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Graphene Oxide Modified with Tetramethylethylenediamine Ammonium Salt as a Powerful Catalyst for Production of Trisubstituted Imidazoles

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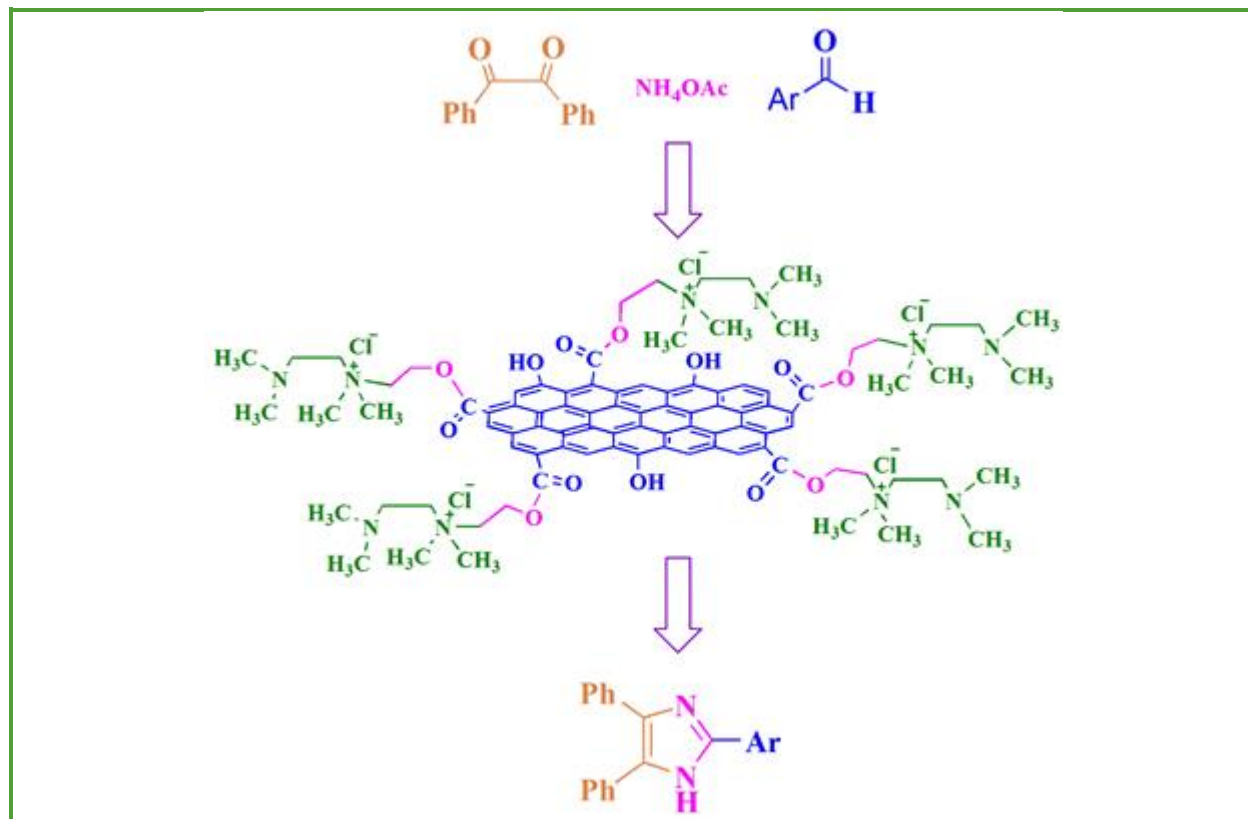
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ABSTRACT

A new and efficient graphene oxide catalyst was synthesized in this study to prepare trisubstituted imidazoles. Graphene oxide was first modified with 2-chloroethanol, and then treated with N,N,N,N-tetramethylethylenediamine. After that, the obtained catalyst was characterized by XRD, FTIR, FESEM, EDAX, and TGA. The reported catalyst was utilized for the synthesis of trisubstituted imidazoles from benzil, aldehydes, and ammonium acetate. Reaction efficiently proceeded via a one-pot multicomponent route under solvent-free conditions. Catalyst offered some advantages over reported ones such as sustainability, cost-effectiveness, ease of handling, storage, and recovery, in addition to non-metal structure. The reported procedure has a series of benefits, including medium conditions, high yields, no by-products, short reaction times, and easy work-up. Reported catalyst can be used in chemistry, material sciences, and related disciplines for diverse applications.

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Graphical Abstract



Introduction

Catalysts are critical in the sustainable synthesis for several advantages, mainly environmental protection in the chemical industry. Chemistry and sciences focus on sustainability to design modern life without harming the ecosystems [1]. Non-metal and carbon-based catalysts are mainly environmentally benign. Numerous carbon-based catalysts have been designed and used for the synthesis of various chemicals [2], among which graphene and graphene oxide are two necessary carbon materials with excellent properties, including flexibility for designing new and safe catalytic systems [3].

Multicomponent reactions play an essential role in the design of sustainable reactions with better selectivity and yield and fewer by-products [4-6]. The mentioned reactions are the

best alternative for multistep reactions in designing safe organic reactions [7-9]. Another protocol for designing sustainable reactions involves no use of solvents, as toxic solvents are the primary source of harming the environment [10, 11]. Trisubstituted imidazoles are an essential class of heterocycles with a series of properties. A series of biological properties have been reported for them, for instance, antifungal, antitumor, analgesic, and antibacterial [12]. Some derivatives accelerate biosynthesis of interleukin-1, used as glucagon receptors, herbicide, and fungicide [13]. Then can be further used in material science as light-sensitive materials as blue-light emitting materials, sensors, and fluorescent agents [14]. The significant properties of trisubstituted imidazoles have been addressed [15]. The one-

pot, three-component synthesis via diketones, ammonium acetate and aldehydes are commonly used in the presence of appropriate catalysts [16]. Numerous catalysts including $\text{CoFe}_2\text{O}_4@\text{SiO}_2@(-\text{CH}_2)_3\text{OWO}_3\text{H}$ NPs [17], graphene oxide-substituted sulfoacetic acid amide [18], $\text{NCP}@\text{SiO}_3\text{PrNHPrSiO}_3\text{TiO}_2$ [19], graphene oxide functionalized diethanolamine sulfate [20], GO-TiO₂ nanocomposite [21], sulfated magnetic cellulose nanoparticles [22], trifluoroacetic acid supported starch/graphene oxide nanocomposite [23], zirconium-based metal-organic framework (Zr-MOF) nanocomposites [24], RGO supported Au nanoparticles [25], sulfated polyborate [26], $\text{BNPs}@\text{SiO}_2\text{-TPPTSA}$ [27], and magnetic $\text{CoFe}_2\text{O}_4/\text{Ni-BTC}$ based MOF composite [28] have been explored. These procedures suffer from some several drawbacks such as long reaction times, the use of toxic catalysts and metals, vigorous reaction conditions, low yields, boring purification process, and high amounts of wastes and by-products, necessitating the development of more sustainable procedures.

In this study, graphene oxide-substituted tetramethylethylenediamine ammonium salt was prepared as an ionic catalyst and its activity was examined for the synthesis of 2,4,5-trisubstituted imidazoles under solvent-free conditions with excellent yield.

