of 2-chlorophenol

1.5 Thesis Organization

This thesis consisted of eight chapters which describe original and novel research on GN based composites for photocatalytic and optoelectronics applications. The first chapter concisely explores the ideas of GN based composites. The research background of GN based material and the issues that lead to the current study were discussed. The four research objectives were identified, followed by the scopes of study used to achieve these objectives. Chapter 2 highlights the recent developments and progress in the synthetic approaches of GN and its composites. The synthesis of graphene through exfoliation, epitaxial growth, direct growth via carbon source as well as the modification approaches by covalent and non-covalent methodology has been reviewed in detail. Moreover, the limitation of each synthesis method has also been reviewed. In addition to this, the applications of graphene based metal and metal oxide composites through photocatalytic process has also been mentioned. Chapter 3 gives the list of chemicals that was used for the synthesis of GO, rGO and further their composites with ZnO, NiO and Cu. This chapter also concisely describes the characterizations that were utilized to analyze the structural, morphological, optical, photocatalytic etc. characteristics of the composites. Chapter 4 deals with the synthesis of GO by facile modified Hummer method. The thin films of GO were deposited on glass substrate by spin coating method. The thin films were deposited at different GO concentration (1.6, 3.2, and 4.8 mg/mL) to optimize the samples for further applications purposes using their structural, optical, chemical state and qualitative analysis. Chapter 5 describes the adoption of low temperature methodology (varied from room temperature to 300 °C) for the reduction of GO to rGO thin films. The whole reduction process from room temperature to 300 °C was analysed at different stages in terms of their structural and surface chemical state composition. The optical, and dielectric properties were calculated by using the UV-visible spectroscopic approach. Furthermore, the role of rGO was studied towards the photo-degradation of toxic recalcitrant 2-chlorophenol (2-CP) by preparing rGO/ZnO composite.

Chapter 6 describes the deposition of GO and rGO thin films were done over glass slides by using spin coating technique. The surface of GO and rGO was further coated with Cu doped ZnO nanoparticle. The change in the structural, optical, dielectric and chemical state of Cu-ZnO thin films was briefly investigated in the presences of GO and rGO. Furthermore, the role of hydroxides along with the sp2 network in GO and rGO for the photo-degradation of 2-chlorophenol (2-CP). The synthesis of GO composites with NiO has been describes in Chapter 7. The prepared GO/NiO thin composite was investigated in terms of its structural and surface chemical state composition. The optical, and dielectric properties were calculated by using the UV-visible spectroscopic approach. Further, the photocatalytic activity of the composite thin films was investigated by the degradation of 2-CP which suggest that GO played a major role along with NiO in the degradation of pollutant in wastewater. Moreover, the comparison between NiO and ZnO was also studied. Finally, Chapter 8 presents the general conclusions from present work and providing a list of some recommendations for future researches.

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APPENDIX A

LIST OF PUBLISTIONS

Jilani, A., Othman, M. H. D., Ansari, M. O., Hussain, S. Z., Ismail, A. F., Khan, I. U. & Inamuddin 2018b. Graphene and its derivatives: synthesis, modifications, and applications in wastewater treatment. *Environmental Chemistry Letters*, 16**,** 1301-1323.

Jilani, A., Othman, M. H. D., Ansari, M. O., Kumar, R., Alshahrie, A., Ismail, A. F., Khan, I. U., Sajith, V. K. & Barakat, M. A. 2017b. Facile spectroscopic approach to obtain the optoelectronic properties of few-layered graphene oxide thin films and their role in photocatalysis. *New Journal of Chemistry*, 41**,** 14217-14227.

Jilani, A., Othman, M. H. D., Ansari, M. O., Kumar, R., Khan, I. U., Abdel-wahab, M. S., Alshahrie, A., Barakat, M. A. & Kurniawan, T. A. 2018c. Structural, optical, and photocatalytic investigation of nickel oxide@graphene oxide nanocomposite thin films by RF magnetron sputtering. *Journal of Materials Science*, 53**,** 15034-15050.

