Project Completion Report

(2013-2017)

Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions.

(F. No.: 42-291/2013(SR) dated 25/03/2013)

Submitted to

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

by

Dr. P. Suresh
Principal Investigator

School of Chemistry
Madurai Kamaraj University
(University with Potential for Excellence)
Madurai 625 021

21. Financial Assistance Provided/ Expenditure incurred:

Consolidated Statement of Accounts

(From the date of commencement 25.03.2013 till 31st March 2017)

Scheme Number: **Order No.: F. 42-291/2013(SR) dated 25/03/2013**
Scheme Number: **Order No.: F. 42-291/2013(SR) dated 20/05/2016**

Title of the Research Scheme: ***" Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions"***

Name of the Principal Investigator: **Dr. P. SURESH**

Date of Commencement: 25/03/2013

Date of Termination: 31/03/2017

S. No.	Items	Amount Approved	Amount Allocated	1st Instalment released	Expenditure (for 1st Instalment) (I)	Balance (from 1st Instalment)	Grant released as 2nd Instalment	Expenditure (for 2nd grand) (II)	Total (₹) I + II	Balance
1.	Books & Journal	-	-	-	-	-	-	-		-
2.	Equipments	4,00,000	4,00,000	4,00,000	4,00,000	-	-	-	4,00,000	-
3.	Honorarium	-	-	-	-	-	-	-		-
4.	Contingency	1,00,000	1,00,000	50,000	49,998	2	40,000	40,000	89,998	-
5.	Travel/fieldwork	-	-	-	-	-	-	-		-
6.	Chemicals & Glassware	2,00,000	2,00,000	1,00,000	99,991	9	80,000	81,800	1,81,791	-
7.	Hiring Services	-	-	-	-	-	-	-		-
8.	Overhead	82,800	82,800	82,800	82,800	-	-	-	82,800	-
9.	Any other items (please specify)	-	-	-	-	-	-	-		-
10.	Honorarium to Principal investigator.	-	-	-	-	-	-	-		-
11.	Staff (date of appointment) (from 06.08.2013 to 06.08. 2016)	5,28,000	4,61,419	2,64,000	2,21,742	42,258	1,51,277	2,07,677	4,29,419	-
	Total			**8,96,800**	**8,54,531**	**42,269**	**2,71,277**	**3,29,477**		-
12.	Other Charges (Interest)	-	-	24,552	9,828#	14,724	1,276	**	9828#	-
	Other Charges (unspent from 1st installment)	-	-	-	-		56,993	***		-
	Other Charges (Bank Charges)	-	-	-	-		-	69	69	-
	Total (₹)	**13,10,800**	**12,44,219**	**9,21,352**	**8,64,359**	**56,993**	**3,29,546**	**3,29,546**	**11,93,905**	-

Sanctioned funds under equipment not sufficient, hence excess expenditure (Rs. 9828/-) has met from accrued interest
** Interest utilized under consumable head
*** 1st Instalment unspent utilized under staff fellowship

It is certified that the grant of **Rs. 11,93,905/-** (including 1st Installment (Rs. 8,96,800 + Interest Rs. 24,552) and 2nd Installment (Rs. 2,71,277 + Interest Rs. 1,276) sanctioned from University Grants Commission under the Scheme of support for Major Research Project entitled "*Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions*. Vide **UGC Letter No. F. 42-291/2013(SR) dated 25/03/2013 and 20/05/2016** and a sum of **Rs. 11,93,905/-** has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission with the **Rs. Nil** is remining unutilized.

27/11/19

28/11/19

PRINCIPAL INVESTIGATOR
Dr. P. SURESH
Principal Investigator
UGC Major Research Project
Functionalized Graphene..........coupling reactions
School of Chemistry
Madurai Kamaraj University
Madurai-625 021

FINANCE OFFICER
FINANCE OFFICER
MADURAI KAMARAJ UNIVERSITY
MADURAI-21.

STAUTORY AUDITOR
DEPUTY DIRECTOR
LOCAL FUND AUDIT
MADURAI KAMARAJ UNIVERSITY AUDIT
MADURAI - 625 021.

4/12/19

4/12/19

REGISTRAR
REGISTRAR
MADURAI KAMARAJ UNIVERSITY
MADURAI-625 021

ज्ञान-विज्ञान विमुक्तये

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 OO2

Utilization Certificate

It is certified that the grant of **Rs. 11,93,905/-** (including 1st Installment (Rs. 8,96,800 + Interest Rs. 24,552) and 2nd Installment (Rs. 2,71,277 + Interest Rs. 1,276) sanctioned from University Grants Commission under the Scheme of support for Major Research Project entitled "*Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions*. Vide **UGC Letter No. F. 42-291/2013(SR) dated 25/03/2013 and 20/05/2016** and a sum of **Rs. 11,93,905/-** has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission with the **Rs. Nil** is remining unutilized.

	25/11/9	R. Sidha 28/11/15	
PRINCIPAL INVESTIGATOR	FINANCE OFFICER	REGISTRAR	STATUTORY AUDITOR
(Seal)	(Seal)	(Seal)	(Seal)
Dr. P. SURESH Principal Investigator UGC Major Research Project *Functionalized Graphene..........coupling reactions* School of Chemistry Madurai Kamaraj University Madurai-625 021	FINANCE OFFICER MADURAI KAMARAJ UNIVERSITY MADURAI-21.	REGISTRAR MADURAI KAMARAJ UNIVERSITY MADURAI-625 021	DEPUTY DIRECTOR LOCAL FUND AUDIT UNIVERSITY AUDIT MADURAI 4/12/15 4/12/15.

C. Staff

Name if the Project Fellow: M. Karthik

Date of Appointment **06-08-2013**

S. No	Items	From	To	Amount Approved (Rs.)	Expenditure incurred (Rs.)
1.	Honorarium to PI (Retired Teachers) @ Rs. 18,000/-p.m.	-	-	-	-
2.	**Project fellow:** **Non-GATE/Non-NET-** Rs. 14,000/- p.m. for initial 2 years and Rs. 16,000/- p.m. for the third year.	06-08-2013	31-01-2016	**4,61419**	**4,29,419**

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.
2. If as a result of check or audit objection some irregularly is noticed at later date, action will be taken to refund, adjust or regularize the objected amounts.

3. Payment @ revised rates shall be made with arrears on the availability of additional funds.
4. It is certified that the grant of **Rs. 4,29,419 (Rs. Four Lakhs Twenty Nine Thousand Four Hundred and Nine-Teen Only)** spent from the University Grants Commission under the scheme of support for Major Research Project entitled ***"Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions"*** vide UGC letter No. F **42-291/2013(SR) dated 25/03/2013 and 20/05/2016** has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

PRINCIPAL INVESTIGATOR
Dr. P. SURESH
Principal Investigator
UGC Major Research Project
Functionalized Graphene..........coupling reactions
School of Chemistry
Madurai Kamaraj University
Madurai-625 021

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5/12/19
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MADURAI-625 021

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
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PROFORMA FOR FINAL REPORT OF THE WORK DONE ON THE PROJECT

1.	TITLE OF THE PROJECT :	***Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions.***
2	NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR **:**	**Dr. P. Suresh** Assistant Professor Department of Natural Products Chemistry School of Chemistry, Madurai Kamaraj University, Madurai-625021
3	NAME AND ADDRESS OF THE INSTITUTION **:**	Department of Natural Products Chemistry School of Chemistry, Madurai Kamaraj University, Madurai-625021
4	UGC APPROVAL LETTER NO. AND DATE **:**	**F. No. : 42-291/2013(SR) dated 25/03/2013**
5	DATE OF IMPLEMENTATION :	01.04.2013
6	TENURE OF THE PROJECT :	From **01.04.2013 to 31.03.17** (01.04.2013 to 31.03.16 Extended up to 31.03.2017 without any financial support)
7	TOTAL GRANT SANCTIONED : TOTAL GRANT REALLOCATED :	₹. 13,10,800.00 ₹. 12,44,219.00
8	TOTAL GRANT RECEIVED :	₹. 11,68,077.00
9	FINAL EXPENDITURE :	₹. 11,93,905.00 (Grant - ₹. 11,68,077 + Interest- ₹. 25828)

10	TITLE OF THE PROJECT :	***Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions.***

11. OBJECTIVES OF THE PROJECT:

- To make graphene more facile for further modification, its reactive functional groups will be pre-functionalized.
- To functionalize the graphene, various bi- and multidentate ligand moieties will be synthesized to hook-on pre-functionalized graphene oxide.
- To chemically functionalized graphene, synthesized chelating ligands will be covalently attached with pre-functionalized graphene oxide.
- To catalyse coupling reaction, catalytically reactive transition metals will be complexed with ligand functionalized graphene.
- To characterize, synthesized nanocomposites they will subjected to spectral and microscopic characterization technique like UV-Vis., FT-IR, NMR, ICP-MS, Raman, XPS, AFM and TEM.
- To optimize the catalytic behaviour, they will used as catalyst for various coupling reactions and will later use as catalyst for various complex molecule synthesis. Their reusability of the catalyst will be studied in their respective reactions to monitor its sustainability nature.

12. WHETHER OBJECTIVES WERE ACHIEVED: **Yes**

The detailed discussion on synthesis and characterization of catalysts and its catalytic applications are as follows.

12.1 Synthesis of Graphene Based Catalyst

12.1.1. Synthesis of Graphene Oxide (GO).

Graphene Oxide (GO) was synthesised from graphite powder using modified Hummers and Hoffman's method.[2] In a typical synthesis, 2.5 g of graphite powder was added to 115 mL of concentrated H_2SO_4 in an ice bath. Then, $NaNO_3$ (2.5 g) and $KMnO_4$ (15.0 g) were added gradually under stirring, and the temperature of the mixture was kept below 5 ºC, and the mixture was stirred for 4 h. After that, the mixture was stirred at room temperature for 12 h, and then diluted with 200 mL of double distilled (DD) water by keeping the mixture in an ice bath. After adding 500 mL of DD water, the mixture was transferred to an oil bath and kept at 98 ºC for 1 h. Then the reaction was quenched by adding 15 mL of 30% H_2O_2 aqueous solution followed by a 5% HCl solution to remove the presence of sulfate. Finally, the resulting graphite oxide was repeatedly washed with DD water and then dialysed for three days to remove residual salts and acids with periodically changing the water. Then the resulting material was dried under a vacuum glass oven at 45 ºC for 24 h to obtain graphite oxide. Before using it in reactions, it was exfoliated under sonication in water / or specific solvent which yield the graphene oxide (GO).

12.1.2 Synthesis of Reduced Graphene Oxide (RGO)

Reduced Graphene Oxide (RGO) was synthesized according to the reported procedure.[3] GO was dispersed in double distilled water by sonication. The resulting GO suspension (400 mL, 1.0 mg/mL) was reduced with sodium borohydride (0.960 g) at 100 ºC for 24 h followed by washing with deionised water for several times. The obtained black precipitate was dialysed with double distilled water for 24 h to get the purified reduced graphene oxide (RGO).

12.1.3 Synthesis of Esterified Graphene Oxide (GO-Ester)

The methyl ester of GO (GO-Ester) was prepared by adopting the reported Steglich esterification procedure.[4] To a dispersed solution of GO (500 mg) in 300 mL anhydrous methanol, 100 mg of 4-dimethylamino pyridine (DMAP) was added. Followed by dicyclohexylcarbodiimide (DCC) was added to the reaction mixture at 0°C in an ice bath, which was then allowed to stir for 5 min. Further, the temperature was raised to 20 °C and continued to stir for 3 h. The resulting black solid was separated by the filtration and washed twice with 0.05 N HCl followed by saturated $NaHCO_3$ solution. Finally, the formed methyl ester of GO was washed with an excess of cold water and then dialysed with DD water for 10 h in order to remove any metal contaminants or salt residues are present. The final product was dried in a vacuum oven for 24 h at 60 °C and characterised using FTIR analysis.

12.1.4 Synthesis of Sulfonated Reduced Graphene Oxide (G-SO_3H)

4-Benzenediazoniumsulfonate was synthesized *via* diazotisation of sulfanilic acid.[5] Sulfanilic acid (10.4 g) was dispersed in 600 mL of aqueous 1M HCl solution in an RB flask. The temperature was maintained at 3–5 ºC in an ice bath. Further, 10% excess of 1M $NaNO_2$ (70 mL) was added dropwise under constant stirring to obtain a clear solution, and the same condition was maintained for another 1 h. Finally formed white precipitate was filtered off and washed with deionised water.

The resulting diazonium salt was mixed with 1:1 DD water and ethanol mixture (200 mL). Then, the suspension of reduced graphene oxide (240 mL 3mg/mL in DD water) was added at 3-5 ºC followed by the addition of 50 wt% H_3PO_2 aqueous solution (100 mL). After 30 min., the same amount of H_3PO_2 has added again and stirred continuously for another 1 h. The obtained sulfonated graphene was carefully washed with double distilled water, and ethanol then dried under vacuum for overnight.

12.2. Graphene Oxide as a Carbocatalyst for Sustainable *ipso*-Hydroxylation of Arylboronic Acids: A Simple and Straightforward Strategy to Access Phenols

A metal-free and straightforward protocol for the synthesis of phenols from aryl and heteroaryl boronic acids has been demonstrated using graphene oxide as a carbocatalyst. This sustainable *ipso*-hydroxylation takes place under relatively mild condition using aqueous H_2O_2 as an oxidant in water medium in short time under base-free and organocatalytic condition. The control experiments clearly demonstrate that the presence of carboxyl groups on the edges of the GO basal plane promotes the *ipso*-hydroxylation. The developed methodology unleashed the role of GO as a benign solid acid catalyst with good sustainability and reused for several times without significant loss in its catalytic activities which was proved by the FT-IR and PXRD studies of the reused catalyst

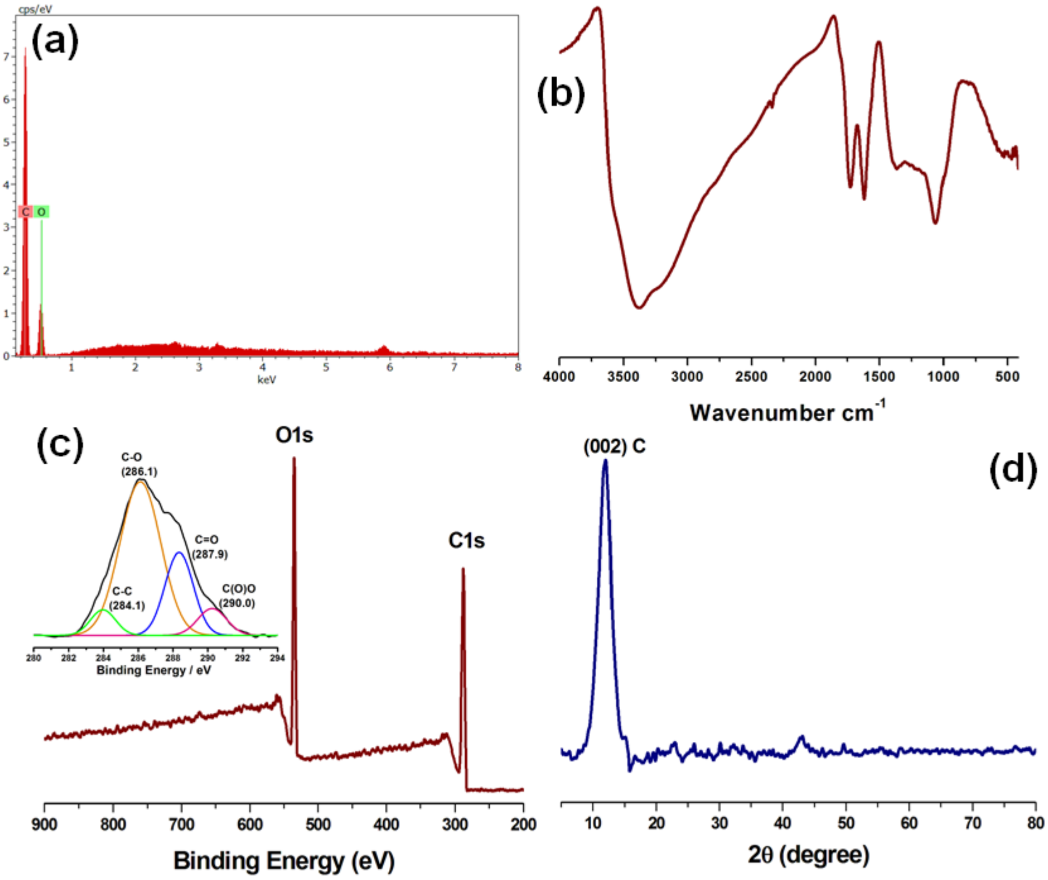


Fig. 1 a) EDS spectrum, b) FT-IR spectrum, c) XPS spectrum (insert deconvoluted C1s Peak), d) PXRD pattern of GO

