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Journal Name

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

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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 pyridine adsorption studies prove the catalytically responsible Brønsted acidity of the Catalyst. 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.

Introduction

Benzimidazole is a class of heterocyclic aromatic organic compound. It starts glows after the discovery of naturally occurring *N*-ribosyl dimethylbenzimidazole, which found in vitamin B12.[1] Benzimidazole scaffold offers a unique set of properties for the designing of bioactive molecules used for the various pharmaceutical requirement.[2] Albeit a number of methods are available for the synthesis of benzimidazole, the two principal synthetic strategies such as (a) condensation of *o*-arylenediamines with carboxylic acids[3] and (b) dehydrogenation of benzimidazoline intermediates generated from the condensation of *o*-arylenediamines with aldehydes in acidic medium[4] are commonly adopted. However, the latter one is most widely followed due to the ease of accessibility of aryl aldehydes. In that context, various oxidative reagents and catalyst such as TEMPO,[5] $Pb(OAc)_4$,[6] $Na_2S_2O_5$,[7] DDQ,[8] MnO_2,[9] oxone,[10] and H_2O_2[11] have reported. Also, metal catalyst such as CuBr,[12] CuCl,[13] and CuO supported silica,[14] were reported.

Readily available Brønsted acids like *p*-toluenesulfonic acid[15], L-proline[16] and various heterogeneous acidic catalyst such as SiO_2-H_2SO_4,[17] xanthan-H_2SO_4,[18] solid supported protic acid,[19] Scolecite,[20] nanoceria,[21] and SDS micelles,[22] were employed to set benzimidazole. However, these methods have several shortcomings like the use of metal catalysts and additives, longer time, tedious workup, purification process, lack of selectivity and high-temperature conditions which adversely affect the eco-friendly nature and the economy of the reaction. Hence it is necessary to develop a catalyst which will overcome all types of shortcomings present in the era.

Graphene the material pivotal in nanochemistry. It has a wide range application in the fields of nanoelectronic devices, sensors, adsorption, energy storage, and catalysis.[23] Its unique physical and chemical characteristics, including a very high specific surface area and distinctive structure, renders an ideal platform to covalently attach a large number of functional groups with accessible active sites and make it as indispensable in catalysis.[24] The properties of graphene have tuned by the chemical functionalization using active intermediates like diazonium radical,[25] carbene,[26] nitrene,[27] and aryn.[28] In addition to that hydrothermal treatment also used for the functionalization of graphene to enhance its properties. By these processes graphene can be decorated with active functional groups like amine,[29] acids,[30] thiols[31] and thioether.[32] Among graphene functionalized with sulfonic acid (-SO_3H) has received more attention and investigated as a solid catalyst for a variety of acid catalyzed reactions such as hydrolysis of ethyl acetate,[33] and etherification of glycerol[34], in addition, its application expanded to photocatalysis,[35] biosensors,[36] electrochemical capacitors,[37] pollutant management,[38] and support material for metal nanocomposite.[39] In the present study we explored the synthetic utility of graphene sulfonic acid as a Brønsted acidic carbocatalyst towards the selective synthesis of 2-substituted benzimidazole under ambient condition.

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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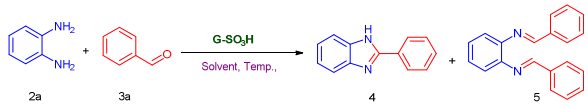
Results and discussion