Experimental

Reagents and chemicals were purchased from Merck chemical company which used as received. The products were characterized by comparing their melting points with previously reported ones. Silica gel SIL G/UV 254 plates were used to study the progress of reactions. JASCO FT-IR spectrometer was employed to record FT-IR spectra using KBr pellets. Melting points were also determined by an electrothermal apparatus. Bruker Avance DRX 400 MHz spectrometer was utilized to afford ¹H-

NMR and ¹³C-NMR spectra. Shimadzu model: XRD 6000 apparatus was used to record XRD patterns. The FESEM images and EDAX studies were further obtained using a TESCAN electron microscope. Thermogravimetric analysis (TGA) was conducted on catalyst using a TA apparatus (model Q600) in the range of 30 °C to 500 °C and heating rate of 10 °C.min⁻¹ under argon atmosphere.

Synthesis of graphene oxide substituted 2-chloroethanol (GO@CE)

Graphene oxide was prepared according to the modified Hummers method [29]. Graphene oxide (1.0 g) was suspended in THF (30 mL) and the mixture was sonicated for 60 min. to afford a colloidal solution. Then, 2-chloroethanol (0.7 mL), triethylamine (0.8 mL) and DCC (0.5 g) was added to the solution. The reaction mixture was stirred at room temperature for 30 h followed by adding DMSO (30 mL) and hot filtration. The precipitate was washed with hot ethanol, hot deionized water and acetone several times and dried to afford GO@CE as a black fine powder.

Synthesis of GO@CE-TMEDA.Cl catalyst

Dimethylacetamide (30 mL) was added to GO@CE (1.0 g) and sonicated for 60 min. to afford a colloidal solution, and then tetramethylethylenediamine (0.5 mL) was added and the mixture was heated at reflux conditions for 24 h. Finally, the mixture was filtered and the precipitate was washed with dry chloroform several times, dried, and stored in a tight vial.

General procedure for the production of trisubstituted imidazoles using the catalyst

To benzil (1 mmol), aldehyde (1 mmol), ammonium acetate (2 mmol) and catalyst (0.02

g) were added. The mixture was heated in an oil bath for appropriate time and after completion (as indicated by TLC using n-hexane/ethyl acetate (3:1)) ethyl acetate was added and filtered hot. The catalyst was collected by the filter paper and mother liquor was stored at room temperature to crystallize trisubstituted imidazole product. The catalyst was recovered and reused for five runs (Figure 7).

Spectral data of 3k

$^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ 5.33 (s, 2H), 7.12-7.14 (m, 2H), 7.20-7.49 (m, 10H), 7.74 (t, $J = 4$ Hz, 2H), 8.00-8.02 (m, 2H), 8.25-8.27 (m, 2H), and 12.51 (s, 1H) ppm. $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6) δ 158.5, 147.5, 146.0, 145.3, 136.8, 132.0, 128.8, 128.8, 128.7, 127.4, 127.3, 124.2, 124.0, 122.4, 115.5, and 68.6.

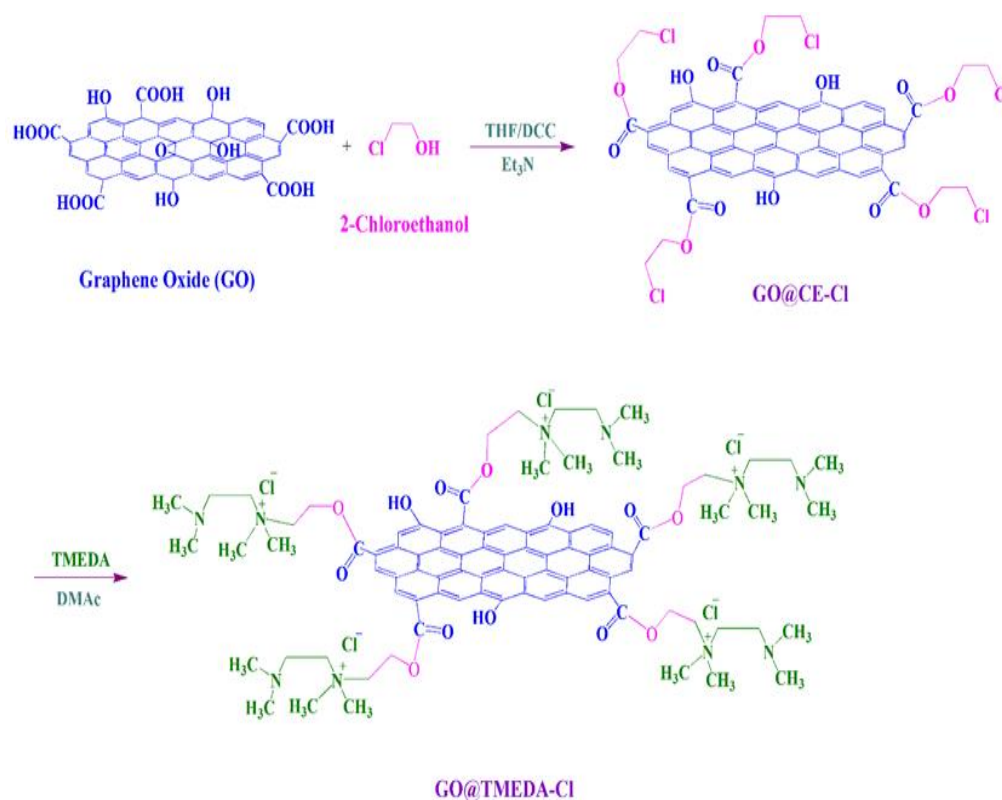
Results and Discussion

Preparation of catalyst

Graphene oxide was prepared according to the modified Hummers method [29]. It was then functionalized with 2-chloroethanol in the presence of triethylamine and DCC in THF solvent (Scheme 1). The mixture was purified using filtration and washed with deionized water and ethanol, dried and treated with tetramethylethylenediamine in dimethylacetamide to afford catalyst (Scheme 1).

Characterization of catalyst and precursors

Intermediates and final catalyst such as graphene oxide (GO), 2-chloroethanol-functionalized graphene oxide (GO@CE), and GO@CE-TMEDA.Cl catalyst were characterized by reliable analytical methods such as FT-IR, XRD, FESEM, EDS, and TGA.



Scheme 1. Production of GO@CE-TMEDA.Cl

FTIR spectra

FTIR spectrum of graphene oxide showed stretching vibrations of carboxylic acid hydroxyl groups at ~ 3419 cm^{-1} and vibrations of carbonyl groups at 1720 cm^{-1} . Moreover, the vibrations of etheric groups (C-O) appeared at 1177 cm^{-1} [30]. FTIR spectrum of GO@CE is depicted in Figure 1a which shows frequency vibrations of hydroxyl of carboxylic acid groups at 3430 cm^{-1} [31], and vibrations of hydroxyls at 3328 cm^{-1} [32]. Furthermore, vibrational frequencies of CH groups were detected at 2851 cm^{-1} and 2926 cm^{-1} [33]. The peak appeared at 1727 cm^{-1} can be also assigned to the carbonyl groups [34], while the bending vibrations of O-H appeared at 1626 cm^{-1} [35]. The peak at 1575 cm^{-1} indicates the vibrational frequencies of C=C bonds [36]. Furthermore, vibrational deformation of CH_2 was detected at 1439 cm^{-1} [37], whereas the bending vibrations of C-N are manifested at 1312 cm^{-1} [38]. Moreover, the

band at 1241 cm^{-1} can be assigned to C-O-C bonds [39], while the frequencies at 1089 cm^{-1} can be attributed to C-O bonds [40]. Furthermore, the peak at 649 cm^{-1} can be ascribed to C-Cl bonds [41].

