Reduced graphene oxide nanosheets decorated with monometallic and bimetallic nanoparticles: Synthesis, characterization and applications

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Materials Sciences & Technology Division
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Jorhat – 785006, Assam

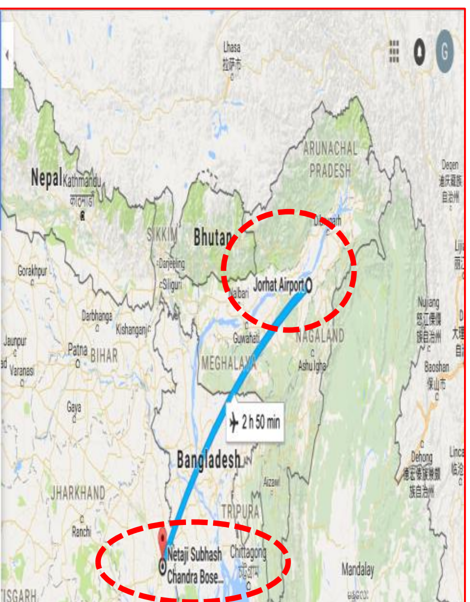
Route from Jorhat, Assam → → Kolkata

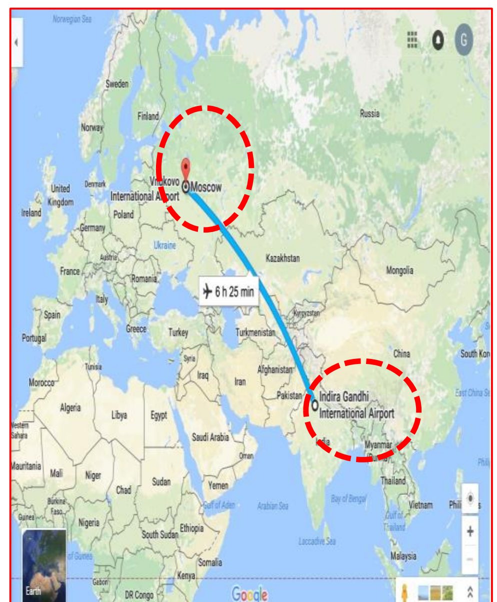
Kolkata → → Delhi

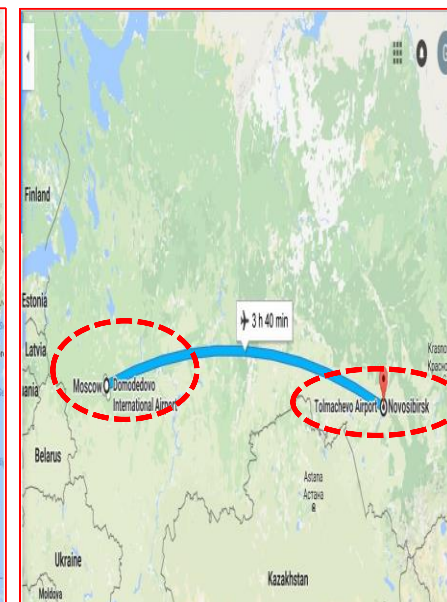
Delhi → → Moscow

Moscow → → Novosibirsk

AIR ROUTE

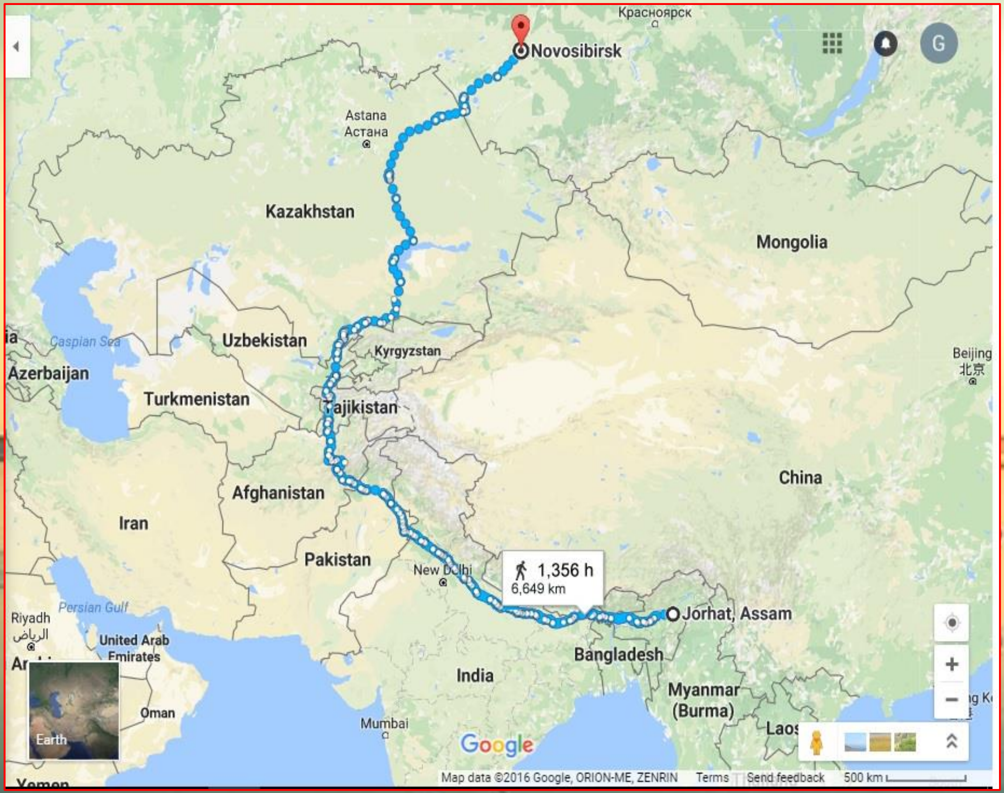






Walking Route
Jorhat-→ Novosibirsk, Russia

Siberian Migratory Birds in Assam



Total Distance: 6,649 km

Time: 1,356 h

Research Group

Dr P Sengupta
Head, MSTD

Present Students

Dr Manash R Das
Scientist, MSTD

Najrul Hussain
(Oct 2012 to present)

Gitashree Darabdhara
(Jan 2014 to present)

Priyakshree Borthakur
(Sept 2014 to present)

Purna K. Baruah
(April 2014 to present)

Bhagyasmeeta Sharma
(May 2015 to present)

Ponchami Sharma (PhD Awarded 2016)

PhD awarded: 01 (2016)
Total Present PhD Students: 06

Prandeep Borthakur
(July 2016 to present)

Current Research Interest

- **Designing metal nanoparticles on the graphene sheets and other 2D materials like g-C_3N_4, h-BN, h-BCN, MoS_2 etc.**

- **Decoration of the bimetallic/core-shell metal nanostructures on the graphene sheets.**

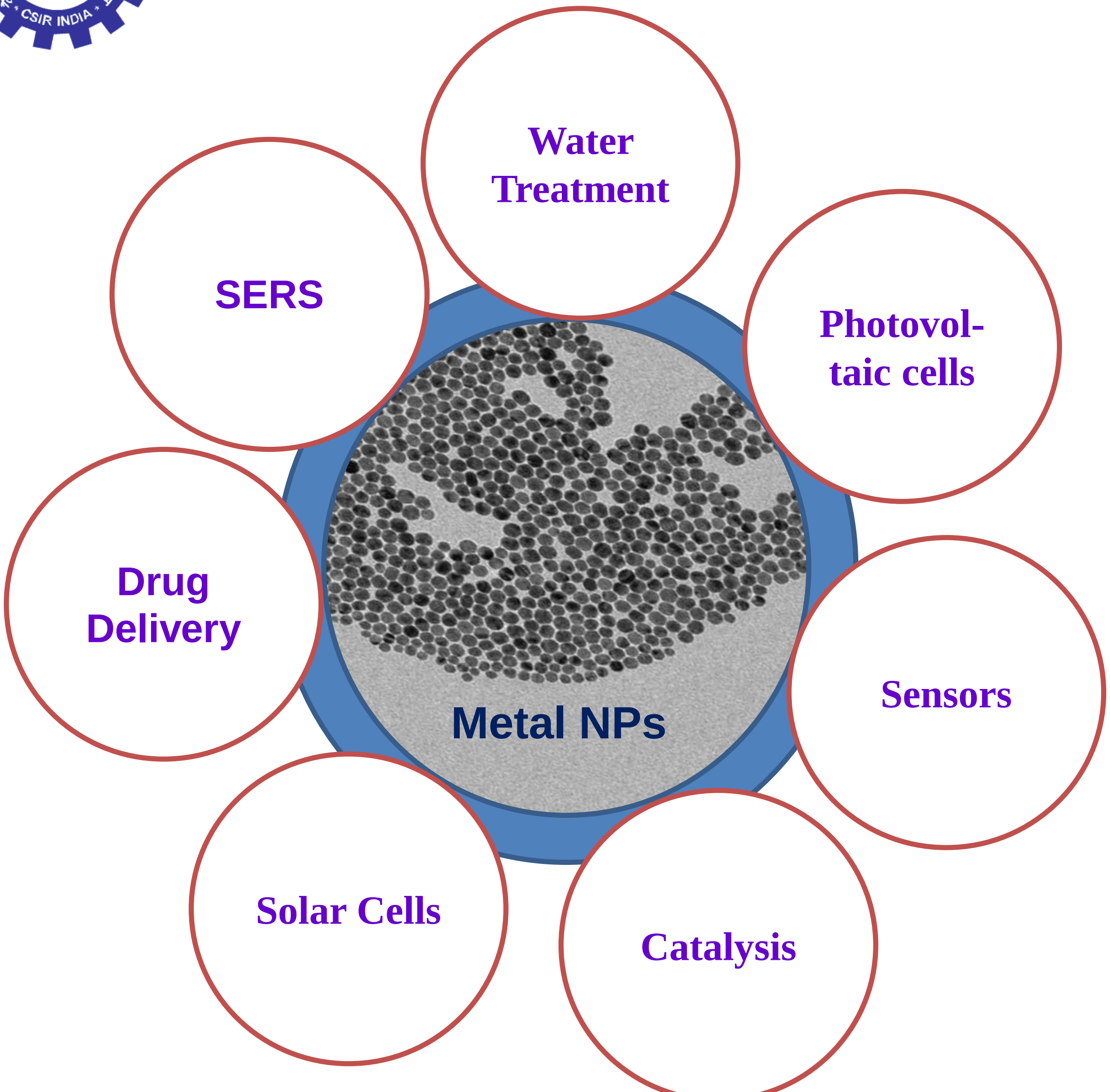
- **Catalytic application of graphene based composite material.**

- **Photocatalytic phenomenon for removal of water pollutant**

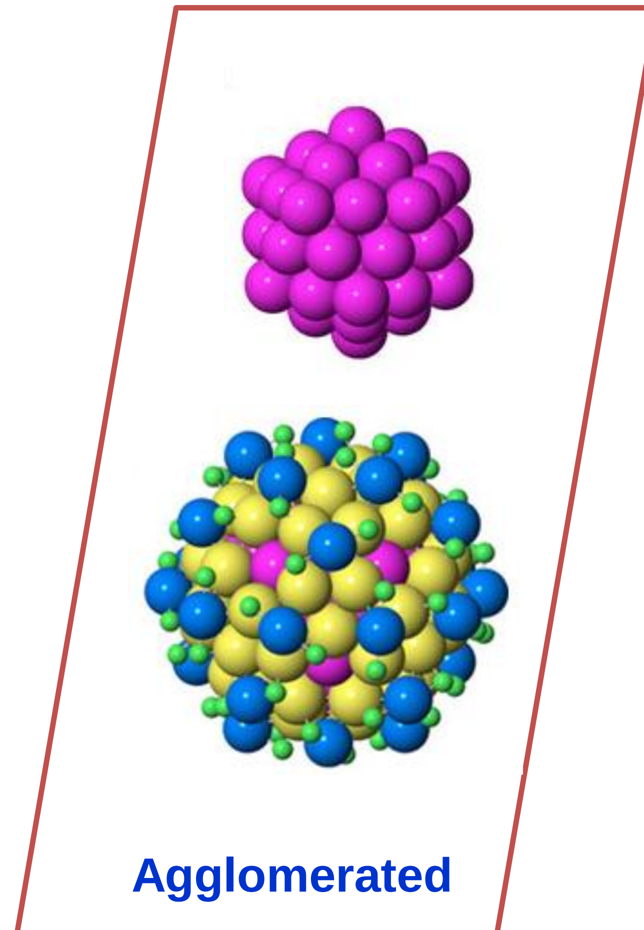
- **Removal of water pollutants using graphene based composite materials by adsorption and reactive extraction technique**

- **Development of colorimetric sensors based on graphene based composite materials**

Introduction

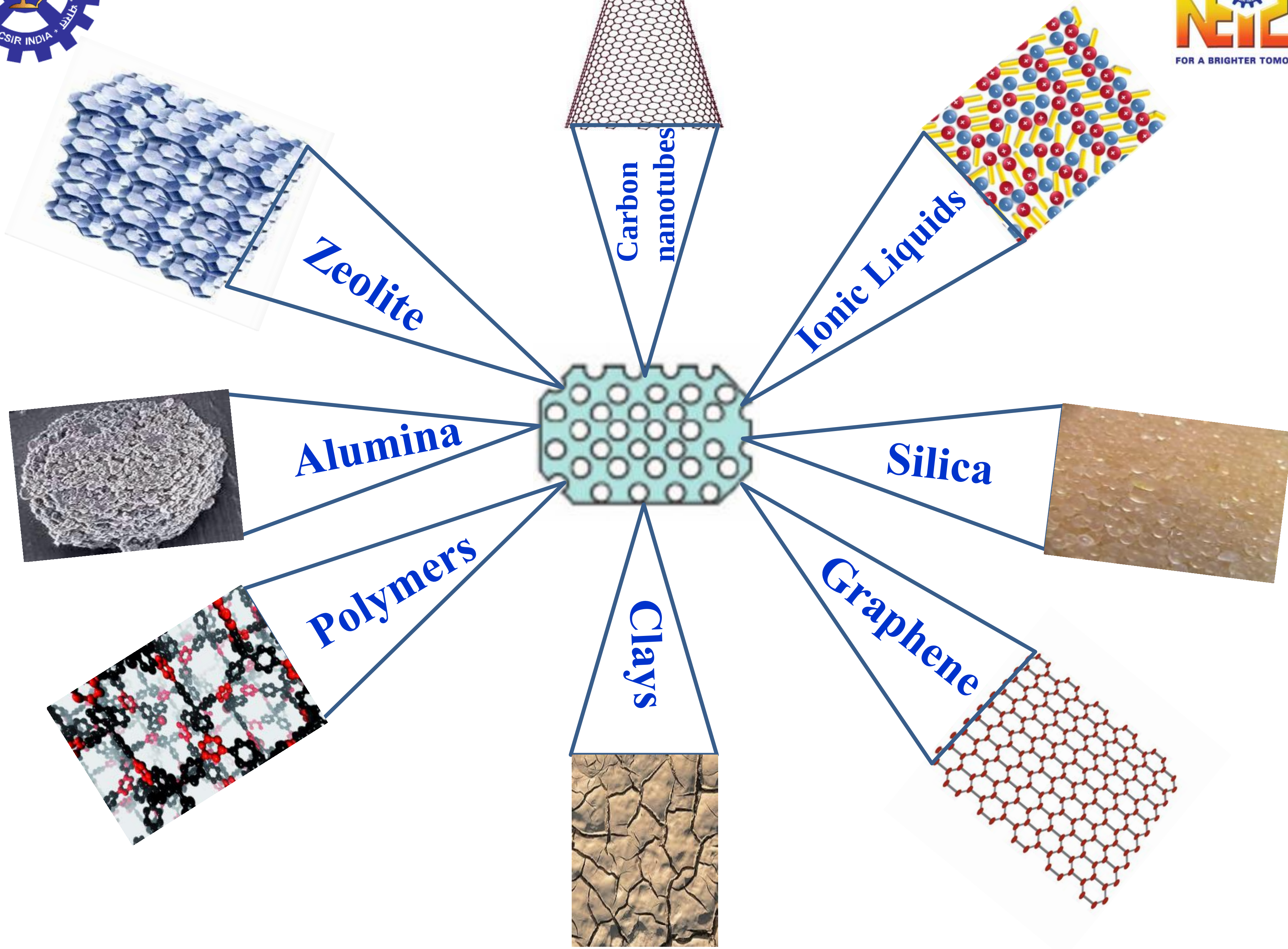


Different Applications



Drawbacks

Supports for Metal NPs



Why graphene ???

Planar structure allows the loading of metal NPs and other inorganic structures even with diameter size of several hundred nanometers

High surface area facilitates the formation and/or deposition of metal NPs over its surface.

Optical properties: Single layer graphene displays a high optical transparency of 97.7%. The high transparency combined with outstanding electrical conductivity make graphene a promising material for applications as a transparent electrode.

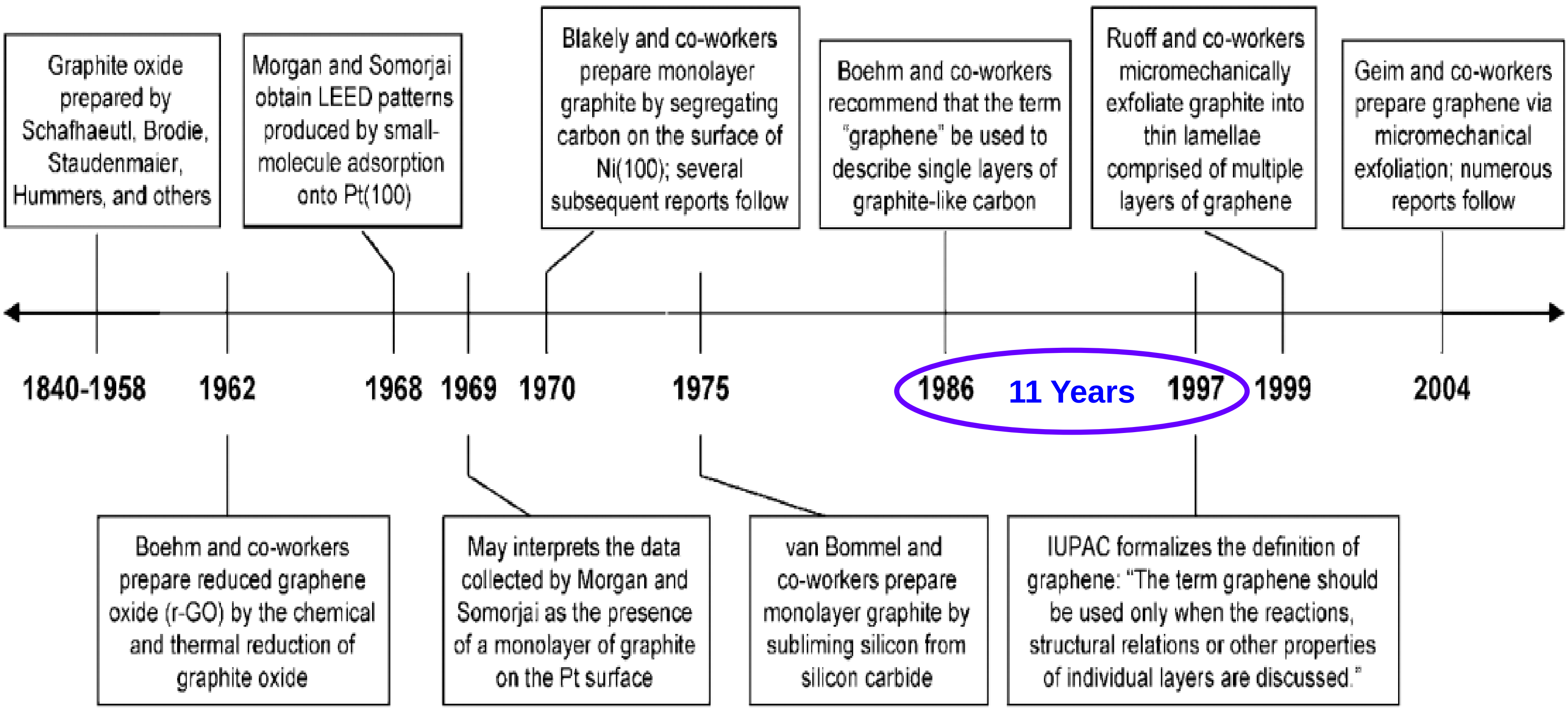
Electrical properties: Graphene shows zero band gap semiconductor properties. The electron mobility is almost independent of temperature and thus a very high mobility can be achieved at room temperature

Mechanical properties: Graphene displays Young's modulus of 1 TPa. Even with some structural defects, graphene shows extraordinary stiffness (Young's modulus 0.25 TPa)

Thermal properties: The room temperature thermal conductivity of a single layer graphene is reported in the range of ~(4.84± 0.44) × 10^3 to (5.30 ± 0.48) × 10^3 W/mK

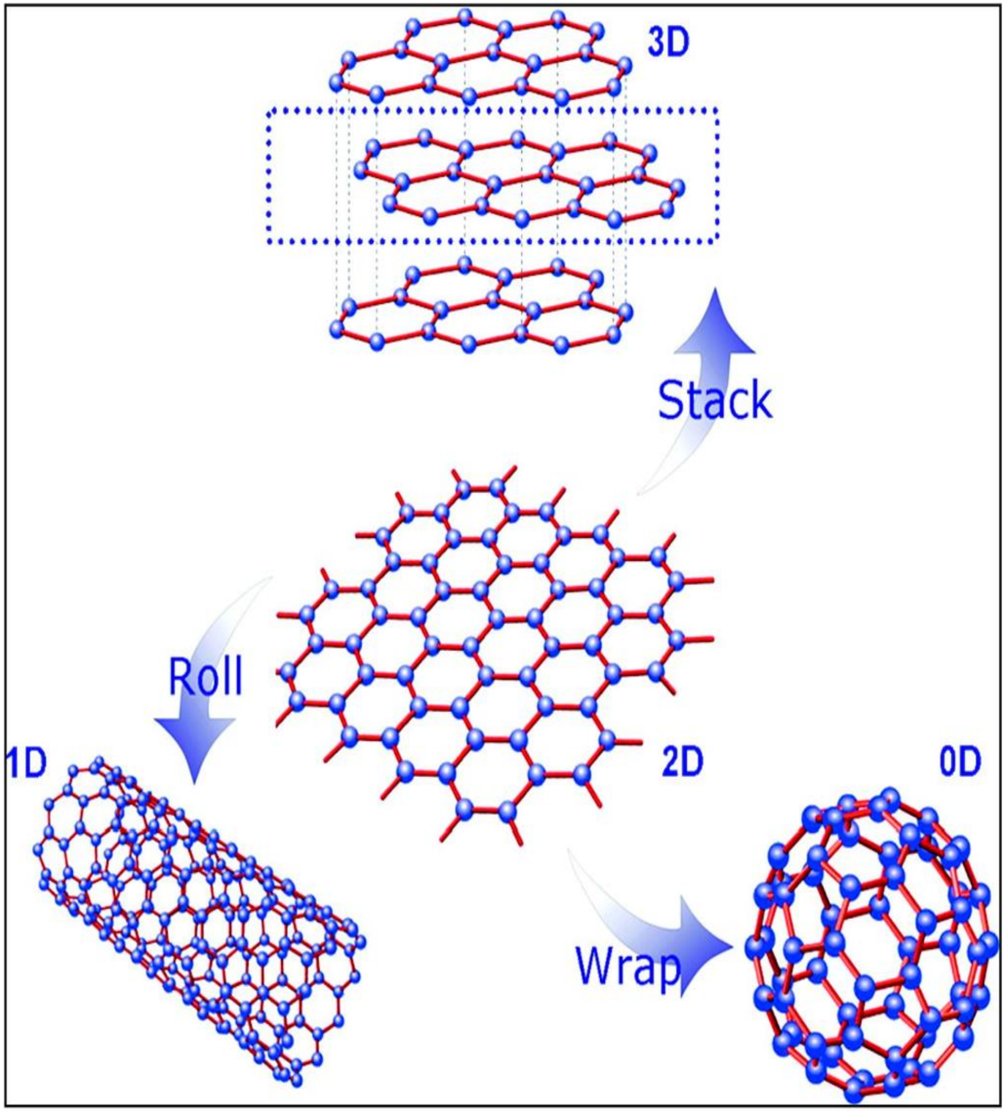
Timeline in the history of Graphene

- Graphene has been theoretically studied as early as 1940 and sixty years later theories proved correct. [Ref: P. R. Wallace, *Phys. Rev.* 1947, Vol. 71, 622]
- The isolation of single-layer graphene sheets from graphite was achieved by Geim, Novoselov and his co-workers from University of Manchester, UK with a "Scotch tape" approach in 2004. [Ref: *Science* 2004, 306, 666]



Angew. Chem. Int. Ed. 2010, 49, 9336

The first isolation of single-layer graphene from graphite was achieved by Geim, Novoselov and his co-workers with a "Scotch Tape" approach in 2004.