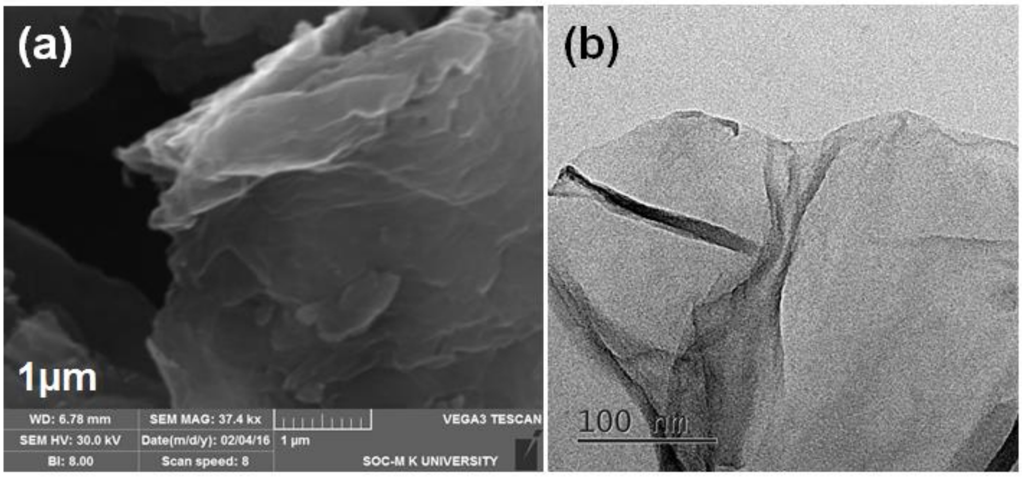
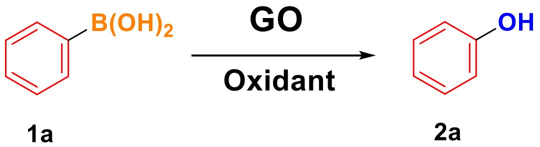


Fig. 2. a) SEM, b) TEM image of GO

Table 1 Optimization of Reaction Conditions for GO Catalysed *ipso*-Hydroxylation



Entry	Solvent	Yield[b] (%)
1	Neat	65
2	Methanol	94
3	Ethanol	86
4	Isopropyl alcohol	85
5	Ethylene glycol	80
6	MeOH:Water (1:1)	88
7	EtOH:Water (1:1)	82
8	Acetonitrile	82
9	Acetone	85
10	DCM	74
11	Ethyl acetate	70
12	DMSO	84
13	THF	78
14	*n*-hexane	74
15	Water	99[c]
16	Water	-[d]
17	Water	35[e],35[f]
18	Water	-[g]

[a] Reaction condition: Phenylboronic acid (0.5 mmol), H_2O_2 (3 mmol) and 40 mg of GO in 2 mL of solvent at room temperature up to 1 h. [b] Isolated yield, [c] reaction completed ≤5 min. other oxidants: [d] molecular oxygen, [e] TEMPO, [f] 8 eq of TEMPO, [g] *t*-butylperoxide.

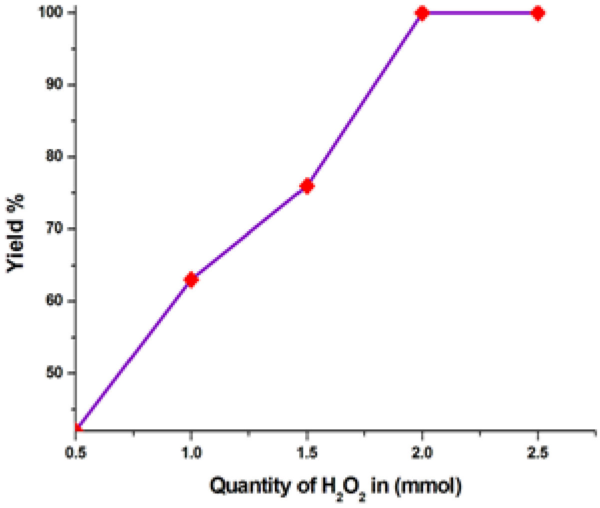


Fig. 3. Oxidant load optimization

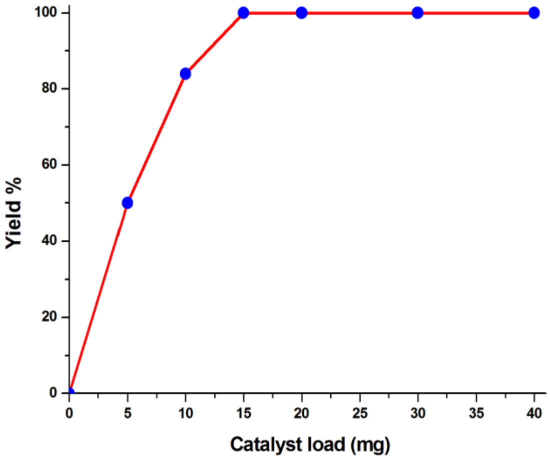


Fig. 4 Catalyst load optimization

Table 2 Control Experiments[a]

Entry	Catalyst	Time (min)	Yield[b] (%)
1	-	60	-
2	GO	60	-[c]
3	GO	5	99
4	Graphite	360	12
5	RGO	360	12
6	Activated Charcoal	360	10
7	GO-Ester	360	14, 14[d]

[a] Reaction condition: Phenylboronic acid (0.5 mmol), 30% H_2O_2 (2 mmol) and 15 mg of catalyst in 2 mL of water at room temperature, [b] isolated yield, [c] without oxidant, [d] after 24h

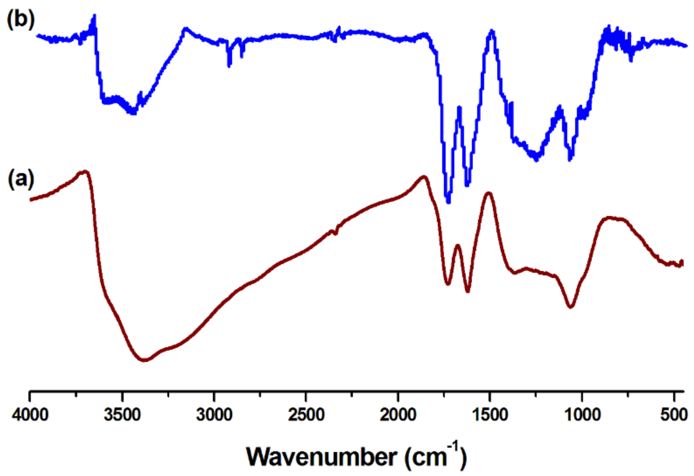
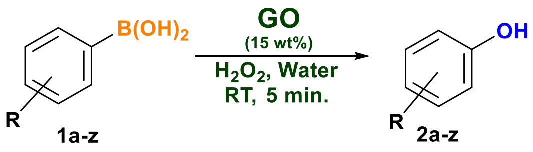
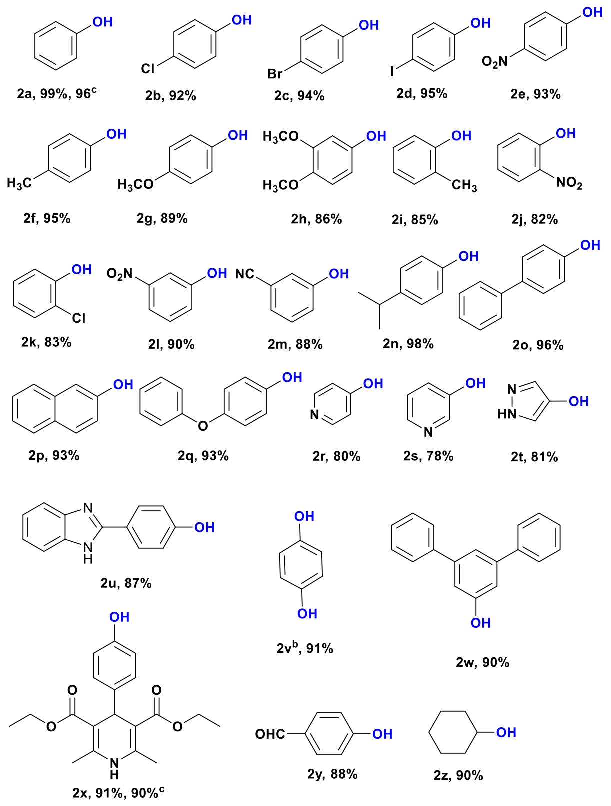


Fig. 5 FT-IR spectra of a) GO, b) Methyl ester of GO (GO-Ester)

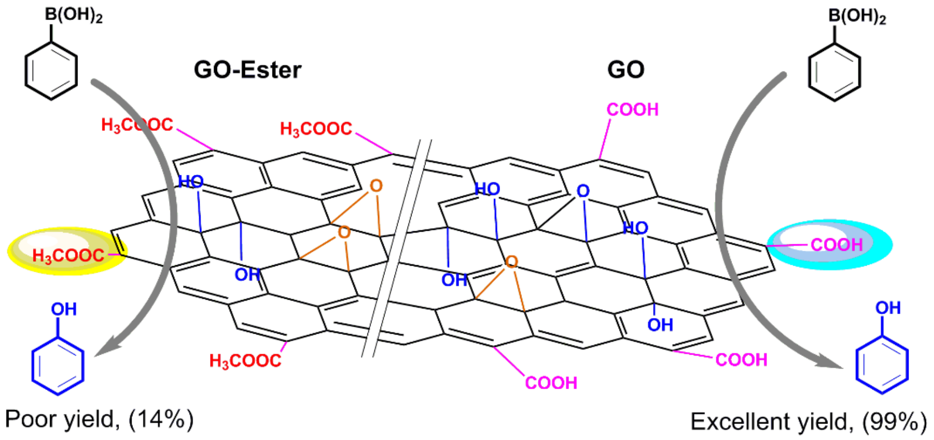
Table 3 Scope of GO Catalysed *ipso*-Hydroxylation of Aryl boronic acids[a]



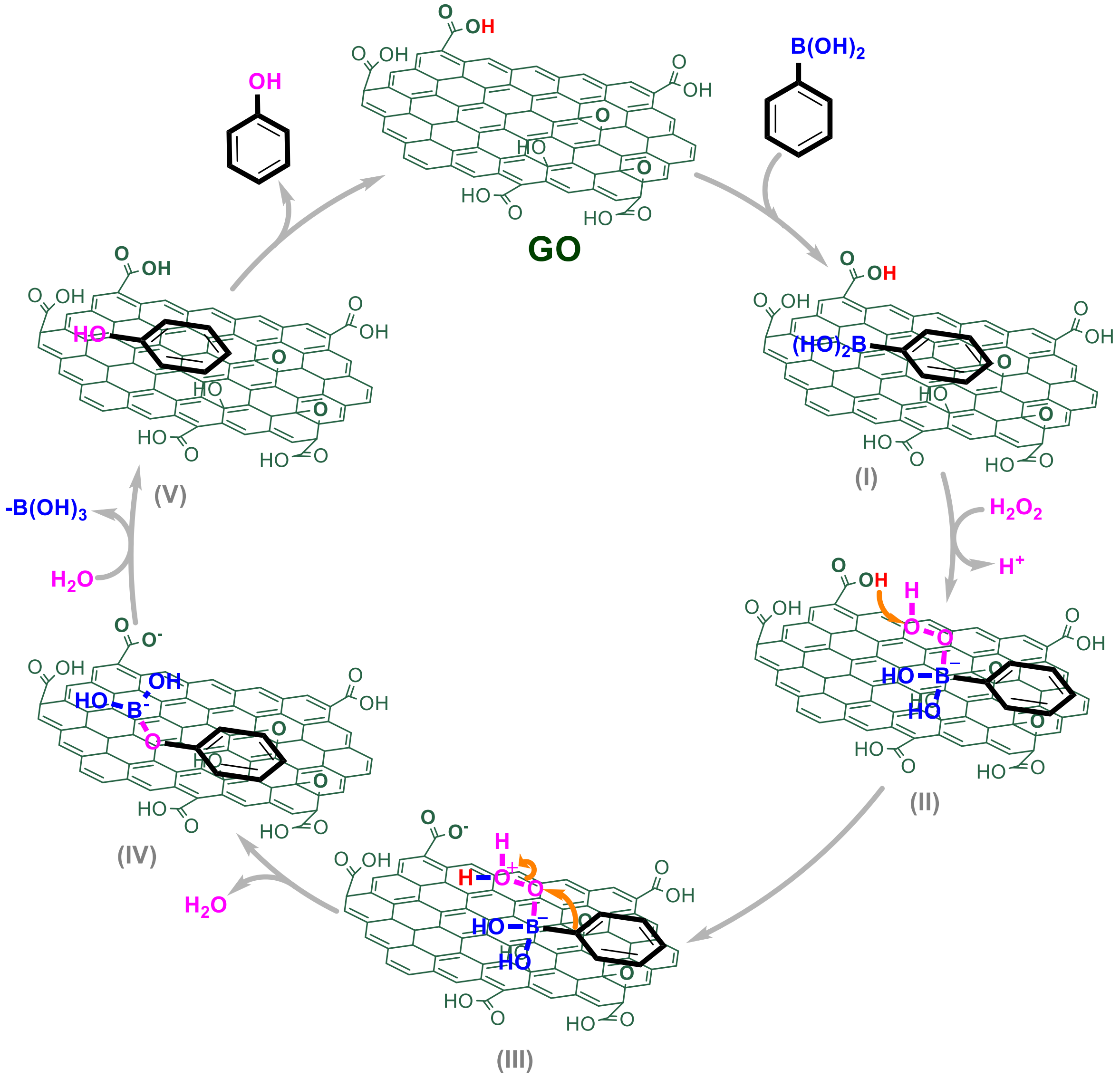


2a, 99%, 96[c]
2b, 92%
2c, 94%
2d, 95%
2e, 93%
2f, 95%
2g, 89%
2h, 86%
2i, 85%
2j, 82%
2k, 83%
2l, 90%
2m, 88%
2n, 98%
2o, 96%
2p, 93%
2q, 93%
2r, 80%
2s, 78%
2t, 81%
2u, 87%
2v[b], 91%
2w, 90%
2x, 91%, 90%[c]
2y, 88%
2z, 90%

[a] Reaction Condition: Arylboronic acid (0.5 mmol), H_2O_2 (2 mmol) and 15 mg of GO in 2 mL of water at room temperature in 5 mins., All are isolated yield, [b] H_2O_2 (3 mmol), [c] Isolated yield in one-gram batch



Scheme 1 Control experiment with GO and GO-ester in *ipso*-hydroxylation of phenyl boronic acid



Scheme 2 Plausible mechanism of GO catalysed *ipso*-hydroxylation

Reusability Studies

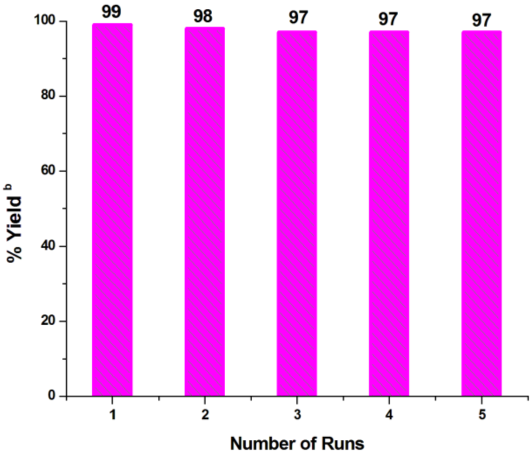


Fig. 3.13 Recycling of the GO Catalyst

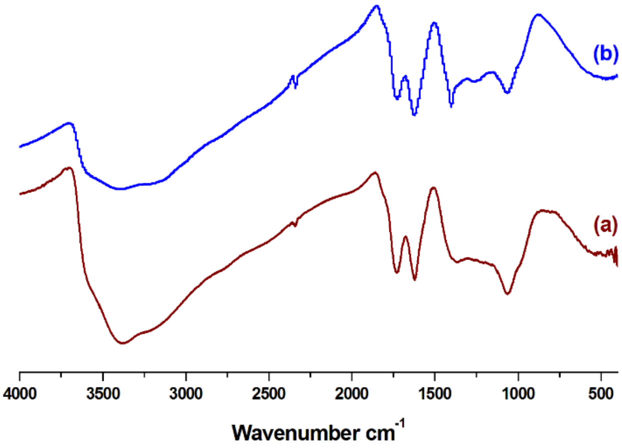


Fig. 6 FTIR pattern of a) GO, b) fifth-time reused-GO

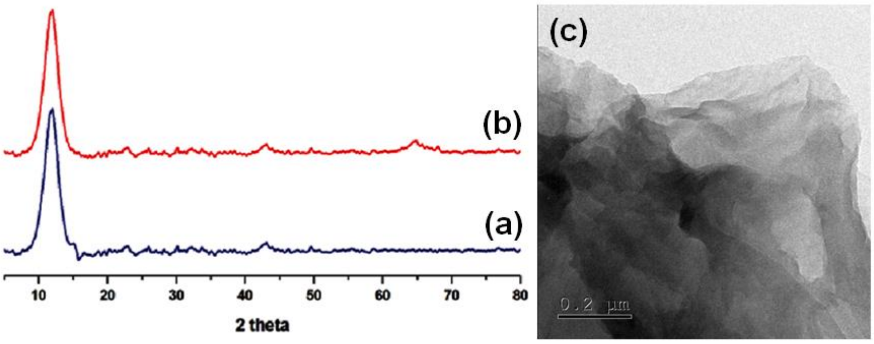


Fig. 7. PXRD pattern of a) GO, b) fifth time reused-GO, & c) TEM image of fifth time reused GO.