FTIR spectrum of GO@CE-TMEDA.Cl catalyst can be found in Figure 1b in which the vibrations of carboxylic acid OH bonds appeared at 3431 cm^{-1} [31]. Likewise, frequency vibrations of aliphatic CH bonds emerged at 2925 cm^{-1} and 2856 cm^{-1} [33]. Vibrations of carbonyl groups emerged at 1713 cm^{-1} [34], while the vibrations of C-N and C=C bonds appeared at 1629 cm^{-1} [42]. Moreover, aromatic C=C vibrations appeared at 1573 cm^{-1} [43], whereas asymmetrical vibrations of CH_2 emerged at 1463 cm^{-1} [44]. Furthermore, the peak at 1112 cm^{-1} can be assigned to COO of ester, C-N and C-O ether bonds [45]. The FTIR spectra confirmed the structure of GO@CE and GO@CE-TMEDA.Cl.

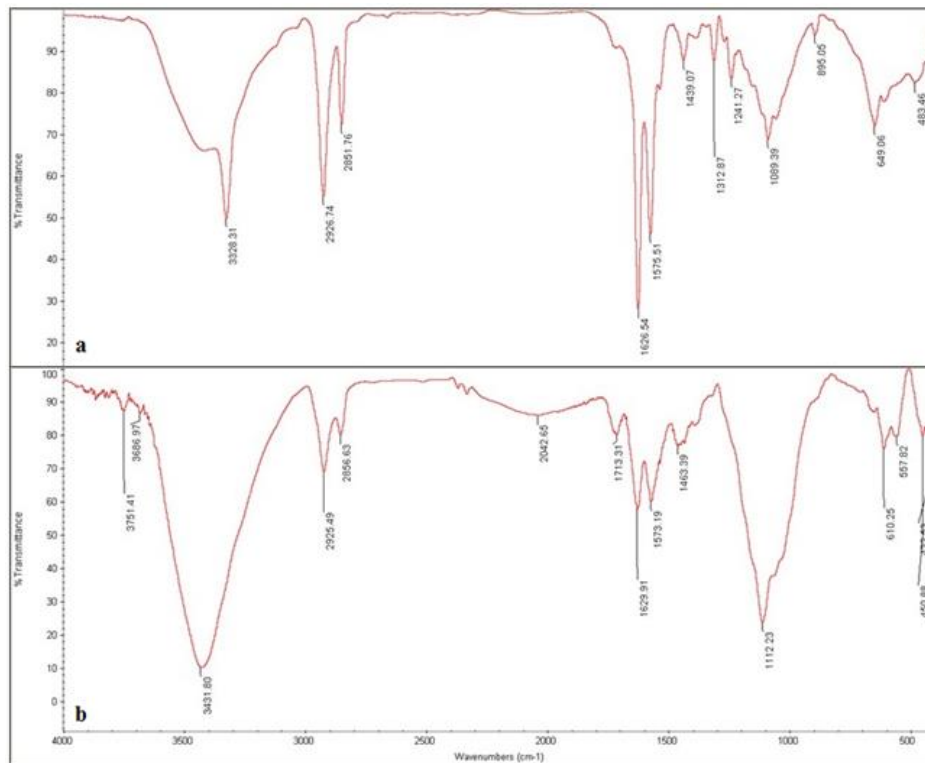


Figure 1. FT-IR spectra of a) GO@CE and b) GO@CE-TMEDA.Cl

XRD patterns

XRD patterns of GO, GO@CE, and GO@CE-TMEDA.Cl are presented in Figure 2. Based on Figure 2a, XRD of graphene oxide showed a sharp peak at 11° and a broad peak, determining reduced graphene oxide between 18° to 22° [46, 47]. Moreover, the XRD pattern of GO@CE (Figure 2b) shows a sharp peak at 8° and 11° and several sharp and broad peaks between 15° to 33° implying the presence of more crystals with various d-spacing. Also, the XRD pattern of GO@CE-TMEDA.Cl in Figure 2c indicate some sharp peaks and two broad peaks. The sharp peaks determine the crystallinity with various d-spacing while the broad peaks showed the nano-sized non-crystalline structures.

Morphology of samples was studied by FE-SEM images (Figure 3). FE-SEM image of GO@CE can be seen in Figure 3a which shows the graphene oxide sheets. FE-SEM image of GO@CE-TMEDA.Cl shows the graphene oxide

sheets with more considerable distances due to its functionalization by tetramethylethylenediamine (Figure 3b).

EDAX analysis (Figure 4) of GO@CE confirms the presence of carbon, oxygen, and chlorine and their percentage in the table. EDAX analysis of GO@CE-TMEDA.Cl shows carbon, nitrogen, oxygen, and chlorine and their percent. Thus, EDAX analysis confirms the preparation of GO@CE and GO@CE-TMEDA.Cl.

Thermogravimetric analysis (TGA) of GO@CE-TMEDA.Cl was conducted under argon atmosphere from 30°C to 500°C (Figure 5). TGA diagram shows two main weight losses. The first weight loss is around 100°C , probably due to evaporation of water and low molecular weight solvents [48]. Second weight loss at 160 to 250°C can be assigned to the isolation of functional groups [49]. The total weight loss and char yield are 27.24 and 72.76%, respectively. Therefore, the catalyst is stable under reaction conditions and can be used up to 200°C in various reaction processes.