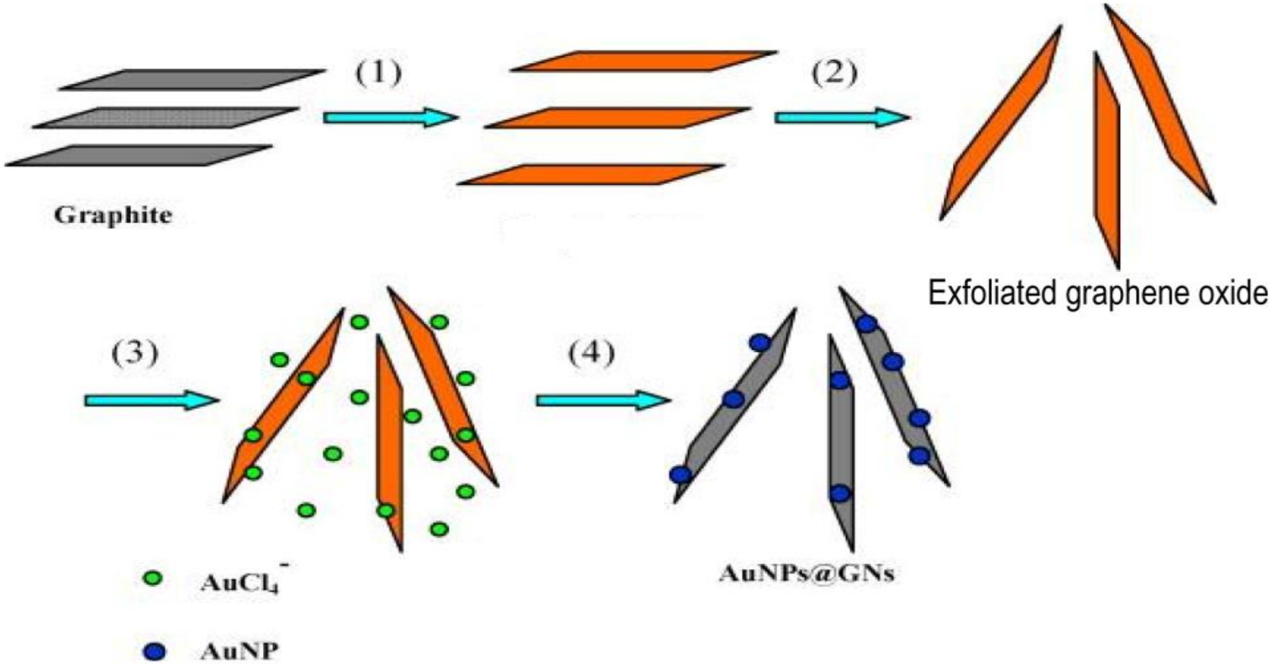


Fullerene 1985
Kroto, H. W., Heath, J. R., O'Brien, S., Curl, R. F. and Smalley, R. F., Nature, 1985, 318, 162–163.

Carbon nanotube 1991
Iijima, S., Nature, 1991, 354, 56–58.

Graphene 2004
Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Science 2004, 306,666.

- Reduced Graphene oxide or graphene sheets tend to restack to form 3D Graphite.
- This aggregation can be prevented by chemical functionalization like insertion of metal nanoparticles.



Metal nanoparticles play important role in several applications like

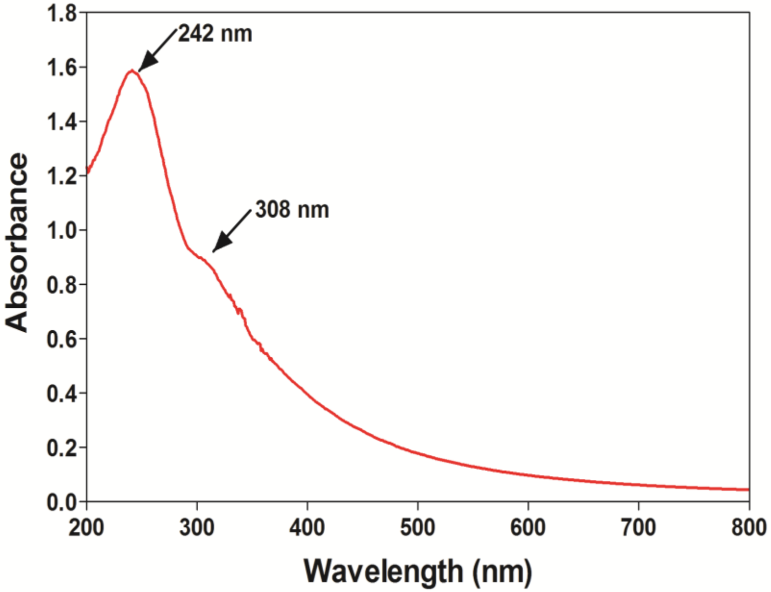
- *Display devices*
- *Catalysis*
- *Microelectronics*
- *light emitting diodes*
- *photovoltaic cells*
- *biological applications*

(1) Oxidation of graphite to graphite oxide
(2) Exfoliation of graphite oxide by sonication in water solution.
(3) Attachment of metal nanoparticles on the graphene oxide sheets.
(4) Formation of graphene-supported metal nanocomposites by reduction using mild reducing agent.

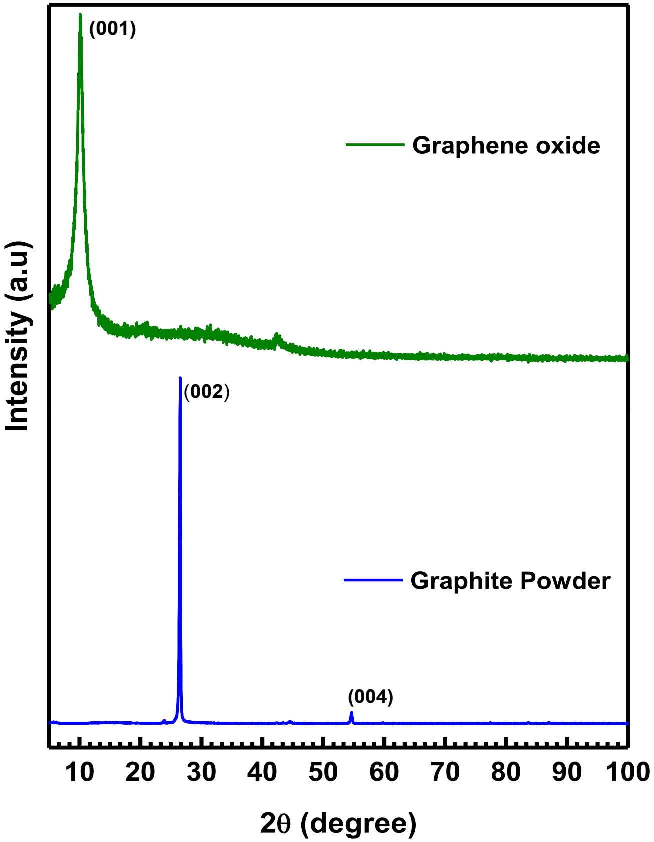
Preparation and Characterization of Graphene Oxide

Graphite oxide is synthesized from Graphite adopting Hummers and Offeman method using H_2SO_4 in presence of $KMnO_4$ and 30% H_2O_2 and graphite Oxide suspension was exfoliated by ultrasonication for 2 hours.

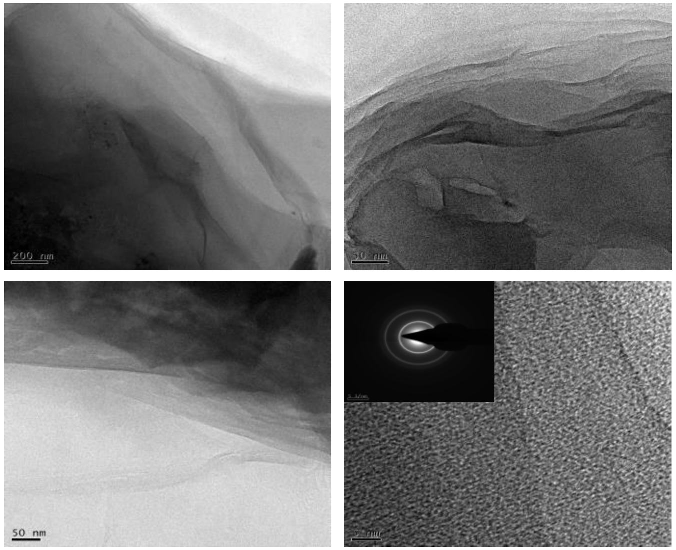
Ref.: Am. Chem. Soc. 1958, 80, 1339



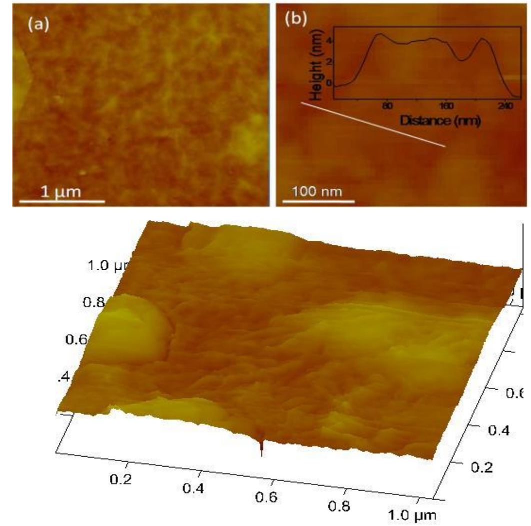
Absorption peak at 242 nm due to $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds, and a shoulder peak at ~308 nm, which can be attributed to $n \rightarrow \pi^*$ transitions of C=O bonds



XRD pattern of Graphite and Graphene oxide



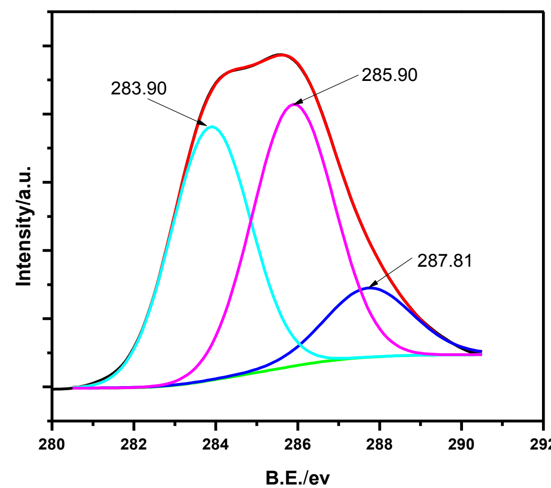
TEM images of Graphene oxide



AFM images of Graphene oxide

Zeta potential value is found to be -50 mV

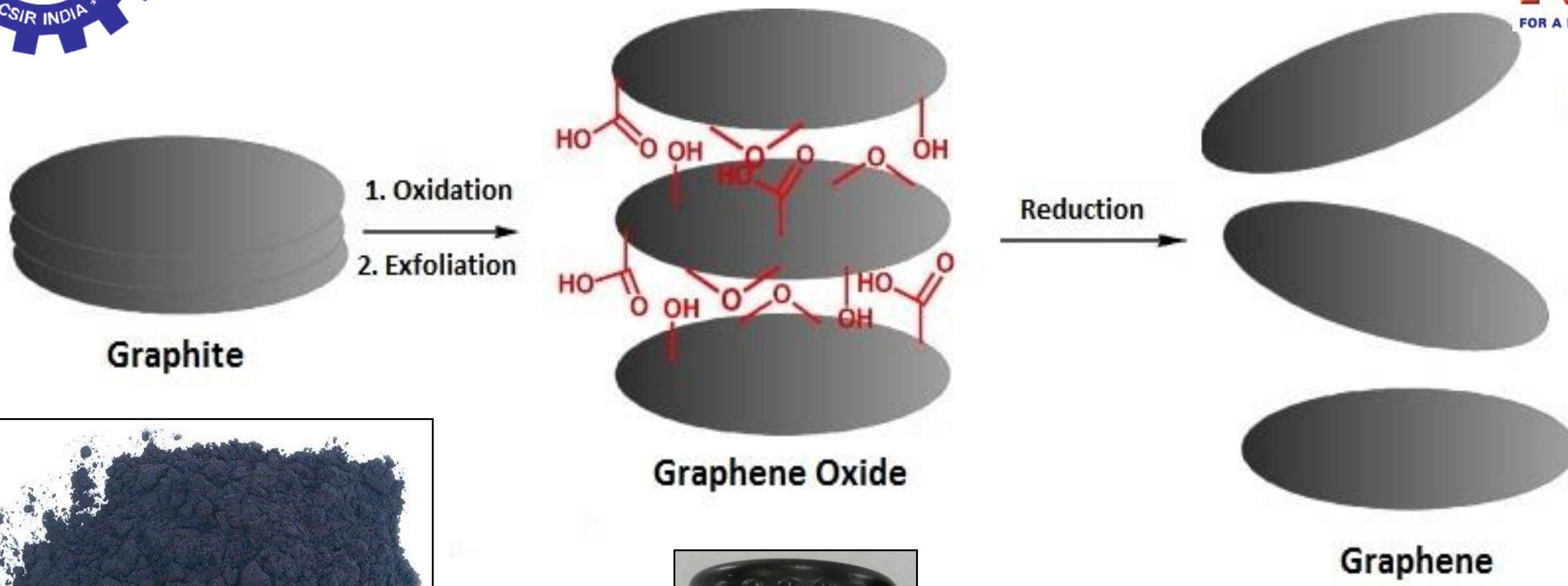
Graphene Oxide-water suspension



XPS of graphene oxide nanosheets

M R Das et al. Colloids & Surfaces B: Biointerfaces 2011, 83, 16-22

Synthesis of Reduced Graphene oxide (RGO)



Reducing Agent used:
- **Ascorbic acid**

M R Das et al. J. Chem. Eng Data 2013, 58, 3477

Synthesis of Metal Nanoparticles on Graphene Oxide/Graphene sheets

In situ

- Solution chemistry approach
- Spontaneous reduction of metal ions on GO/graphene surface
- Photochemical & photothermal method
- Microwave assisted synthesis
- Electrochemical deposition
- Cation exchange
- UV Irradiation
- Ultrasonication

Ex situ

In the ex-situ method, the metal NPs and graphene sheets are synthesized separately. Then combine by:

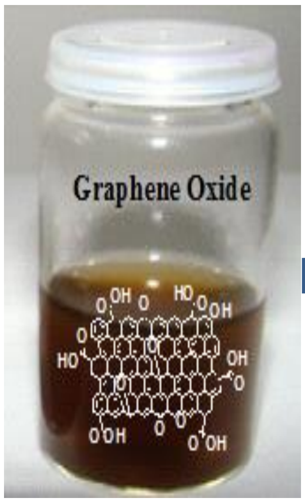
- Electrostatic interaction
- π-π interaction
- van der Waal’s interaction

Synthesis of Metal Nanoparticles on Graphene Oxide/Graphene Surfaces

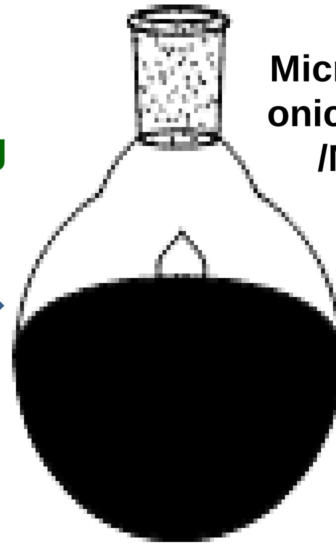
Solution Chemistry Approach

Metal Salt Solution

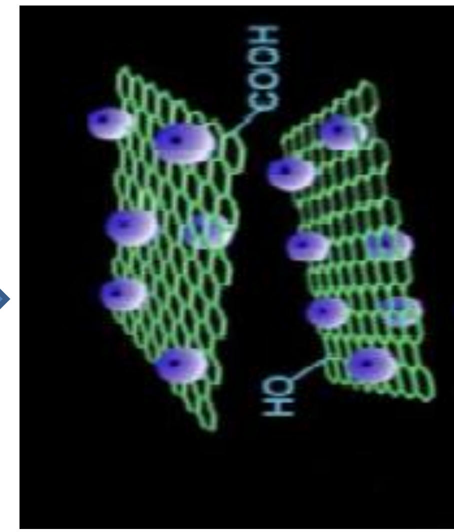
+



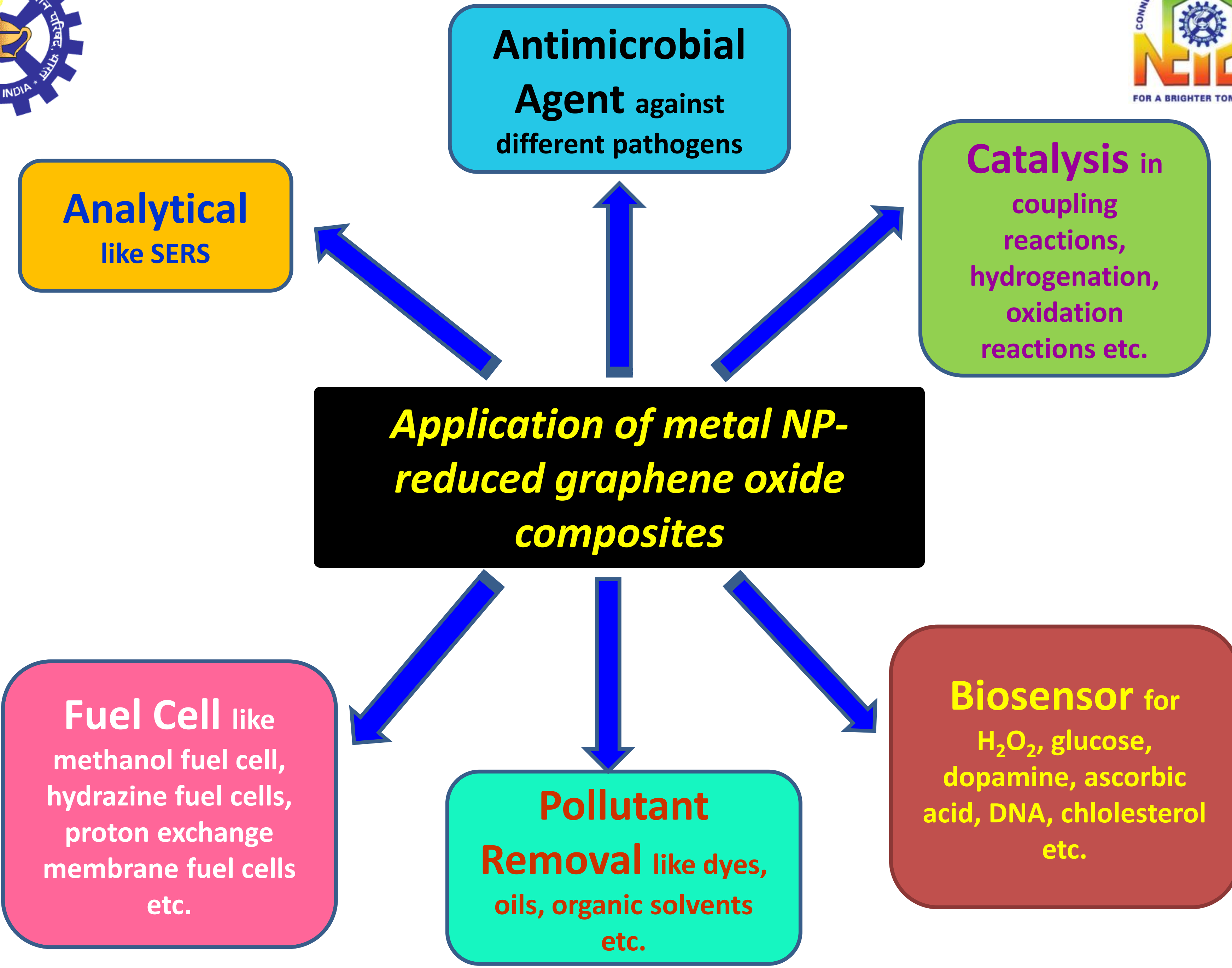
Reducing agent



Microwave/Ultrasonication/Heating /Mechanical Stirring



Metal nanoparticles decorated Graphene Oxide/Graphene sheets


Application of metal NP-reduced graphene oxide composites
Antimicrobial Agent against different pathogens
Analytical like SERS
Catalysis in coupling reactions, hydrogenation, oxidation reactions etc.
Fuel Cell like methanol fuel cell, hydrazine fuel cells, proton exchange membrane fuel cells etc.
Pollutant Removal like dyes, oils, organic solvents etc.
Biosensor for H_2O_2, glucose, dopamine, ascorbic acid, DNA, chlolesterol etc.