The graphene sulfonic acid (G-SO_3H, **1)** used in this work was prepared by simple diazonium radical chemistry.[30] The reduced graphene oxide (RGO) obtained through the reduction of graphene oxide (GO) was reacted with 4-benzenediazoniumsulfonate gave the corresponding benzenesulfonic acid functionalized graphene oxide (G-SO_3H). The chemical nature of G-SO_3H was characterized by FT-IR analysis (Fig.1a). The intense broad peak at 3347, 1167, 1110 and 1031 cm^{-1} are attributed the presence -OH, S-O, S-C and S=O functional group stretching frequencies of the '-SO_3H' of the benzenesulfonic acid crafted on RGO surface. Another peak at 2915 cm^{-1} represents the aromatic C-H of the phenyl ring attached with sulfonyl moiety. These preliminary data from FT-IR studies confirm the covalent functionalization of RGO sheets by benzenesulfonyl moiety.[40] further, the amorphous nature of the as-prepared G-SO_3H was examined by PXRD pattern (Fig.1b). After sulfonation of RGO, a new broad peak appeared at 24.67° owing to the covalent incorporation benzenesulfonic acid group on the surface of the RGO. The appearance of new peak strongly evidences the formation of graphene sulfonic acid. FT- Raman analysis of G-SO_3H, the I_D/I_G ratio is higher than (1.044) that of RGO, due to the covalent attachment of abundant benzenesulfonic acid groups on the RGO surface. Usually, a red or blue shift of the band can be used to evaluate the degree of structural changes during chemical functionalization. Further, the G bands of G-SO_3H shifted from 1586 cm^{-1} to 1581 cm^{-1} this observable redshift strongly supports the covalent anchoring of benzenesulfonic acid moiety on RGO. SEM image of G-SO_3H (Fig.1e) shown a smooth, silky layered structure that reveals the sulphonation did not make any distractive changes on the morphology of RGO sheets. Further XPS spectrum for G-SO_3H of high-resolution survey scan (Fig. 1g) shows the presence of C1s, O1s, and S2p elemental signals. An S2p peak at 167.6 eV associated with S-O bond of G-SO_3H demonstrate the functionalization of benzene sulfonic acid group on RGO.[37]

In addition, the elemental mapping by energy dispersive X-ray spectroscopy (EDS) (Fig.S5) also exhibits the uniform distribution of sulphur atom on the surface of RGO sheets which conclusively evident the sulfonation of GO. Finally, the microstructures of G-SO_3H nanosheets was characterized by TEM analysis, (Fig.1f) which discloses the crumpled sheet-like morphology, and had good agreement with the images obtained in SEM. The SEM and TEM images collectively visualize the sheet like surface morphology of G-SO_3H. It evident the sulfonation does not majorly alter the morphology of RGO. All the above analytical techniques hands together support the successful covalent crafting of benzene sulfonic acid moiety on the reduced graphene oxide sheets.

Table 1 Optimization of G-SO_3H catalyzed benzimidazole synthesis[a]



Entry	Solvent	Temp. (°C)	Yield [b] (%)	
			4	**5**
1	Neat	RT	-	-
2	Water	RT	50	49
3	ACN	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.

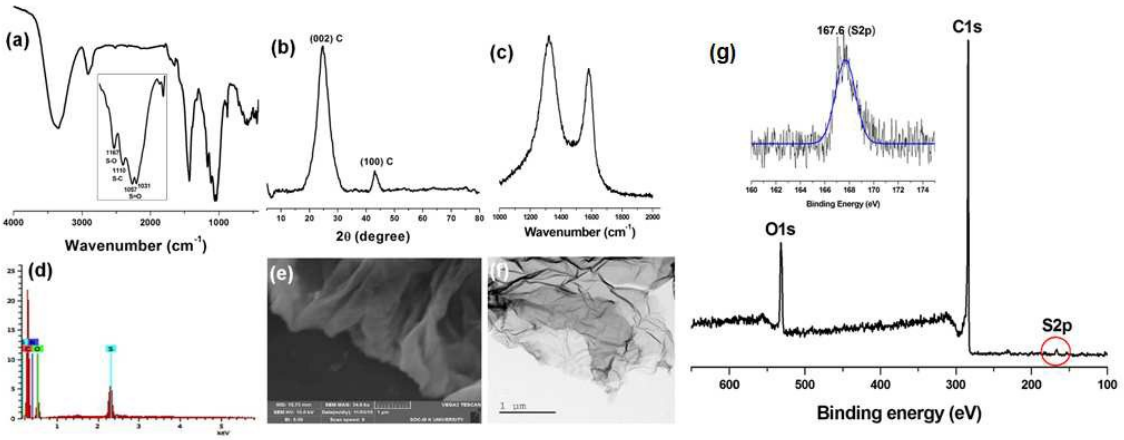


Fig. 1 a) FT-IR, b) PXRD, c) FT-Raman spectrum, d) EDS, e) SEM image and f) TEM Image, g) XPS of G-SO_3H

