UNRAVELING THE POTENTIAL OF PRISTINE GRAPHENE AS A VALUABLE CATALYST SUPPORT MATERIAL FOR NANOPARTICLES.

A Thesis

submitted

by

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(Roll No: D12052)

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Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis is the result of investigations carried out by me in the **School of Basic Sciences**, Indian Institute of Technology Mandi, under the supervision of **Dr. Prem Felix Siril**, and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

Place: **IIT Mandi**

Date: **16/03/2018**

Signature:

Name: **Tripti Vats**

Declaration by the Research Advisor

I hereby certify that the entire work in this Thesis has been carried out by **Tripti Vats**, under my supervision in the **School of Basic Sciences**, Indian Institute of Technology Mandi, and that no part of it has been submitted elsewhere for any Degree or Diploma.

Signature:

Name of the Guide: **Dr. Prem Felix Siril**

Date: **16/03/2018**

Affectionately

Dedicated

To

My Parents,Almighty God

&

My loving family

न चोरहार्यं न च राजहार्यं न भ्रातृभाज्यं न च भारकारि।
व्यये कृते वर्धत एव नित्यं विद्याधनं सर्वधनप्रधानम्॥

The Wealth that cannot be stolen, neither abducted by state, nor can be divided amongst brothers, neither it is burdensome to carry, the wealth that increases by giving.

That wealth is education and is supreme of all possessions.

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Chapter 2 Graphene synthesis and characterization: Data set

Abbreviations

AFM……………………………………………………………………..Atomic force microscopy

$CDCl_3$..Deuterated chloroform

CMC…………………………………………………………...Critical micelle concentration

CNTs……………………………………………………….................Carbon nanotubes

cryo-TEM……………………………………………….cryo-Transmission electron microscopy

CTAB……………………………………………………...Cetyltrimethyl ammonium bromide

CuAAC...Copper(I)catalyzed alkyne-azide cycloaddition

CuO_{nano}..Copper oxide nanoparticle

CV……………………………………………………………………….Cyclic voltammetry

CVD...Chemical vapour deposition

DCM...Dichloromethane

EtOH...Ethanol

EDX or EDS...……………………………………………..Energy dispersive X-ray spectroscopy

FE-SEM……………………………………………Field emission-Scanning electron microscopy

FTIR………………………………………………….....Fourier transform infrared spectroscopy

G…………………………………………………………………………….Pristine Graphene

G_{CuO}...Copper oxide/ Pristine graphene nanocomposites

G_{Fe2O3}...Iron oxide/Pristine graphene nanocomposites

$GPd_{0.001M}$..Palladium nanoparticles (0.001M)/Pristine Graphene

$GPd_{0.01M}$... Palladium nanoparticles (0.01M)/Pristine Graphene

GPr...Palladium nanorods/Pristine graphene

GO…………………………………………………………………………………Graphene oxide

HR-TEM……………………………………...High resolution Transmission electron microscopy

ICP-MS…………………………………………..Inductively coupled plasma mass spectrometry

LCs……………………………………………………………………………….Liquid crystals

LLCs……………………………………………………………...Lyotropic liquid crystals

LPE..Liquid Phase exfoliation

NMP…………………………………………………………………N-methyl pyrrolidone

NaCl..Sodium chloride

$NaBH_4$..Sodium borohydride

$Nano_{Fe2O3}$..iron oxide nanoparticles

OER...Oxygen evolution reaction

ORR...Oxygen reduction reaction

Pd...Palladium

$Pd(DBA)_2$.. Bis(dibenzylideneacetone)palladium(0)

$Pd_{0.001M}$.. Pd nanoparticles

Pr..Palladium nanorods

Pt…………………………………………………………….............................Platinum

POM…………………………………………………………...Polarizing optical microscopy

RGO……………………………………………………..……….Reduced graphene oxide

RGO_{CuO}...Copper oxide/Reduced graphene oxide nanocomposites

RGO_{Fe2O3}...Iron oxide/Reduced graphene oxide nanocomposites

$RGOPd_{0.001M}$.......................................Palladium nanoparticles (0.001M)/Reduce graphene oxide