A simple, inexpensive and reusable graphene oxide catalysed *ipso*-hydroxylation of arylboronic acid has been demonstrated using readily available hydrogen peroxide as an oxidant under very mild condition. The present GO carbocatalyst provides a clear strategy to get a wide range of phenols and heteroaryl phenols under the benign condition without any undesired by-products and tedious chromatographic separation. The role of free carboxylic groups of graphene oxide in promoting the hydroxylation has been proven. The developed methodology offers a practical and benign alternate to industrial scale phenol synthesis as well for the facile functional group transformation in natural products synthesis and medicinal chemistry with an excellent scope.

12.3. Brønsted Acidic Reduced Graphene Oxide as a Sustainable Carbocatalyst: A Selective Method for the Synthesis of C-2 Substituted Benzimidazole

Brønsted acidic reduced graphene acts as an efficient and sustainable carbocatalyst for the selective synthesis of C-2-substituted benzimidazoles under ambient conditions. A massive influx of sulphonic acid group on reduced graphene oxide surface gives graphene sulfonic acid (G-SO_3H) which act as a Brønsted acidic catalyst for synthesis of a series of benzimidazole under mild conditions. Present methodology is a revamp of the benzimidazole synthesis with broad functional group tolerance in a shorter time. G-SO_3H provides an operationally simple, metal free condition and amenable to the gram scale production. The catalytically responsible Brønsted acidity of the Catalyst is proved by the pyridine adsorption studies. The catalyst is highly stable for several cycles without loss in its activity which evidenced by the FT-IR, PXRD and TEM characterization of the reused catalyst.

Characterization of G-SO_3H

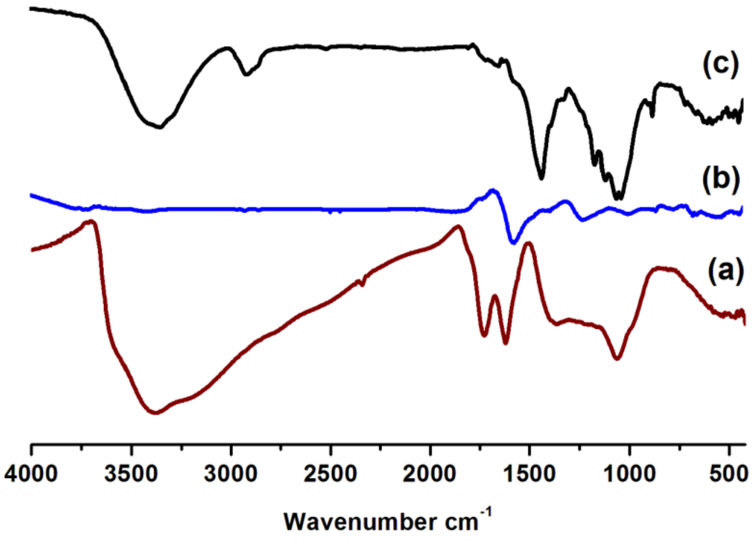


Fig. 8 FT-IR Spectra a) GO, b) RGO, c) G-SO_3H

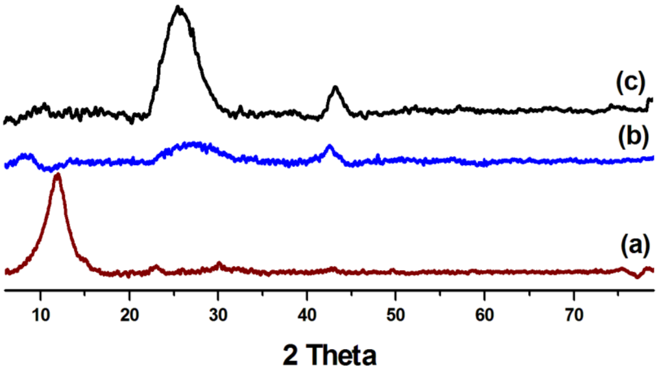


Fig. 9 PXRD Pattern of a) GO, b) RGO, c) G-SO_3H

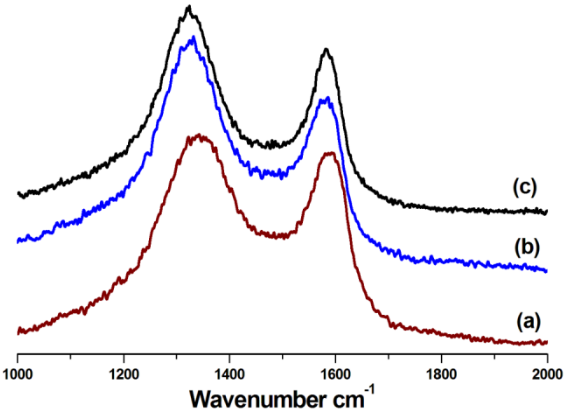


Fig. 10 Raman spectra of a) GO, b) RGO, c) G-SO_3H

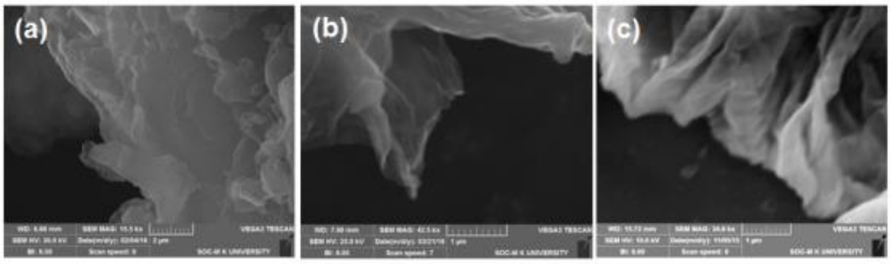


Fig.11 SEM Images of a) GO b) RGO c) G-SO_3H

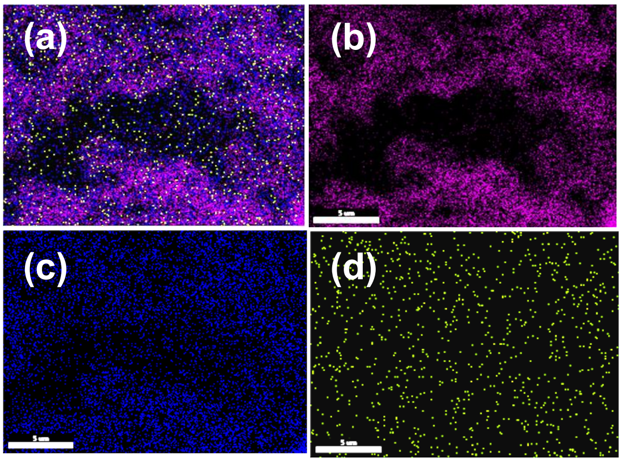


Fig.12 SEM elemental mapping of a) G-SO_3H, b) C, c) O, d) S

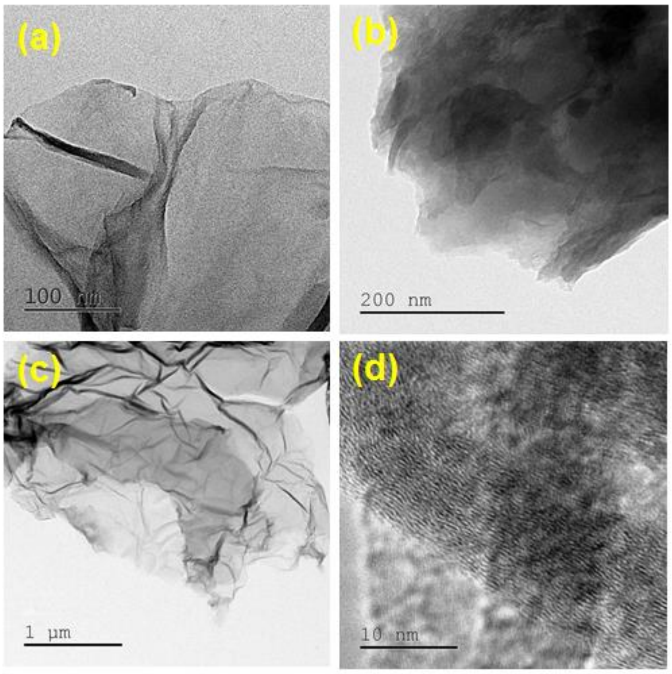
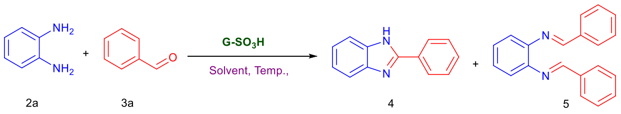


Fig. 13 TEM images of a) GO, b) RGO, c & d) G-SO_3H

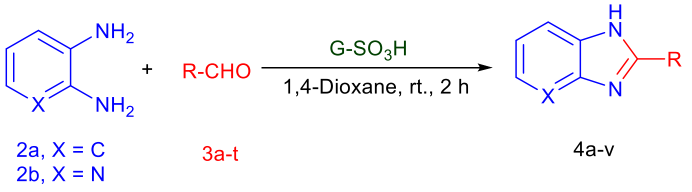
Table 4 Optimization of G-SO_3H catalyzed benzimidazole synthesis[a]

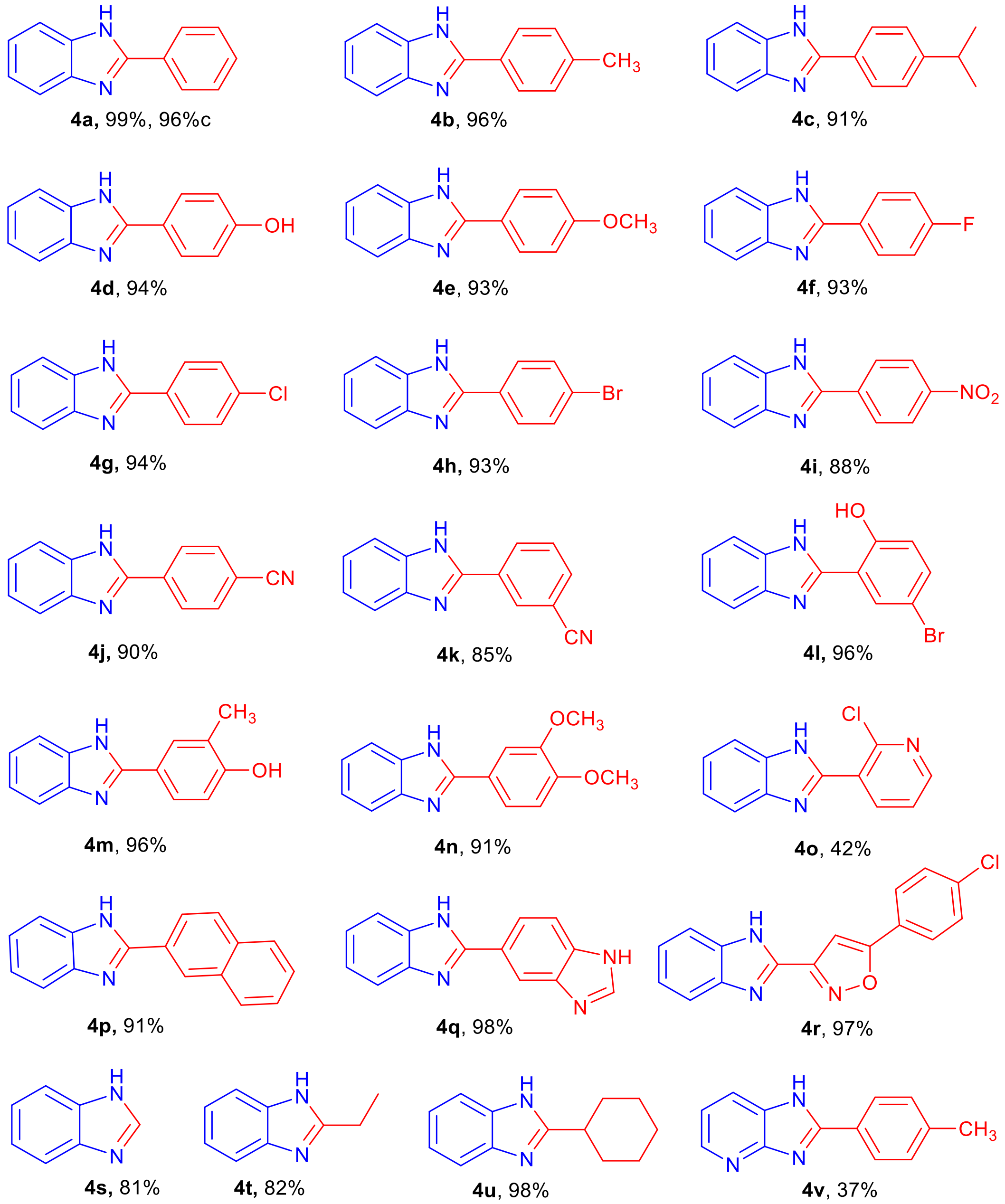


Entry	Solvent	Temp. (˚C)	Yield [b] (%) **4**	Yield [b] (%) **5**
1	Neat	RT	-	-
2	Water	RT	50	49
3	CAN	RT, 80	36, 44	64, 56
4	ACN-Water(1:1)	80	26	52
5	Methanol	RT, 40	22, 40	43, 58
6	Ethanol	RT, 80	48 ,-	34, 82
7	Ethanol-Water(3:1)	80	46	38
8	Hexane	RT, 60	-	-
9	THF	RT, 60	82, 74	7, 21
10	THF-Water (1:1)	RT, 60	41, 44	23, 3
11	1,4-Dioxane	RT, 80	99 [c], 79	-, 20
12	1,4-Dioxane-Water(1:1)	RT, 80	40, 40	41, 24
13	1,4-Dioxane [d]	RT	-	-

[a] Reaction condition: G-SO_3H catalyst (10 mg, 18.5 wt %), benzene-1,2-diamine (0.5 mmol) & benzaldehyde (0.5 mmol) at RT, 6 h. [b] HPLC yield. [c] 2 h. [d] Without Catalyst.

Table 5 Graphene Sulfonic Acid Catalyzed Synthesis of Benzimidazole [a]





4a, 99%, 96%c

4b, 96%

4c, 91%

4d, 94%

4e, 93%

4f, 93%

4g, 94%

4h, 93%

4i, 88%

4j, 90%

4k, 85%

4l, 96%

4m, 96%

4n, 91%

4o, 42%

4p, 91%

4q, 98%

4r, 97%

4s, 81%

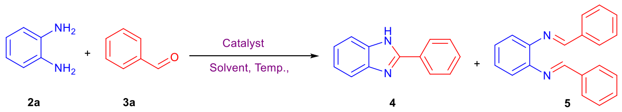
4t, 82%

4u, 98%

4v, 37%

[a] Reaction condition: G-SO$_3$H catalyst (6 mg, 11 wt %), 0.5 mmol of benzene-1,2-diamine and 0.5 mmol of aldehyde at RT, 2 h. [b] isolated yield, [c] Isolated yield in gram scale.

Table 6 Catalytic Control Experiments^a



S. No.	Catalyst	Yield^b (%)	
		4	5
1	GO	37	54
2	RGO	-	-
3	*p*-TSA	32	59
4	G-SO_3H	99	-
5	G-SO_3H-PY	7	-

^{a} Reaction condition: catalyst (6 mg), benzene-1,2-diamine (0.5 mmol) & benzaldehyde (0.5 mmol) at RT, 2 h, ^{b} HPLC yield.