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After unambiguously characterized the structure of the as-prepared G-SO_3H (**1**), to explore its potential in organic synthesis as a catalyst, it has been employed as a carbocatalyst for the synthesis of medicinally important benzimidazole under metal-free condition. Initially, to use G-SO_3H as a Brønsted acid catalyst, a model reaction was carried out using benzene-1,2-diamine (**2a**) and benzaldehyde (**3a**), and other reaction controlling parameters such as solvent, temperature, time and catalyst load were also optimized. The observed results are presented in table-1. In the absence of a catalyst and solvent, the reaction was inert without any conversion (Table-1, entry 1). To identify a reliable solvent for G-SO_3H (**1**) catalyzed benzimidazole synthesis, a series of solvent such as water, ethanol, methanol, acetonitrile, DMF, hexane, The

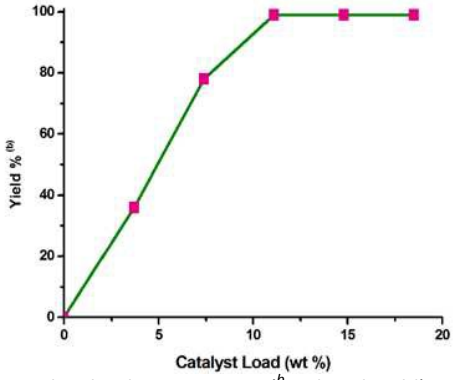
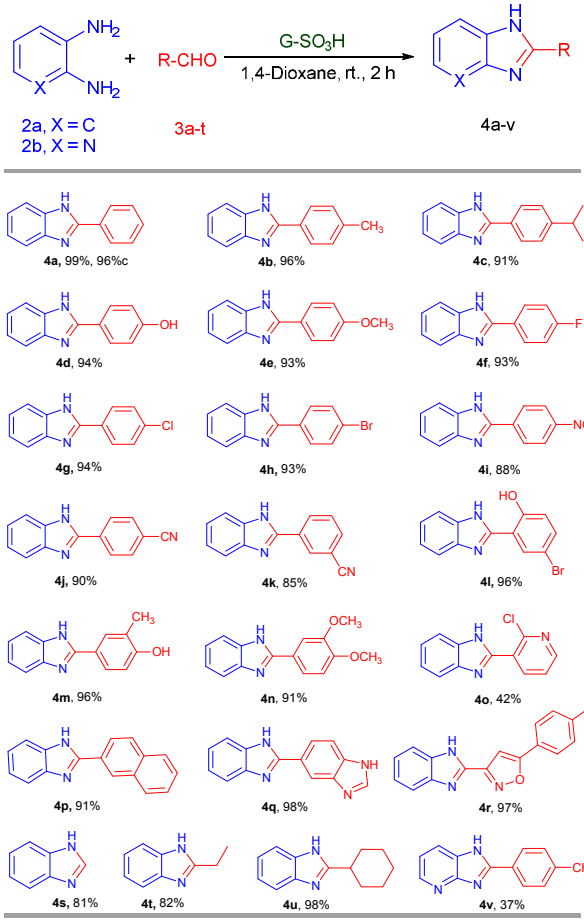


Fig. 2 Catalyst load optimization ([b] isolated yield)

tetrahydrofuran, and dioxane were employed. To improve more benign nature of the carbocatalyst and practice greener protocols, the reaction was performed using water as a medium, however, the desired benzimidazole formation was not encouraging, but in addition, another condensation product, *N,N'*-(1,2-phenylene)*bis*(1-phenylmethanimine) (**5**) was formed. It shown that the catalyst is not selective due to poor solubility of the precursors in water. (Table-1, entry 2). Further other polar solvents such as acetonitrile, methanol, and ethanol were employed to improve the yield and resulted the moderate amount of benzimidazole along with the condensation product, both in room and higher temperature ranges (Table-1, entries 3, 5-6). When moved to non-polar solvents the catalyst was idle in hexane medium, (Table-1, entry 8) due to poor dispersion. Meantime, both THF and dioxane were behaved better than the polar solvents, however, with THF, a notable diimine formation was observed (Table-1, entry 9). Among the screened solvents, dioxane behaves superiorly, and gave benzimidazole selectively as a sole product with the excellent yield at room temperature and formation of diimine was circumvented entirely (Table-1, entry 11). Though 1,4-dioxane is a six-membered cyclic diether; it behaves like cyclohexane and exists in both boat, and chair forms, among boat form is slightly polar than chair form. Polarity of the 1,4-dioxane shuttled owing to the structural flipping which enhances the complete dispersion of Brønsted acidic reduced graphene oxide (G-SO_3H) and facilitates the good mass transfer of reactants to products. Due to the chameleon polarity nature of the 1,4-dioxane, it promotes the G-SO_3H catalysed formation of C-2 substituted benzimidazole.