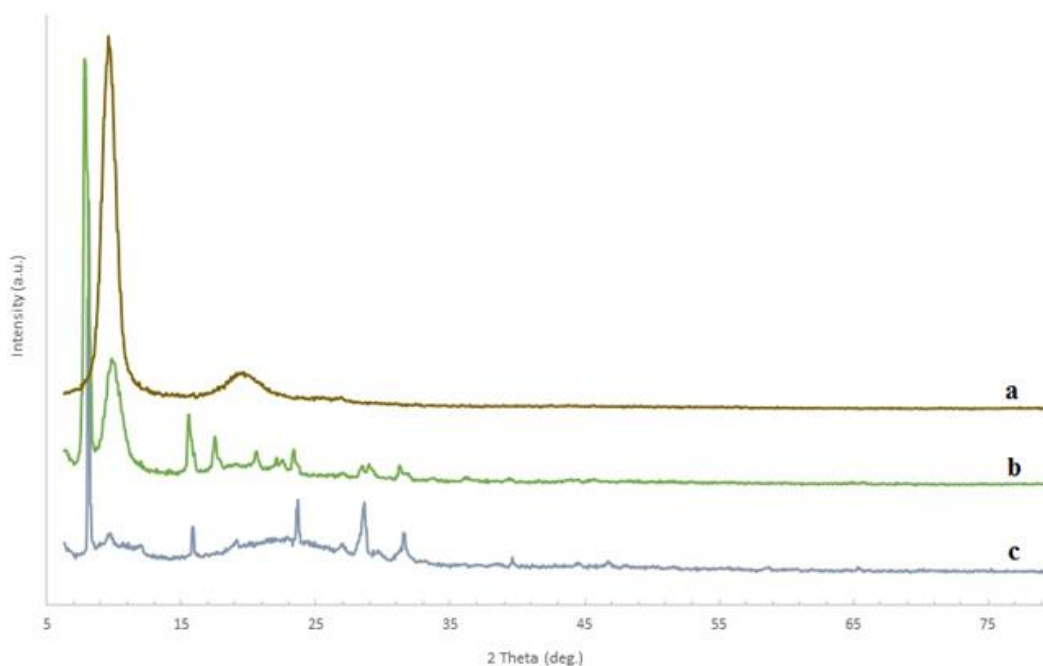


Figure 2. XRD pattern of a) GO, b) GO@CE and c) GO@CE-TMEDA.Cl

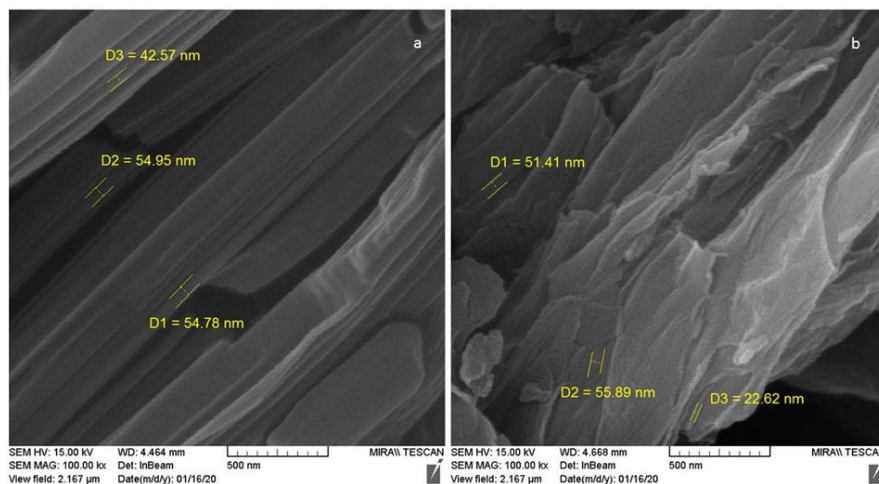


Figure 3. FE-SEM images of a) GO@CE and b) GO@CE-TMEDA.Cl

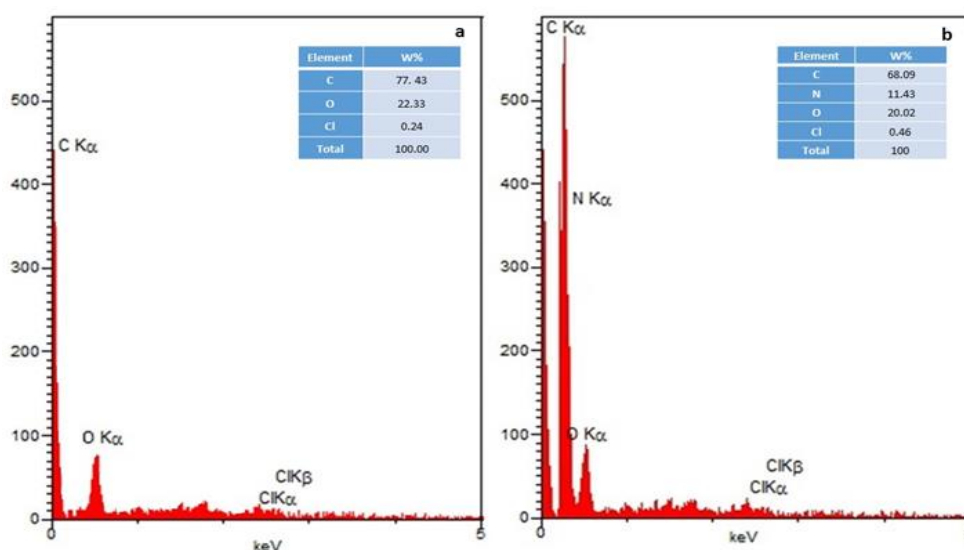


Figure 4. EDAX analysis of a) GO@CE and b) GO@CE-TMEDA.Cl

Synthesis of trisubstituted imidazoles using the catalyst

GO@CE-TMEDA.Cl was utilized to produce 2,4,5-trisubstituted imidazoles under solvent-free conditions via benzil, aldehydes, and ammonium acetate. The reaction of diketone, aldehyde, and ammonium acetate is the most used route for the production of trisubstituted imidazoles [50]. This route was studied using various catalysts. According to green chemistry principles, it suffers from some disadvantages

[51]. Therefore, this work focuses on the removal or minimize disadvantages, mainly, environmental problems by employing a new graphene oxide based catalyst. In order to find optimum conditions, four variables such as catalyst, time, solvent, and temperature are examined for production of **3b** (Scheme 2, Table 1). Optimized conditions for the production of imidazoles include 30 min., solvent-free conditions, 80 °C, 0.02 g of catalyst loading, and 95% yield (Table 1, entry 10).

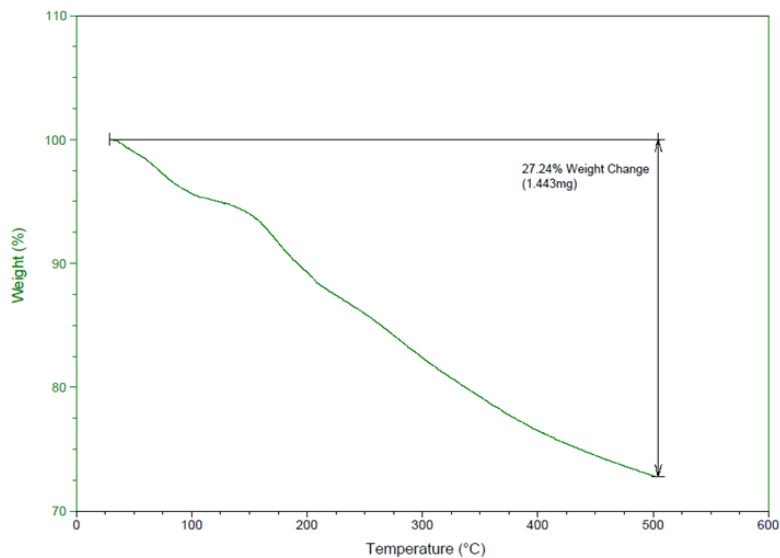


Figure 5. TGA analysis of GO@CE-TMEDA.Cl

Table 1. Effect of catalyst (GO@CE-TMEDA.Cl) loading, temperature and time on the model reaction for the production of **3b**

Entry	Solvent	Catalyst (g)	Temperature (°C)	Time (min)	Yielda (%) ^a
1	EtOH	-	Reflux	90	trace
2	EtOH	0.02	Reflux	90	83
3	Water	0.02	90	90	45
4	DMSO	0.02	100	90	49
5	CH ₃ CN	0.02	Reflux	90	76
6	DMF	0.02	100	90	54
7	MeOH	0.02	Reflux	90	79
8	Solvent-free	0.02	100	60	98
9	Solvent-free	0.02	90	40	96
10	Solvent-free	0.02	80	30	95
11	Solvent-free	0.01	80	30	84
12	Solvent-free	0.005	80	30	78
13	Solvent-free	0.01	70	30	72
14	Solvent-free	0.02	70	30	87
15	Solvent-free	0.03	70	30	88
16	Solvent-free	0.02 ^b	80	30	35

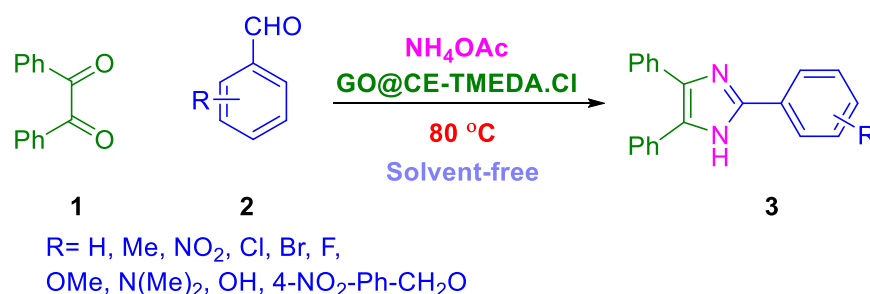
^aIsolated yield

^bGraphene oxide

The capability of GO@CE-TMEDA.Cl catalyst was explored in the synthesis of 2,4,5-trisubstituted imidazoles from aldehydes (Scheme 2). Findings on the successful synthesis of 2,4,5-trisubstituted imidazoles are reported in Table 2 with a broad scope of functional groups, high yields, and sustainable conditions. Aldehydes with electron withdrawing-groups, and halogens offered higher yields of trisubstituted imidazoles compared to aldehydes with electron-donating substituents [52]. Electron-withdrawing groups accelerate nucleophilic attacks of ammonia on

the carbonyl group by inducing a positive charge on the carbon of aldehyde. Moreover, they can facilitate water removal from the intermediate to attain final trisubstituted imidazole [53].