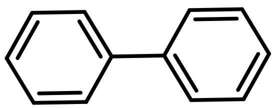
Organic coupling reaction using Metal NP-Graphene composite materials

One Component Coupling
(Homocoupling)

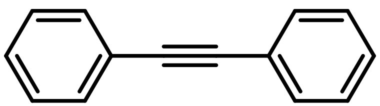
Two Component Coupling
(Suzuki, Heck, Sonogashira)

Three Component Coupling
(A3 Coupling and other)

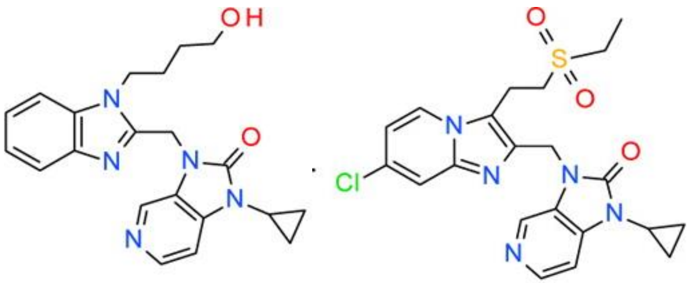
Biaryl, Biphenylacetylene, Heteroaromatic compounds containing nitrogen atoms



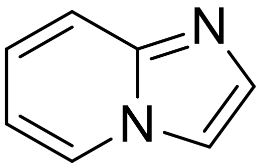
Biaryl



Biphenylacetylene



Imidazopyridine derivatives

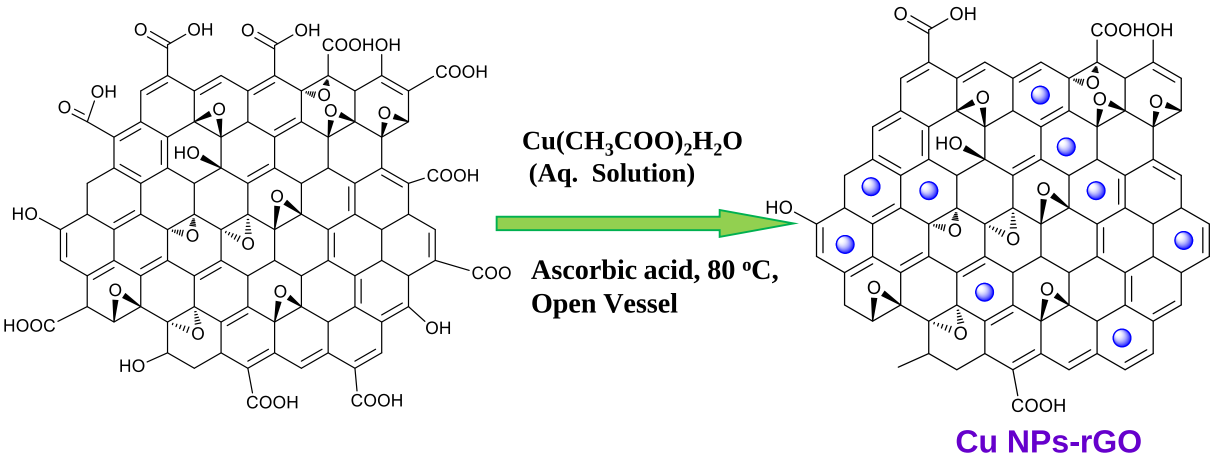


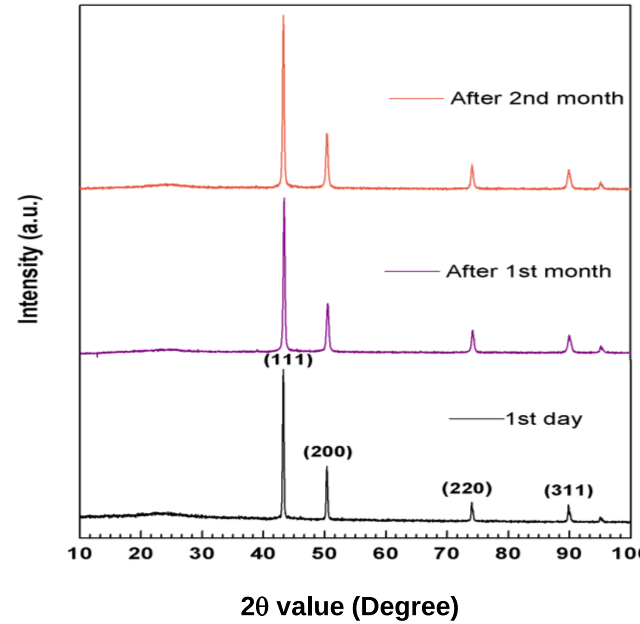
Imidazo[1,2-a]pyridine

Drawback associated with the previous literature of metal-graphene composite material catalysed coupling reaction

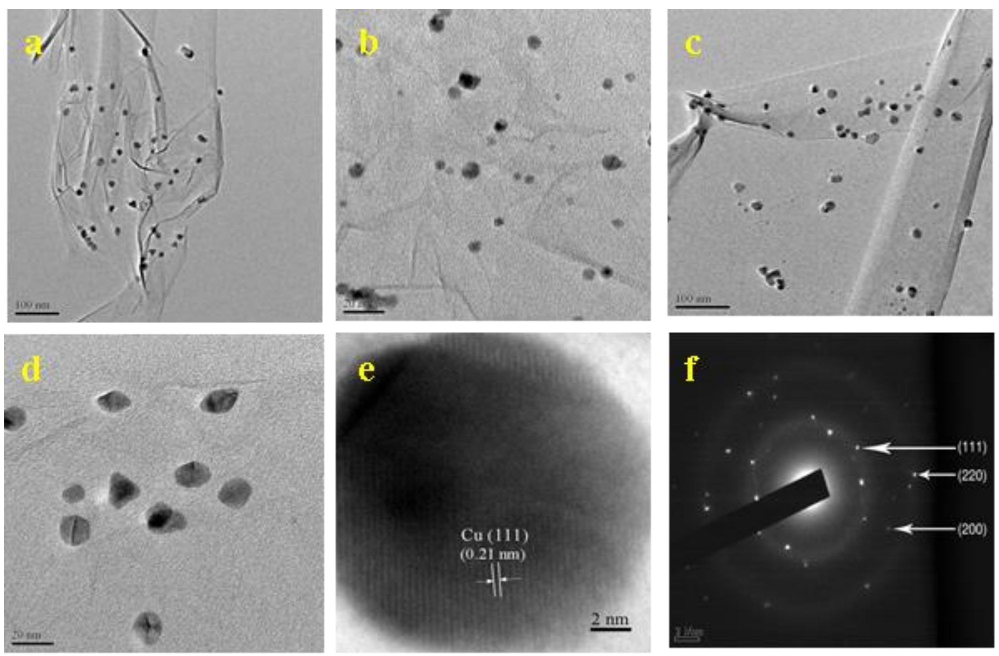
- ✓ **Use of toxic reducing agent**
- ✓ **Use of toxic ligand and capping agent**
- ✓ **Separation problem of the catalyst.**
- ✓ **Reusability of the catalyst**

Synthesis of Cu(0) NPs on to reduced graphene oxide sheets (CuNPs-rGO)

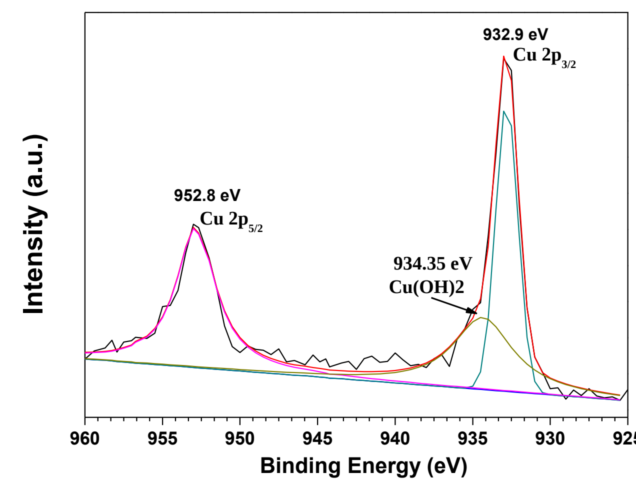




XRD Patterns CuNP on rGO



TEM images of CuNP on rGO



XPS spectra of CuNP on rGO

Catalytic activity of synthesized Cu NPs on rGO towards homocoupling of Phenylboronic acid

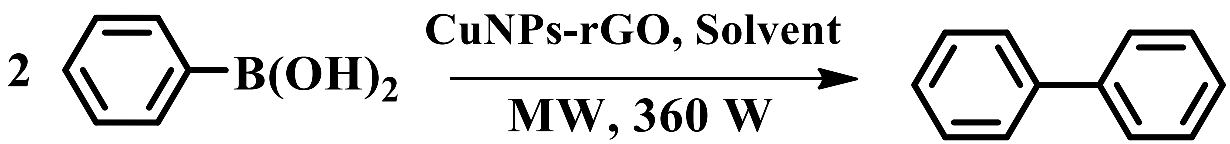
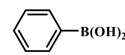
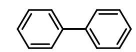
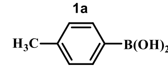
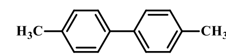
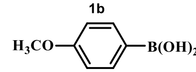
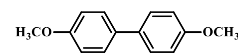
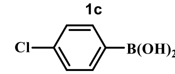
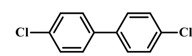
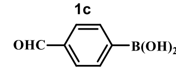
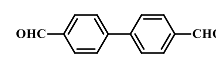
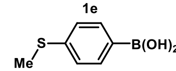
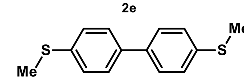
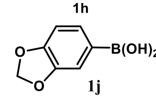
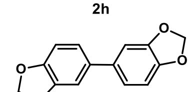
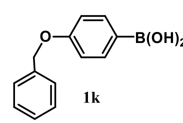
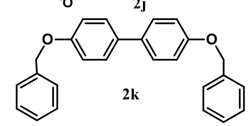
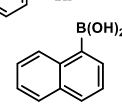
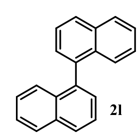
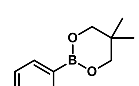
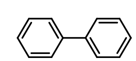


Table 1: Effect of solvent and catalyst loading on the homocouplig reactions of phenylboronic acid catalyzed by CuNPs-rGO

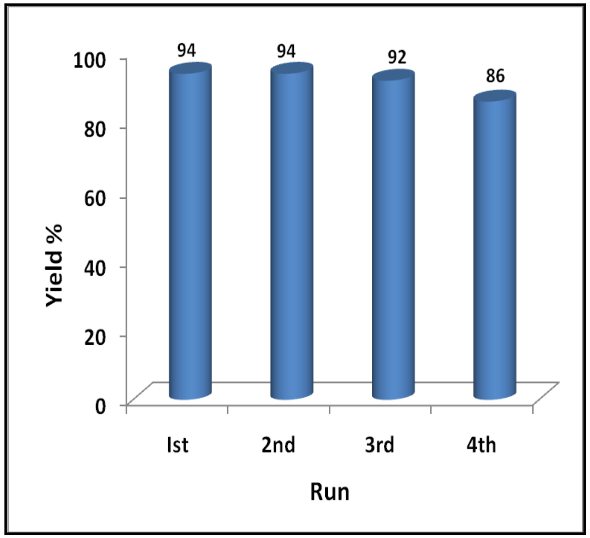
Entry	Solvent	Catalyst loading mg/mL	Time (min)	Yield[b] (%)
1	Water	28	14	42
2	DMSO	25	15	80
3	DMF	25	12	94
4	Toluene	30	14	54
5	Xylene	26	12	65
6	Dichloroethane	25	15	37
7	Ethanol	28	12	42
8	DMF	10	20	77
9	DMF	50	12	90

Reaction conditions: Phennylboronic acid (1.0 mmol),catalyst (10-50 mg/mL), solvent (2 mL), MW 360 W;
[b] isolated yield

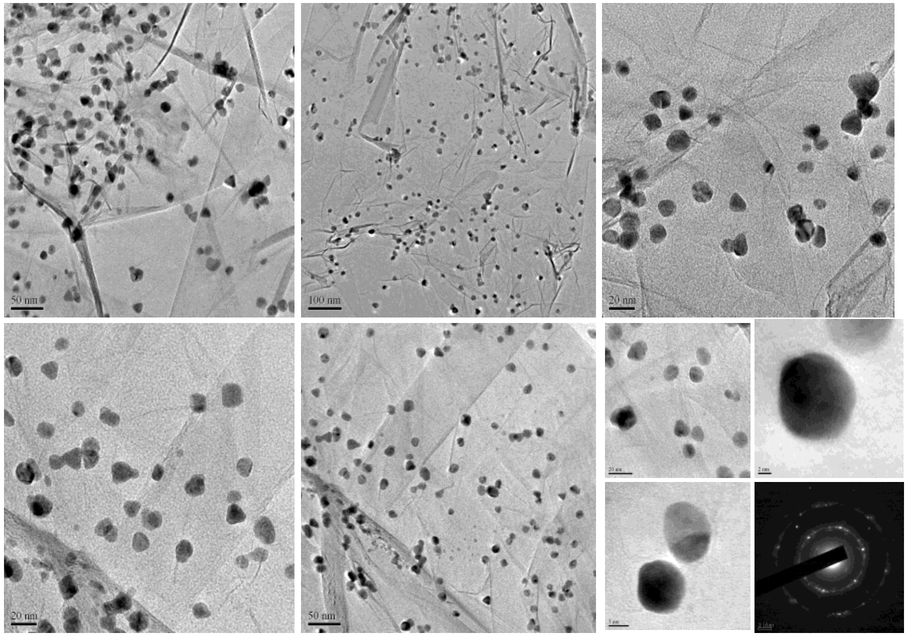
Table 2. Microwave assisted homocoupling of various arylboronic acid

Boronic acid	Biphenyl	Time (min)	Yield (%)[b]
 1a	 2a	12	94
 1b	 2b	12	92
 1c	 2c	13	94
 1c	 2c	15	92
 1e	 2e	15	86
 1h	 2h	12	94
 1j	 2j	12	94
 1k	 2k	15	90
 1l	 2l	12	94
 1k	 2a	15	90

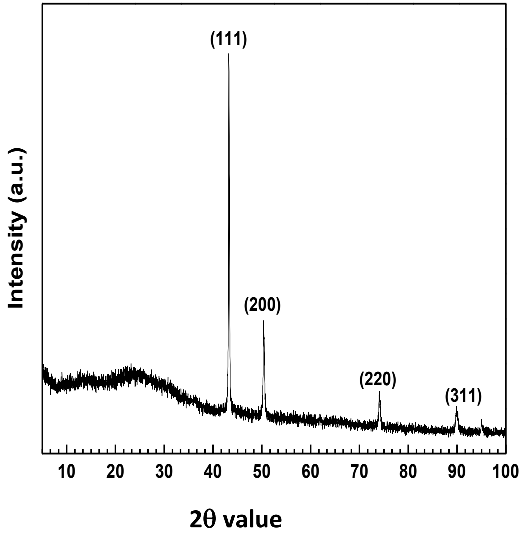
Characterization of the catalyst after reaction



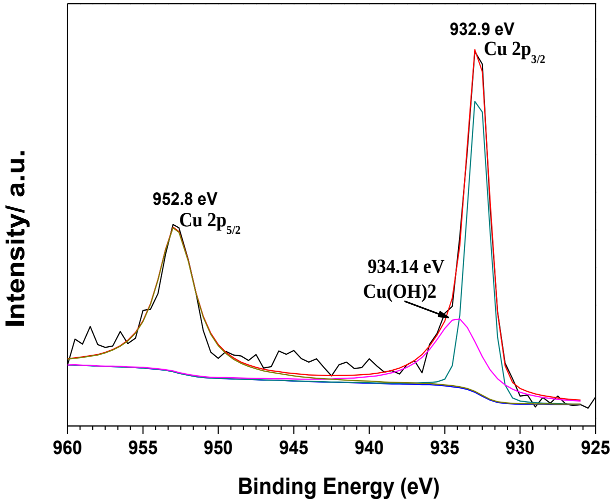
Recycling activity of the Cu(0) nanoparticle -rGO composites

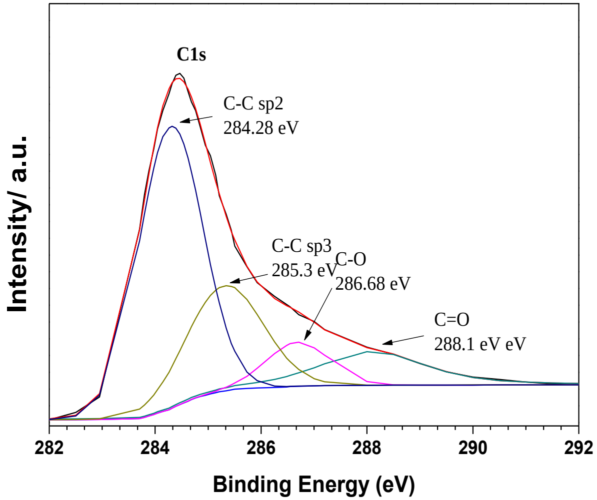


TEM & HRTEM images



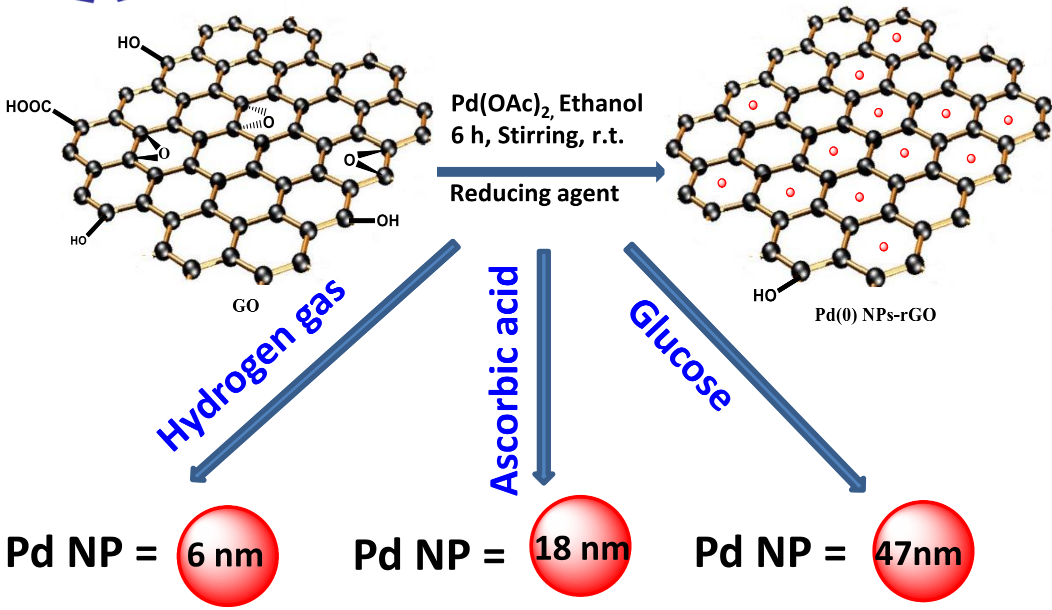
XRD pattern

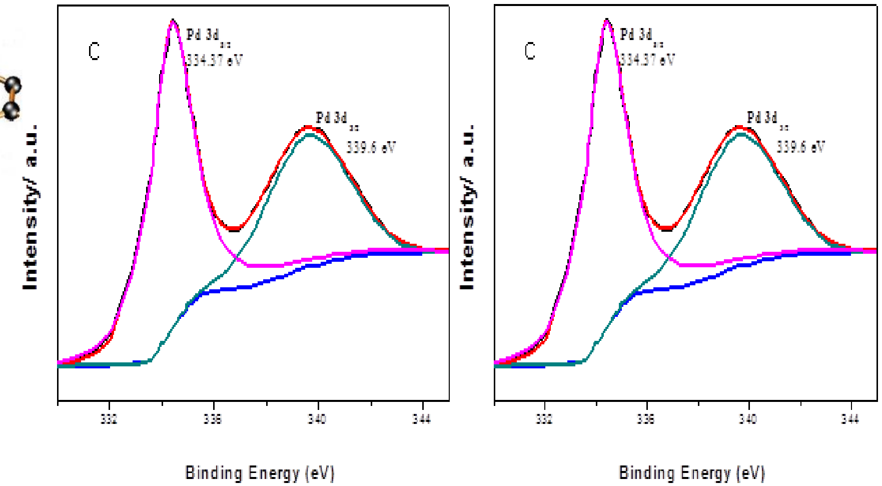




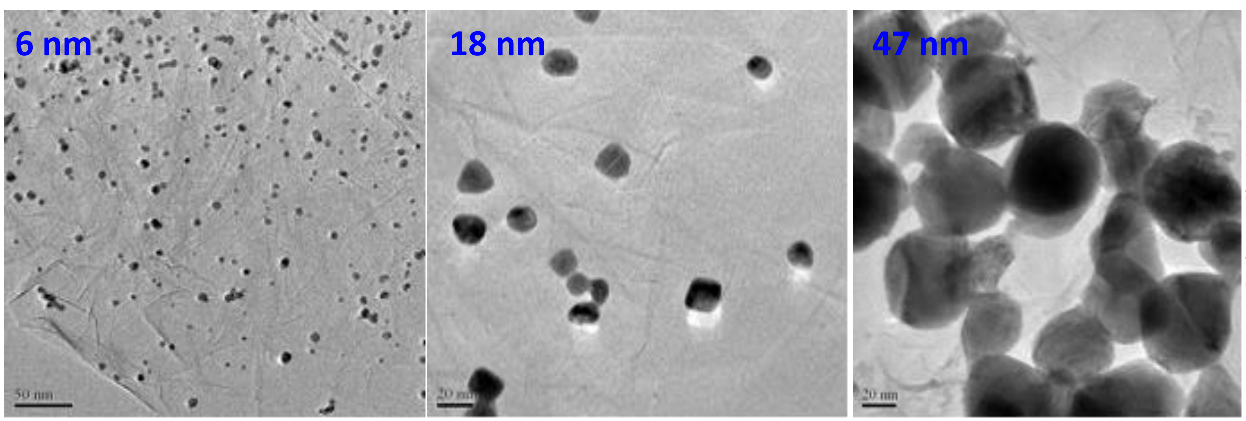
XPS analysis

Pd nanoparticles of different size and shape on to reduced graphene oxide nanosheets (PdNPs-rGO)