To enhance the greenness of the reaction, aqueous mixture was tried with all solvent system, but the results were not encouraging, and diimine formation was predominant in all the cases. (Table-1, entries 4, 7 & 10). Finally, dioxane at room temperature was chosen as an optimum medium for the G-SO_3H catalyzed benzimidazole synthesis. Furthermore, catalyst load has a pivotal role in organic synthesis. Most of the benzimidazole synthesis involves the stoichiometric amount of the catalyst. Even though, the solvent and temperature optimization involve 18.5 wt % (10 mg) of catalyst and further catalyst load optimization showed that 11 wt % (6 mg) of the G-SO_3H is adequate for the complete conversion of the diamine and aldehyde to the corresponding benzimidazole, with >99% selectivity and without any by-

Table 2 Graphene Sulfonic Acid Catalyzed Synthesis of Benzimidazole [a]



[a] Reaction condition: G-SO_3H 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.

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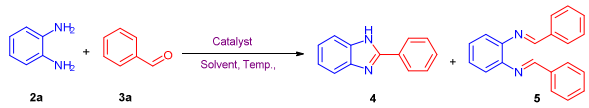
Table 3 Catalytic Control Experiments[a]



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.

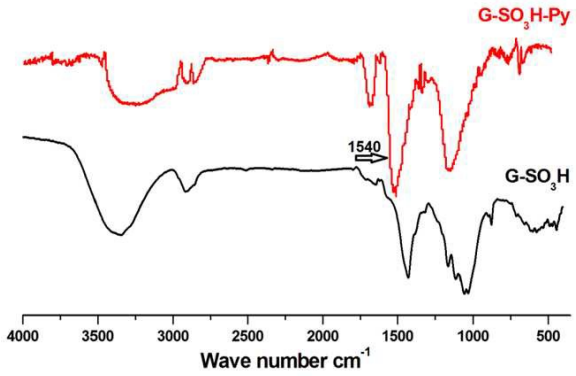


Fig. 3 FT-IR spectra of G-SO_3H and G-SO_3H-Py

products. Similarly, time optimization results revealed that within two hours all the reactants were consumed and converted into the desired benzimidazole. Furthermore, the present catalytic system is highly specific towards the formation of C-2 substituted benzimidazole, rather than 1,2-disubstituted benzimidazole even in the presence of excess equivalence of aldehyde. From the screening results, the as-prepared G-SO_3H acts as a catalyst for the synthesis of benzimidazole in dioxane using 11 wt % of the catalyst at ambient temperature. With the mild optimized condition in hand, to explore the inherent potential of the G-SO_3H catalyst in synthetic chemistry, the benzimidazole synthesis was successfully extended by using a spectrum of aromatic, heteroaromatic and aliphatic aldehydes with benzene-1,2-diamine (**3**), which affords the respective products in good to excellent yield without any by-products or intermediates such as diimine and disubstituted benzimidazoles. The observed substrate versatility has been depicted in Table 2. All aldehydes were efficiently converted into the corresponding benzimidazoles within the optimized time, among aromatic aldehydes were found more reactive irrespective of the substituents electronic nature present on the aryl ring. The present catalyst works very well for a wide range of *para*-substituted aldehydes possessing both electron releasing like methyl, isopropyl, hydroxyl, and methoxy (Table 2, **4b-4e**) and withdrawing substituents halogens, nitro and nitrile (Table 2, **4f-4j**) with good to excellent isolated yield. Meanwhile, a notable decrease in the yield was observed when the nitrile group present in the *meta*-position (Table 2, **4k**). Aldehydes with disubstituent (Table 2, **4l-4n**) were also smoothly underwent the reaction and gave relatively good yield without any steric effect. It is noticed that when the nitrogen present either in aldehyde or diamine's ring system, which suppress the reaction and result in moderate yield (Table 2, **4o, 4v**), because of the catalytic poisoning of the pyridine moiety which hampers the catalytic acidic sites of the G-SO_3H. Aldehydes with a fused ring system having native, heteroaromatic and heteroaromatic bicyclic system gave excellent yield (Table 2, **4p-4r**). Aliphatic aldehydes such as formaldehyde, propionaldehyde and cyclohexane aldehydes are compatible with the present methodology and result good to excellent yield of corresponding benzimidazoles (Table 2, **4s- 4u**). To demonstrate the potential of the present catalyst, for the preparative purpose, the reaction was also carried out on a gram scale, giving the isolated yield (Table 2, **4a**) which is comparable to those obtained for a small-scale reaction.