Jilani, A., Othman, M. H. D., Ansari, M. O., Oves, M., Alshahrie, A., Khan, I. U. & Sajith, V. K. 2018d. A simple route to layer-by-layer assembled few layered graphene oxide nanosheets: Optical, dielectric and antibacterial aspects. *Journal of Molecular Liquids*, 253**,** 284-296.

Jilani, A., Othman, M. H. D., Ansari, M. O., Oves, M., Hussain, S. Z., Khan, I. U. & Abdel-wahab, M. S. 2019. Structural and optical characteristics, and bacterial decolonization studies on non-reactive RF sputtered Cu–ZnO@ graphene based nanoparticles thin films. *Journal of Materials Science*, 54**,** 6515-6529.

APPENIDIX B

CALCULATIONS OF BAND GAP FOR PURE NiO THIN FILMS

The band gap calculation for pure NiO thin films was through Equation 3.6. A decrease in the band gap of pure NiO thin films was observed with an increase in the deposition time of NiO. The pure NiO thin films with deposition time 400 sec have band gap 3.09 eV while 800 sec and 1200 sec have 2.93 eV and 2.74 eV, respectively.

APPENIDIX C

PHOTOCATALYTIC ACTIVITY OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE

The Photocatalytic activity of pure GO and rGO thin films was tested for the degradation of 2-CP as shown Figure S1. The results showed that in comparison of GO, the rGO is more active in pure form which might be due to the presence of sp2-hybridization cause by eradication of oxygenated moieties on surface of GO.

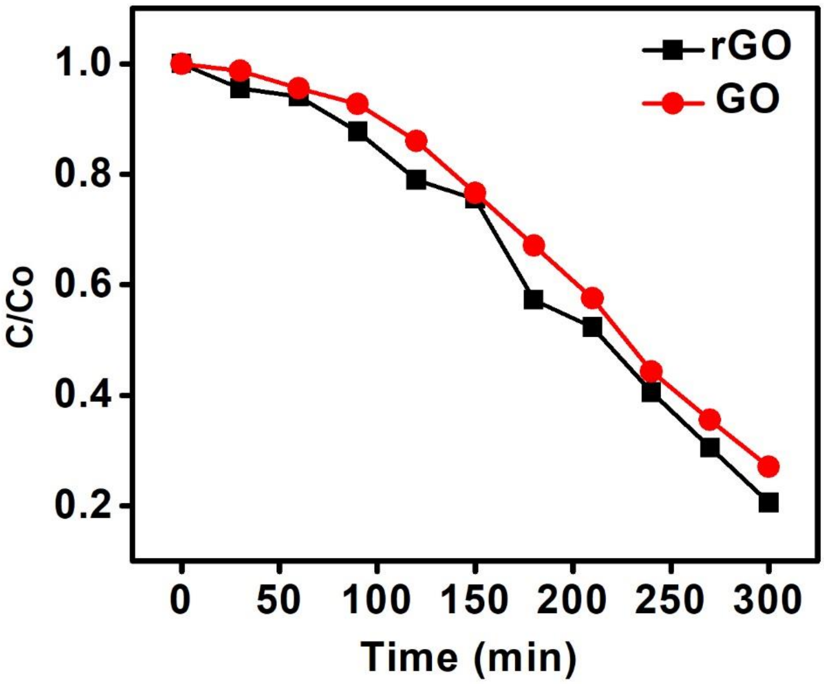

Figure S1 Photocatalytic activity for GO and rGO thin films

The reduced band-gap in rGO is the reason for its high photocatalytic activity towards the degradation of 2-CP (Sjong et al., 2019). In our case, the composites of metal or metal oxide with rGO exhibited higher photocatalytic activity than pure GO or rGO. This is because, GO and rGO assists the metal oxide in the charge transfer process and also lowers the recombination rate by dispersing the charge carriers in their heavily rich π bonded structure (Jaihindh et al., 2018)