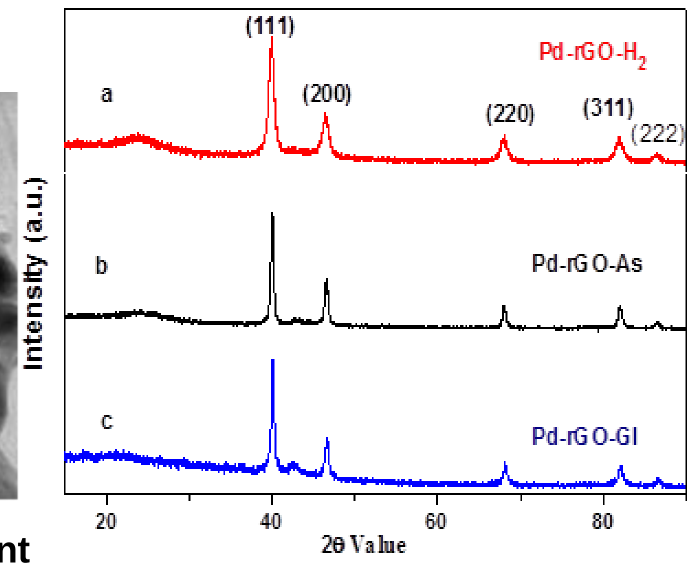




Pd 3d XPS core level spectra of Pd-rGO-H_2 and Pd-rGO-As

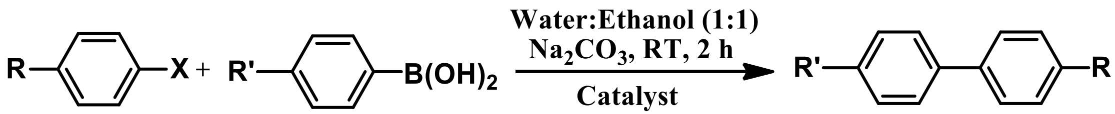


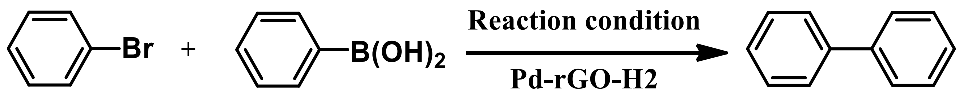
TEM images of Pd NPs on rGO synthesized by different reducing agent



XRD Patterns PdNP on rGO

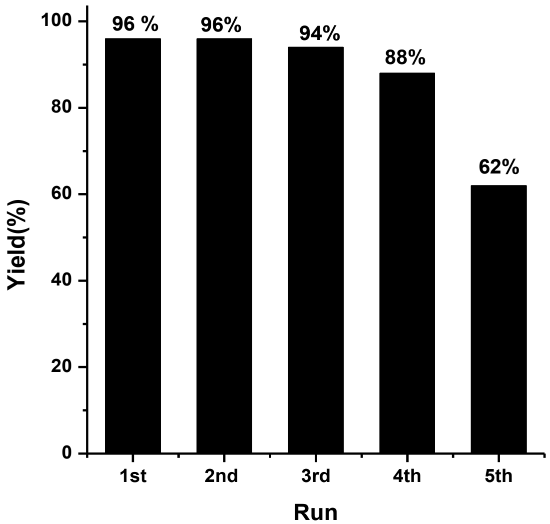
Catalytic activity of synthesized Pd NPs of different size and shape towards Suzuki cross-coupling reaction



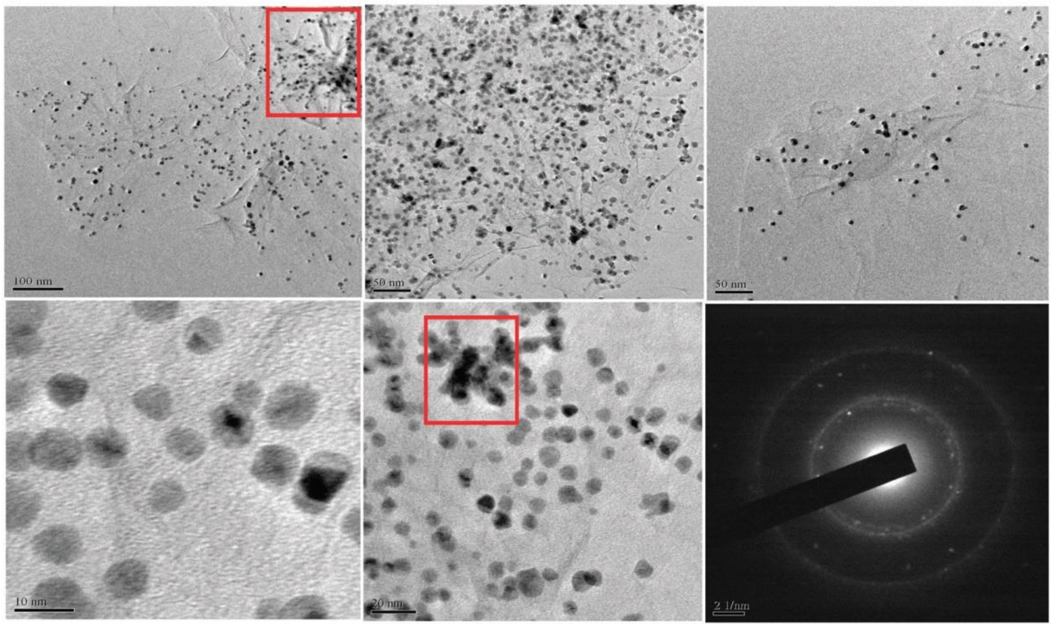


Catalyst	Elemental Contents			Particle Diameter (nm)	R-X	R´-B(OH)$_2$	Yield (%)
	C	H	O				
Pd-rGO-H$_2$	55.0	2.3	42.5	6 ± 2	R= Ph-; X= Br	R´= Ph-	96
					R= p(OMe)Ph-; X=Br	R´= Ph-	95
Pd-rGO-As	45.2	2.4	52.2	18 ± 9	R= Ph-; X= Br	R´= Ph-	81
					R= p(OMe)Ph-; X=Br	R´= Ph-	76
Pd-rGO-Gl	44.2	1.9	53.8	47 ± 5	R= Ph-; X= Br	R´= Ph-	72
					R= p(OMe)Ph-; X=Br	R´= Ph-	65

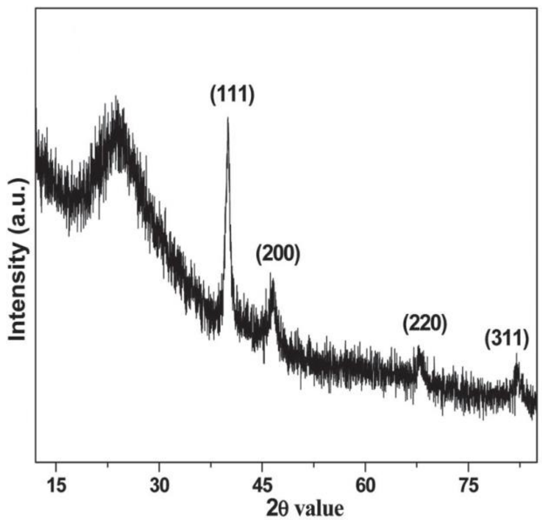
Characterization of the catalyst after reaction



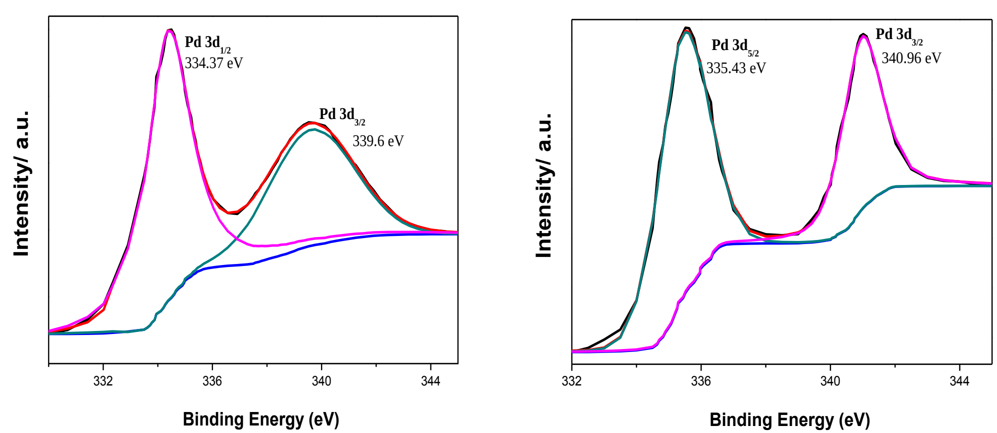
Recycling of the Pd -rGO-H_2 catalyst



TEM & HRTEM images



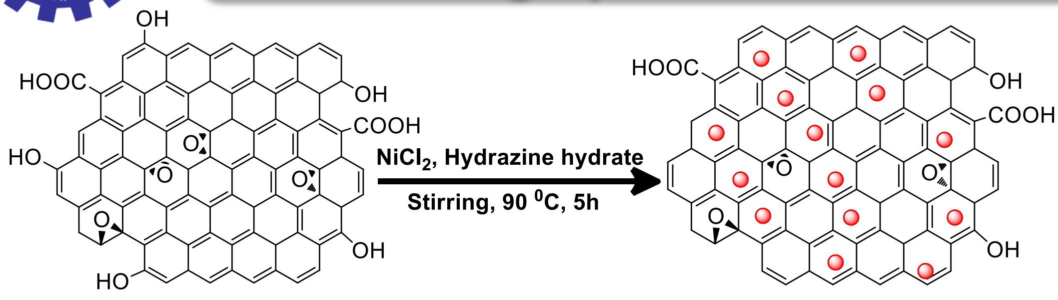
XRD pattern



XPS analysis

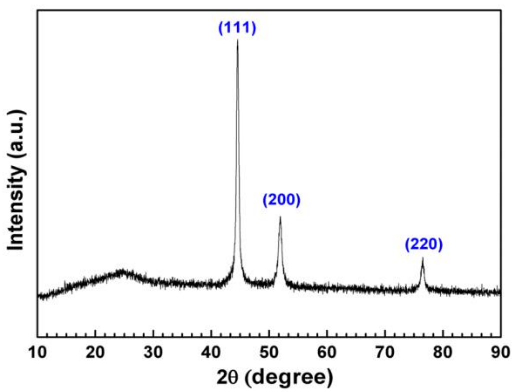
M R Das et al. New J. Chem, 2015, 39, 6631.

Magnetically recoverable Ni NPs supported on reduced graphene oxide nanosheets (NiNPs-rGO)

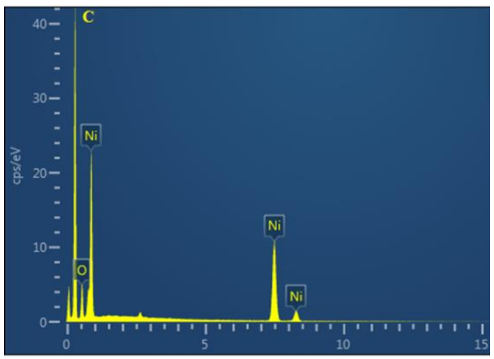


GO

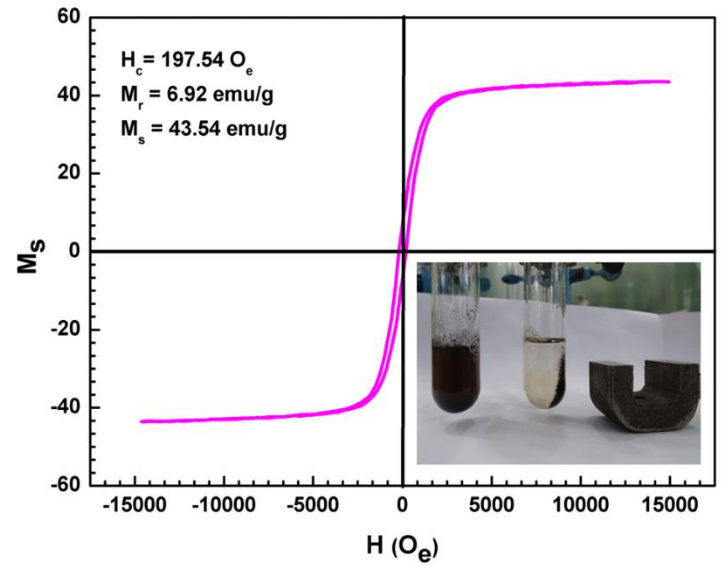
NiNPs-rGO



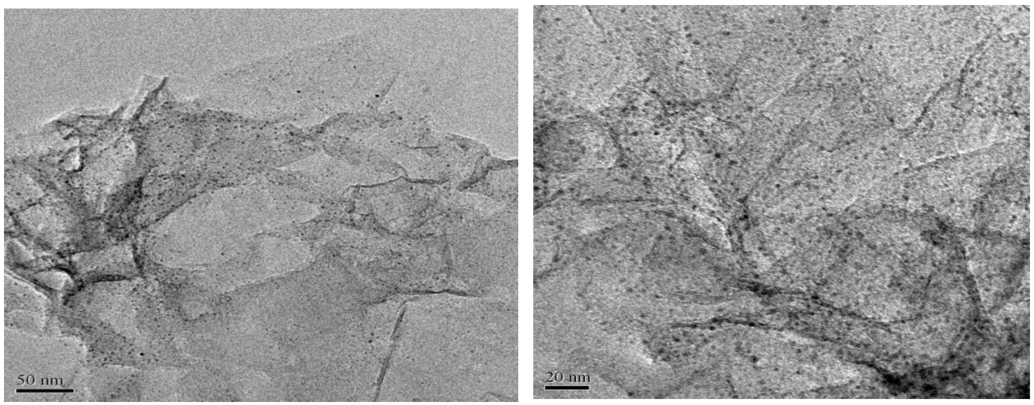
XRD Patterns NiNPs on rGO



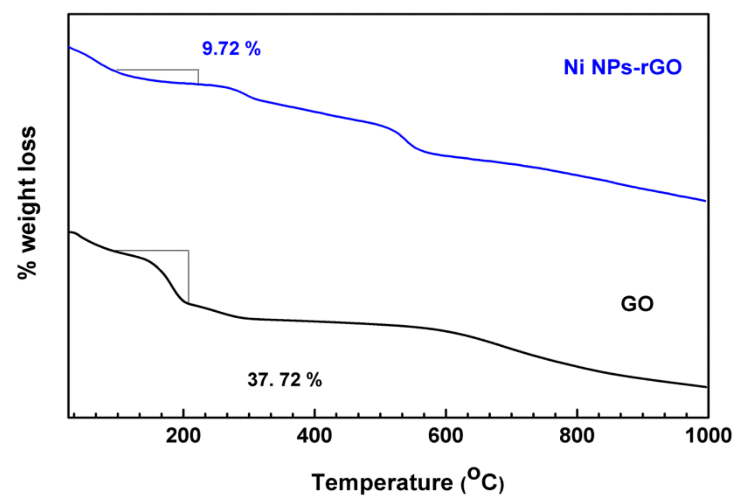
EDS analysis of NiNPs-rGO



Variation of magnetization (M) with magnetic field (H) at room temperature for NiNPs-rGO

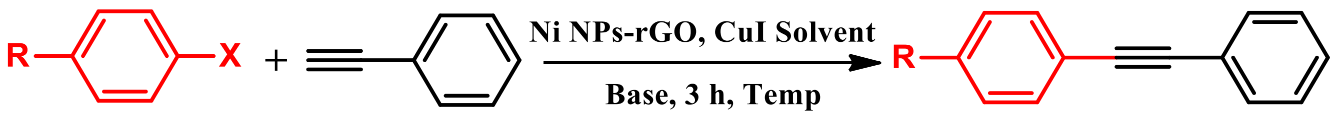


TEM images of NiNPs on rGO

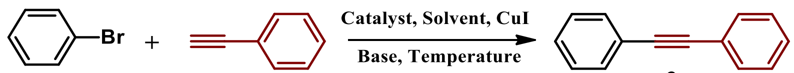


TGA curve of (a) GO and (b) NiNPs -rGO composites

Catalytic activity of synthesized Ni NPs-rGO towards the Sonogashira cross-coupling reaction



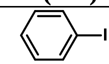
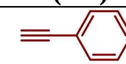
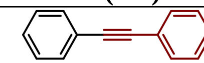
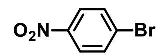
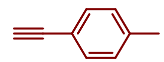
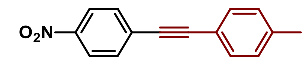
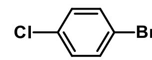
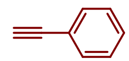
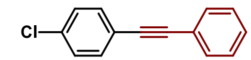
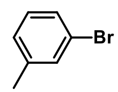
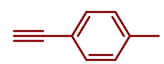
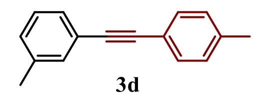
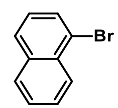
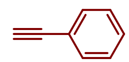
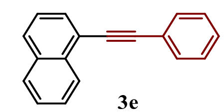
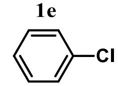
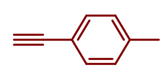
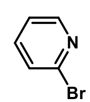
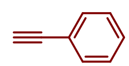
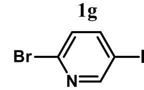
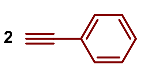
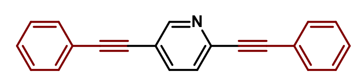
Biphenylacetylene



1e 2a 3a

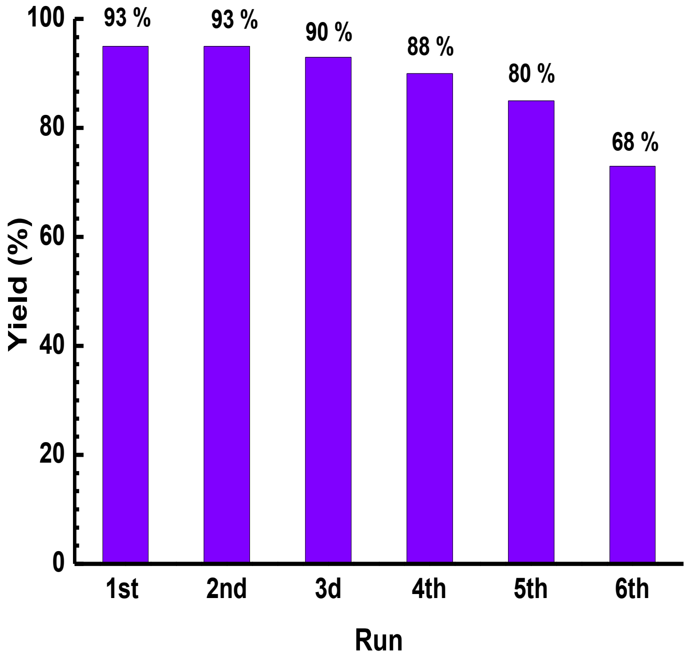
Solvent	Base	Temperature (^{O}C)	Yield (%) [b]
H_2O	K_2CO_3	110	15
DMF	K_2CO_3	60	40
DMF	K_2CO_3	120	45
Toluene	K_2CO_3	120	30
NMP	K_2CO_3	60	70
NMP	K_2CO_3	100	85
NMP	**K_2CO_3**	**120**	**93**
DMSO	K_2CO_3	100	80
DMSO	K_2CO_3	120	80
NMP	KOH	120	50
NMP	Na_2CO_3	120	92
NMP	K_3PO_4	120	90
NMP	NaOH	120	58

[a] Reaction conditions: Bromobenzene (1 mmol), Phenyl acetylene (1.2 mmol), CuI (0.08 mmol), catalyst (25 mg, 0.15 mmol Ni), base (3 mmol), Solvent (5 mL), 4 h. [b] Isolated Yield

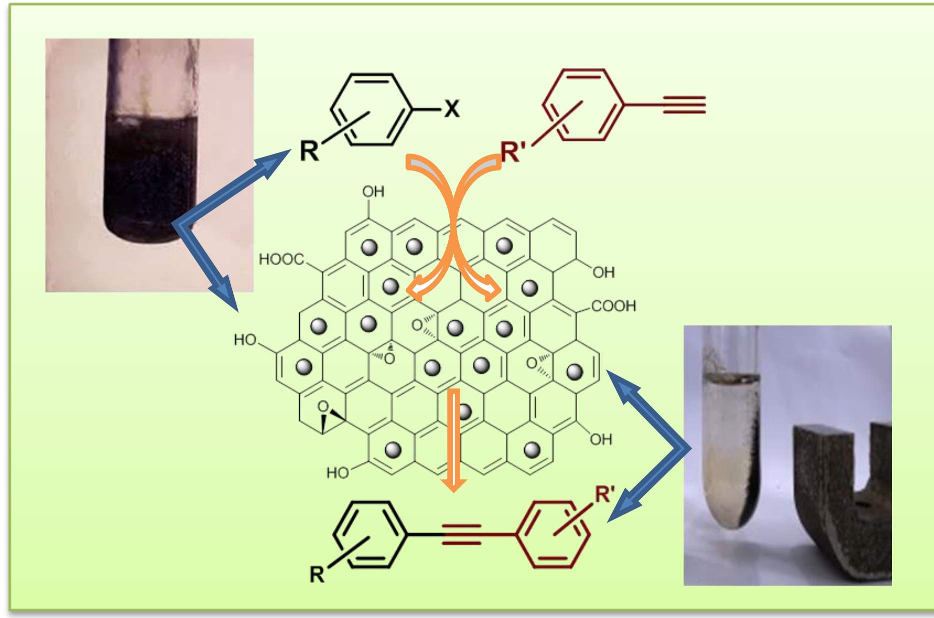
Aryl halide 1(a-h)	Alkynes 2(a-b)	Product 3(a-h)	Yield [b] (%)
 1a	 2a	 3a	95
 1b	 2b	 3b	88
 1c	 2a	 3c	91
 1d	 2b	 3d	93
 1e	 2a	 3e	93
 1f	 2b	 3f	72 [c]
 1g	 2a	 3g	86
 1h	2  2a	 3h	95

Aryl halide (1 mmol), Phenyl acetylene (1.2 mmol), CuI (0.08 mmol), catalyst (25 mg, 0.15 mmol of Ni), K_2CO_3 (3 mmol), NMP (5 mL, 120 °C, 4 h. [b] Isolated Yield. [C] The reaction was performed at 140 °C for 16h.