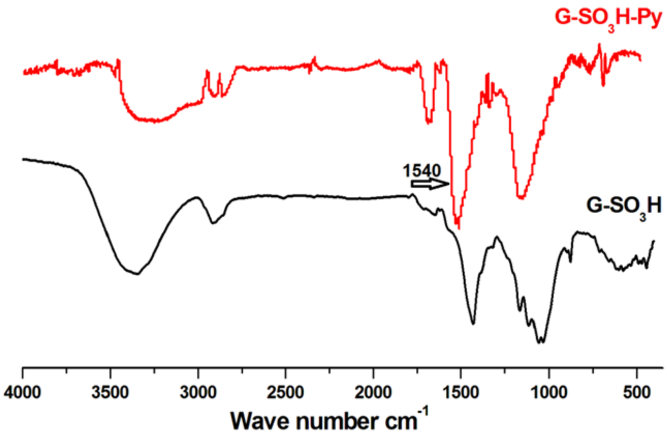


Fig. 14 FT-IR spectra of G-SO_3H and G-SO_3H-Py

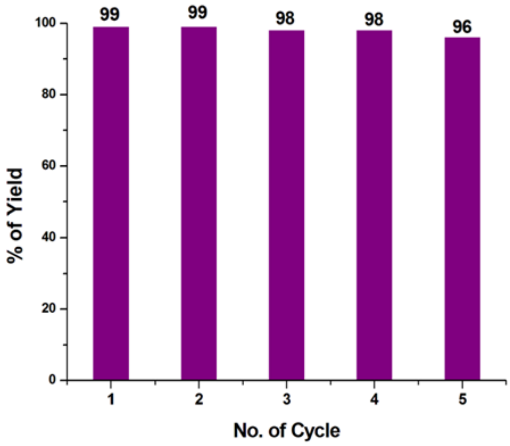


Fig. 15 Reusability of G-SO_3H catalyst.

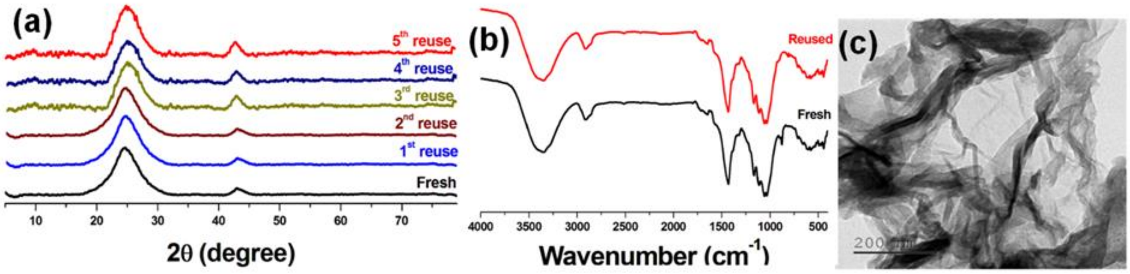
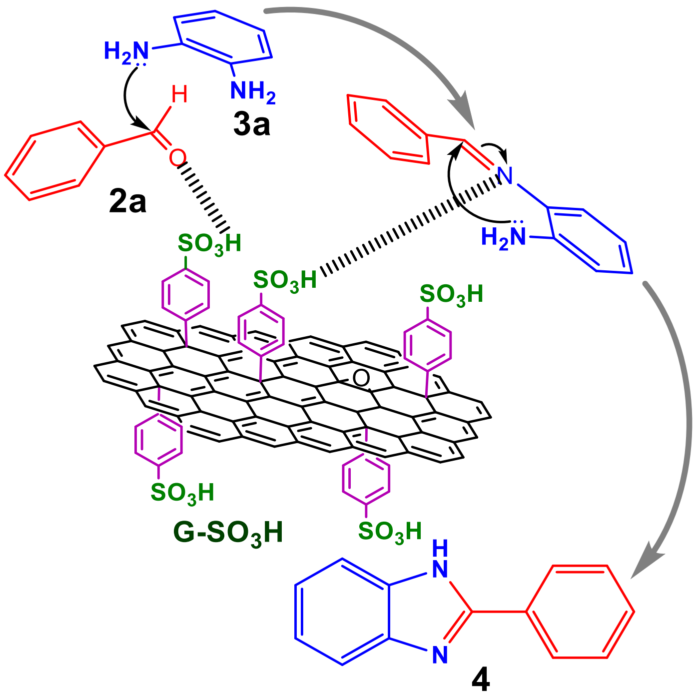


Fig. 16 (a) PXRD, (b) FT-IR and (c) HRTEM Image of reused G-SO_3H

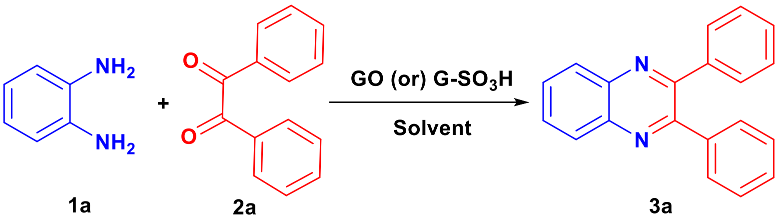


Scheme 3 Proposed Mechanism

A simple, metal-free and benign methodology for the synthesis of C-2 substituted benzimidazole has been developed using sulfonic acid functionalized graphene as a solid Brønsted acid catalyst under ambient condition. Catalyst exhibits good functional group tolerances and selectively, yields a wide spectrum of C-2 substituted benzimidazoles under chromatography free pure condition. The pyridine adsorption studies evidenced the catalytically responsible sulfonic acid cites. This sustainable carbon-based organocatalyst is highly stable, and no loss in activity and could be recovered by simple filtration. The as-prepared G-SO_3H catalyst had shown sustained recyclability over five consecutive cycles for the synthesis of pharmaceutically essential benzimidazoles. To our delight, this carbocatalyst may find broad applications in synthetic as well in medicinal chemistry.

12.4 Rationalising the Catalytic Strength of Graphene Oxide and Functionalised Graphene Oxide on the Synthesis of Quinoxaline

Catalytic potential of carbon-based materials, namely, Graphene Oxide (GO) and it's sulfonic acid functionalised sulfonated reduced graphene oxide ($G\text{-}SO_3H$), have been compared as solid-acid heterogeneous catalysts in quinoxaline synthesis under two different, conventional and ultrasonication conditions. Catalytic activities of these two solid acids are diverge depending on the reaction parameters.



Scheme 4 GO and $G\text{-}SO_3H$ catalysed quinoxaline synthesis

Table 7 Solvent Optimisation for GO Catalysed Quinoxaline Synthesis[a]

Entry	Solvent	Ultrasonication Yield[b] (%)	Conventional Yield[b] (%)
1	Methanol	99	97
2	Ethanol	95	97
3	2-Propanol	64	92
4	Acetonitrile	72	92
5	1,4-Dioxane	91	97
6	THF	76	96
7	Water	80	99
8	DCM	89	89
9	DMSO	71	89
10	DMF	86	90
11	MeOH: Water	77	99

[a]Reaction condition: GO catalyst (10 mg) benzene-1,2-diamine (0.25 mmol) and benzil (0.25 mmol) at RT, 1 h. [b]HPLC yield.

Systematically optimised reaction conditions demonstrate that the functionalised $G\text{-}SO_3H$ performs better than the native GO in quinoxaline synthesis. From this comparative study, it understands that the presence of strong and stable Brønsted acid sites on the G-SO_3H and the clear graphitic domain made G-SO_3H as a better catalyst under conventional condition. The present studies used as a tool to unleash the catalytic latent of native and modified GO in organic synthesis.

Table 8 Solvent Optimisation of G-SO_3H Catalysed Quinoxaline Synthesis[a]

Entry	Solvent	Ultrasonication Yield[b] (%)	Conventional Yield[b] (%)
1	Methanol	100	99
2	Ethanol	99	99
3	2-propanol	94	98
4	Acetonitrile	56	98
5	1,4 Dioxane	88	85
6	THF	48	58
7	Water	51	93
8	DCM	57	90
9	DMSO	58	95
10	DMF	72	91
11	MeOH: Water	74	90

[a] Reaction condition: G-SO_3H catalyst (10 mg) benzene-1,2-diamine (0.25 mmol) and benzil (0.25 mmol) at RT, 5 min. [b] HPLC yield.

Comparison of Catalyst's Activity with different Solvents Under Conventional Condition

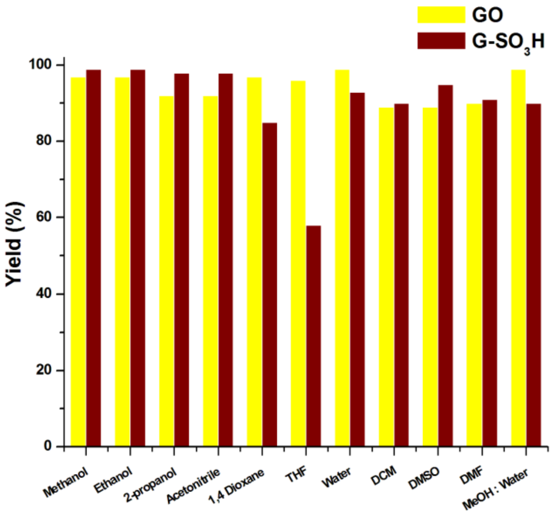


Fig. 17 Comparison of catalyst's activity with solvents under conventional condition. Reaction condition: Catalyst (10 mg) benzene-1,2-diamine (0.25 mmol) and benzil (0.25 mmol) at RT, HPLC yield. reaction time 1 h for GO, 5 min for G-SO_3H.

Comparison of Catalyst's Activity in different Solvent under Ultrasonication Condition

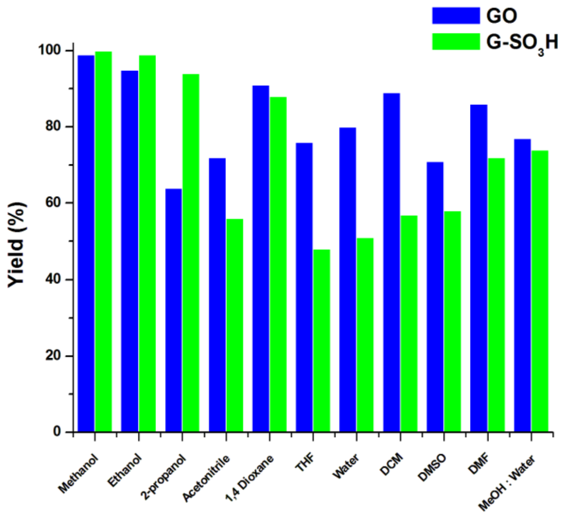


Fig. 18 Comparison of catalyst's activity in different solvents under ultrasonication condition.
Reaction condition: Catalyst (10 mg) benzene-1,2-diamine (0.25 mmol) and benzil (0.25 mmol) at RT, HPLC yield. reaction time 1 h for GO, 5 min for G-SO$_3$H.

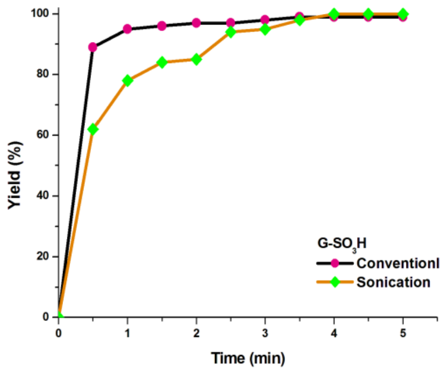


Fig. 19 Time optimisation for G-SO$_3$H catalysed quinoxaline synthesis
Reaction condition: G-SO$_3$H Catalyst (10 mg) benzene-1,2-diamine (0.25 mmol) and benzil (0.25 mmol) at RT, in ethanol, HPLC yield.

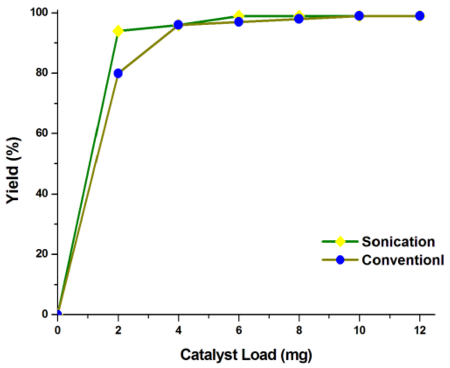
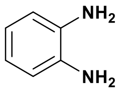
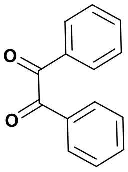
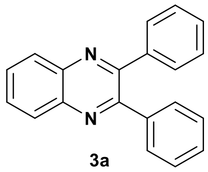
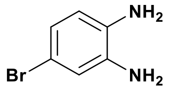
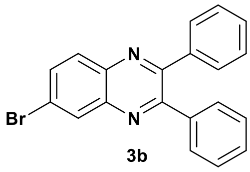
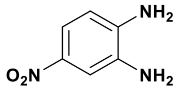
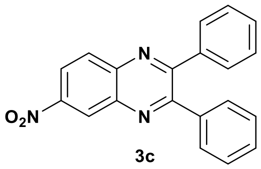
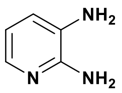
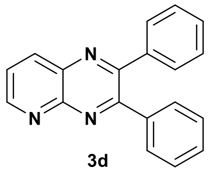
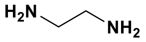
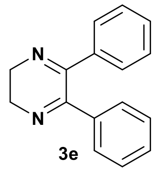
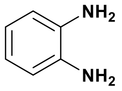
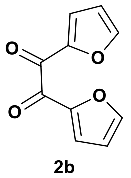
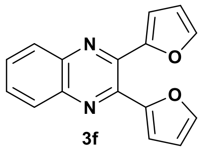


Fig. 20 Catalyst load optimisation for GO catalysed quinoxaline synthesis
Reaction condition: GO catalyst benzene-1,2-diamine (0.25 mmol) and benzil (0.25 mmol) at RT, 12min, HPLC yield, methanol solvent for ultrasonication, water solvent for conventional.

Table 9 G-SO_3H Catalysed Synthesis of Quinoxaline Derivatives^a

S. No.	Reactants		Product	Yield^b (%)
	Diamine	Diketone		
1	 1a	 2a	 3a	99
2	 1b		 3b	96
3	 1c		 3c	94
4	 1d		 3d	80
5	 1e		 3e	90
6	 1a	 2b	 3f	95

^{a}Reaction condition: G-SO_3H catalyst 6 mg, benzene-1,2-diamine (0.5 mmol) and benzil (0.5 mmol) at RT in 2 mL ethanol, < 4 min, ^{b}Isolated yield.

The Bronsted acidic sites present on GO and G-SO_3H were compared in terms of their acidity and catalytic efficiency in the acid catalysed the synthesis of quinoxalines under two different conditions such as conventional room temperature stirring and ultrasonication. For the better understanding of the activity, reaction parameters were screened for both the catalyst under identical reaction conditions. In the rivalry between the two- acidic graphitic catalysts, though both are showed better reactivity in the quinoxaline synthesis, presence of strong Brønsted acidic sulfonic acid sites on G-SO_3H has shown good reactivity without any deactivation or decomposition than the simple carboxylic acid and other oxygen functionalities present on native GO. Besides, under the ultrasonication condition, the activities of both catalysts are reduced except in polar protic solvents. The comparative studies reveals that the Brønsted acidic G-SO_3H shown better reactivity owing to its high stability over the GO towards the synthesis of biologically important quinoxaline synthesis.

12.5 Greener Synthesis of Reduced Graphene Oxide-Nickel Nanocomposite: Rapid and Sustainable Catalyst for the Reduction of Nitroaromatics

An efficient one-pot method for the preparation of reduced graphene oxide-nickel nanocomposite (RGO-Ni) has been developed using L-ascorbic acid as a greener reducing agent, which simultaneously reduces both graphene oxide and Ni^{II}. The as-prepared nanocomposite was characterized using various analytical techniques. The ICP-OES confirms the presence of 19.7% nickel loading and TEM shows the average size of the particles to be 10 nm. Subsequently, RGO-Ni nanocomposite was used as a sustainable catalyst for the reduction of nitroaromatics to the corresponding amines using $NaBH_4$ in an aqueous methanol medium. A series of aromatic and aliphatic nitro compounds are chemoselectively reduced to amines over other reducible functionalities. RGO-Ni nanocomposite is highly stable and can be recovered by simple magnetic separation and recycled for at least five consecutive cycles. The present catalytic system has achieved the dual requirements for reactivity and selectivity in a nitro reduction in short reaction time with minimum nickel load in greener media.

Preparation of RGO-Ni Nanocomposite

GO (20 mg) was dispersed in 10 mL of DD water by sonication. 60 mg of $NiCl_2.6H_2O$ in water (2 mL) was added dropwise under stirring. The mixture was sonicated for 1 h to ensure complete adsorption of nickel on GO. Meanwhile, a 0.1 M L-ascorbic acid (142 mg in 8 mL water) was added slowly with vigorous stirring and the mixture was sonicated for 60 min. Finally, the above suspension was transferred into a 50 mL Teflon-lined autoclave and placed in a hot air oven at 120 °C for about 16 h. It was then cooled to room temperature, and the resultant black precipitate was separated by centrifugation, washed with a large amount of water and ethanol, and was dried under vacuum at 60 °C.