As mentioned in experimental section, final products were characterized by comparing their melting points with previously reported ones. Likewise, Nuclear magnetic resonance (NMR) spectroscopy confirmed the structure of **3k** using DMSO-d₆ as solvent and tetramethylsilane (TMS) as standard.



Scheme 2. Synthesis of 2,4,5-trisubstituted imidazoles catalyzed by GO@CE-TMEDA.Cl catalyst

Table 2. Synthesis of 2,4,5-trisubstituted imidazoles catalyzed by GO@CE-TMEDA.Cl catalyst

Entry	R	Product	Time (min)	Yield (%) ^a	mp (°C)	
					Found	Reported
1	H	3a	40	92	276-277	276-278 [54]
2	4-Cl	3b	30	95	262-263	260-262 [54]
3	2-Cl	3c	30	93	198-199	197-199 [55]
4	4-MeO	3d	40	88	227-228	228-230 [54]
5	2,4-diCl	3e	30	95	177-178	176-178 [56]
6	4-F	3f	30	96	260-261	258-260 [55]
7	4-Me	3g	40	87	229-230	228-230 [57]
8	4-NO ₂	3h	30	96	202-203	200-201 [56]
9	3-NO ₂	3i	30	97	301-302	297-300 [56]
10	4-(CH ₃) ₂ N	3j	45	86	256-257	255-258 [56]
11	4-NO ₂ -Ph-CH ₂ O [58]	3k	45	85	216-217	215-216 [23]
12	4-OH	3l	45	88	270-271	269-271 [54]

^aIsolated yield

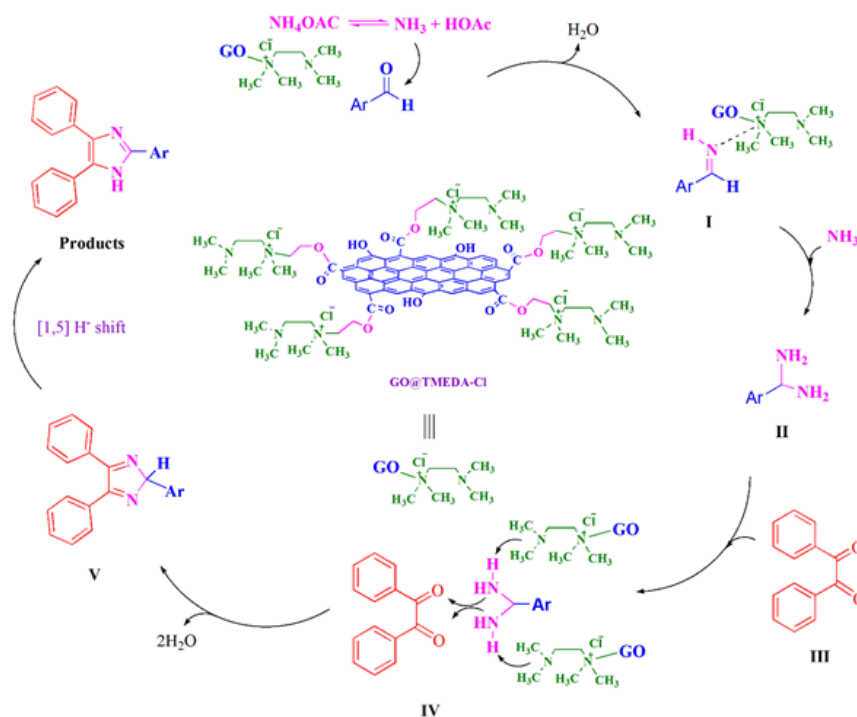
Table 3. Calculated values of turnover number (TON) and turnover frequency (TOF) for 2,4,5-trisubstituted imidazoles

Product	TON	TOF (min ⁻¹)	Product	TON	TOF (min ⁻¹)
3a	13.6	0.34	3g	13.4	0.33
3b	15.6	0.52	3h	16.3	0.54
3c	15.3	0.51	3i	16.5	0.55
3d	14.3	0.35	3j	14.5	0.32
3e	17.3	0.57	3k	18.99	0.42
3f	15	0.50	3l	13.7	0.30

To assess efficiency of GO@CE-TMEDA.Cl catalyst for production of trisubstituted imidazoles, turn over number (TON) and turn over frequency (TOF) values were calculated (Table 3). Turn over number (TON) was obtained using the equation: TON = product yield (g) / amount of catalyst (g) and turn over frequency (TOF) was afforded utilized the equation: TOF = product yield (g) / [reaction time (min) × amount of catalyst (g)] or TOF = TON / reaction time (min) [59].

Mechanism of reaction

A plausible mechanism of reaction is demonstrated in Figure 6. Ammonia was initially released from ammonium acetate and attacked to catalyst activated aldehyde to afford imine intermediate by releasing water (I), and then a second ammonia molecule attacked the imine to obtain II. In the next step, benzil (III) was attached by catalyst activated II via an adduct (IV) to achieve V. Ultimately, products were afforded by [1,5] hydride shift from intermediate V.

**Figure 6.** Plausible mechanism of reaction

Reusability and durability of catalyst

The recovery and reuse of the catalyst in the synthesis of **3b** was explored for five runs to examine the stability of the catalyst under reaction conditions (in Figure 7) showed no vital changes in the catalyst recovery and reuse. Thus, the catalyst has sufficient stability and activity toward synthesizing 2,4,5-trisubstituted imidazoles.

Comparison with other reported catalysts

The efficiency of the reported catalyst was evaluated by the synthesis of **3e** using the reported catalysts and comparing that with our catalyst (Table 4) in terms of reaction time, solvent, temperature, and catalyst loading, and this catalyst has priorities over previously reported ones.

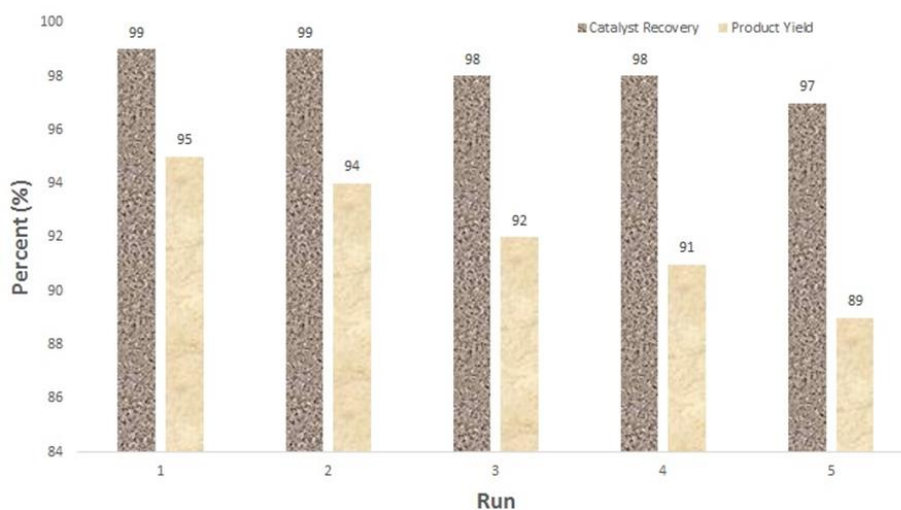


Figure 7. Product yield of **3b** and GO@CE-TMEDA.Cl catalyst recovery and reuse for five runs