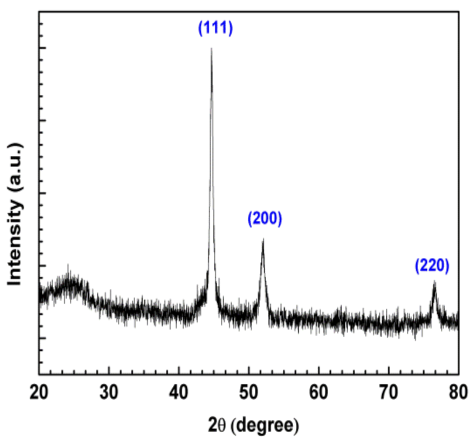
Reusability studies of Ni NPs-rGO

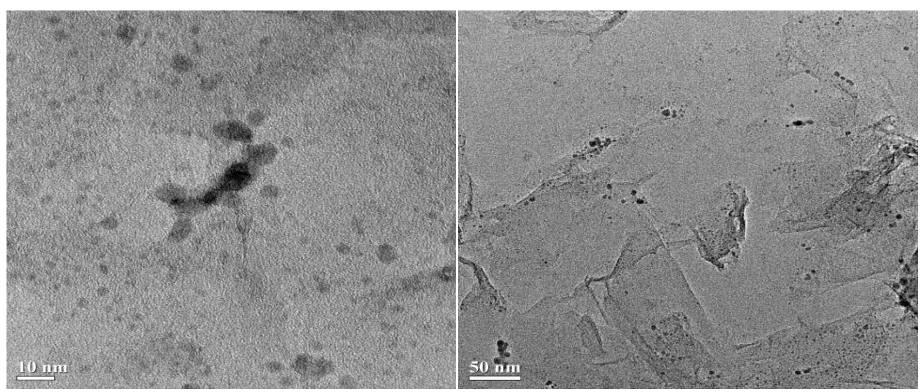


Ni NPs-rGO catalyst can be reused uoto six times without significant loss of catalytic activity



Ni NPs-rGO catalyst can be recovered from the reaction mixture by using an external magnet

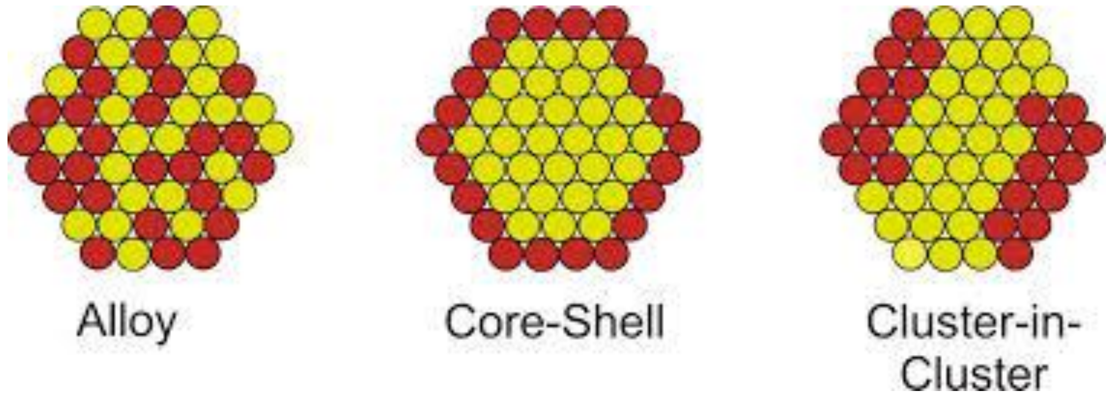




Characterization of the Ni NPs-rGO catalyst after performing the reaction

RSC Advances, 2015, 2015, 5, 103105

Bimetallic Nanoparticles



- **Bimetallic NPs consists of two metal components within a single particle.**

- **Different nanostructures are alloy/intermetallics, core-shell, cluster-in-cluster etc.**

- **Exhibits synergistic effects.**

- **Bimetallic-graphene nanocomposites exhibits exciting properties and finds applications in several fields.**

Applications of Bimetallic Graphene Nanocomposites

Bimetallic-graphene Nanocomposites

Photothermal therapy for treatment of different cancer cells

Biosensors for detection of molecules like glucose, uric acid, dopamine etc.

Hydrogen evolution & Oxygen Reduction Reaction

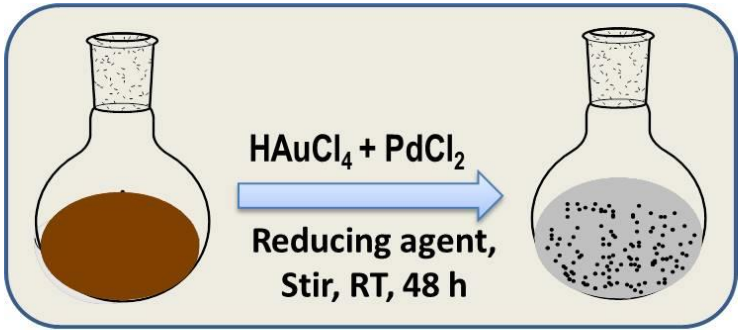
Photocatalysis for removal of pollutants

Organic catalytic reactions (reduction of 4-nitrophenol, coupling reactions etc.)

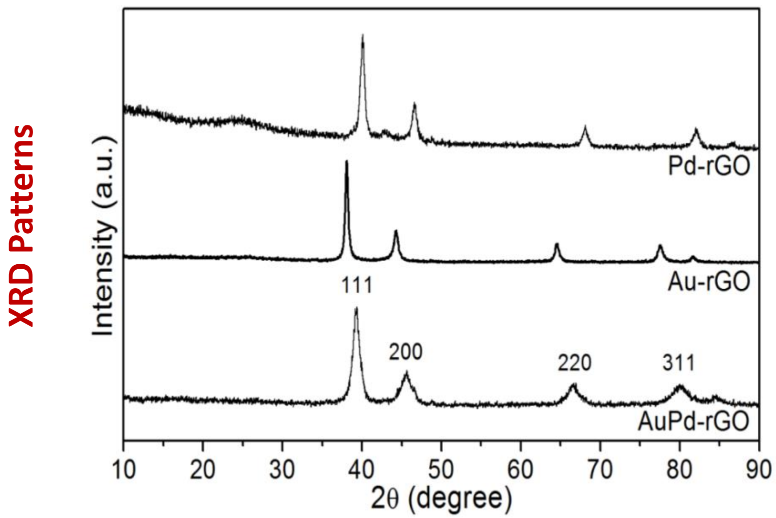
Targeted drug delivery & Bioimaging

Au-Pd alloy bimetallic nanoparticles on reduced graphene oxide

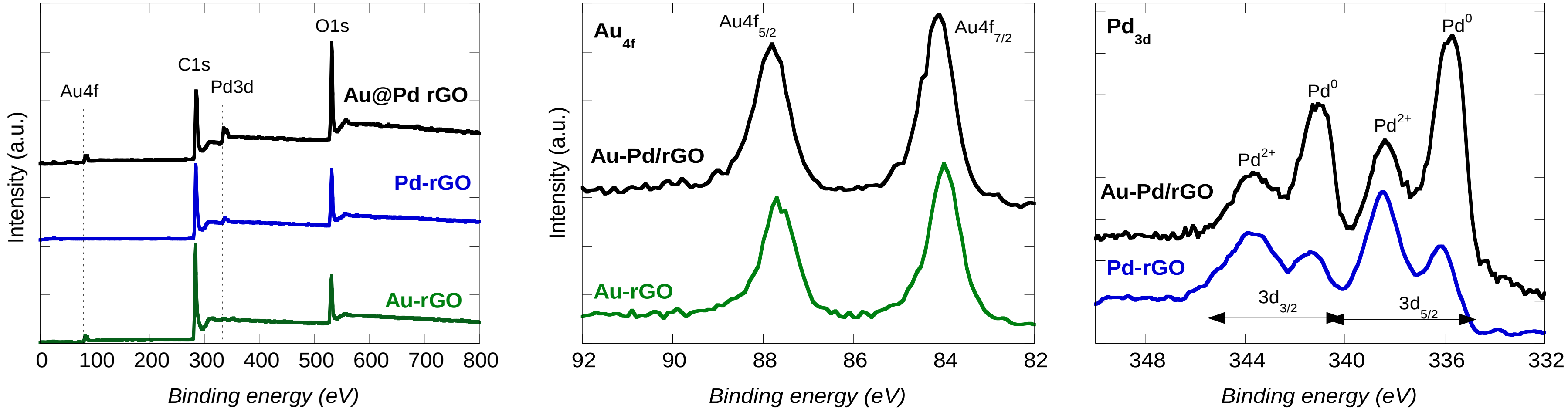
- A simple solution chemistry technique was adopted for synthesis of Au-Pd NPs/rGO nanocomposites.
- Use of an eco-friendly reducing agent like ascorbic acid during synthesis.



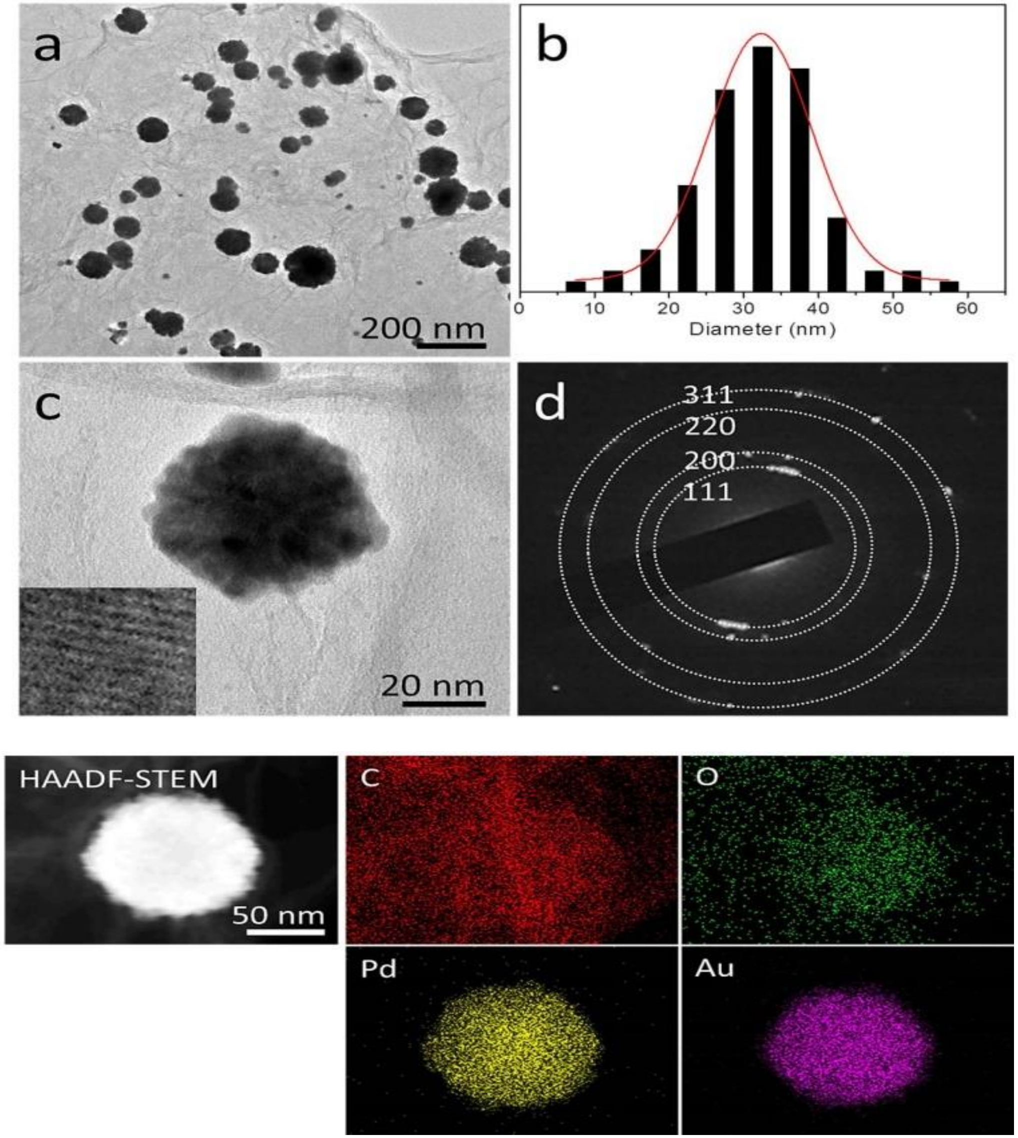
Synthesis of AuPd NPs/rGO nanocomposites



XPS analysis of AuPd NPs-rGO



HRTEM and HAADF-STEM analysis of Au-Pd NPs/rGO

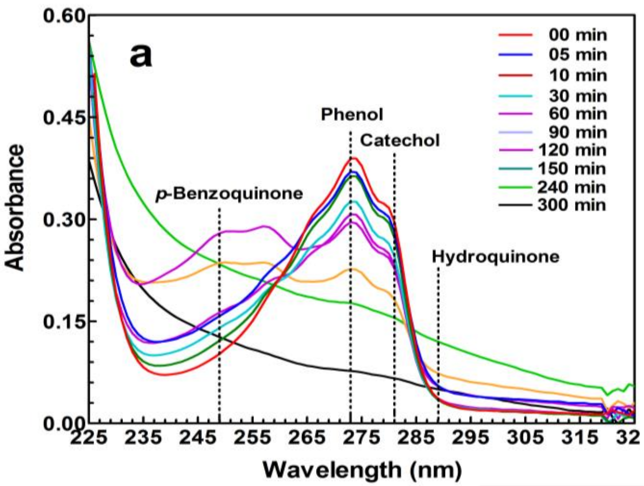


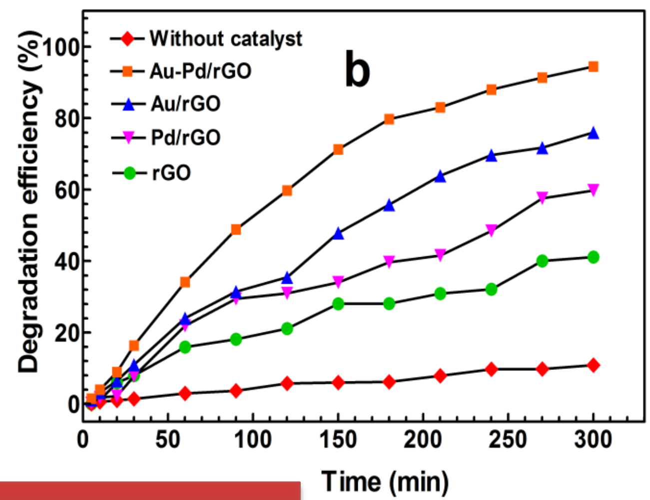
- Au-Pd NPs/rGO of size 32 ± 0.4 nm was obtained from TEM analysis
- Alloy structure of Au-Pd NPs/rGO was confirmed from both HRTEM and HAADF-STEM analysis.

Photocatalytic degradation using AuPd NPs-rGO nanocomposites

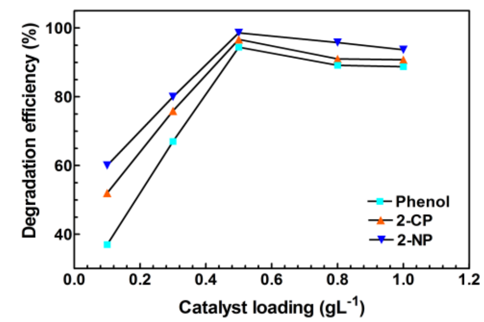
- Photocatalytic degradation of phenol, 2-chlorophenol and 2-nitrophenol studied in presence of sunlight
- Above 90% degradation was observed for all the organic molecules

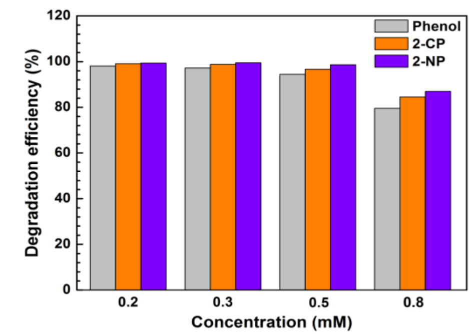
Degradation of phenol

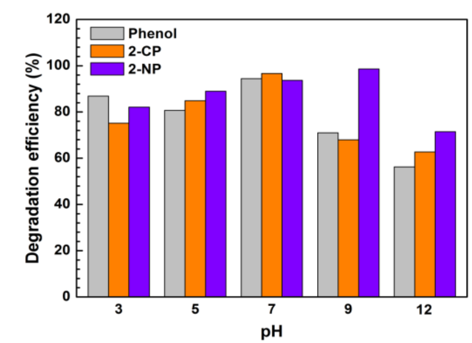




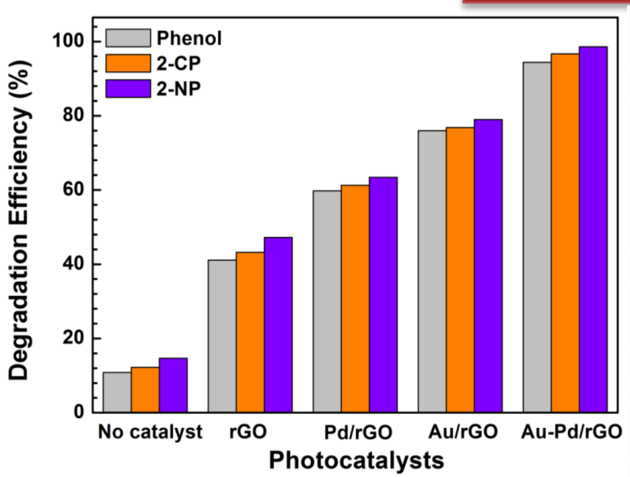
Analysis of different parameters on degradation

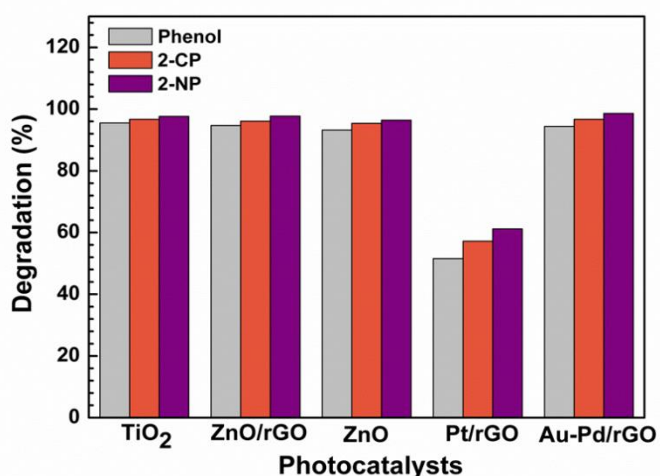




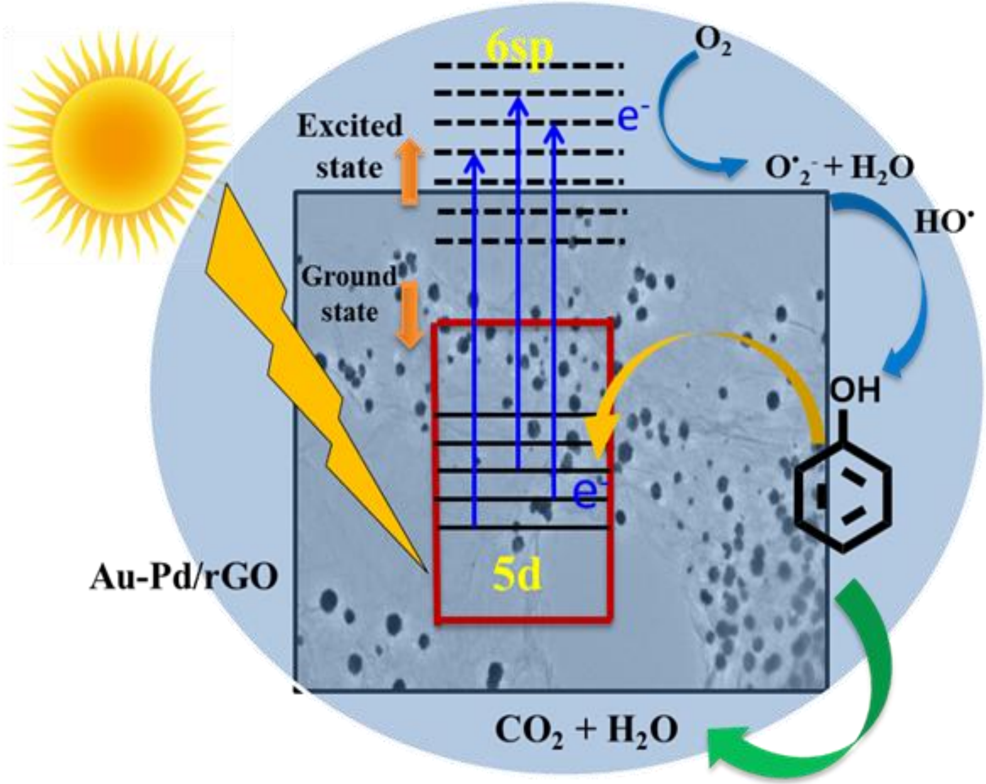


Catalyst comparison

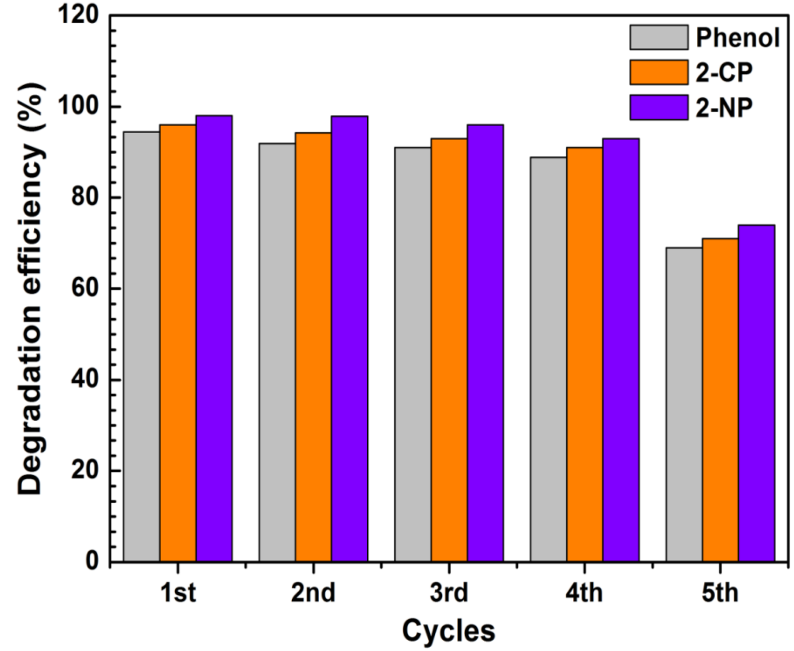




Mechanism of photocatalytic degradation and reusability studies



Reusability Study



$O_2 + e^- \rightarrow O^{\bullet}{}_2^-$

$O^{\bullet}{}_2^- + H_2O \rightarrow HO_2^{\bullet} + OH^-$

$e^- + HO_2^{\bullet} + H^+ \rightarrow H_2O_2$

$e^- + H_2O_2 \rightarrow OH^{\bullet} + OH^-$

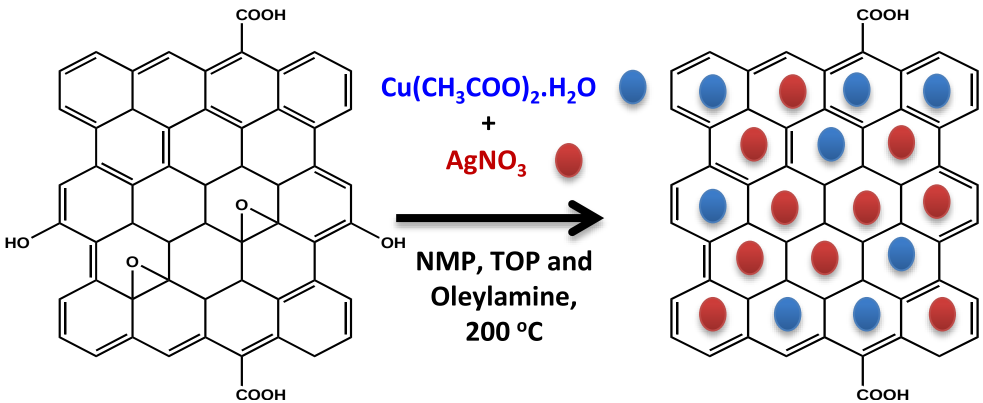
$OH^{\bullet}$ + Phenols → Degraded products

