

Green Synthesis of Pyrimido [2,1-b] Benzothiazoles Using Graphene Oxide Substituted Tris(hydroxymethyl) Aminomethane Sulfonic Acid as Environmentally Friendly Carbon Catalyst

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ABSTRACT

In this study, graphene oxide was modified with tris(hydroxymethyl) aminomethane using an amide formation reaction and treated with chlorosulfonic acid to produce a sulfonated catalyst. The catalyst was characterized using reliable analytical methods including Fourier Transform Spectroscopy (FTIR), X-ray diffraction analysis (XRD), Field Effect Scanning Electron Microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDAX), and Thermogravimetric Analysis (TGA). The production process of Pyrimido [2,1-b] benzothiazoles was efficiently conducted using the new catalyst, resulting in high product yields without the use of a solvent. The synthesis proceeded effectively using 2-aminobenzothiazole, aldehydes, and ethyl or methyl acetoacetate with the catalyst. Various products were synthesized using different aldehydes with diverse functional groups. The reported procedure and catalyst offer several advantages, including being carbon-based, operating under solvent-free conditions, having short reaction times, being a recoverable catalyst, featuring simple purification, and being environmentally friendly. With these excellent properties, the synthesized functionalized graphene oxide can be utilized in various research areas, and its properties can be further expanded.

KEYWORDS: Pyrimido [2,1-b] benzothiazoles, Graphene oxide, Tris(hydroxymethyl)aminomethane sulfonic acid, Green Chemistry

1. Introduction

Green chemistry provides efficient conditions for the development and use of more beneficial systems to address deficiencies such as low yields, isolation and separation problems, selectivity of reactions and environmental issues [1]. The use of toxic reagents and solvents can be harmful to ecosystems, while utilizing safe and environmentally friendly chemicals can help protect the environment [2,3]. Therefore, a key focus of green chemistry is to create new eco-friendly reagents and solvents, as well as promote the use of safer materials [4]. Reactions with fewer steps and by-products in solvent-free conditions

offer the same advantages and can address concerns from scientists about the chemical industry [5]. One-pot, multicomponent reactions involve three or more components to produce products in a single step with significant benefits [6]. These reactions eliminate intermediates, require less toxic reagents and solvents or no solvents, produce no by-products, have short reaction times, high yields, and are easy to work with [7].

Graphene oxide has a wide range of properties and is an excellent material for research in various disciplines, including chemistry and materials science [8]. Functionalization with different groups, such as organic species [9], metal nanostructures,

metal and covalent organic frameworks (MOFs and COFs), polymeric materials, and inorganic solid supports, expands the applications and properties of graphene oxide [10]. Modified graphene oxide, used as a heterogeneous catalyst, is significant due to the nontoxic and chemically inert nature of carbon allotropes, as well as the nanoscale graphene oxide backbone [11,12]. Sulfonated carbon catalysts, including graphene oxide, have been found to be strong heterogeneous catalysts in organic synthesis and heterocyclic chemistry [13], with several reported methodologies for sulfonic acid functionalization of carbon [14]. These catalysts have advantages over others, such as being sustainable, easy to produce and store, insoluble in organic solvents, chemically stable under reaction conditions, safe to handle, and having a two-dimensional structure like graphene oxide [15].

Pyrimido [2,1-b] benzothiazoles have biological activity and are important constituents in natural products, as well as being applied in medicinal chemistry research [16]. Due to their significance in medicinal chemistry and biological research [17], a large number of studies have been conducted on their preparation and properties [18]. Various synthetic routes have been explored for the synthesis of these compounds, with several catalysts being reported [19]. One-pot three-component reactions involving 2-aminobenzothiazole, aldehydes, and acetoacetates in the presence of catalysts are important pathways for their production [20]. Numerous catalysts, including heterogeneous ones, have been described, such as FeF_3 [21], trypsin [22], nano-kaolin/ $\text{Ti}^{4+}/\text{Fe}_3\text{O}_4$ [23], sulfonic acid-functionalized carbon@titania composites [24], Fe_3O_4 @nano-cellulose/ Cu(II) [25], Fe_3O_4 @nano-cellulose/ Sb(V) [26], and Fe_3O_4 @ SiO_2 - TiCl_3 NPs [27]. However, the reported routes and catalysts have their disadvantages, and new, more efficient procedures and catalysts should be explored to address environmental crises.