Table 4. Comparison with previously reported catalysts

Entry	Catalyst	Time (min)	Temp. (°C)	Solvent	Yields [Ref.]
1	GO@CE-TMEDA.Cl (0.02 g)	30	80	solvent-free	95 [-]
2	Fe ₃ O ₄ @SiO ₂ -EPIM ^a (0.02 g)	25	100	PEG-200	91 [60]
3	Cu/C (1 mol%)	180	100	PEG-200	91 [61]
4	CoFe ₂ O ₄ NPs (0.01 g)	25	US ^b , 40	EtOH	92 [62]
5	UHP ^c (10 mol%)	240	Reflux	EtOH	88 [63]
6	Fe ₃ O ₄ @SiO ₂ -Imid-PMA (0.03g)	75	110	solvent-free	91 [64]
7	MIL-101 (0.005 g)	8	120	solvent-free	95 [65]
8	NiCoFe ₂ O ₄ (0.004 g)	17	110	solvent-free	85 [66]
9	LDH-APS-PEI-DTPA (0.005g)	65	Reflux	EtOH	95 [56]
10	MC-SO ₃ H (0.012 g)	120	80	EtOH	83 [67]
11	Fe ₃ O ₄ @SiO ₂ -TMA-Me (0.005g)	45	Reflux	EtOH	84 [68]
12	Cu(II)/PL-COF (0.1 g)	2	MW ^d	solvent-free	95 [69]

^aEpichlorohydrine-Imidazole

^bUltrasound

^cUrea-Hydrogen peroxide

^dMicrowave

Conclusion

Graphene oxide functionalized tetramethylethylenediamine ammonium salt was prepared, characterized, and used as catalyst. Synthesis of 2,4,5-trisubstituted imidazoles was achieved successfully, using the catalyst, under solvent-free conditions via a one-pot reaction of benzil, ammonium acetate, and aldehydes. The developed catalyst offered several priorities over previously reported ones, including, nontoxic and carbon-based, recoverable under reaction conditions, easy handling and storage, and inexpensive. The reported process is sustainable and requires moderate conditions while offering high yields, and short reaction times. Considering the findings, the reported graphene oxide derivative can be employed in various fields in chemistry and material science.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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References

- [1]. Astruc D. Introduction: Nanoparticles in catalysis, *Chemical Reviews*, 2020, **120**:461 [Crossref], [Google Scholar], [Publisher]
- [2]. Devi B.L.A.P., Vijayalakshmi K., Reddy T.V.K. Highly efficient SO₃H-carbon catalysed solvent-free synthetic protocol for wax esters via esterification of long chain fatty acids and alcohols, *Asian Journal of Green Chemistry*, 2023, **7**:239 [Crossref], [Publisher]
- [3]. Yan Y., Shin W.I., Chen H., Lee S.M., Manickam S., Hanson S., Zhao H., Lester E., Wu T., Pang C.H. A recent trend: application of graphene in catalysis, *Carbon Letters*, 2021, **31**:177 [Crossref], [Google Scholar], [Publisher]
- [4]. Ahankar H., Taghavi Fardood S., Ramazani A. One-pot three-component synthesis of tetrahydrobenzo [b] pyrans in the presence of Ni₀. 5Cu₀. 5Fe₂O₄ magnetic nanoparticles under microwave irradiation in solvent-free conditions, *Iranian Journal of Catalysis*, 2020, **10**:195 [Google Scholar], [Publisher]
- [5]. Moradnia F., Taghavi Fardood S., Ramazani A. Green synthesis and characterization of NiFe₂O₄@ ZnMn₂O₄ magnetic nanocomposites: An efficient and reusable spinel nanocatalyst for the synthesis of tetrahydropyrimidine and polyhydroquinoline derivatives under microwave irradiation, *Applied Organometallic Chemistry*, 2023, e7315 [Crossref], [Google Scholar], [Publisher]
- [6]. Fardood S.T., Ramazani A., Asiabi P.A., Fard Y.B., Ebadzadeh B. Microwave-assisted multicomponent reaction for the synthesis of 2-amino-4H-chromene derivatives using ilmenite (FeTiO₃) as a magnetic catalyst under solvent-free conditions, *Asian Journal of Green*

- Chemistry*, 2017, **1**:34 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [7]. Muslim Muhiebes R., Fatolahi L., Sajjadifar S. L-proline catalyzed multicomponent reaction for simple and efficient synthesis of tetrahydropyridines derivatives, *Asian Journal of Green Chemistry*, 2023, **7**:121 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [8]. Taghavi Fardood S., Ramazani A., Ayubi M., Moradni F., Abdpour S., Forootan R. Microwave Assisted Solvent-free Synthesis of 1-phenyl-1, 2-dihydro-3H-naphtho [1, 2-e][1, 3] oxazin-3-one Catalyzed by FeCl₃, *Chemical Methodologies*, 2019, **3**:519 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [9]. Taghavi Fardood S., Ramazani A., Moradni F., Afshari Z., Ganjkanlu S., Yekke Zare F. Green synthesis of ZnO nanoparticles via Sol-gel method and investigation of its application in solvent-free synthesis of 12-Aryl-tetrahydrobenzo [α] xanthene-11-one derivatives under microwave irradiation, *Chemical Methodologies*, 2019, **3**:632 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [10]. Zangade S., Patil P. A review on solvent-free methods in organic synthesis, *Current Organic Chemistry*, 2019, **23**:2295 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [11]. Taghavi Fardood S., Ebadzadeh B. and Ramazani A. Green synthesis and characterization of Ni-cu-mg ferrite nanoparticles in the presence of Tragacanth gum and study of their catalytic activity in the synthesis of Hexanitrohexaazaisowurtzitane, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, 2019, **38**:21 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [12]. Kumar P., Syal B., Seboletswe P., Cele N., Olofinson K., Singh P., Shahidul Islam M., Singh D., Gupta P. Synthesis, Biological Evaluation, Molecular Docking and Kinetic Investigation of New 2, 4, 5-Trisubstituted Imidazole Derivatives as Antidiabetic Agents, *ChemistrySelect*, 2023, **8**:e202300924. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [13]. Heppner D.E., Günther M., Wittlinger F., Laufer S.A., Eck M.J. Structural basis for EGFR mutant inhibition by trisubstituted imidazole inhibitors, *Journal of Medicinal Chemistry*, 2020, **63**:4293 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [14]. Adhikary S., Majumder L., Pakrashy S., Srinath R., Mukherjee K., Mandal C., Banerji B. Polysubstituted imidazoles as LysoTracker molecules: Their synthesis via iodine/H₂O and cell-imaging studies, *ACS Omega*, 2020, **5**:14394 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [15]. Kerru N., Bhaskaruni S.V., Gummidi L., Maddila S.N., Maddila S., Jonnalagadda S.B. Recent advances in heterogeneous catalysts for the synthesis of imidazole derivatives, *Synthetic Communications*, 2019, **49**:2437 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [16]. Rani N., Sharma A., Singh R. Trisubstituted imidazole synthesis: A review, *Mini Reviews in Organic Chemistry*, 2015, **12**:34 [[Google Scholar](#)], [[Publisher](#)]
- [17]. Kermanizadeh S., Naeimi H., Mousavi S. An efficient and eco-compatible multicomponent synthesis of 2, 4, 5-trisubstituted imidazole derivatives using modified-silica-coated cobalt ferrite nanoparticles with tungstic acid, *Dalton Transactions*, 2023, **52**:1257 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [18]. Zadeh M.M.A., Rostami E., Farhadi A. An Extremely Productive and Sustainable Procedure for the Synthesis of 2, 4, 5-Trisubstituted Imidazoles Using Graphene Oxide-Substituted Sulfoacetic Acid Amide, *Russian Journal of Organic Chemistry*, 2022, **58**:1487 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [19]. Rabiei K., Pouramiri B., Neshati M., Imanvand A. Eco-friendly synthesis of various tri-substituted imidazole derivatives by using a novel functionalized NCP@