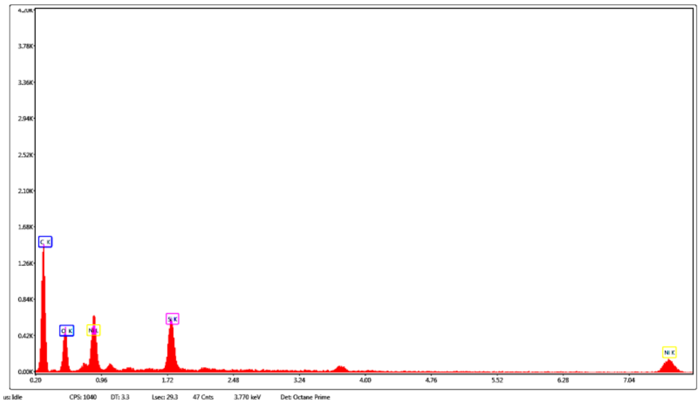


Fig. 21 EDS spectrum of RGO-Ni nanocomposite

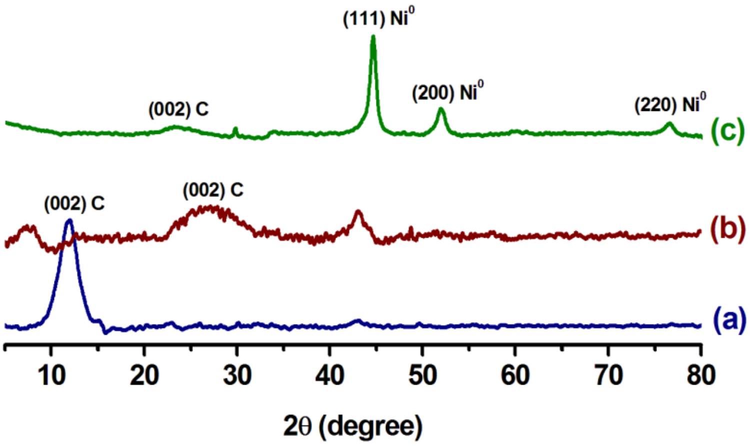


Fig. 22 PXRD patterns of a) GO, b) RGO and c) RGO-Ni.

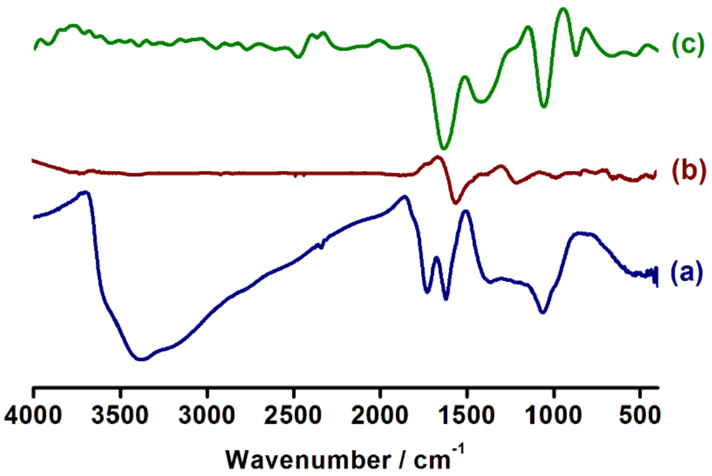


Fig. 23 FTIR spectra of a) GO, b) RGO and c) RGO-Ni.

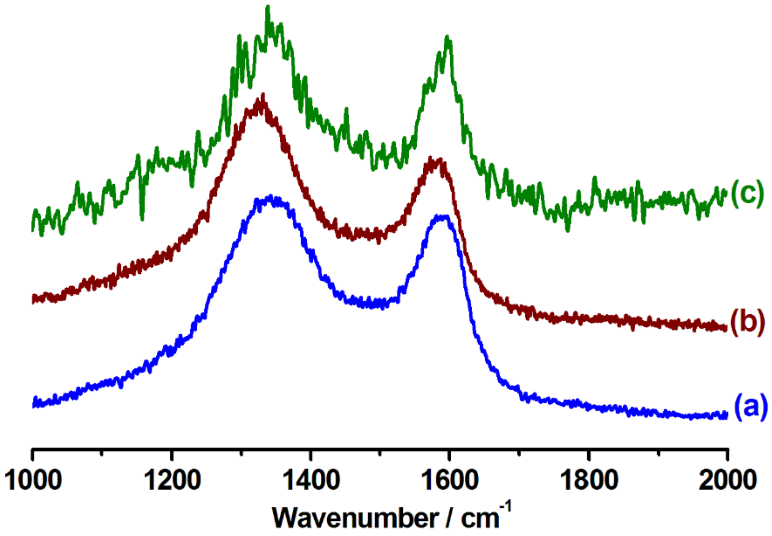


Fig. 24 Raman spectra of a) GO, b) RGO and c) RGO-Ni.

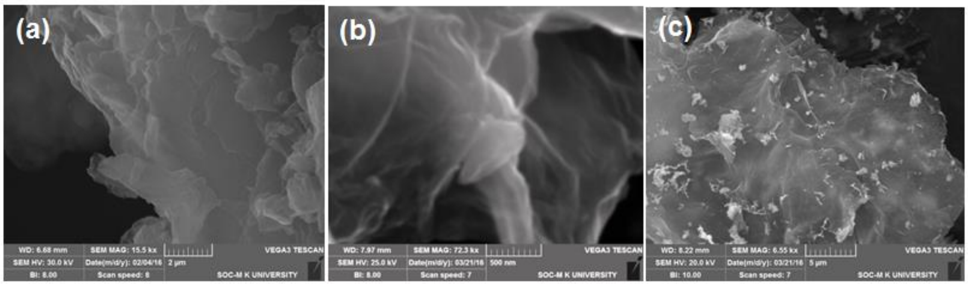


Fig. 25 SEM images of a) GO, b) RGO, and c) RGO-Ni.

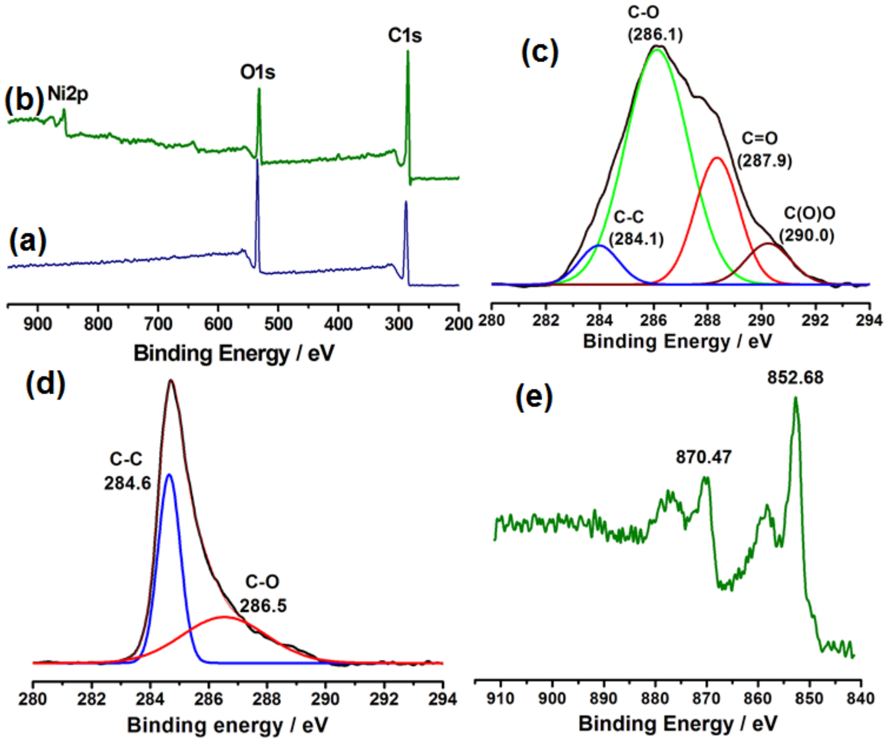


Fig. 26 XPS spectra of a) GO, b) RGO-Ni, deconvoluted peaks: c) GO - C 1s, d) RGO-Ni- C 1s and e) RGO-Ni Ni 2p.

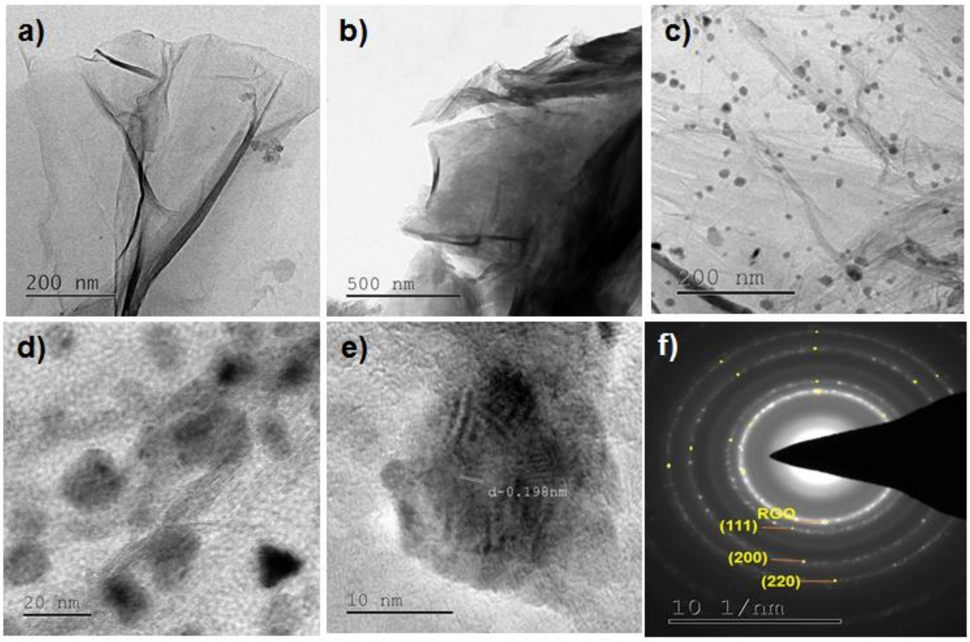


Fig. 27 TEM images a) GO, b) RGO, c) and d) RGO-Ni nanocomposite, e) lattice fringes of Ni nanoparticle, f) SAED pattern of RGO-Ni.

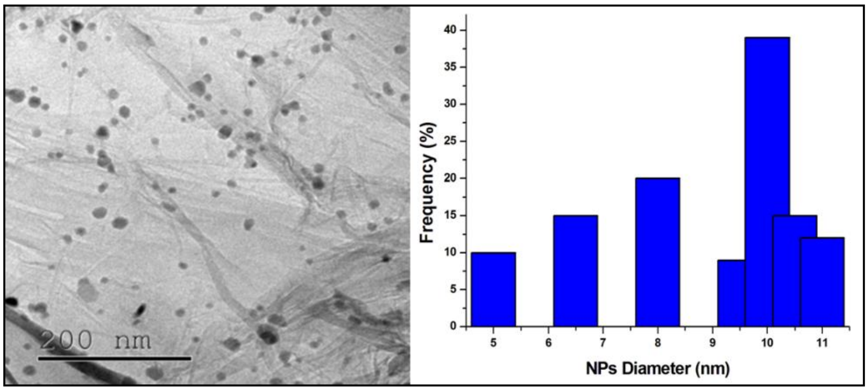


Fig. 28 Particle size distribution of RGO-Ni nanocomposite

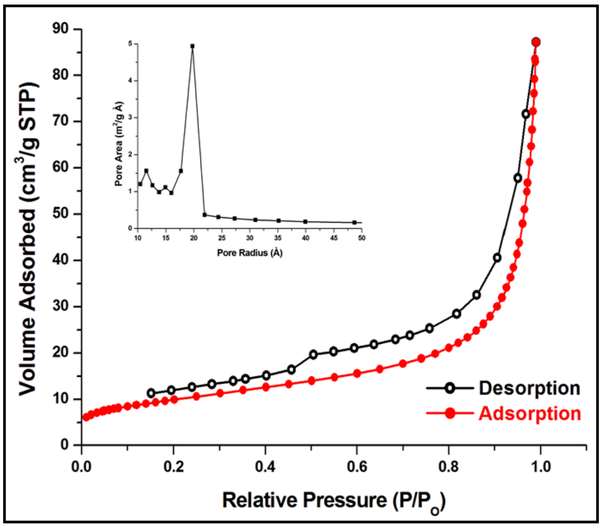
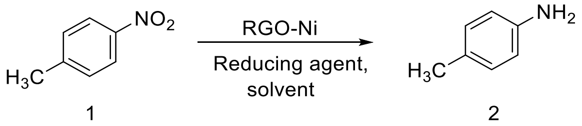


Fig. 29 Nitrogen adsorption and desorption isotherms of RGO-Ni at 77 K

Table 10 Optimisation of Reaction Condition for RGO-Ni Catalyzed Reduction of *p*-nitrotoluene[a]



Entry	Solvent	Reducing agent	Eq. of reducing agent	Yield[b] (%)
1	Methanol	$NaBH_4$	2	5
2	Ethanol	$NaBH_4$	2	-
3	Acetonitrile	$NaBH_4$	2	-
4	Isopropyl alcohol	$NaBH_4$	2	-
5	DMF	$NaBH_4$	2	-
6	DMSO	$NaBH_4$	2	-
7	Water	$NaBH_4$	2	-
8	THF	$NaBH_4$	2	-
9	1,4-Dioxane	$NaBH_4$	2	-
10	Toluene	$NaBH_4$	2	-
11	Methanol	$NH_2NH_2.H_2O$	2,15	-,-
12	Methanol	HCOOH	2,15	-,-
13	Methanol	$HCOONH_4$	2,15	-,-
14	Methanol	Isopropyl alcohol	2,15	-,-
15	Methanol:H_2O (1:1)	$NaBH_4$	2	5
16	Acetonitrile:H_2O (1:1)	$NaBH_4$	2	-
17	Methanol:H_2O (1:1)	$NaBH_4$	2	5[c,d]
18	Methanol:H_2O (1:1)	$NaBH_4$	15	100[e]
19	Ethanol	$NaBH_4$	15	58
20	Ethanol:H_2O (1:1)	$NaBH_4$	15	-

[a] Reaction condition: *p*-nitrotoluene (0.5 mmol), reducing agent, 10 mg of RGO-Ni catalyst in 4 mL solvent at RT, 24 h. [b] GC yield. [c] Reaction carried at 45 °C. [d] 45 °C under N_2 atm. [e] 30 min.

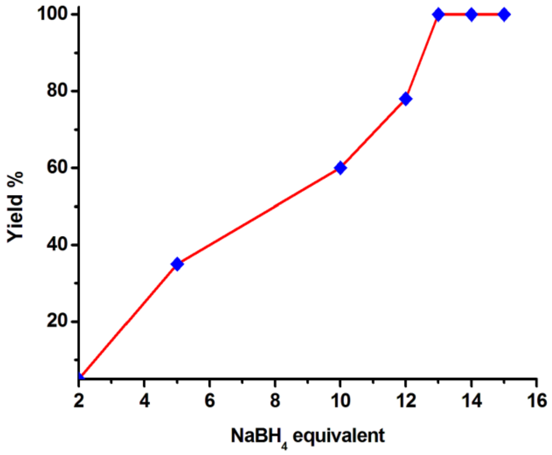


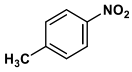
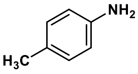
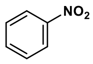
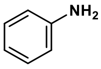
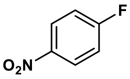
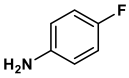
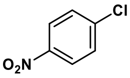
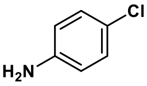
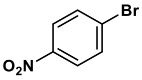
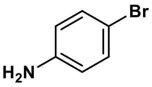
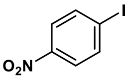
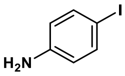
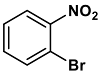
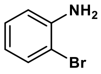
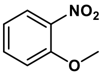
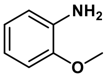
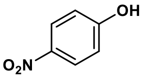
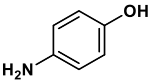
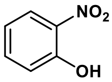
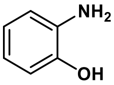
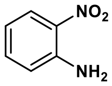
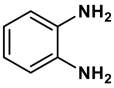
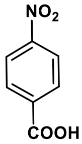
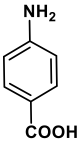
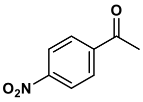
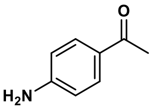
Fig. 30 Optimisation of sodium borohydride equivalent in RGO-Ni mediated *p*-nitrotoluene reduction.