In this research project, a catalyst was initially created using graphene oxide functionalized with tris(hydroxymethyl)aminomethane, followed by treatment with chlorosulfonic acid to generate a sulfonic acid-modified carbon catalyst ($\text{GO@THMAM-SO}_3\text{H}$). Subsequently, pyrimido [2,1-b] benzothiazoles were synthesized in high yields using the catalyst in the presence of 2-aminobenzothiazole, functionalized aryl aldehydes, and ethyl acetoacetate under

environmentally friendly and solvent-free reaction conditions.

2. Experimental

2.1. Materials and instrumentation

All chemicals were of chemical grade and were purchased from Aldrich, Fluka, and Merck, and used without further purification. A Bruker Avance 300 MHz spectrometer was used to record ^1H and ^{13}C NMR spectra in DMSO-d_6 solvent. Fourier Transform Infrared spectra (FT-IR) were obtained using KBr pellets and a JASCO FT/IR-6300 FT-IR spectrometer. A Bruker AXSD 8 Advance X-ray diffractometer was utilized to conduct powder X-ray diffraction analysis (XRD) with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) at a scan rate of $0.1^\circ \text{ min}^{-1}$. To achieve homogeneous colloidal dispersed solutions, an IMECO 34 kHz frequency, 500W sonicator was employed. Melting points were determined using Stuart Scientific melting point apparatus. Morphological studies, Field Emission Scanning Electron Microscopy (FESEM) images, and *Energy Dispersive Spectroscopy (EDS)* spectra were acquired using a TE-SCAN microscope. Thermal analysis (TGA) of the catalyst was conducted using a SDT Q600 V20.9 Build 20 apparatus under an argon atmosphere.

2.2. Preparation of graphene oxide modified with tris (hydroxymethyl) aminomethane

The modified Hummers method was utilized to produce single-layer nanostructured graphene oxide [28]. To begin, 1.0 g of graphene oxide was combined with 30 mL of THF and sonicated for 60 minutes to create a colloidal solution. Next, Tris (hydroxymethyl) aminomethane (THMAM, 0.6 mL), triethylamine (8.8 mL), and DCC (1.20 g) were added to the mixture. The reaction was allowed to proceed at room temperature for 48 hours. Afterwards, 5.0 mL of water and 15 mL of DMSO were added, and the resulting precipitate was filtered while still hot. The purified product was obtained by washing the precipitate several times with hot ethanol, hot deionized water, and acetone. It was then dried at room temperature and stored in a tightly sealed, dry vial.

2.3. Production of $\text{GO@THMAM-SO}_3\text{H}$ catalyst

To a solution of GO@THMAM (1.0 g) in THF (20 mL), sonication was applied for 60 minutes to create a colloidal solution. Subsequently, a solution of chlorosulfonic acid (0.6 mL) and THF (10 mL) was added dropwise under a N_2 atmosphere. The

reaction proceeded for 12 hours, followed by purification through centrifugation, washing with THF and chloroform several times, drying, and stored in a sealed, dry place.

2.4. General procedure for production of pyrimido benzothiazoles using the catalyst

A mixture of 2-Aminobenzothiazole (1 mmol), ethyl acetoacetate (1 mmol), aldehyde (1 mmol), and GO@THMAM catalyst was prepared. The mixture was homogenized and heated using an oil bath for an appropriate amount of time. Ethyl acetate (5 mL) was then added and filtered while hot. The resulting precipitate was purified by washing with ethyl acetate sequentially, dried under vacuum, and reused as a catalyst for the same reaction to study catalyst recovery (five times recovery, see Table 2, entry 3). The remaining liquid was evaporated and the residue was recrystallized in ethanol to obtain a pure product.