- SiO₃PrNHPrSiO₃TiO₂ under solvent-free conditions, *Journal of Organometallic Chemistry*, 2023, **1001**:122888 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [20]. Zadeh M.M.A., Rostami E. and Zare S.H. Graphene oxide functionalized diethanolamine sulfate as a novel, highly efficient and sustainable catalyst for the synthesis of 8-aryl-7 H-acenaphtho [1, 2-d] imidazoles, *Research on Chemical Intermediates*, 2022, **48**:4537 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [21]. Samal K., Swain M.R., Pati A. GO-TiO₂ Nanocomposite: An Efficient Catalyst for the Conventional and Ultrasonically Mediated Multicomponent Synthesis of 2, 4, 5-Trisubstituted Imidazole Derivatives, *ChemistrySelect*, 2023, **8**:e202302026 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [22]. Uozumi Y., Hattori S. Nanohybrid Photocatalyst for the Synthesis of Aryl Carbonyl Compounds and Benzimidazoles, *Synfacts*, 2022, **18**:0774 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [23]. Rostami E., Nejad M.S.G. Preparation, characterization and utilization of a novel trifluoroacetic acid supported starch/graphene oxide green nanocomposite for efficient synthesis of 2,4,5-trisubstituted trisubstituted imidazoles. *Cellulose Chem Technol.*, 2021, **55**:1095 [[Google Scholar](#)], [[Publisher](#)]
- [24]. Kumar G., Mogha N.K., Masram D.T. Zr-Based Metal-Organic Framework/Reduced Graphene Oxide Composites for Catalytic Synthesis of 2, 3-Dihydroquinazolin-4 (1 H)-One Derivatives, *ACS Applied Nano Materials*, 2021, **4**:2682 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [25]. Sinha D., Biswas S., Das M., Ghatak A. An eco-friendly, one pot synthesis of tri-substituted imidazoles in aqueous medium catalyzed by RGO supported Au nano-catalyst and computational studies, *Journal of Molecular Structure*, 2021, **1242**:130823 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [26]. Indalkar K., Malge S.S., Mali A.S., Chaturbuj G.U. Expeditious and Highly Efficient One-Pot Synthesis of Functionalized Imidazoles Catalyzed by Sulfated Polyborate, *Organic Preparations and Procedures International*, 2021, **53**:387 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [27]. Khodamorady M., Ghobadi N., Bahrami K. Homoselective synthesis of 5-substituted 1H-tetrazoles and one-pot synthesis of 2, 4, 5-trisubstituted imidazole compounds using BNPs@ SiO₂-TPPTSA as a stable and new reusable nanocatalyst, *Applied Organometallic Chemistry*, 2021, **35**:p.e6144 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [28]. Yadav S., Dixit R., Sharma S., Dutta S., Arora B., Rana P., Kaushik B., Adholeya A., Gawande M.B., Sharma R.K. Unlocking the catalytic potency of a magnetic responsive CoFe₂O₄/Ni-BTC MOF composite for the sustainable synthesis of tri- and tetra-substituted imidazoles, *Materials Chemistry Frontiers*, 2021, **5**:7343 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [29]. Chen J., Yao B., Li C., Shi G. An improved Hummers method for eco-friendly synthesis of graphene oxide, *Carbon*, 2013, **64**:225 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [30]. Liu C., Qiu S., Du P., Zhao H., Wang L. An ionic liquid-graphene oxide hybrid nanomaterial: synthesis and anticorrosive applications, *Nanoscale*, 2018, **10**:8115 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [31]. Nikdel M., Salami-Kalajahi M., Hosseini M.S. Synthesis of poly (2-hydroxyethyl methacrylate-co-acrylic acid)-grafted graphene oxide nanosheets via reversible addition-fragmentation chain transfer polymerization, *RSC Advances*, 2014, **4**:16743 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [32]. Kulal D.K., Khose R.V., Pethsangave D.A., Wadekar P.H., Some S. Biomass-Derived Lignocellulosic Graphene Composite: Novel Approach for Removal of Oil and Organic

- Solvent, *ChemistrySelect*, 2019, **4**:4568 [Crossref], [Google Scholar], [Publisher]
- [33]. Rahman M.S., Hamed W.A., Yahyah R., Mahmud H.N.M.E. Optoelectrical and photoluminescence quenching properties of poly (N-vinyl carbazole)-polypyrrole/reduced graphene oxide nanocomposites, *Synthetic Metals*, 2017, **226**:188 [Crossref], [Google Scholar], [Publisher]
- [34]. Liu H., Xi P., Xie G., Shi Y., Hou F., Huang L., Chen F., Zeng Z., Shao C., Wang J. Simultaneous reduction and surface functionalization of graphene oxide for hydroxyapatite mineralization, *The Journal of Physical Chemistry C*, 2012, **116**:3334 [Crossref], [Google Scholar], [Publisher]
- [35]. Haubner, K., Murawski, J., Olk P., Eng L.M., Ziegler C., Adolphi B., Jaehne E. The route to functional graphene oxide, *ChemPhysChem*, 2010, **11**:2131 [Crossref], [Google Scholar], [Publisher]
- [36]. Kabel K.I., Farag A.A., Elnaggar E.M., Al-Gamal A.G. Improvement of graphene oxide characteristics depending on base washing, *Journal of Superhard Materials*, 2015, **37**:327 [Crossref], [Google Scholar], [Publisher]
- [37]. Lamiel C., Kharismadewi D., Shim J.J. Covalently bonded reduced graphene oxide/polyaniline composite for electrochemical sensors and capacitors, *Journal of Electroanalytical Chemistry*, 2015, **758**:148 [Crossref], [Google Scholar], [Publisher]
- [38]. Hassan G., Sajid M., Choi C. Highly sensitive and full range detectable humidity sensor using PEDOT: PSS, methyl red and graphene oxide materials, *Scientific Reports*, 2019, **9**:15227. [Crossref], [Google Scholar], [Publisher]
- [39]. Sepehri E., Mousavi S.M., Saljoughi E., Bahreini M., Doaei M., Kiani S. Enhancing anti-biofouling property by incorporating graphene oxide-silver nanocomposite into polycaprolactone membrane for ultrafiltration application, *Journal of Chemical Technology & Biotechnology*, 2023, **98**:2517 [Crossref], [Google Scholar], [Publisher]
- [40]. Liu A., Zhou W., Shen K., Liu J., Zhang X. One-pot hydrothermal synthesis of hematite-reduced graphene oxide composites for efficient removal of malachite green from aqueous solution, *RSC Advances*, 2015, **5**:17336 [Crossref], [Google Scholar], [Publisher]
- [41]. Chen X., Tong X., Gao J., Yang L., Ren J., Yang W., Liu S., Qi M., Crittenden J., Hao R. Simultaneous nitrite resourcing and mercury ion removal using mxene-anchored goethite heterogeneous fenton composite, *Environmental Science & Technology*, 2022, **56**:4542 [Crossref], [Google Scholar], [Publisher]
- [42]. Hu R., Gou H., Mo Z., Wei X., Wang Y. Highly selective detection of trace Cu²⁺ based on polyethyleneimine-reduced graphene oxide nanocomposite modified glassy carbon electrode, *Ionics*, 2015, **21**:3125 [Crossref], [Google Scholar], [Publisher]
- [43]. Spanò S.F., Isgrò G., Russo P., Fragalà M.E., Compagnini G. Tunable properties of graphene oxide reduced by laser irradiation, *Applied Physics A*, 2014, **117**:19 [Crossref], [Google Scholar], [Publisher]
- [44]. Hamam K.A., Gaabour L.H. Verification of the changes in the structural and physical properties of PU/PEO embedded with graphene oxide, *Results in physics*, 2017, **7**:2427 [Crossref], [Google Scholar], [Publisher]
- [45]. Maravi S., Bajpai A.K., Bajpai J. Poly (vinyl alcohol) supported thermally reduced graphene oxide (TRGO) nanosheets exhibit enhanced electrical and mechanical behavior, *Nano-Structures & Nano-Objects*, 2018, **14**:73 [Crossref], [Google Scholar], [Publisher]
- [46]. Stobinski L., Lesiak B., Malolepszy A., Mazurkiewicz M., Mierzwa B., Zemek J., Jiricek P., Bieloshapka I. Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods, *Journal of*