Although G-SO_3H catalyzes the benzimidazole synthesis with minimum catalyst load under ambient condition, to demonstrate the inherent catalytic activity of G-SO_3H, control experiments were carried out with another similar type of materials such as GO and RGO under the optimized reaction condition (Table 3). GO gave only 37 % of the benzimidazole along with diimine (**5**) derivative (54 %) (Table 3, entry 1) owing to the presence of acidic oxygen functionalities. Meantime, RGO was entirely idle under the optimized condition (Table 3, entry 2). Commercially available *p*-toluenesulphonic acid (Table 3, entry 3) acts as a homogeneous catalyst and yield the mixture of both benzimidazole and diimine (**5**) under the present condition. Though, the above catalysts promote the benzimidazole formation, selectivity is completely lost which enlighten the uniqueness of the present catalyst

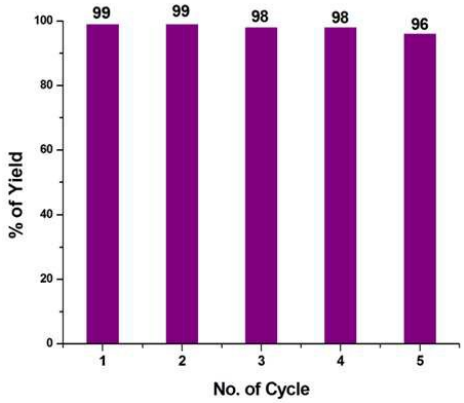


Fig. 4 Reusability of G-SO_3H catalyst.

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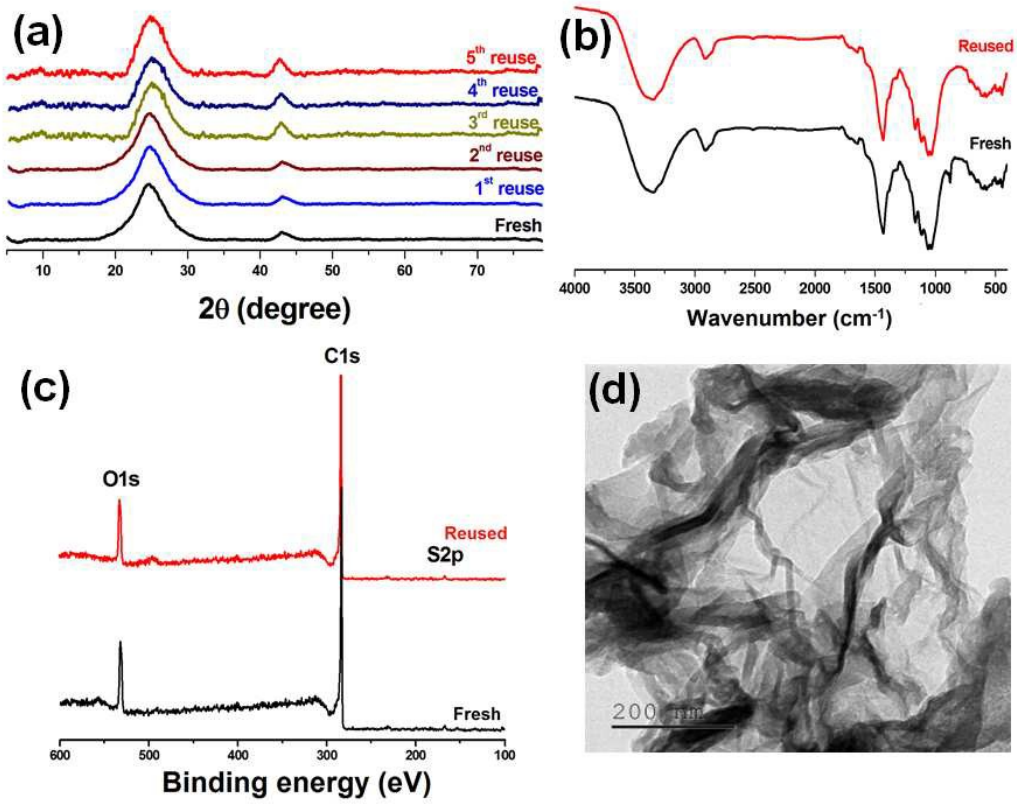