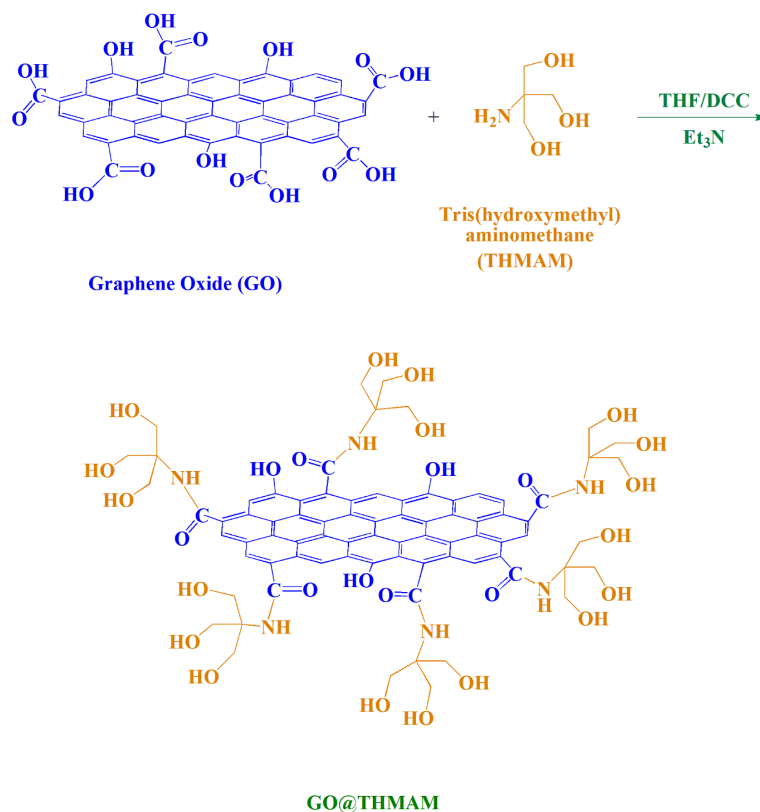
2.5. Spectral data of methyl-2-methyl-4-(3-nitrophenyl)-4H-pyrimido [2,1-b] [1,3] benzothiazole-3-carboxylate (4n)

^1H NMR (300 MHz, DMSO-d_6) δ : 2.33 (s, 3H), 3.64 (s, 3H), 6.70 (s, 1H), 7.21-7.34 (m, 2H), 7.55-7.63 (m, 2H), 7.76-8.09 (m, 3H), 8.33 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ : 166.26, 163.58, 155.67, 148.33, 143.93, 137.65, 133.82, 130.88, 127.47, 124.80, 123.78, 123.44, 123.35, 122.01, 112.79, 102.38, 56.32, 51.49, 40.84, 40.57, 40.29, 40.01, 39.73, 39.46, 39.18, 23.84. Anal. Cal. For $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$: C, 59.83; H, 3.96; N, 11.02; S, 8.41; Found: C, 59.81; H, 3.97; N, 11.05; S, 8.44.

3. Results and discussion

3.1. Preparation and characterization of catalyst

The modified Hummers method was utilized to prepare graphene oxide from graphite flakes [28]. This material was further enhanced with tris (hydroxymethyl) aminomethane (THMAM) using triethylamine and DCC in THF at room temperature to produce functionalized graphene oxide (GO@THMAM) (Scheme 1). Subsequently, Chlorosulfonic acid was used to treat GO@THMAM to create the catalyst in high yield (Scheme 2).