Electron Spectroscopy and Related Phenomena, 2014, **195**:145 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[47]. Xue J., Wu L., Hu N., Qiu J., Chang C., Atobe S., Fukunaga H., Watanabe T., Liu Y., Ning H., Li J. Evaluation of piezoelectric property of reduced graphene oxide (rGO)-poly (vinylidene fluoride) nanocomposites, *Nanoscale*, 2012, **4**:7250 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[48]. Park S., An J., Potts J.R., Velamakanni A., Murali S., Ruoff R.S. Hydrazine-reduction of graphite-and graphene oxide, *Carbon*, 2011, **49**:3019 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[49]. Zhang G., Wen M., Wang S., Chen J., Wang J. Insights into thermal reduction of the oxidized graphite from the electro-oxidation processing of nuclear graphite matrix, *RSC Advances*, 2018, **8**:567 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[50]. Shabalin D.A., Camp J.E. Recent advances in the synthesis of imidazoles, *Organic & Biomolecular Chemistry*, 2020, **18**:3950 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[51]. Gebre S.H. Recent developments in the fabrication of magnetic nanoparticles for the synthesis of trisubstituted pyridines and imidazoles: A green approach, *Synthetic Communications*, 2021, **51**:1669 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[52]. Bansal R., Soni P.K., Halve A.K. Green Synthesis of 1, 2, 4, 5-Tetrasubstituted and 2, 4, 5-Trisubstituted Imidazole Derivatives Involving One-pot Multicomponent Reaction, *Journal of Heterocyclic Chemistry*, 2018, **55**:1308 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[53]. Sakhdari M., Amoozadeh A., Kolvari E. Magnetic nanoparticle-supported sulfonic acid as a green catalyst for the one-pot synthesis of 2, 4, 5-trisubstituted imidazoles and 1, 2, 4, 5-tetrasubstituted imidazoles under solvent-free conditions, *Heterocyclic Communications*, 2021, **27**:71 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[54]. Kadu V.D., Mali G.A., Khadul S.P., Kothe G.J. Simple practical method for synthesis of trisubstituted imidazoles: an efficient copper catalyzed multicomponent reaction, *RSC Advances*, 2021, **11**:21955 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[55]. Asressu K.H., Chan C.K., Wang C.C. TMSOTf-catalyzed synthesis of trisubstituted imidazoles using hexamethyldisilazane as a nitrogen source under neat and microwave irradiation conditions, *RSC Advances*, 2021, **11**:28061 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[56]. Ghanbari N., Ghafuri H. Design and preparation of nanoarchitectonics of LDH/polymer composite with particular morphology as catalyst for green synthesis of imidazole derivatives, *Scientific Reports*, 2022, **12**:11288 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[57]. Gholap D.P., Huse R., Dipake S., Lande M.K. Silica supported lanthanum trifluoroacetate and trichloroacetate as an efficient and reusable water compatible Lewis acid catalyst for synthesis of 2, 4, 5-triarylimidazoles via a solvent-free green approach, *RSC Advances*, 2023, **13**:2090 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[58]. Rostami E., Zare S.H. Double Brønsted Acidic Media Immobilized on Carbonized Sugarcane Bagasse (CSCB) as a New and Efficient Solid Acid Catalyst for the Synthesis of Coumarins, Dicomarols and Xanthenes, *ChemistrySelect*, 2019, **4**:13295 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[59]. Chowdhury S.H., Ahsan M., Kabir M.H., Alam S.S., Hasnat M.A. Decomposition of hydrogen peroxide using chemical and catalytic methods: A reactor-based approach, *Asian Journal of Chemistry*, 2022, **34**:1263 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

[60]. Khalifeh R., Naseri V., Rajabzadeh M. Synthesis of Imidazolium-Based Ionic Liquid on Modified Magnetic Nanoparticles for

- Application in One-Pot Synthesis of Trisubstituted Imidazoles, *ChemistrySelect*, 2020, **5**:11453 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [61]. Khalifeh R., Niknam A. Nanoparticle-promoted synthesis of trisubstituted imidazoles in a green medium, *Organic Preparations and Procedures International*, 2020, **52**:91 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [62]. Eidi E., Kassae M.Z., Nasresfahani Z. Synthesis of 2, 4, 5-trisubstituted imidazoles over reusable CoFe₂O₄ nanoparticles: an efficient and green sonochemical process, *Applied Organometallic Chemistry*, 2016, **30**:561 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [63]. Maleki A., Alirezvani Z. A highly efficient synthesis of substituted imidazoles via a one-pot multicomponent reaction by using urea/hydrogen peroxide (UHP), *Journal of the Chilean Chemical Society*, 2016, **61**:3116 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [64]. Esmailpour M., Javidi J., Zandi M. One-pot synthesis of multisubstituted imidazoles under solvent-free conditions and microwave irradiation using Fe₃O₄@SiO₂-imid-PMA n magnetic porous nanospheres as a recyclable catalyst, *New Journal of Chemistry*, 2015, **39**:3388 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [65]. Manteghi F., Zakeri F., Guy O.J., Tehrani Z. MIL-101 (Cr), an efficient heterogeneous catalyst for one pot synthesis of 2, 4, 5-trisubstituted imidazoles under solvent free conditions, *Nanomaterials*, 2021, **11**:p.845. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [66]. Hemmesi L., Naeimi H. Preparation and Characterization of NiCoFe₂O₄ Nanoparticles as an Effective Catalyst for the Synthesis of Trisubstituted Imidazole Derivatives Under Solvent-free Conditions, *Acta Chimica Slovenica*, 2022, **69**:876 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [67]. Saeedi S., Rahmati A. MNP-cellulose-OSO₃H as an efficient and biodegradable heterogeneous catalyst for green synthesis of trisubstituted imidazoles, *RSC Advances*, 2022, **12**:11740 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [68]. Fattahi B., Dekamin M.G. Fe₃O₄/SiO₂ decorated trimesic acid-melamine nanocomposite: a reusable supramolecular organocatalyst for efficient multicomponent synthesis of imidazole derivatives, *Scientific Reports*, 2023, **13**:401 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [69]. Sedaghat M., Moeinpour F., Mohseni-Shahri, F.S. Copper (II)/polyimide linked covalent organic framework as a powerful catalyst for the solvent-free microwave irradiation-based synthesis of 2, 4, 5-trisubstituted imidazoles, *Analytical Science Advances*, 2023, **5**:1 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

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