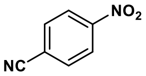
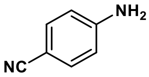
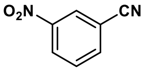
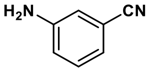
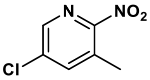
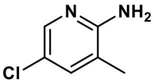
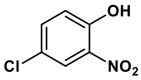
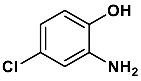
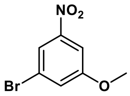
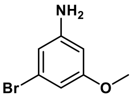
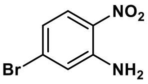
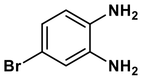
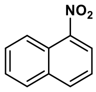
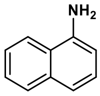
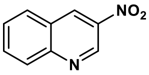
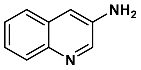
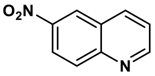
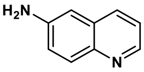
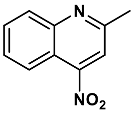
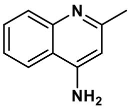
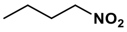
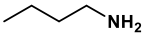
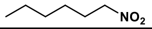
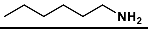
Table 11 Optimisation of RGO-Ni Nanocomposite Catalyst Load in *p*-Nitrotoluene Reduction[a]

Entry	Catalyst load[b] (mg)	Yield[c] (%)
1	4	84
2	5	100
3	6	100
4	7	100

[a] Reaction condition: *p*-nitrotoluene (0.5 mmol), 13 eq. of $NaBH_4$, in 4 mL methanol-water (1:1) at RT, 30 min. [b]RGO-Ni nanocomposite, [c] GC yield.

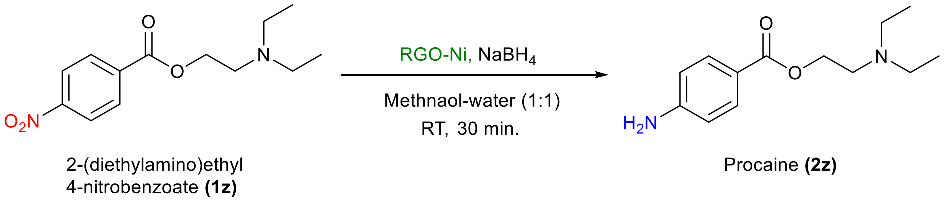
Table 12 Reduction of Nitroaromatics by RGO-Ni Nanocomposite with Sodium borohydride[a]

Entry	Nitroaromatics		Amines		Time (min.)	Yield[b] (%)
1		**1a**		**2a**	30	98,100[c], 96 [d]
2		**1b**		**2b**	30	99
3		**1c**		**2c**	30	95
4		**1d**		**2d**	30	98
5		**1e**		**2e**	30	98
6		**1f**		**2f**	30	98
7		**1g**		**2g**	30	98
8		**1h**		**2h**	30	97
9		**1i**		**2i**	10	99
10		**1j**		**2j**	10	99
11		**1k**		**2k**	40	92
12		**1l**		**2l**	30	97
13		**1m**		**2m**	30	95

14		**1n**		**2n**	30	99
15		**1o**		**2o**	30	99
16		**1p**		**2p**	40	90
17		**1q**		**2q**	40	92
18		**1r**		**2r**	40	96
19		**1s**		**2s**	40	93
20		**1t**		**2t**	30	98
21		**1t**		**2t**	30	95
22		**1v**		**2v**	30	91
23		**1w**		**2w**	40	91
24		**1x**		**2x**	30	74
25		**1y**		**2y**	30	72

[a] Reaction conditions: Nitroaromatics (0.5 mmol), $NaBH_4$ (13 eq.), RGO-Ni catalyst (5 mg), methanol:water (1:1) (4 mL), RT. [b] All are isolated yield, [c] GC Yield, [d] Isolated yield in 1 g batch.

Application of RGO-Ni in the Synthesis of a Local Anesthetic Agent - Procaine



Scheme 4 Synthesis of procaine using RGO-Ni nanocomposite as catalyst

Table 13 Other Materials in Reduction of Nitroaromatics[a]

Entry	Catalyst	Conversion[b] (%)
1	No catalyst	-
2	Graphite	-
3	GO	4.9
4	RGO	-

5	$NiCl_2.6H_2O$	28[c]
6	Nickel powder	53
7	Raney nickel	96[d]

[a] Reaction conditions: Nitroaromatics (0.5 mmol), $NaBH_4$ (13 eq.), Catalyst materials (10 mg), 1:1 Methanol:Water (4 mL), RT. [b] GC Yield. [c] Contains 0.98 mg of Nickel. [d] Entry from reference 28.

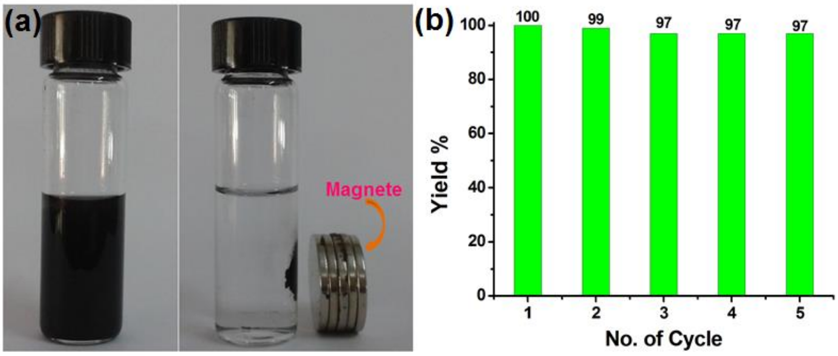


Fig. 31 a) Facile magnetic separation of RGO-Ni catalyst from the reaction media b) Reusability of heterogeneous RGO-Ni nanocomposite catalyst in nitroaromatic (**1**) reduction

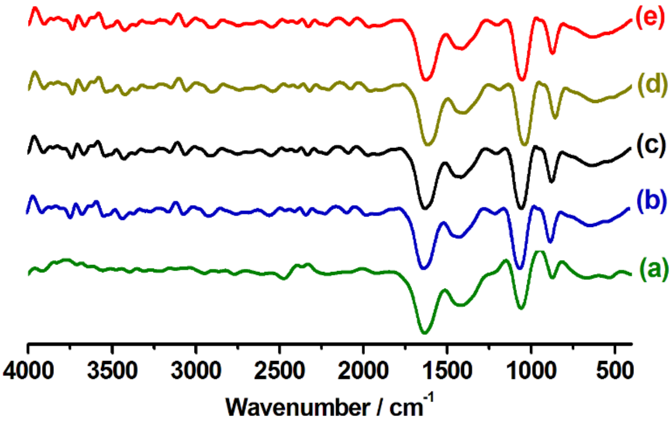


Fig. 32 FTIR spectra of a) Fresh RGO-Ni, b) after1st use RGO-Ni, c) 2nd use RGO-Ni, d) 3rd use RGO-Ni, e) 5th use RGO-Ni.

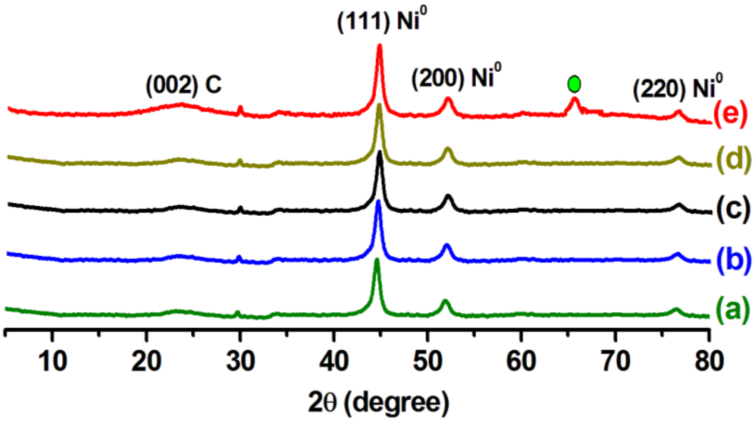
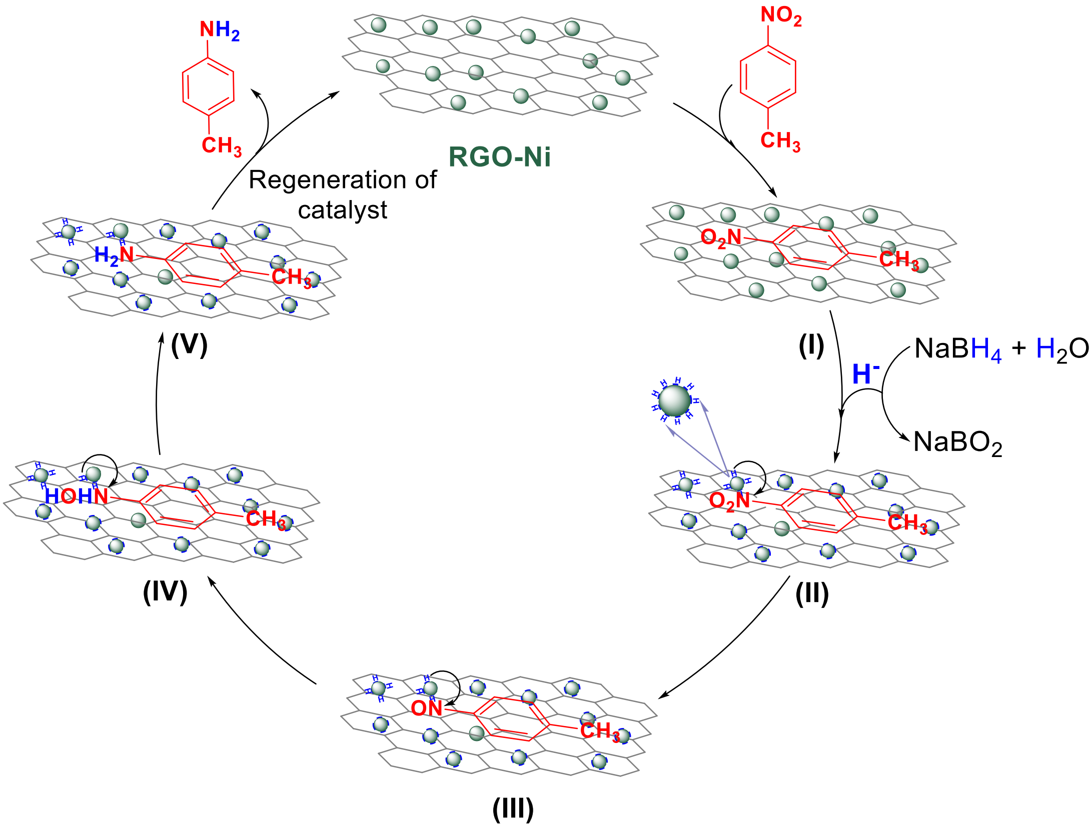


Fig. 33 PXRD patterns of a) Fresh RGO-Ni, b) After1st use RGO-Ni, c) 2nd use RGO-Ni, d) 3rd use RGO-Ni, e) 5th use RGO-Ni. (green dot shows new peak).

Table 14 Filtration Test for RGO-Ni Nanocomposite Catalyst[a]

Catalyst	Yield[b] (%)	
	15 min	15 + 15 min
RGO-Ni nanocomposite	48	48[c]

[a] Reaction condition: *p*-nitrotoluene (0.5 mmol), 13 eq. of $NaBH_4$, RGO-Ni nanocomposite (5 mg), in 4 mL methanol-water (1:1) at RT for 30 min. [b] GC yield. [c] After removing the catalyst.



Scheme 5. Plausible mechanism for reduction of nitroaromatics catalyzed by RGO-Ni nanocomposite and sodium borohydride.

We have demonstrated a greener and efficient method to synthesis RGO-Ni nanocomposite using L-ascorbic acid as an eco-friendly reducing agent under hydrothermal condition, which eliminates the hazardous reducing agents, stabilizers, and tricky purification methods. In the present strategy, graphene oxide and nickel salts reduced simultaneously and form a stable RGO-Ni nanocomposite, it has been meticulously characterized using various spectroscopic and microscopic techniques. All analysis undoubtedly confirmed the formation of stable nanocomposite with minimum nickel load, without any aggregation and oxidation. The as-prepared RGO-Ni nanocomposite act as a potential catalyst for the reduction of diverse nitroaromatics under a mild condition in a benign aqueous methanol medium within a brief time with low catalyst load. Furthermore, the catalyst is compatible with various vulnerable functional groups and reduces nitro groups selectively. The catalytic behavior of RGO-Ni is higher than supported Ni NPs, and other metal catalysts which enlighten the synergistic effect between the reduced graphene oxide and nickel nanoparticles. The sustainability of the catalyst was proved by simple magnetic separation and reused for several times without a decrease in catalytic activity.

12.6. Nickel Nanoparticles on Reduced Graphene Oxide as an Active and Selective Catalyst for the C-C Coupling Reaction

A mild and environmentally benign methodology to syntheses biaryls and 1,3-diynes has been demonstrated using the nickel nanoparticles supported on reduced graphene oxide (RGO-Ni) as a heterogeneous catalyst which is prepared using green reagents. A series of substituted biaryls and 1,3-diynes has been synthesised in good to excellent yields through C-C homocoupling reaction of arylboronic acids and terminal alkynes respectively using 1,4-dioxane as a benign solvent. The present ligand-free catalytic system proceeds smoothly under mild conditions, avoids noble and stoichiometric metal reagents, tolerates sensitive functional groups, has a wide substrate scope, and is feasible with other nitrogen and sulphur containing heteroaryl boronic acids. Hot filtration test unambiguously proves the true heterogeneity of the catalyst and which support for the further reusability of the catalyst for several times without any change in the activity. The easy preparation and simple magnetic separation, stability and reusability reveal that as-prepared RGO-Ni as a versatile catalyst for the synthesis of polyaromatic compounds both in academia and industries.

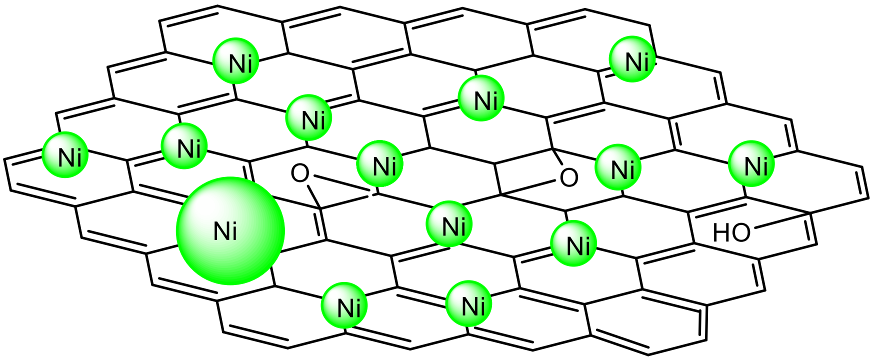
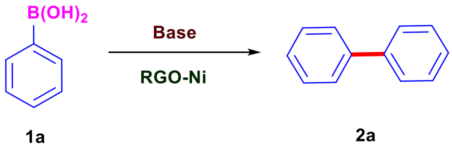


Fig. 34 Proposed structure of the synthesised RGO-Ni composite.