Fig. 5 (a) PXRD, (b) FT-IR, (c) XPS and (d) HRTEM Image of reused G-SO_3H

Furthermore, to ensure the role of the sulfonic acid group present in G-SO_3H, pyridine adsorption studies were performed. In this typical study, an excess of pyridine was added to the G-SO_3H catalyst dispersed in dioxane under sonication, and the resultant black precipitate was used as a catalyst in benzimidazole synthesis with the same optimized condition. Before the adsorption of pyridine on G-SO_3H was confirmed by FT-IR analysis (Fig.3).[41] Pyridine is a relatively strong base hence, it shows three modes of interaction with solid acids *via* hydrogen bonding, coordinative bonding, and chemisorption as a pyridinium ion. This pyridine adsorption study discloses the considerable information about the acidity of G-SO_3H by studying changes in the "ring' vibrations of pyridine and other bands in the region of 1700 cm^{-1} to 1400 cm^{-1}. The band at 1540 cm^{-1} indicates the interaction of pyridine with sulfonic acid group of the G-SO_3H catalyst through the formation of positively charged pyridinium ions chemisorbed on the surface of G-SO_3H. The absence of a band around 1440-1465 cm^{-1} indicates that no physically or coordinately bonded pyridine is present. These detailed analyses suggest that the irreversible chemisorption inhibits the active acidic sites *via* pyridinium ion formation which deliberately explains the catalytic poisoning of G-SO_3H by pyridine and reason outs the lower yield (table 3, entry 5) for the pyridine-based entities in the reaction.

Furthermore, to understand the stability and sustainable nature of the G-SO_3H, which is recovered by simple filtration after the reaction finished, then washed, dried under vacuum. Another fresh batch reaction was preceded with the recovered catalyst under the identical condition. The reuse results establish that G-SO_3H remains equally active and exhibits high stability for five consecutive cycles without any noticeable decay in the activity (Fig.4). The outcome of the recycling behaviour of the present catalyst clearly demonstrates the robustness and sustainable nature of the catalyst. Further, to confirm the stability of the catalyst, the reused G-SO_3H was subjected for further analysis after the reaction.

The vacuum dried catalyst was subjected to FT-IR, PXRD, XPS and HRTEM analyses, to examine the functional group, and morphological changes of the catalyst during the reaction (Fig. 5). PXRD pattern and FT-IR analysis of the fresh and reused catalyst are identical without any notable changes even after five consecutive runs. It was supported by the TEM images of the fifth time reused catalyst where the surface morphology and microstructures are remains intact. In addition, the chemical composition of the reused sample was tested by XPS analysis that reveals the sustainable nature of the catalyst. Followed by the filtrate was subjected to ICP-OES analysis to find any sulphur was leached of after the reaction, and results show the absence of a detectable amount of