Catalyst could be repeatedly used upto 4th cycle after which it activity decreases

Nanoscale, 2016, 8, 8276 (IF 7.76)

Bimetallic Cu-Ag alloy nanoparticles on reduced graphene oxide sheets (Cu-Ag/rGO)

Synthesis

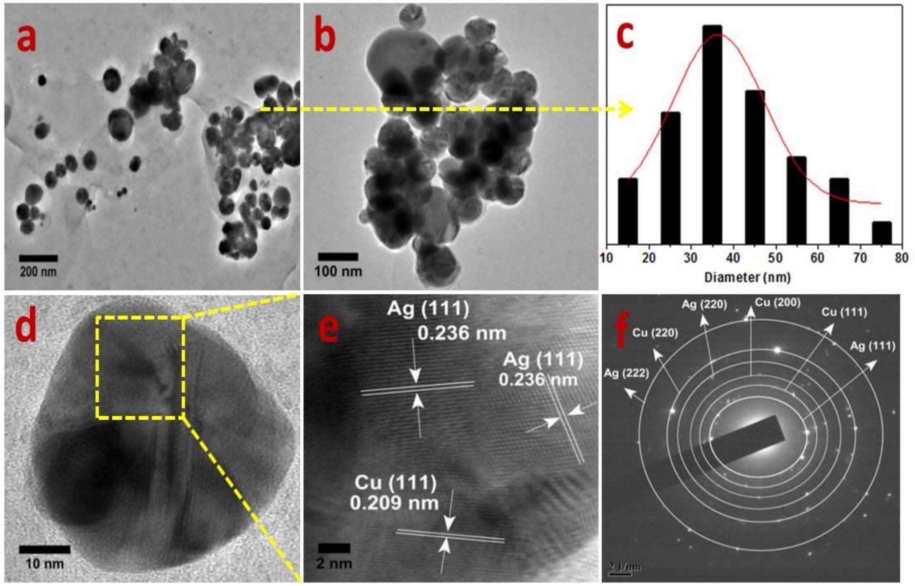


GO

Cu-Ag/rGO

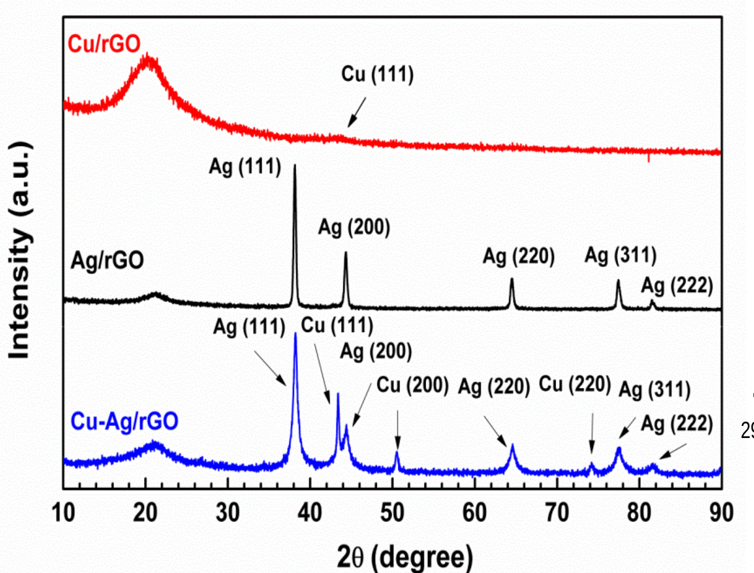
NMP: N-methyl-2-pyrrolidone
TOP: Trioctylphosphine

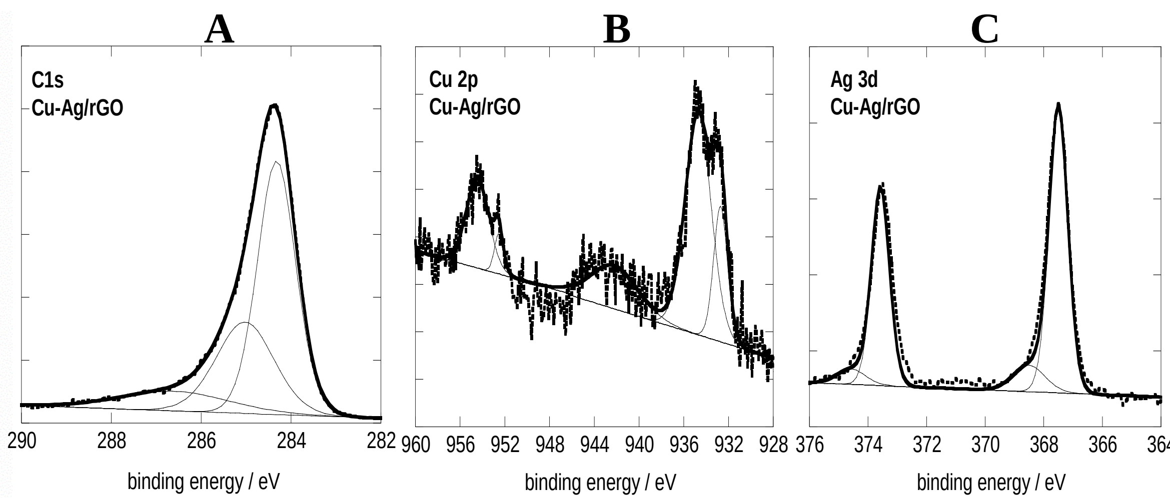
TEM images of Cu-Ag/rGO



Characterization

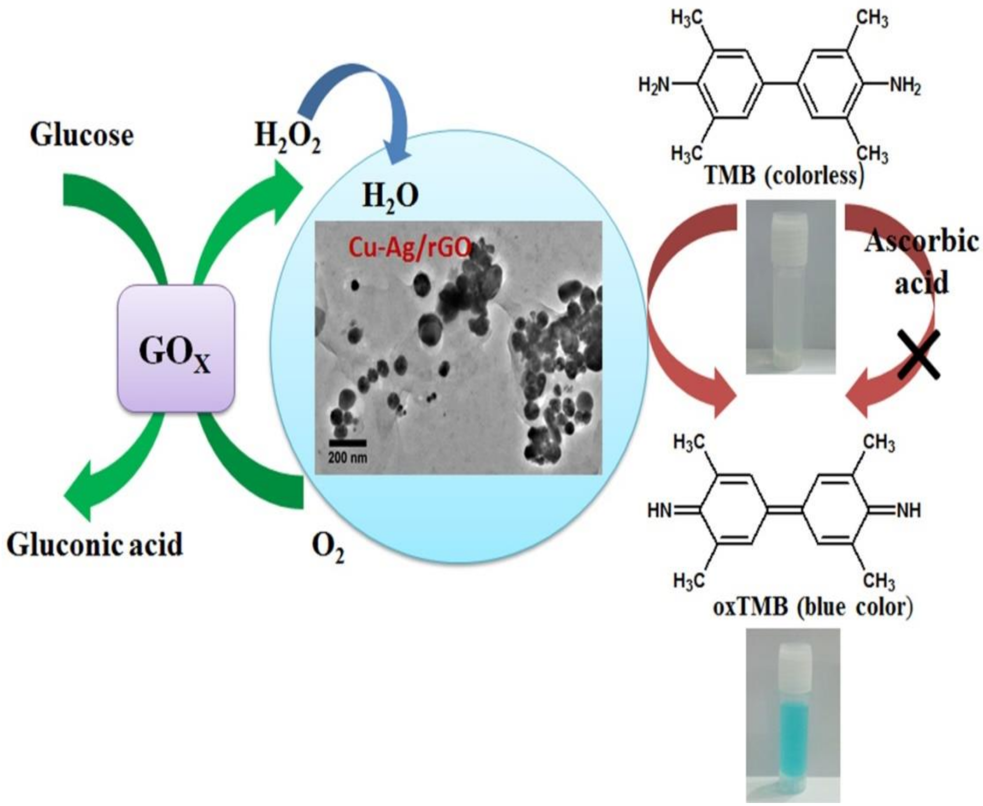
XRD of Cu-Ag/rGO, Cu/rGO, Ag/rGO





XPS core level spectra of Cu-Ag/rGO: (A) C_{1s} (B) Cu_{2p} and (C) Ag_{3d}

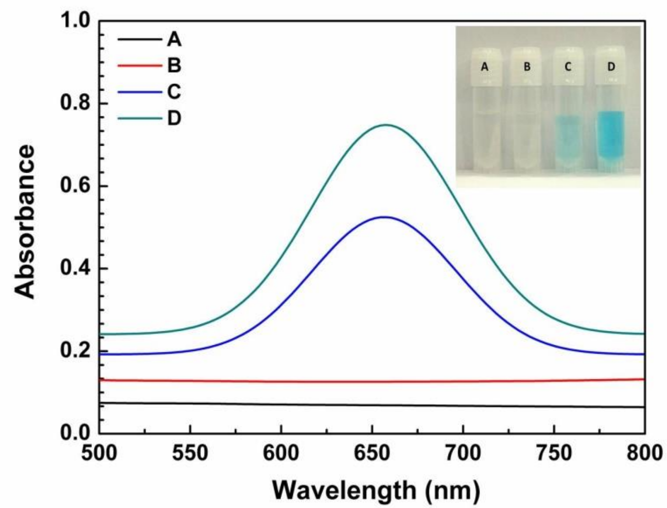
Cu-Ag/rGO as peroxidase mimic for detection of glucose and ascorbic acid



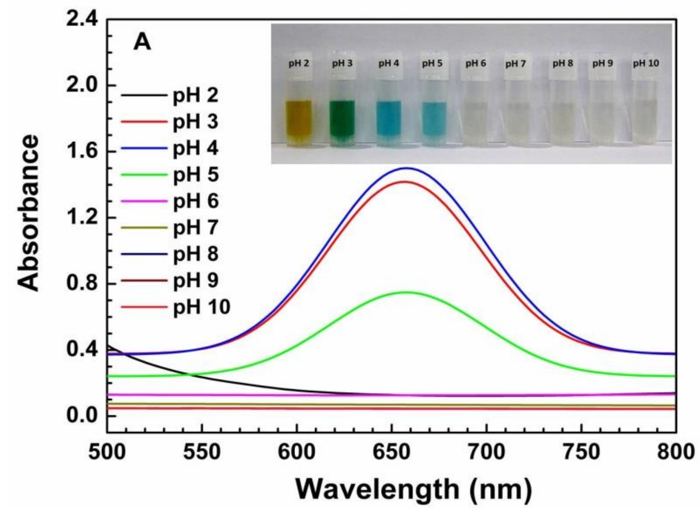
Colorimetric detection of glucose and ascorbic acid using Cu-Ag/rGO nanocomposites

- **Cu-Ag/rGO nanocomposites acts as artificial enzymes notably as peroxidase mimetic catalyst.**
- **It helps in the oxidation of peroxidase substrate 3,3',5,5'-tetramethylbenzidine (TMB) in presence of H_2O_2 to give a blue colour solution of oxidized TMB with an absorbance maximum located at 652 nm .**
- **Cu-Ag/rGO was found to follow Michaelis Menten enzyme kinetics.**
- **The change in colour change was used to study the detection of biologically relevant molecules glucose and ascorbic acid.**

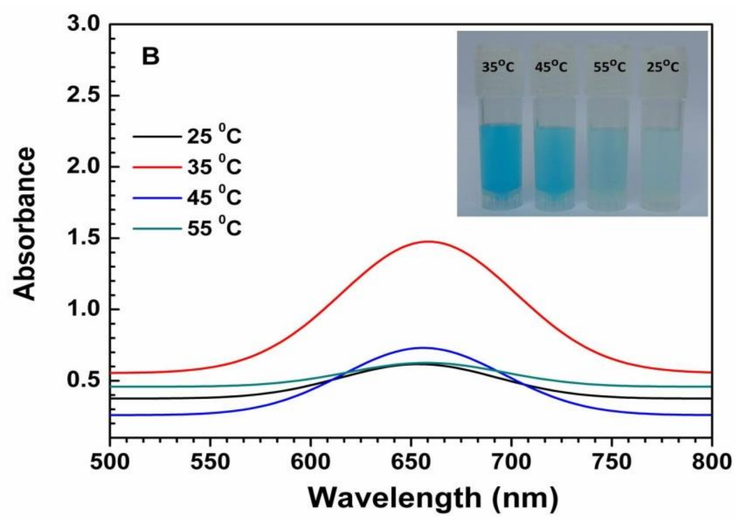
Peroxidase like activity of Cu-Ag/rGO nanocomposites



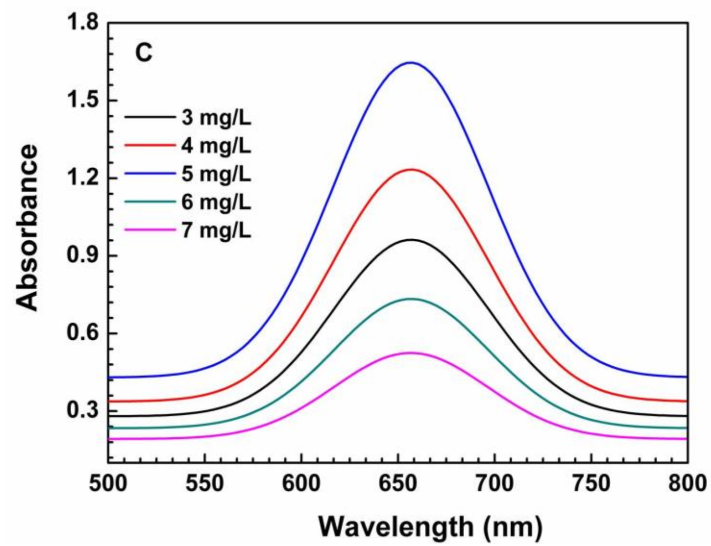
UV absorbance of TMB in presence of (A) 50 mM H_2O_2, (B) 5 mg L^{-1} Cu-Ag/rGO, (C) both H_2O_2 and GO and (D) both H_2O_2 and Cu-Ag/rGO



Oxidation of TMB at varying pH



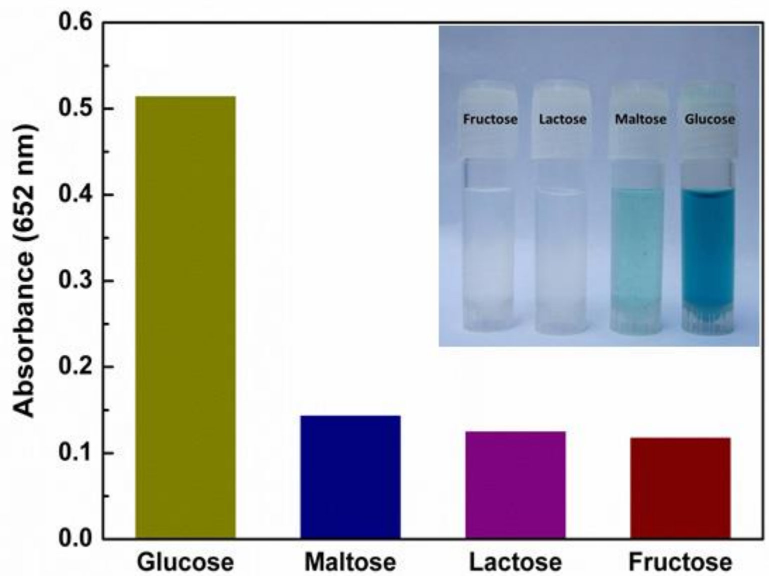
Oxidation of TMB at varying temperature



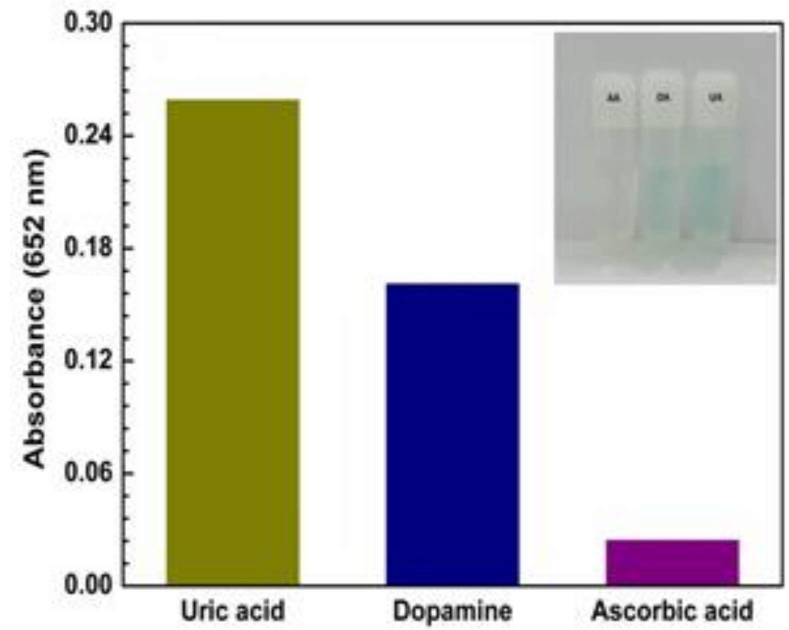
TMB oxidation at varying Catalyst concentration

Detection of glucose & ascorbic acid using Cu-Ag/rGO nanocomposites

Selectivity study of glucose



Selectivity study of ascorbic acid



Glucose Detection in real sample

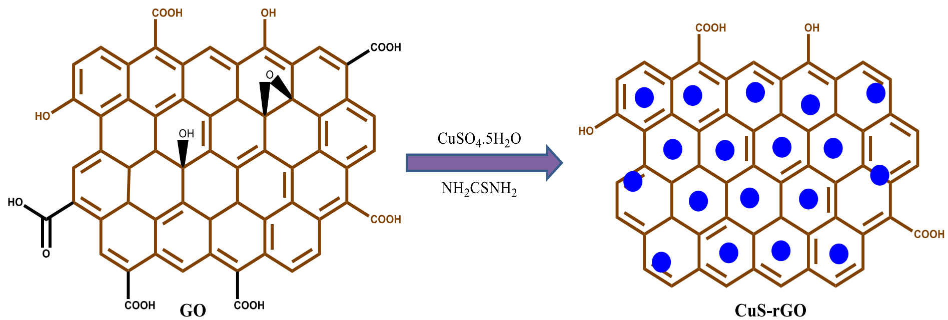
Sample No.	Sensor Result (mM)	Hospital Method (mM)	Relative Deviation (%)
1	4.134	4.5	8.13
2	6.49	6.731	3.713

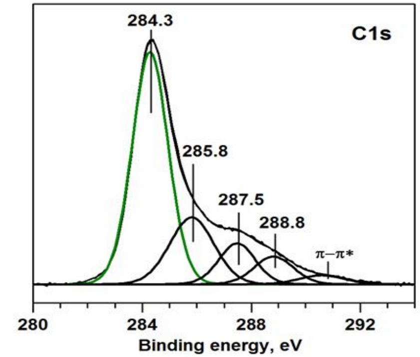
Sensors. and Actuators, B, 2017, 238, 842 (IF 4.758)

Metal Nanoparticles on Graphene, h-BN and Low Dimensional (2D) Transition Metal Chalcogenides

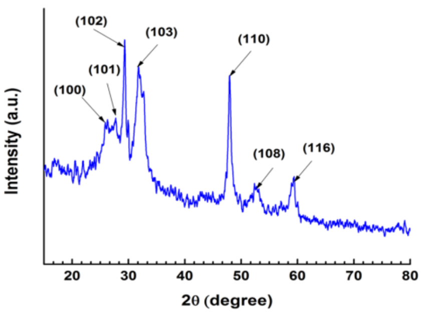
**A Project Under Joint Research programme of
Department of Science and Technology, Govt. of India
and
Russian Federation of Basic Research, Russia**