Table 15 Optimisation of RGO-Ni Catalysed Homocoupling of Boronic acids[a]



Entry	Solvent	Base	Yield[b] (%)
1	1,4-Dioxane	K_3PO_4	-[c]
2	Methanol	K_3PO_4	-
3	Ethanol	K_3PO_4	-
4	Water	K_3PO_4	-
5	DMSO	K_3PO_4	95
6	DMF	K_3PO_4	-
7	1,4-Dioxane	K_3PO_4	99
8	1,4-Dioxane	K_3PO_4	-[d], 68[e], 82[f], 99[g]
9	DCM	K_3PO_4	-
10	THF	K_3PO_4	trace
11	ACN	K_3PO_4	78
12	1,4-Dioxane: Water	K_3PO_4	35
13	1,4-Dioxane	Cs_2CO_3	-
14	1,4-Dioxane	K_2CO_3	-
15	1,4-Dioxane	Na_2CO_3	-
16	1,4-Dioxane	Et_3N	15

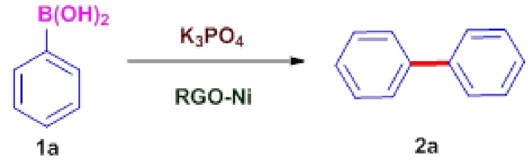
[a] Reaction Conditions: phenylboronic acid (0.5 mmol), base (1.5 mmol) and 60 mg of RGO-Ni in 2 mL of solvent at 100 °C up to 12 h. [b] Isolated yield. [c] without catalyst, [d] without base, Yields in [e] 1h, [f] 2 h, and [g] 3 h

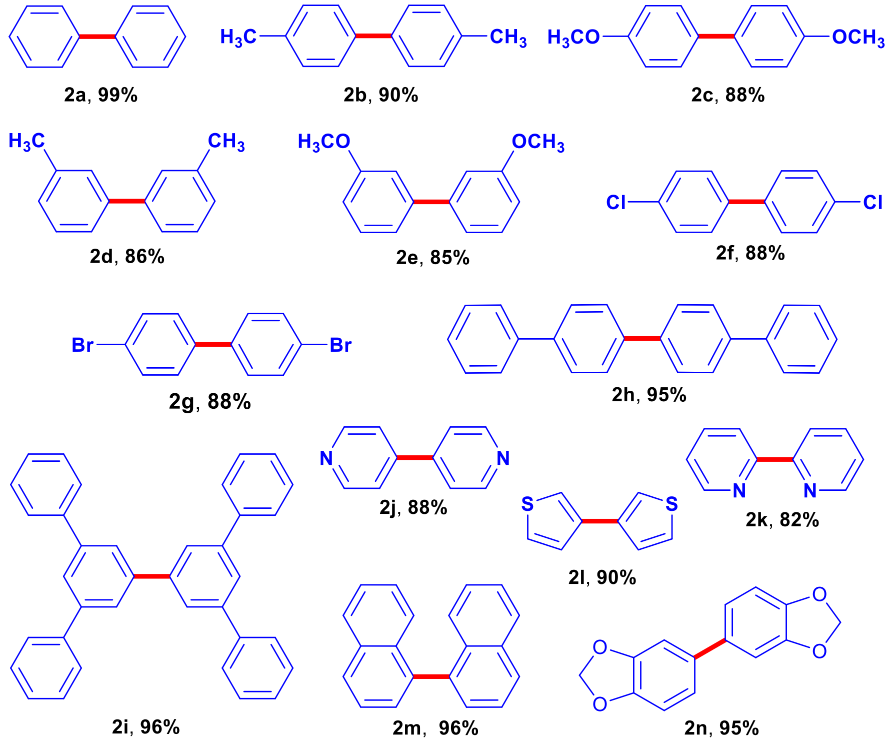
Table 16 Control experiment for the catalytic efficiency of RGO-Ni in the homocoupling of phenylboronicacid[a]

Entry	Catalyst	Yield [b] (%)
1	RGO-Ni	99
2	GO	-
3	Graphite	-
4	RGO	12,12[c]
5	$NiCl_2.6H_2O$	38,38[c]
6	Nickel nanoparticle	75[d]

[a] Reaction condition: Phenylboronic acid (0.5 mmol), K_3PO_4 (1.25 mmol) and 50 mg of catalyst in 2 mL of 1,4-dioxane at 85 °C up to 3 h. [b] isolated yield. [c] reaction carried out up to 24 h. [d] 9.5 mg of catalyst

Table 17 RGO-Ni nanocomposite catalysed homocoupling of arylboronic acids[a]





2a, 99%
2b, 90%
2c, 88%
2d, 86%
2e, 85%
2f, 88%
2g, 88%
2h, 95%
2j, 88%
2l, 90%
2k, 82%
2i, 96%
2m, 96%
2n, 95%

[a]Reaction conditions: RGO-Ni catalyst (50 mg), phenylboronic acid (0.5 mmol), K_3PO_4 (1.25 mmol) 1,4-dioxane (2.0 mL) at 85 °C up to 3 h. All are isolated yields.

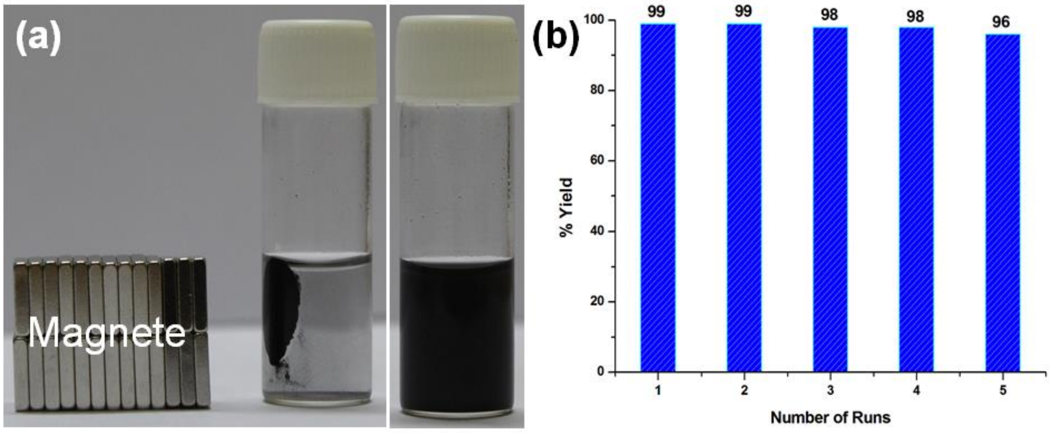
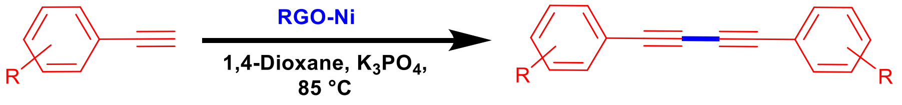
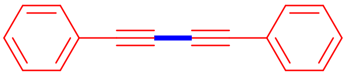


Fig. 35 a) Magnetic separation of the catalyst; (b) Reusability profile of RGO-Ni in homocoupling of phenylboronic acid. Reaction conditions: RGO-Ni catalyst (50 mg), phenylboronic acid (0.5 mmol), K_3PO_4 (1.25 mmol) 1,4-dioxane (2.0 mL) at 85 °C up to 3 h. All are isolated yields.

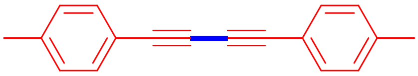
Table 18 RGO-Ni nanocomposite catalysed Glaser–Hay coupling of terminal alkynes[a]



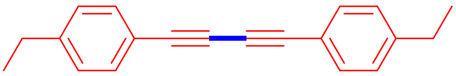
3a **4a**



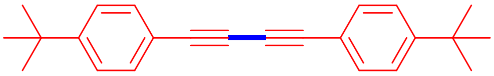
4a, 99%



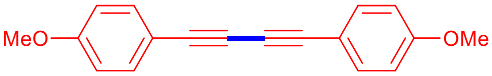
4b, 94%



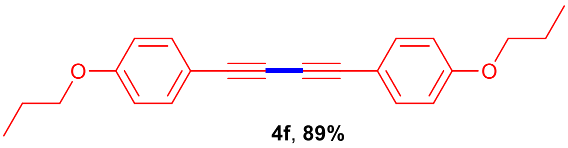
4c, 92%



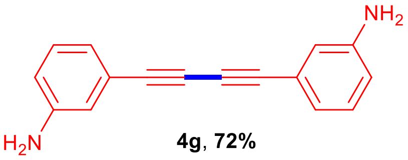
4d, 87%



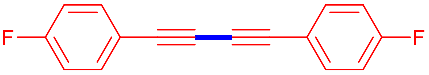
4e, 90%



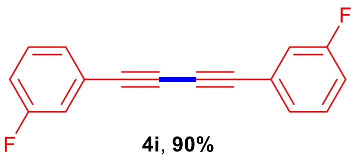
4f, 89%



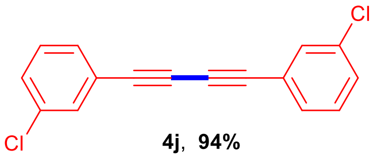
4g, 72%



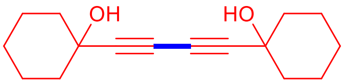
4h, 91%



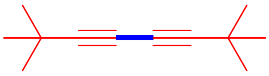
4i, 90%



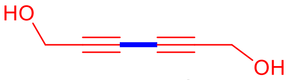
4j, 94%



4k, 42%



4l, 38%[b]



4m, 38%[b]

[a] Reaction conditions: RGO-Ni nanocomposite catalyst (50 mg), alkynes (0.5 mmol), K_3PO_4 (1.25 mmol) 1,4-dioxane (2.0 mL) at 85 °C up to 3 h. All are isolated yields. [b] reaction time was extended to 10 h

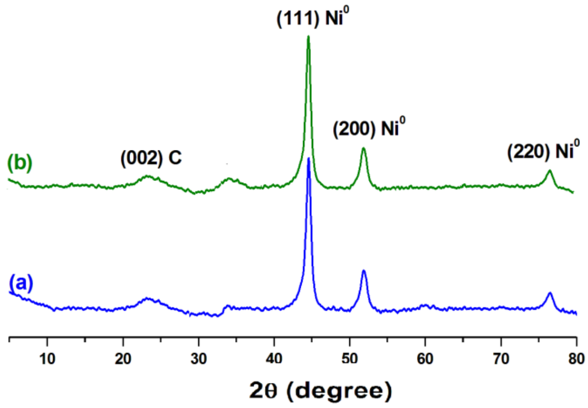


Fig. 36 Powder-XRD patterns of fresh RGO-Ni (a), and reused catalysts after the fifth run (b).

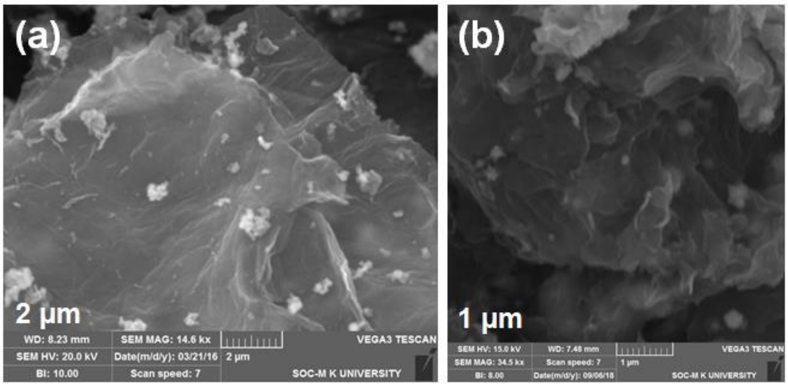


Fig. 37 SEM images of (a) fresh and (b) reused RGO-Ni after the fifth run.

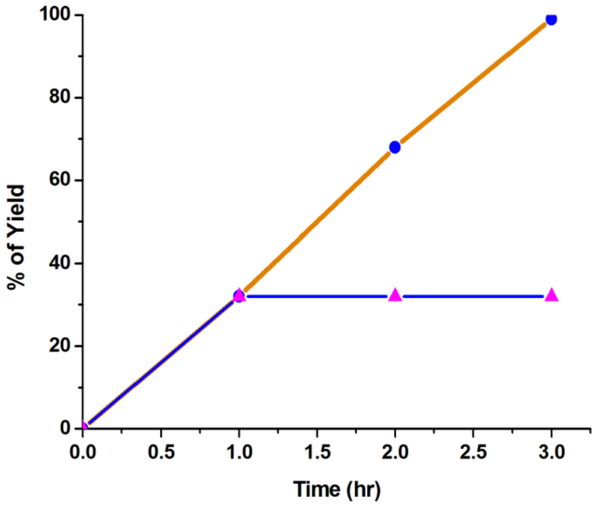
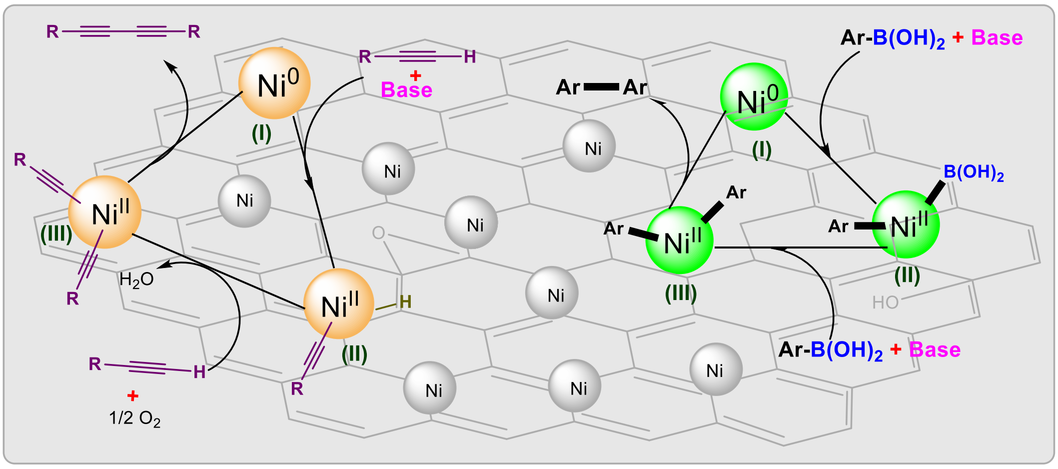


Fig. 38 Hot filtration test of RGO-Ni in the homocoupling of phenylboronic acid.



Scheme 6 Plausible mechanism for RGO-Ni catalysed homocoupling of arylboronic acid/aryl alkynes.

Apart from as a reducing catalyst, the present work discloses another potential catalytic application of the as-prepared RGO-Ni nanocomposite in C_{sp}^2- C_{sp}^2 Suzuki type homocoupling and C_{sp}–C_{sp} Glaser–Hay coupling reactions. Here, a simple, efficient and greener methodology has been developed for the synthesis of both symmetrical biphenyls and 1,3-diynes using the heterogeneous nickel-based catalytic system with good to excellent yields. This multicatalytic behaviour of the RGO-Ni nanocomposite has more advantageous when compared to the existing commercial catalyst due to the utilisation of a non-Noble and readily available nickel metal without any ligand or additives under optimum temperature with the minimum nickel loading. Also, the RGO-Ni nanocomposite is highly stable and could be reused for five times without any significant loss in catalytic behaviour with a mild drop in the yield. The developed catalytic methodology offers to develop a commercially viable heterogeneous nanocomposite based sustainable catalytic system for synthesis of industrially demanding diverse biaryl and 1,3-diynes compounds.

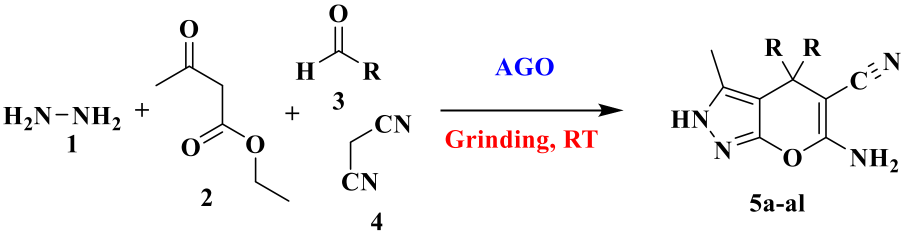
12.7. Nitrogen Doped Graphene Oxide as a Green Organocatalyst for Michael Addition Reactions

Nitrogen doped graphene oxide (NGO) used as a solid base organocatalyst for michael addition under ambient conditions. Myriad nitrogen doped GO was synthesized from graphene oxide by simple hydrothermal method and characterized using various analytical techniques like elemental analysis, PXRD, FT-IR, EDX, SEM, TEM and XPS. The prepared catalyst activity was confirmed with the Michael addition between chalcone and various michael donors. Sustainable nature of the catalyst is good, more stable and reactive even after four cycles. Present catalyst works smoothly under very mild condition without any external bases or additives.

12.8 Amino Graphene as a Sustainable Organocatalyst for Solvent free multicomponent synthesis of pyranopyrazole

An environmentally benign protocol was developed with amino graphene (AGO) which act simultaneously as an efficient solid base catalyst and sustainable organocatalyst for the solvent free four component reaction at room temperature has been developed for the synthesis of 6- amino-5- cyano-3-methyl-4-aryl/heteroaryl-2H,4H-dihydropyrano[2,3-c] pyrazoles. The AGO was synthesized from graphene oxide by simple hydrothermal method and characterized using various analytical techniques like elemental analysis, PXRD, FT-IR, EDX, SEM, TEM and XPS. The prepared catalyst activity was confirmed with the synthesis of pyranopyrazoles. This protocol, includes a milder procedure, does not involve any hazardous work-up and results in quantitative yields. The catalyst can be reused at least five times without loss of its catalytic activity.