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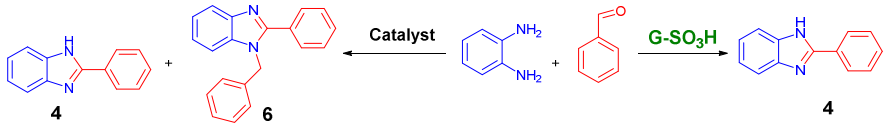
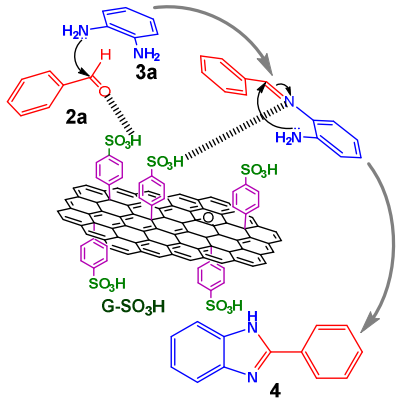
Table 4 Comparison of Catalytic Selectivity of G-SO_3H



S. No.	Catalyst	Condition			Yield (%)		Ref.
		Solvent	Temp (°C)	Time (h)	**4**	**6**	
1	G-SO_3H	1,4-Di-oxane	RT	2	99	-	This work
2	L-Proline	$CHCl_3$	RT	5	-	95	16
3	Oxalic acid	EtOH: H_2O	RT	3	14	70	19
4	Silica sulfuric acid (LiCl)	EtOH: H_2O	RT	2	0	90	17
5	Montmorillonite K-10	EtOH	RT	2	22	42	19
6	SiO_2-$HClO_4$	EtOH	RT	2	0	90	19
7	Nano ceria	H_2O	RT	0.5	-	92	21
8	Scolecite	EtOH	70	1	94	-	20
9	Cu-MOF	EtOH	RT	6	97	-	40
10	GO	MeOH	60	4	81	-	41

sulphur. This advocacy indicates that there is no markable change in the chemical and structural morphology of the catalyst even after the fifth use.



Scheme 1 Proposed Mechanism

In accordance with previous report[42] and based on the experimental observations, a plausible mechanism for the G-SO_3H catalyzed synthesis of C-2 substituted benzimidazoles has been proposed (Scheme 1). In the case of 2-substituted benzimidazole, the reaction proceeds through imine intermediate. It is form by the activation of the aldehydic carbonyl oxygen by the Brønsted acidic sulfonic acid of G-SO_3H and subsequent condensation with one of amine of Benzen-1,2- diamine to form imine intermediate. Due to the to the presence of the aromatic system they stabilized on graphene surface through π- π stacking. Then the lone pair of electron in the free amine attacks the imine bond lead to cyclization to yield C-2 substituted benzimidazole.

The uniqueness of the as-prepared G-SO_3H is rationalized based on its selectivity in benzimidazole synthesis over the other existing system which is spectacle by comparison with the reported catalyst. In the present work G-SO_3H accord specifically mono C-2 substituted benzimidazole without any other by-product. Meanwhile, other homogeneous catalyst such as L-proline, oxalic acid and heterogeneous systems such as silica sulphuric acid, K-10 montmorillonite, SiO_2-$HClO_4$, and nanoceria gave a mixture of mono (C-2 substituted) and 1,2-disubstituted benzimidazoles, among later one formed as a predominant product (Table 4, Entries - 2-7). Similarly, with other heterogeneous solid acid catalyst such as Scolecite, and metal-based Cu-MOF shown good reactivity, however, they work with high temperature and long reaction time. (Table 4, Entry 8-9). Recently GO is also studied in the synthesis of benzothiazole and benzimidazole but required high temperature and time with moderate yield. (Table 4, Entry 10). Present sulfonic acid functionalized graphene exhibits a better catalytic activity in concerning the synthesis of benzimidazole in terms of catalyst load, reaction time, temperature and selectivity. In analogy, G-SO_3H is a metal-free, eco-friendly fanfare catalyst for the selective synthesis of benzimidazole.

Conclusions

In summary, 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 sites. 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

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essential benzimidazoles. To our delight, this carbocatalyst may find broad applications in synthetic as well in medicinal chemistry.