CuS nanoparticles on graphene nanosheets

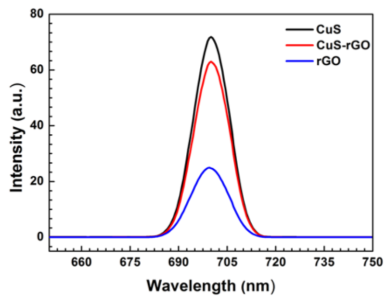




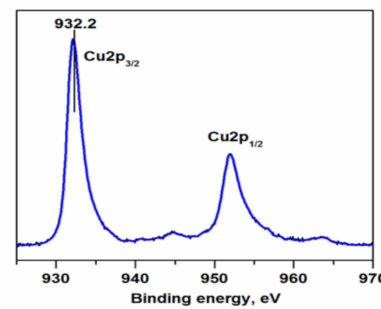
C1s XPS spectra of rGO sheet after deposition of CuS



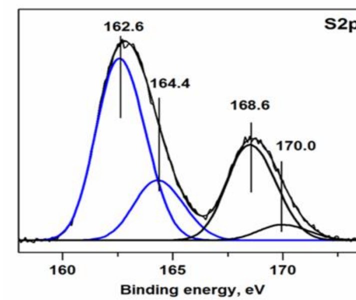
XRD pattern of CuS-rGO nanocomposites



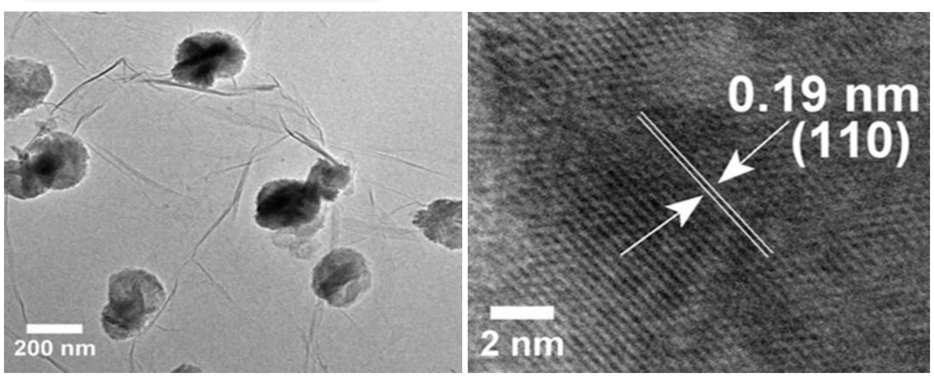
PL spectra of CuS, CuS-rGO and rGO sheets



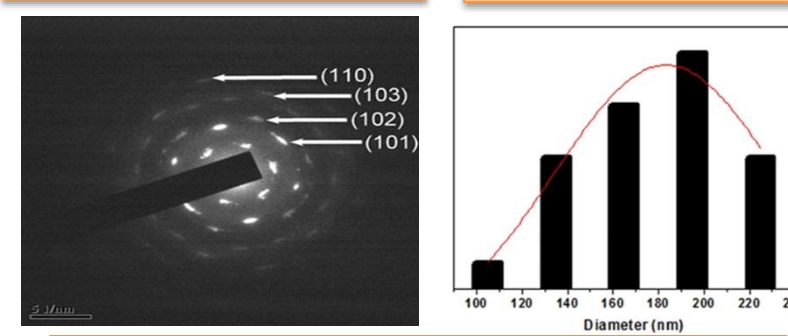
Cu2p XPS spectra of CuS-rGO



S2p XPS spectra of CuS-rGO

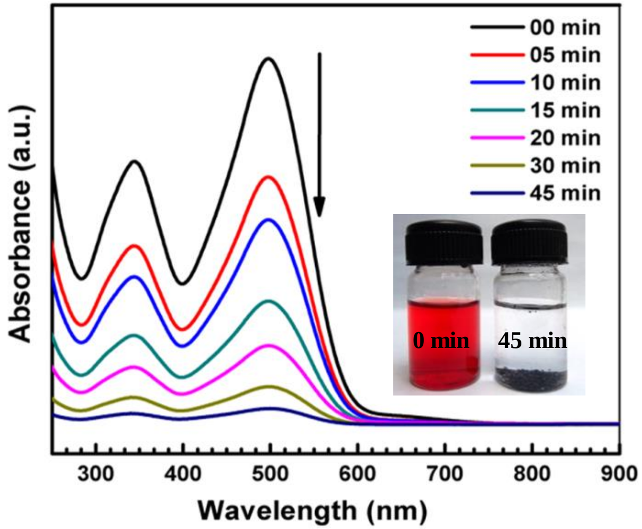


TEM and HRTEM images of CuS-rGO

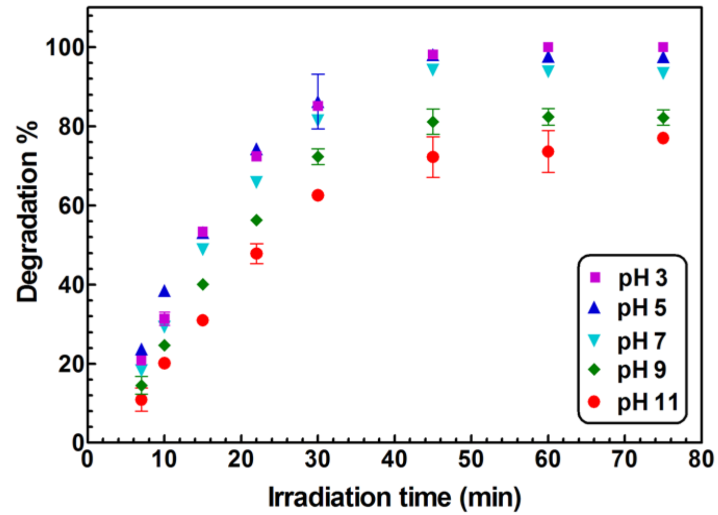


SAED pattern and particle size analysis of CuS-rGO

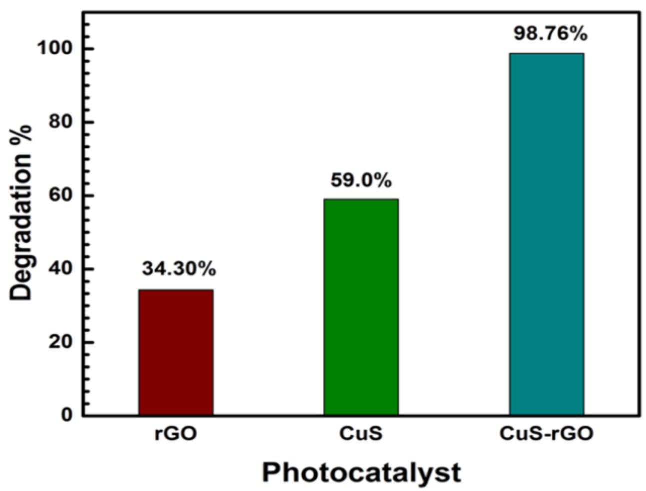
Photocatalytic activity of CuS-rGO nanocomposites towards degradation of Congo-Red dye molecule



Degradation of CR in presence of CuS-rGO



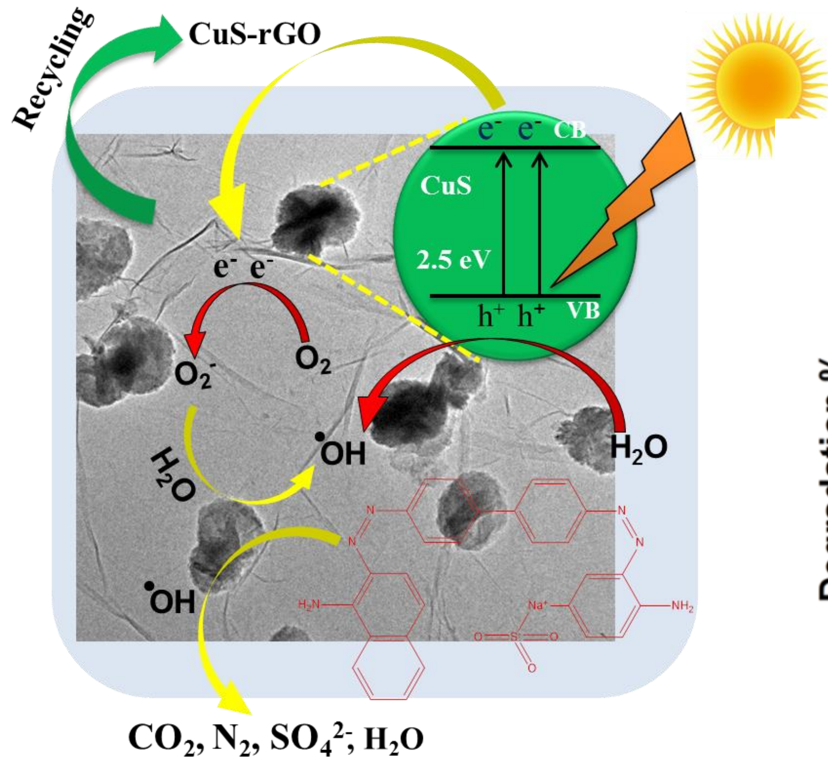
Degradation at different pH



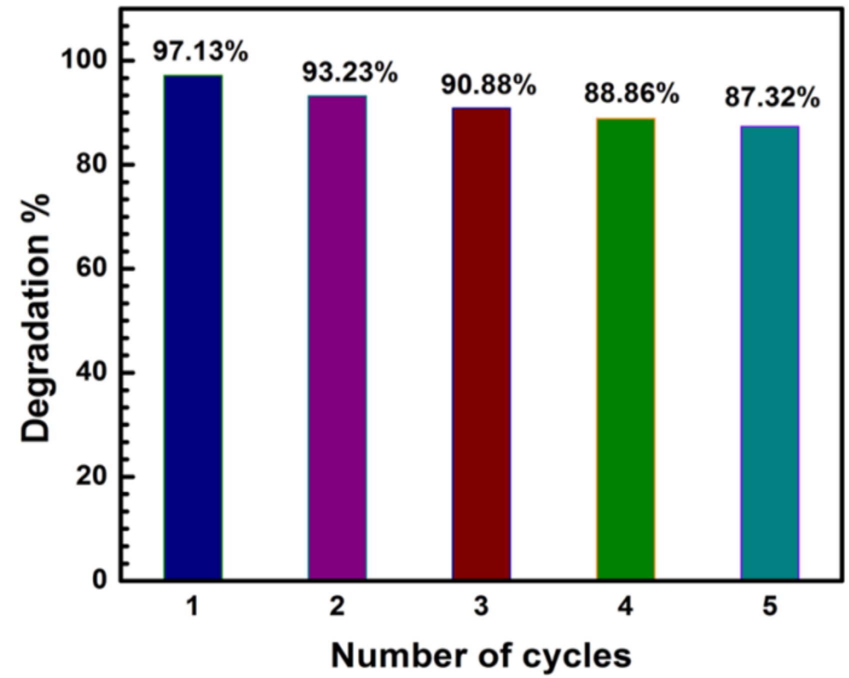
Degradation in presence of different catalysts

Photocatalyst	Light Source	Irradiation Time (min)	Degradation Efficiency (%)
TiO_2	Sunlight	45	88.98
ZnO-rGO	Sunlight	45	94.56
Pt-rGO	Sunlight	45	52.13
CuS-rGO	**Sunlight**	**45**	**98.80**

Degradation mechanism and usability study



Reusability



$CuS\text{-}rGO + h\upsilon \rightarrow CuS\ (h^+) + rGO\ (e^-)$

$O_2 + e^- \rightarrow O_2^{\cdot -}$

$O_2^{\cdot -} + H_2O \rightarrow HO_2^{\cdot} + OH^-$

$OH^- + h+ \rightarrow {}^{\cdot}OH$

Dye molecule + $^{\cdot}OH \rightarrow CO_2, H_2O, N_2, SO_4^{2-}$ etc.

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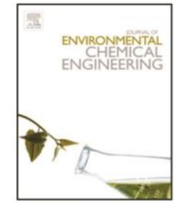

Microwave assisted synthesis of CuS-reduced graphene oxide nanocomposite with efficient photocatalytic activity towards azo dye degradation

Priyakshree Borthakur[a,b], Purna K. Boruah[a,b], Gitashree Darabdhara[a,b], Pinaki Sengupta[a,b], Manash R. Das[a,b,*], Andrei I. Boronin[c,e], Lidiya S. Kibis[c,e], Mariia N. Kozlova[d], Vladimir E. Fedorov[d,e]

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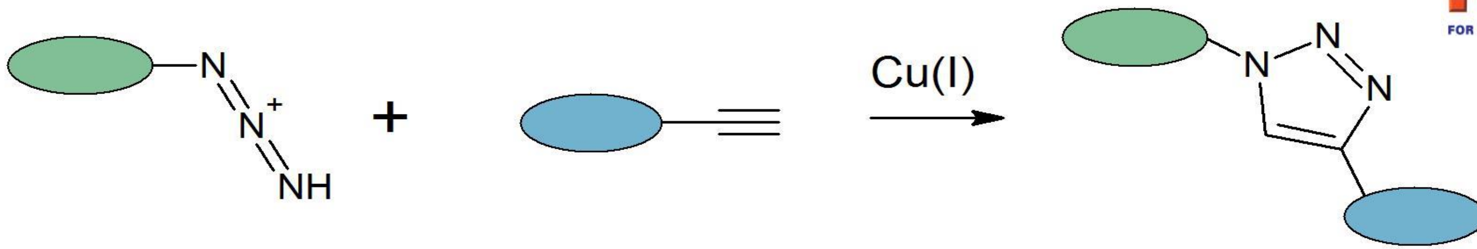
Reduced graphene oxide
Congo red (CR)
Photocatalytic degradation

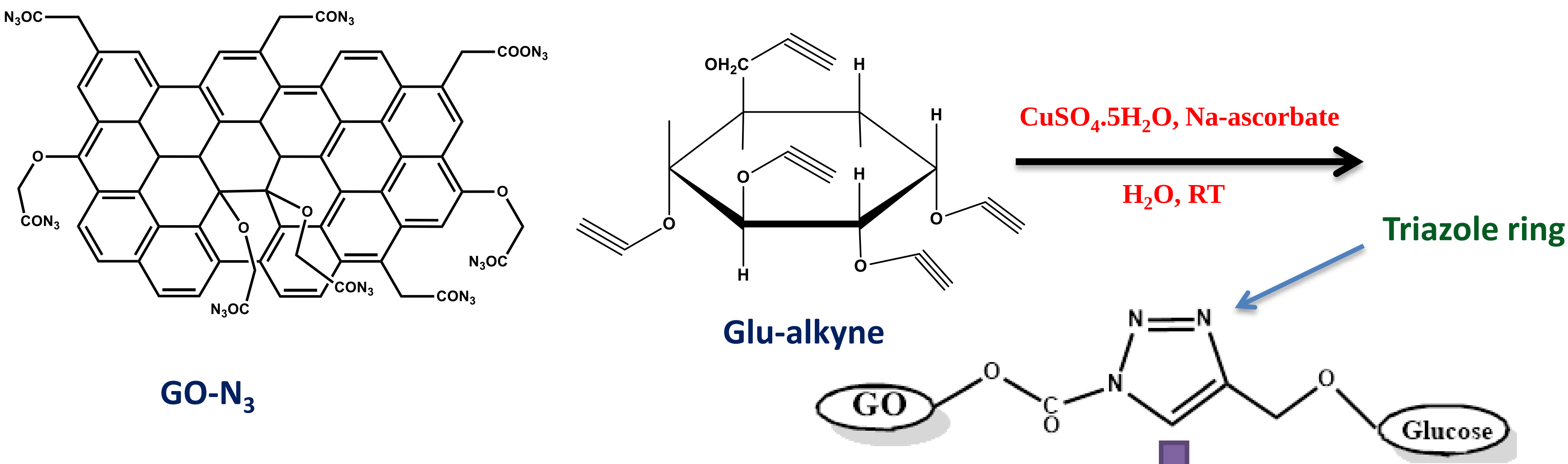
ABSTRACT

Semiconductor based CuS-rGO nanocomposite materials have drawn a considerable attention towards photodegradation of organic dye molecules due to the low band gap (~2.5 eV) of CuS nanoparticles. Presence of reduced graphene oxide (rGO) in CuS-rGO nanocomposite induced synergistic effect between CuS and rGO sheets which led towards better photocatalytic degradation efficiency as compared to CuS nanoparticles (without rGO support) and rGO alone. In this study CuS-rGO nanocomposite was synthesized by a simple microwave irradiation technique and characterized by High resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and Photoluminescence (PL) spectroscopy studies. The synthesized nanocomposite behaved as efficient photocatalyst towards diazo Congo Red (CR) dye molecule under natural sunlight irradiation with a maximum degradation efficiency of 98.76%. Effect of initial dye concentration, catalyst loading, pH of the reaction medium and role of different inorganic ions as well as the amount of graphene content in the photocatalyst on photocatalytic degradation of CR dye molecule was investigated in this study. The present study also focussed on the effect of different inorganic ions on the surface potential of the photocatalyst and their effect on the degradation process.

Functionalisation of Graphene Surface via 'Click' Chemistry Approach



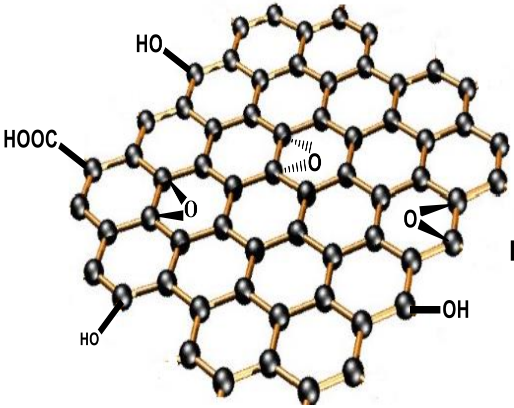
azide | alkyne | triazole



Decoration of the metal/bimetallic nanoparticles

Application in
Organic Catalysis,
Photocatalysis
Sensor

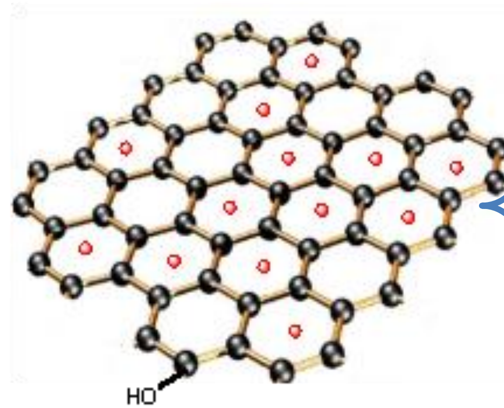
Synthesis of different types of Cu based nanoparticles on Graphene /functionalized h-BN sheets



Graphene Oxide sheet

Metal precursor (M.P)

Reaction Condition (R.C)

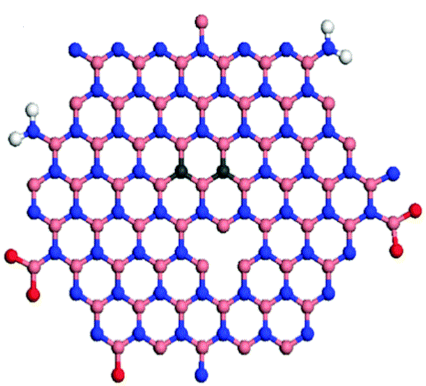


Graphene based 2D material, Metal = Cu(0), CuO, CuS

For Cu(0)-graphene
M.P= $Cu(CH_3COO)_2H_2O$
R.C= Chemical reduction with ascorbic acid

For CuO-graphene
M.P= $Cu(CH_3COO)_2H_2O$
R.C= Hydrothermal treatment

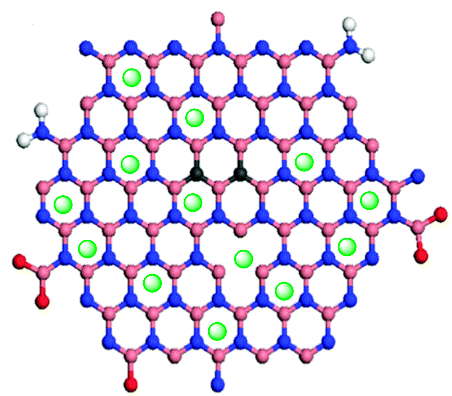
For CuS-graphene
M.P= $Cu(NO_3)_2.3H_2O$
R.C= Mechanical stirring with $Na_2S_2O_3$ as S source



Functionalized h-BN sheet

Metal precursor (M.P)

Reaction Condition (R.C)



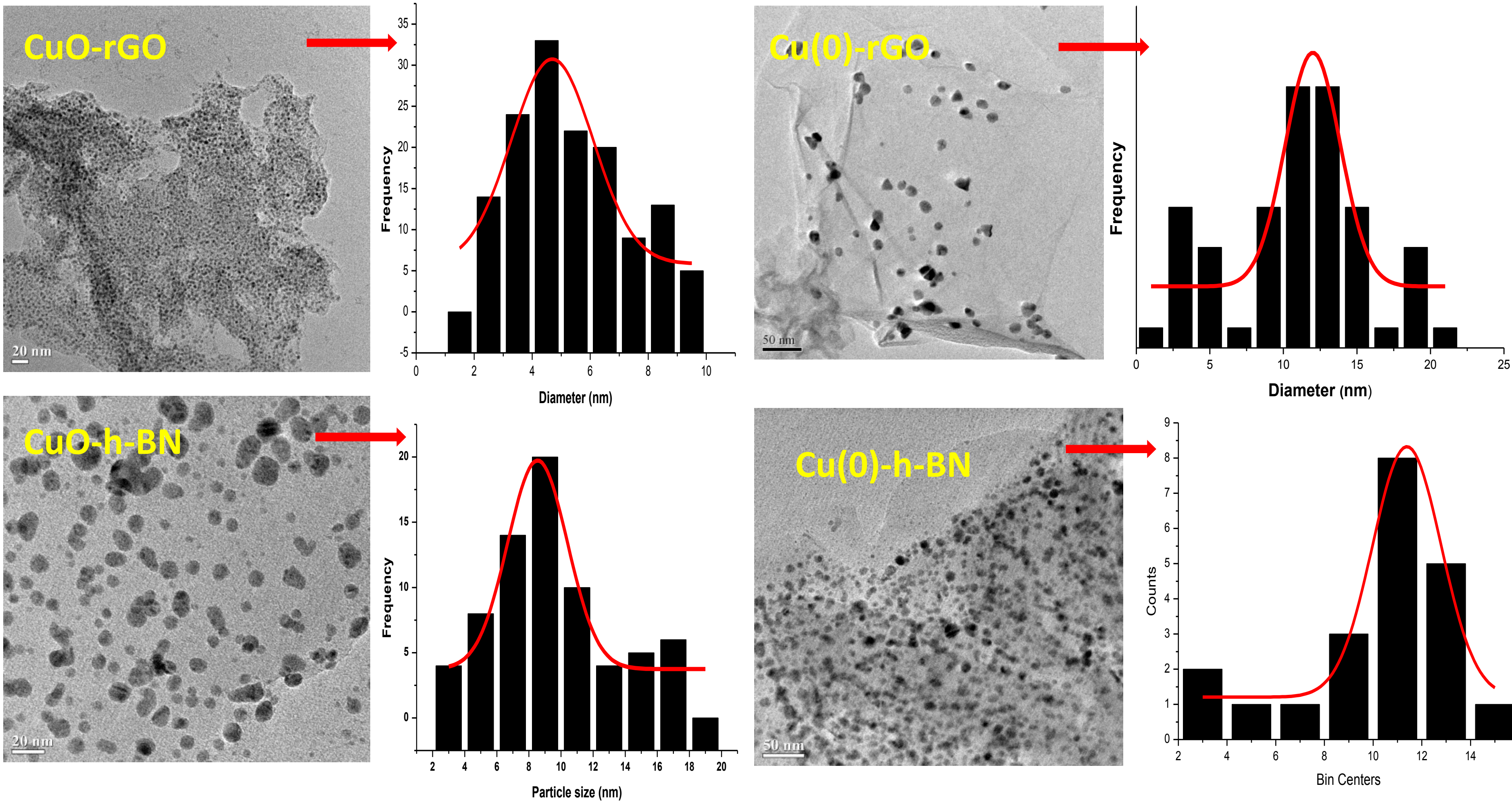
h-BN based 2D material, Metal = Cu(0), CuO, CuS