RGOPr...Palladium nanorods/Reduced graphene oxide

SAED…………………………………………………………Selected area electron diffraction

SAXS………………………………………………………...Small-angle X-ray scattering

SDS…………………………………………………………………..Sodium dodecyl sulfate

SiC..Silicon Carbide

SLCs……………………………………………………………………..Swollen liquid crystals

TEM…………………………………………………………Transmission electron microscopy

TGA……………………………………………………………..Thermogravimetric analysis

UV……………………………………………………………………………...Ultra violet

Vis……………………………………………………………………………………..Visible

XPS…………………………………………………………X-ray photo electron spectroscopy

XRD……………………………………………………………………....X-ray diffraction

Abstract

Graphene is an allotrope of carbon, where 2-D arrangement of carbon atoms offers a plethora of amazing properties. Carbon atoms arrange themselves in sp^2 hybridized honeycomb structures where long-range of π -conjugated graphitic system yields extraordinary thermal, high theoretical surface area, amazing mechanical and electrical properties. These extraordinary properties make graphene a perfect support material for catalytically active nanoparticles. Infact, graphene in the form of reduced graphene oxide is widely used as a catalyst support. Reduced graphene oxide sheets, formed due to the reduction of graphene oxide contains marginal amount of residual oxygen that are bonded to carbon atoms in the sheets forcing them to be in sp^3 hybridized state. Due to the presence of these sp^3 sites the flow of charge carriers through sp^2 clusters get disrupted. The presence of such functional groups also decreases the π electron cloud and disturb the π-π interaction property of graphitic sheets with other electron rich molecules. However, the reduced graphene oxide is a popular choice as support material mainly due to its hydrophilicity, better interaction with metal or metal oxide nanoparticles through the functional groups and the familiar chemical method of synthesis. The primary postulate of the present thesis was that pristine graphene with minimal defect concentration and uniform distribution of π electrons throughout the 2-D sheets should make it a better catalyst support material. The studies that are embodied in the present thesis proved our postulate to be true.

The pristine graphene was synthesized using a sonication assisted liquid phase exfoliation is aqueous solution of surfactants. The method was initially optimized for obtaining maximum yield of exfoliated thin layer graphene without introducing significant amounts of defects. Two methods were developed to make nanocomposites of pristine graphene with metal or metal oxide nanoparticles. First approach was to use swollen liquid crystals (SLCs) as soft templates for the

preparation of nanocomposites of pristine graphene. SLCs are a class of lyotropic liquid crystals that are usually formed from a mixture of water, oil, surfactant and co-surfactant. The aspects such as diameter of the micelles and the distance between them can be varied in SLCs and hence the name. It has been shown in the past that the SLCs can be used as versatile templates for the synthesis of a variety of noble metal nanostructures. In this thesis, SLCs were used as soft templates to synthesize spherical and rods shaped metal nanostructures that are preferentially attached to pristine graphene sheets. The nanocomposites were prepared by entrapping the pristine graphene in the SLCs along with a metal precursor which on exposure to hydrazine vapor yielded the nanocomposites. The present studies also proved that the nanocomposites of pristine graphene could be synthesized by using hydrothermal methods also. All the prepared nanomaterials were thoroughly characterized using advanced characterization techniques. These nanocomposites were found to have better catalytic activities than the corresponding nanocomposites of RGO for various chemical and electrochemical reactions.

The present thesis entitled 'Unraveling the potential of pristine graphene as a valuable catalyst support material for nanoparticles" contains seven chapters. Chapter 1 includes a brief introduction about graphene, its properties, synthesis, effect as a support material and its applications. A discussion about the general aspects of the two methods that were used for making the nanocomposites of pristine graphene, i.e. SLC and hydrothermal has also been included in this chapter. The liquid phase exfoliation, optimization of different experimental parameters to obtain maximum yield of graphene and the detailed characterization of pristine graphene vis-à-vis RGO are detailed in Chapter 2. Chapter 3 describes an approach for the synthesis of pristine graphene/palladium nanocomposites by confining pristine graphene and metal salt in the oil phase of SLCs. Chapter 3 mainly focuses on the synthesis and the application of pristine graphene/palladium nanocomposites, where small palladium nanospheres (approx. size 4±1 nm) were preferentially got deposited over pristine graphene sheets. The pristine graphene-Pd nanocomposite showed very good catalytic activities in C-C coupling reactions and hydrogenation of nitrophenol. Chapter 4 conveys the ability of soft templates in controlling the morphology of palladium nanorods over the pristine graphene support. This chapter also includes the exploration of its activity in different C-C coupling reactions. In chapter 5, synthesis of pristine graphene/iron oxide nanocomposites using SLC template assisted method is discussed. The catalyst showed very high electro-catalytic activity as a bifunctional catalyst in water splitting reactions. Chapter 6 includes the synthesis and application in pristine graphene/copper oxide nanocomposites in copper catalysed azide-alkyne cycloaddtion reactions. The synthesis and application of this catalyst was performed in a green environment where we used water as a solvent and microwave for the temperature control during the reaction.

Chapter 7 presents the key findings of our research work and the future scope of the present work. Overall, the study clearly established that pristine graphene is a better catalyst support than RGO for the catalyst systems and applications that were studied. The nanocomposites of pristine graphene with Pd, iron oxide and CuO were not only having better activities, but exhibited very good stability and hence recyclability, thus proving the utility of pristine graphene as a better catalyst support material.