Experimental

General Information

All reagents and starting materials were purchased commercially from Sigma–Aldrich, Alfa-Aesar, Merck, or Spectrochem and used as received without any further purification unless otherwise noted. The powder X-ray diffraction was recorded in XPERT-PRO instrument using Cu Kα (λ = 0.1542 nm) radiation operated at a voltage of 40 kV and a current of 40 mA at room temperature. FT-IR spectra were recorded in a Shimadzu instrument from 4000 cm^{-1} to 500 cm^{-1} with samples being dispersion using KBr pellet technique. Raman spectra were recorded in Shimadzu laser 630 nm. SEM analysis was carried out in TESCAN VEGA3 instrument using SE detector and equipped with EDX (AMETEK EDAX, Model Octane Prime with Active area = 10 mm^1) detector. ICP-OES was analysis was carried out in Perkin Elmer OPTIMA 5300 DV. Samples for high-resolution transmission electron microscopy (HRTEM) analysis were done by dispersing the prepared samples in acetone using ultrasonication, then deposit a drop of that dispersed solution on amorphous carbon-coated copper grids. Images were obtained on TEF 20 TECNAI G2 200kv TEM (FEI). X-ray photoelectron spectroscopy (XPS) were collected on Omicron Nanotechnology spectrometer with Al Ka as the excitation source (hm = 1486.6 eV). All ^1H NMR and ^{13}C NMR were measured either in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard in 300/75 or 400/100 MHz on a Bruker spectrometer unless otherwise noted. LC-MS analysis was carried out using a Thermo Fisher Scientific instrument LTQ Fleet using C18 column (XTerra - 5µ) with a flow rate of 0.8 mL/min. (0.01 mol ammonium acetate buffer and acetonitrile) at the absorption wavelength of 254 nm.

Synthesis of Graphene Sulfonic acid (G-SO_3H)

4-Benzenediazoniumsulfonate was synthesized *via* diazotization of sulfanilic acid. Sulfanilic acid (10.4 g) was dispersed in 600 mL of aqueous 1M HCl solution in a 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 with constant stirring to obtain clear solution and the same condition was maintained for another 1 h. Finally formed white precipitate was filtered off and washed with deionized 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 was 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.

General Procedure for the Synthesis of Substituted Benzimidazole

In a typical procedure, 6 mg of the catalyst was dispersed in 1 mL of 1,4-dioxane under sonication. Add 0.5 mmol (1 eq) of benzene-1,2-diamine in 2 mL of 1,4-dioxane with constant stirring followed by dropwise addition of 0.5 mmol (1 eq) of benzaldehyde. The course of the reaction was monitored by TLC. After completion of the reaction, the catalyst was recovered by simple filtration and washed twice with methanol and water and dried under vacuum for further use. The filtrate was evaporated to dryness under reduced pressure to obtain the pure product for NMR and ESI-MS analysis.

Conflicts of interest

There are no conflicts to declare.

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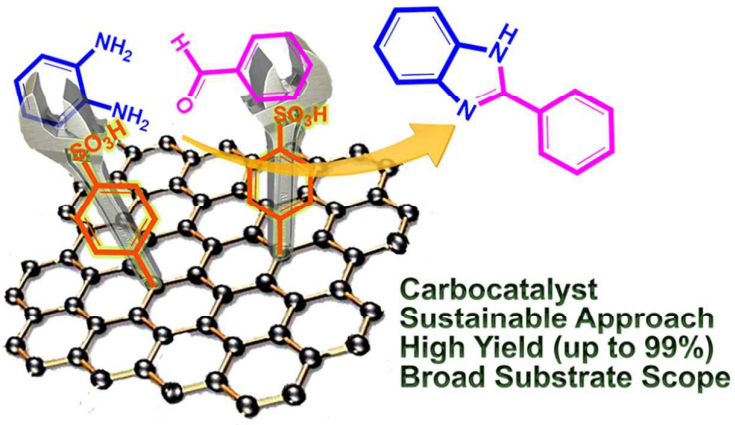
Brønsted Acidic Reduced Graphene Oxide as a Sustainable Carbocatalyst: A Selective Method for the Synthesis of C-2 Substituted Benzimidazole

Murugan Karthik, Palaniswamy Suresh*

A selective and sustainable methodology for the synthesis of C-2 substituted benzimidazole has been demonstrated using benzenesulfonic acid grafted reduced graphene oxide as a Brønsted acidic carbocatalyst.



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