Table 24 Optimization of Amino Graphene (AGO) catalyzed by synthesis of pyranopyrazole [a]



S.No	Solvent	Catalyst	Catalyst load (mg)	Yield [b] (%)
1	Ethanol	AGO	5	68
2	Ethanol : water	AGO	5	65
3	Methanol : water	AGO	5	57
4	Acetonitrile	AGO	5	68

5	Tetrahydrofuran	AGO	5	52
6	Isopropyl alcohol	AGO	5	70
7	Toluene	AGO	5	68
8	Methanol	AGO	5	54
9	**Neat**	**AGO**	**5**	**98**
10	Neat	AGO	-	20
11	Neat	AGO	1	25
12	Neat	AGO	2	32
13	Neat	AGO	3	55
14	Neat	AGO	4	77
15	Neat	AGO	10	75
16	Neat	AGO	20	70

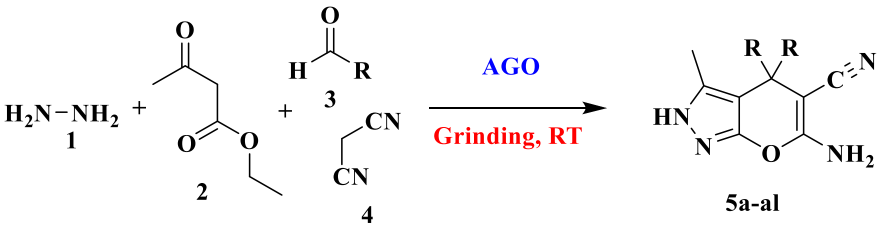
[a] Reaction was carried out at 1mmol scale of all reactants with 5 mg of AGO in a solvent free conditions for 2 min at room temperature. [b] Isolated yield

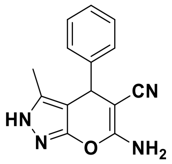
Table 25 Control experiment with other graphene catalyzed by synthesis of pyranopyrazole [a]

S.No	Solvent	Catalyst	Catalyst load (mg)	Yield [b] (%)
1	**Neat**	**AGO**	**5**	**98**
2	Neat	RGO	5	-
3	Neat	GO	5	35
4	Neat	GO-APTES	5	86

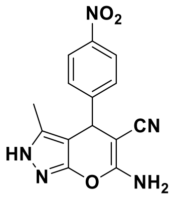
[a] Reaction was carried out at 1mmol scale of all reactants with 5 mg of catalyst in a solvent free conditions for 2 min at room temperature. [b] Isolated yield

Table 26 Synthesis of pyranopyrazole with various substituted aldehydes [a]

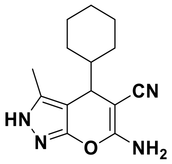




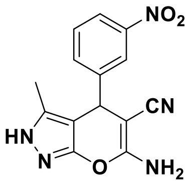
Entry 1; **5a,** 98%
M.P (253-257) °C



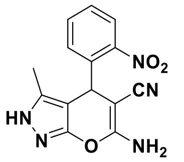
Entry 2; **5b,** 99%
M.P (253-257) °C



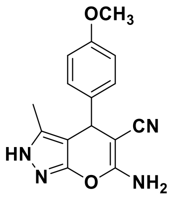
Entry 3; **5c,** 78%
M.P (253-257) °C



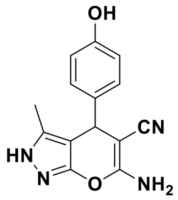
Entry 4; **5d,** 99%
M.P (253-257) °C



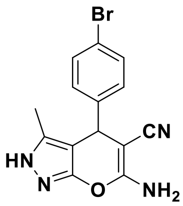
Entry 5; **5e,** 99%
M.P (253-257) °C



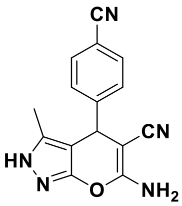
Entry 6; **5f,** 89%
M.P (253-257) °C



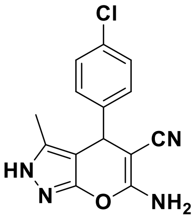
Entry 7; **5g,** 85%
M.P (253-257) °C



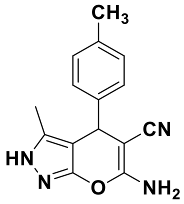
Entry 8; **5h,** 87%
M.P (253-257) °C



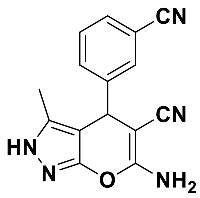
Entry 9; **5i,** 98%
M.P (253-257) °C



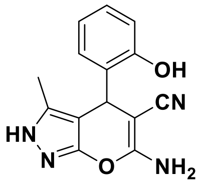
Entry 10; **5j,** 85%
M.P (253-257) °C



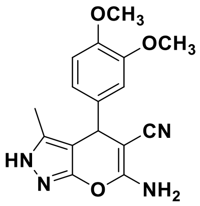
Entry 11; **5a,** 78%
M.P (253-257) °C



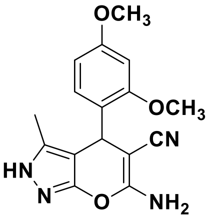
Entry 12; **5b,** 95%
M.P (253-257) °C



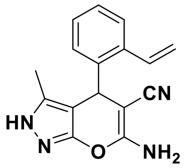
Entry 13; **5c,** 80%
M.P (253-257) °C



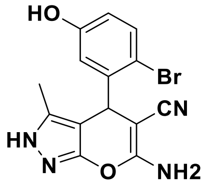
Entry1 4; **5d,** 74%
M.P (253-257) °C



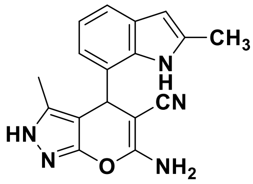
Entry1 5; **5e,** 76%
M.P (253-257) °C



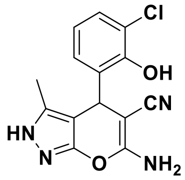
Entry 16; **5a,** 5%
M.P (253-257) °C



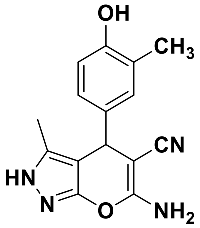
Entry 17; **5b,** 67%
M.P (253-257) °C



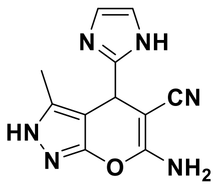
Entry 18; **5c,** 72%
M.P (253-257) °C



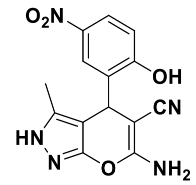
Entry 19; **5d,** 56%
M.P (253-257) °C



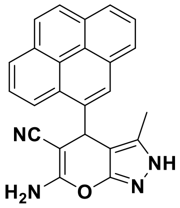
Entry 20; **5e,** 79%
M.P (253-257) °C



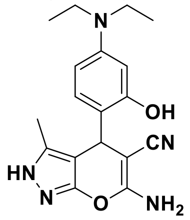
Entry 21; **5a,** 4%



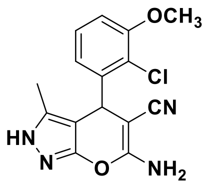
Entry22; **5b,** 90%



Entry23; **5c,** 86%

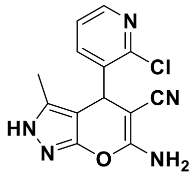


Entry 24; **5d,** 67%



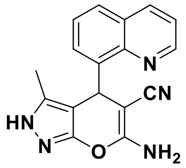
Entry 25; **5e,** 70%

M.P (253-257) °C



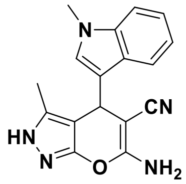
Entry 26; **5a,** 78%
M.P (253-257) °C

M.P (253-257) °C



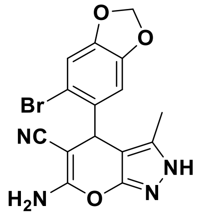
Entry 27; **5b,** 82%
M.P (253-257) °C

M.P (253-257) °C



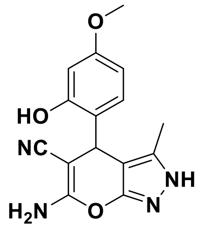
Entry 28; **5c,** 74%
M.P (253-257) °C

M.P (253-257) °C



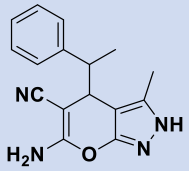
Entry 29; **5d,** 67%
M.P (253-257) °C

M.P (253-257) °C

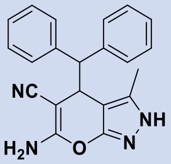


Entry 30; **5e,** 75%
M.P (253-257) °C

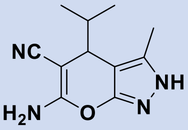
Lists of ketone substrates



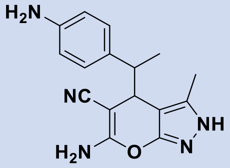
Entry 1; **5a,** 72%
M.P (253-257) °C
%



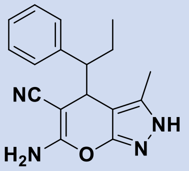
Entry 2; **5b,** 62%
M.P (253-257) °C



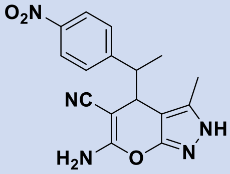
Entry 3; **5c,** 77%
M.P (253-257) °C



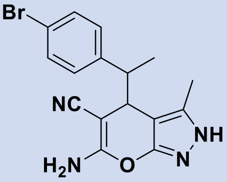
Entry 4; **5d,** 86%
M.P (253-257) °C



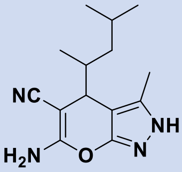
Entry 5; **5e,** 57%
M.P (253-257) °C



Entry 6; **5a,** 4%
M.P (253-257) °C



Entry 7; **5b,** 6%
M.P (253-257) °C



Entry 8; **5c,** 24%
M.P (253-257) °C

Table 27 Reusability and recovery of the amino graphene in the model reaction

Cycle	Recovered catalyst (%)	Reaction yield (%)
1	98	99
2	98	99
3	97	98
4	97	97
5	96	97
6	95	97

Amino graphene were synthesized via simple hydrothermal method. A simple, clean, and efficient solvent free one pot synthesis of pyranopyrazole derivatives were synthesized over metal-free, amino graphene as a base catalyst under green method. Reaction conditions are very simple for substituted aldehydes and ketone. The detailed surface analysis for a prepared amino graphene was explained. Like elemental analysis, PXRD, FT-IR, Raman spectroscopy, EDS and HRTEM, all the techniques were combined together and show graphene oxide was well functionalized with nitrogen. The amino graphene displayed a superior basicity and exhibited remarkable catalytic activity. Sustainable nature of the catalyst is very high and more stable even after few cycles.

13. ACHIEVEMENTS FROM THE PROJECT:

The major achievement of the present project is the successful development of greener methodology for the synthesis of graphene-metal nanocomposites. It has been used as a sustainable catalyst for the C-C coupling reactions and the reduction of nitroaromatics. Preparation and functionalization of graphene oxide open a new opportunity in the solid acid and solid base catalysis as a reusable organocatalyst. In future, these methodologies and carbon-based catalyst will make a fruitful contribution in the field of heterogeneous catalysis.

14. SUMMARY OF THE FINDINGS:

The present work entitled "*Functionalized Graphene Oxide and Transition Metal Nanocomposite: An Efficient Hybrid Catalyst for Coupling Reactions*" describes the studies on exploring the catalytic potential of a "Graphene Oxide" and its derivatives and metal nanocomposites in diverse synthetic organic transformations. Primarily, the catalytic behaviours of graphene oxide as a carbocatalyst in *ipso*-hydroxylation of arylboronic acids and Mannich reaction were developed. Then functionalized form of GO, *ie.*, Brønsted acidic reduced graphene oxide (G-SO_3H) was used as a solid-acid catalyst for the selective synthesis of C-2 substituted benzimidazole. Followed by we have deliberated a rival catalytic studies between the graphene oxide and graphene sulphonic acid (G-SO_3H) in the synthesis of quinoxaline under two different conditions such as a sonication and conventional stirring conditions. In another study a novel and greener methodology for the synthesis of reduced graphene oxide–nickel nanocomposite (RGO-Ni) material was developed and its catalytic application tested in the reduction of nitroaromatics, as well as in C-C homocoupling of arylboronic acids and Glaser-Hay coupling of terminal alkynes.

Additionally we prepared number of chemically modified graphene materials and used as a sustainable catalyst in various organic reactions like Michael addition, pyranopyrazole synthesis and asymmetric Michael addition.

15. CONTRIBUTION TO THE SOCIETY:

From this project, sustainable and heterogeneous carbon-based as well as metal nanoparticles immobilized graphene-based catalyst has been developed from the commercially available graphitic materials. The prepared carbon-based materials tested as a catalyst for various synthetically important organic transformations. All the catalysts are not only tested under laboratory scale, but they also scaled up for industrial scale applications. From the observed results, the catalyst will be synthesised in a large scale and could be commercialized. Particularly the RGO-Ni nanocomposite showed excellent activity towards nitro reduction reaction and better activity than the commercial Raney-Ni. This catalyst might scale up for commercial use. Overall the carbon based graphene materials has found wide scope as a catalyst in industrial application and few applications are explored in the academic level.

16. WHETHER ANY PhD ENROLLED/PRODUCED OUT OF THE PROJECT:

Ph.D Enrolled	:	Yes
Candidate Name	:	M. Karthik
Enrolled on	:	June 2015
Status	:	Ph. D Degree awarded

17. NO. OF PUBLICATIONS OUT OF THE PROJECT:

S. No.	Authors	Title of the paper	Name of the Journal	Vol	Pages	Year
1.	M. Karthik**,** **P. Suresh,***	Graphene oxide as a carbocatalyst for sustainable ipso-hydroxylation of arylboronic acids: A simple and straightforward strategy to access phenols.	***ACS Sustainable Chem. Eng.,*** (IF **6.140**)	7	9028–9034	2019
2.	M. Karthik**,** **P. Suresh,***	Brønsted acidic reduced graphene oxide as a sustainable carbocatalyst: a selective method for the synthesis of C-2-substituted benzimidazole.	***New J. Chem.,*** (IF **3.277**)	42	17931–17938.	2018
3	M. Karthik, **P. Suresh**,*	Greener Synthesis of Reduced Graphene Oxide-Nickel Nanocomposite: Rapid and Sustainable Catalyst for the Reduction of Nitroaromatics	***ChemistrySelect*** (IF **1.505)**	2	6916 – 6928	2017
4.	N. Devarajan, M. Karthik, **P. Suresh**,*	Copper catalyzed oxidative homocoupling of terminal alkynes to 1,3-diynes: A $Cu_3(BTC)_2$ MOF as an efficient and	***Org. Biomol. Chem.,*** (IF **3.564**)	15	9191–9199	2017

		ligand free catalyst for Glaser–Hay coupling				
5.	N. Devarajan, **P. Suresh***	Copper-catalyzed oxidative coupling of arylboronic acids with aryl carboxylic acids: $Cu_3(BTC)_2$ MOF as a sustainable catalyst to access aryl esters	***Org. Chem. Front.,*** (IF **5.455**)	5	2322–2331	2018
6.	N. Devarajan, **P. Suresh***	Framework Copper Catalyzed C-N Cross Coupling of Arylboronic Acids with Imidazole: Convenient and Ligand Free Synthesis of *N*-Arylimidazoles	***ChemCatChem*** (IF **4.803)**	8	2953–2960	2016
7.	P. Puthiaraj, **P. Suresh** and K. Pitchumani	Aerobic Homocoupling of Arylboronic Acids Catalysed by Copper Terephthalate Metal Organic Frameworks	***Green Chemistry*** (IF **9.125**)	16	2865–2875	2014
8.	M. Karthik, N. Devarajan, **P. Suresh**,*	Nickel nanoparticles on reduced graphene oxide as an active and selective catalyst for the C-C coupling reaction,	***Catal. Sci. Technol.,)***	To be communicated	-	-
9.	M. Karthik, **P. Suresh**,*	Design, synthesis and characterization of graphene	***ACS Sustainable Chem. Eng.,***	To be communicated	-	-

oxide-based bifunctional catalyst: An acid-base co-operative catalyst for the conversion of HMF into value-added products

(PRINCIPAL INVESTIGATOR)

Dr. P. SURESH
Principal Investigator
UGC Major Research Project
Functionalized Graphene.........coupling reactions
School of Chemistry
Madurai Kamaraj University
Madurai-625 021

RSudha
21/06/19

(REGISTRAR)

REGISTRAR,
MADURAI KAMARAJ UNIVERSITY,
MADURAI-625 021