For Cu(0)-h-BN
M.P= $Cu(CH_3COO)_2H_2O$
R.C= Chemical reduction with ascorbic acid

For CuO-h-BN
M.P= $Cu(CH_3COO)_2H_2O$
R.C= Hydrothermal treatment

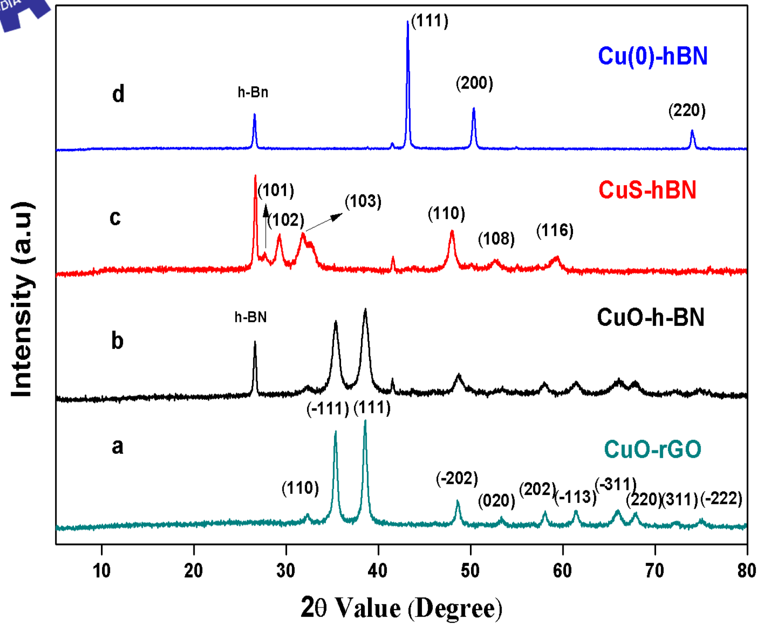
For CuS-h-BN
M.P= $Cu(NO_3)_2.3H_2O$
R.C= Mechanical stirring with $Na_2S_2O_3$ as S source

Characterization of the synthesized different types of composite material

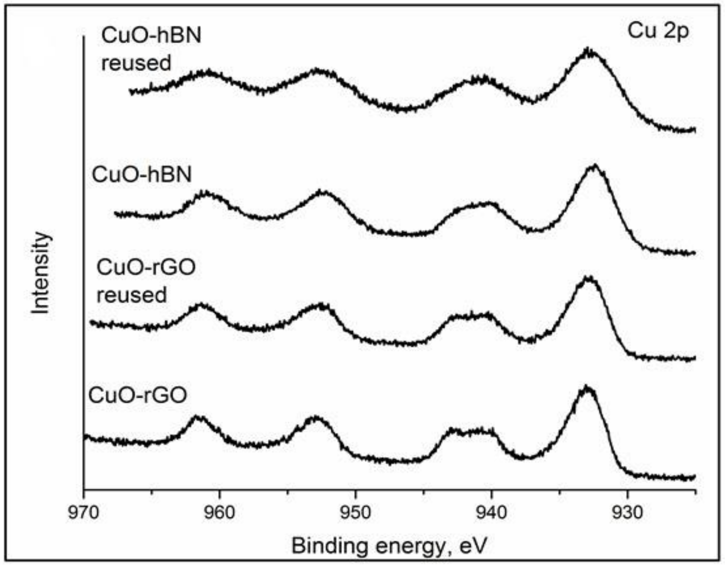


TEM images of different types of Cu composite of 2D materials along with their size distribution of nanoparticles

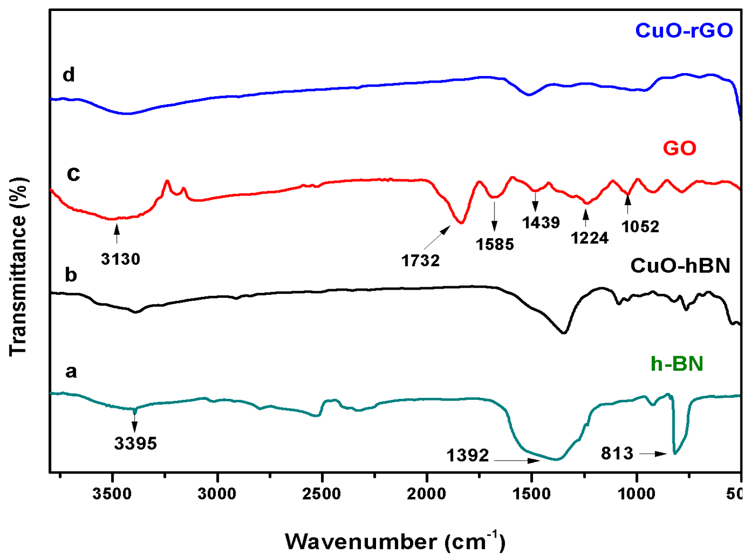
Continued…….



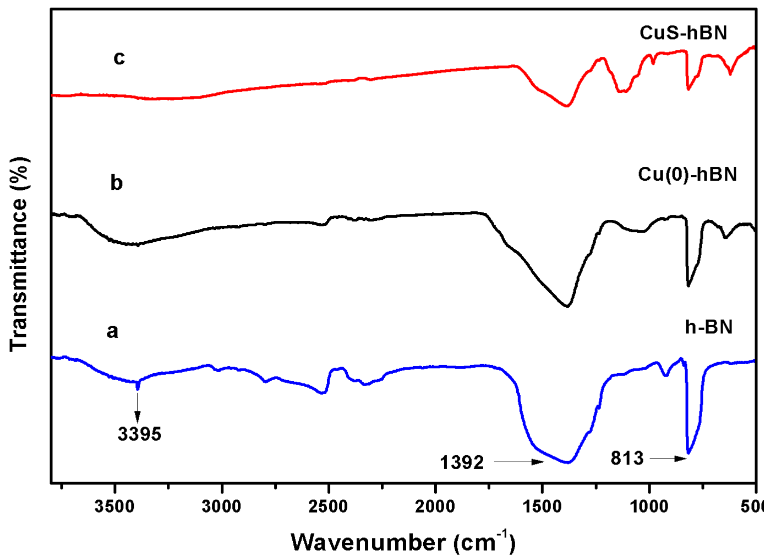
XRD pattern



XPS analysis



FTIR spectra



FTIR spectra

Catalytic activity towards three component coupling reaction

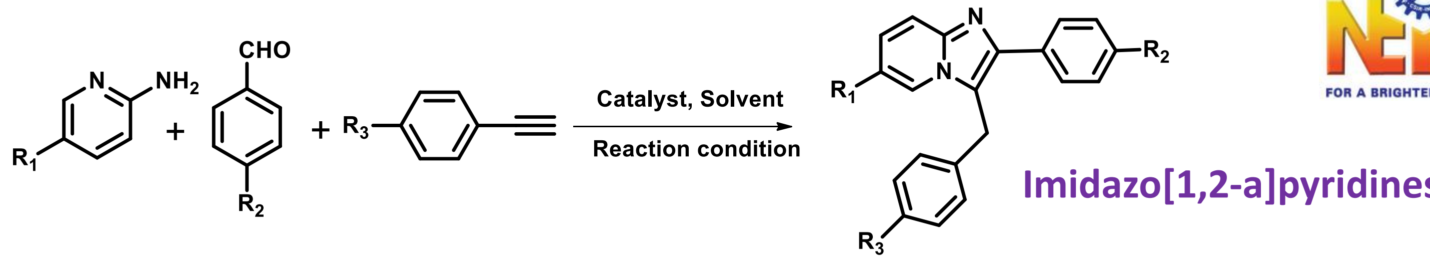
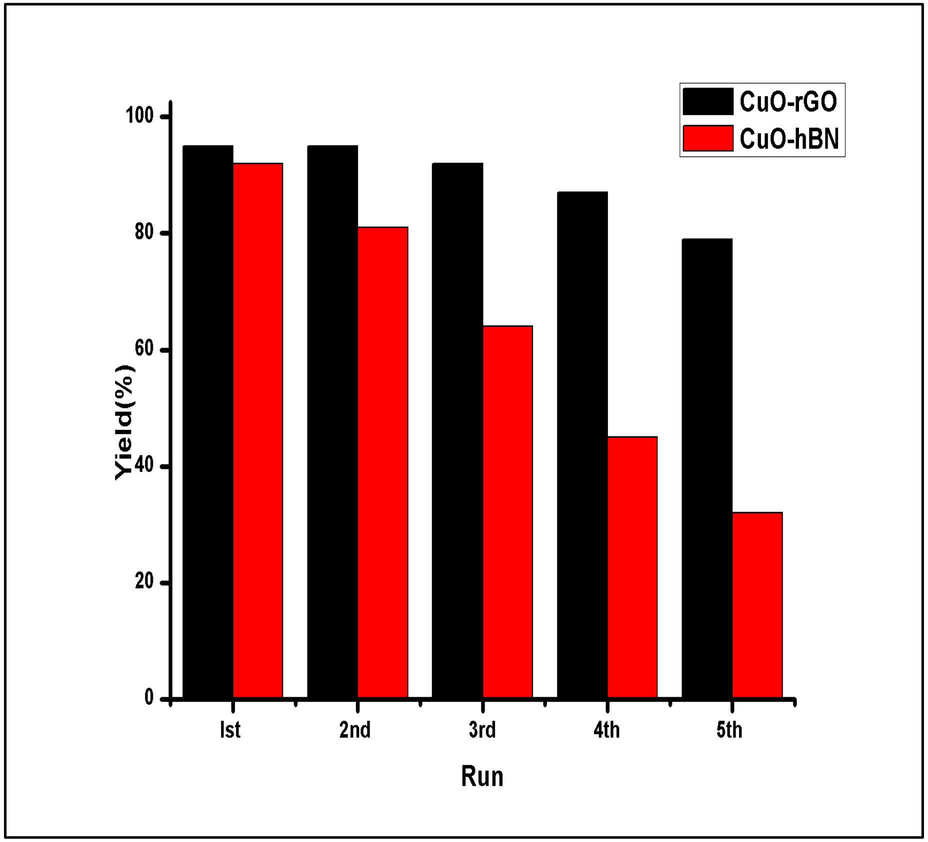


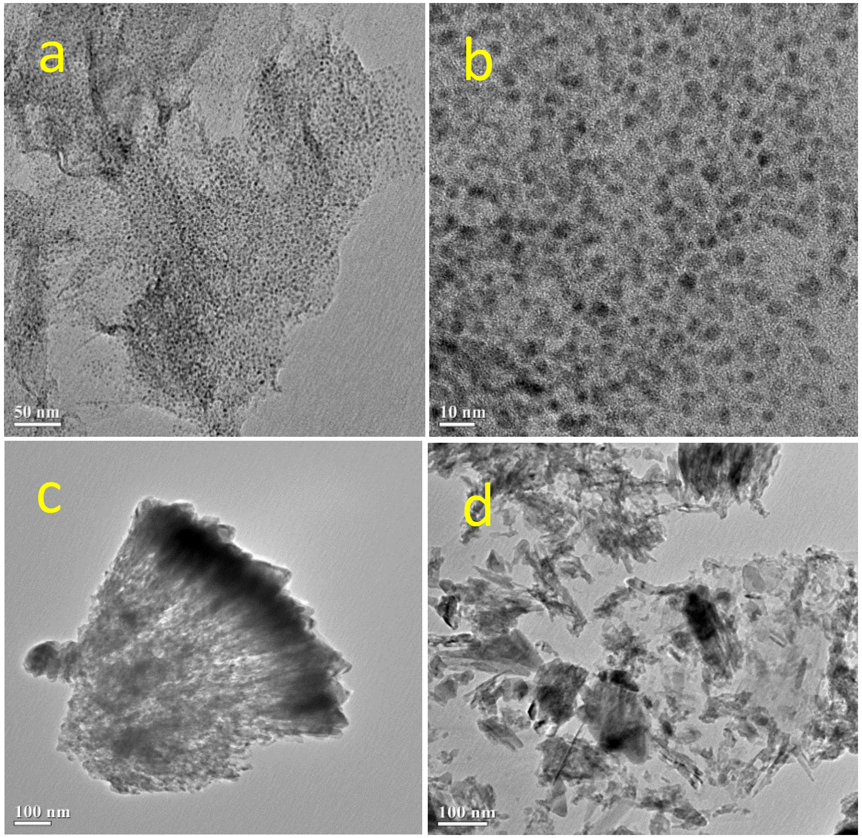
Table: Comparison of catalytic activity of different synthesized composite materials [a]

Entry	Catalysts	Particle Diameter [c] (nm)	R_1	R_2	R_3	Yield [d] (%)
1	CuO-rGO	4.6 ± 1.4	H	Cl	H	95
2			H	H	H	91
3			Me	H	Me	92
1	CuO-hBN	8.5± 1.8	H	Cl	H	92
2			H	H	H	90
3			Me	H	Me	91
1	Cu(0)-rGO	12 ± 4.8	H	Cl	H	87
2			H	H	H	88
3			Me	H	Me	89
1	Cu(0)-hBN	13.9 ± 0.48	H	Cl	H	86
2			H	H	H	85
3			Me	H	Me	84
1	CuS-rGO	183+48.51	H	Cl	H	62
2			H	H	H	59
3			Me	H	Me	40
1	CuS-hBN	>> 190 (Cluster type Structure)	H	Cl	H	58
2			H	H	H	55
3			Me	H	Me	49

[a] Reaction conditions: 2-aminopyridine (1 mmol), benzaldehyde (1.2 mmol), phenylacetylene (1.2 mmol), catalyst (0.015 g), Solvent (3 mL,) 110 ^{0}C, 8 h; [b] Average size with standard deviation as measured by TEM analysis; [d] Isolated Yield

Reusability study of CuO-rGO and CuO-hBN catalyst towards three component coupling reaction





Reusability study of CuO-rGO and CuO-hBN composite material after performing reaction

(a-b) TEM images of CuO-rGO composite material after performing reaction; (c-d) TEM images of CuO-hBN composite material after performing reaction

Future Prospects

- Exploration of new support material such as *h*-BN, BCN, g-C_3N_4 for synthesis of metal/bimetallic nanoparticles.

- Development of new metal and bimetallic nanoparticles such as Au-Ni, Cu-Pd, Cu-Ni, Au-Fe_3O_4 etc.

- Application of these synthesized nanocomposites in different areas as
  - ✓ Photocatalyst in environmental remediation
  - ✓ Catalyst in organic transformations
  - ✓ As sensors in detection of biological as well as environment pollutants etc.

International Collaborators

National Institute for Materials Science (NIMS), Japan

North-East Institute of Science & Technology, Jorhat, Assam

Institute de Recherche Interdisciplinaire (IRI, USR 3078), Universite Lille 1, France

Nikolaev Institute of Inorganic Chemistry, Russia

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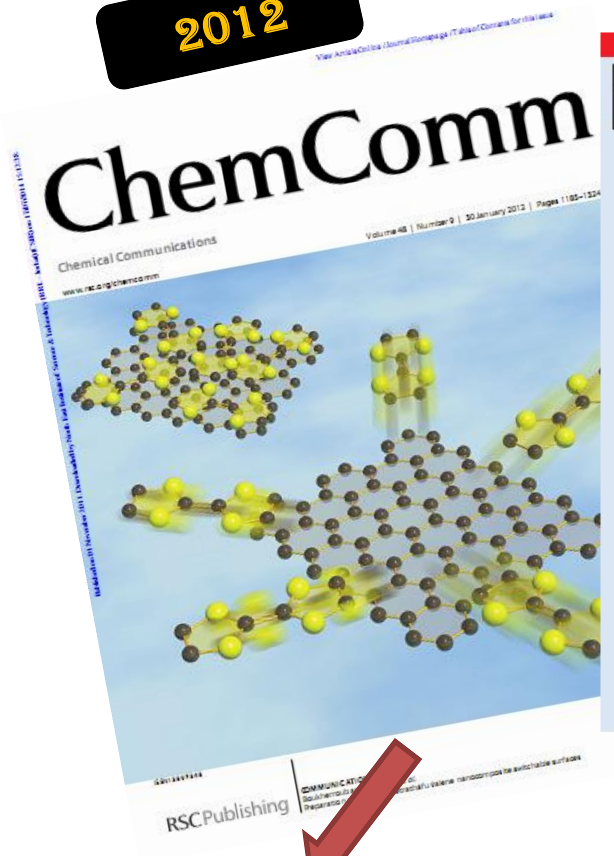
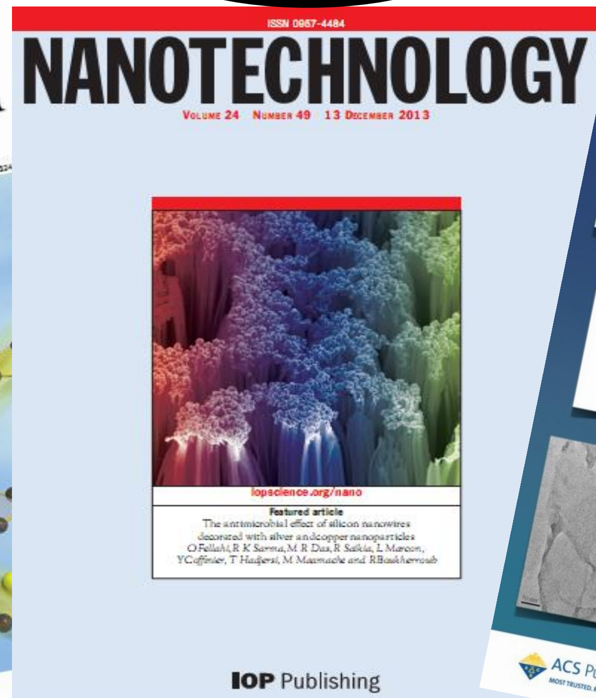
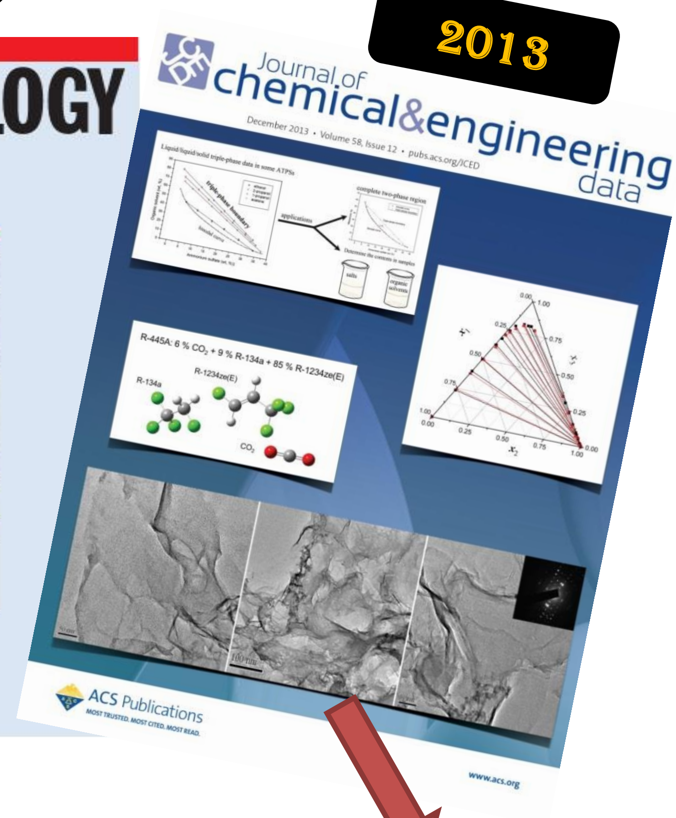
2012



2013



2013



Title: Preparation of graphene/tetrathia-fulvalene nanocomposite switchable surface.
Vol.48, Pg-1221

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Vol.24, Pg-495101

Title: Kinetics and Adsorption Behavior of the Methyl Blue at the Graphene Oxide/Reduced Graphene Oxide Nanosheet-Water Interface: A comparative study.
Vol.58, Pg-3477

BOOK CHAPTERS

Title: Metal Nanoparticles/Graphene-based Composite Materials: Synthesis and Applications
Publisher: Smithers Rapra, UK, 2013

Title: Metal-oxide Graphene Nanocomposites
Publisher: IGI Global, USA, 2014

Title: Graphene Oxide and Reduced Graphene Oxide as Efficient Carbon Based Materials for Removal of Dye From Aqueous Solution
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Title: Gold nanoparticles-graphene composites material: Synthesis, characterization and catalytic application
Publisher: Scrivener Publisher, USA, 2015

Title: Iron oxide nanoparticles-graphene composite materials: Synthesis, characterization and applications
Publisher: World Scientific, UK, 2015

Title: Metal oxide nanoparticles: Toxicological impact on bacteria
Publisher: Nova, USA, 2015

Title: Nano emulsion: preparation and its application in Food Industry
Publisher: Elsevier, Netherlands, 2016

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- DST, New Delhi, CSIR, New Delhi and RFBR, Russia for financial support
- All the Students of my group
- Last but not the least, my sincere thanks to all for your kind listening

Heritage of Assam


Thank You
THE MIGHTY BRAHMAPUTRA