Scheme 1. Production of GO@THMAM

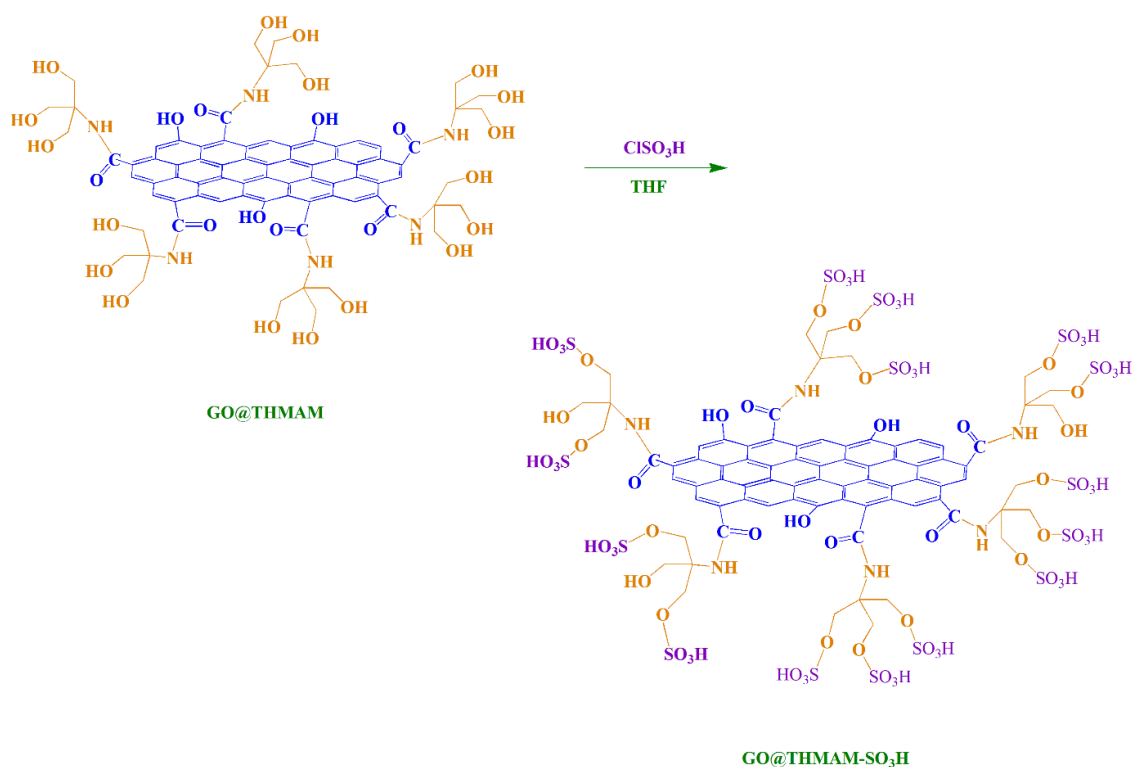
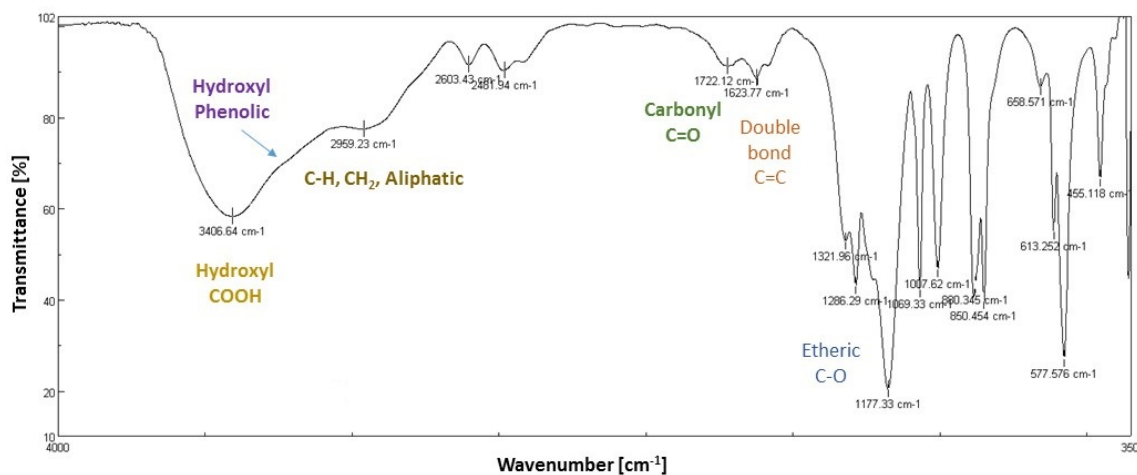
Scheme 2. Production of GO@THMAM-SO₃H

Fig. 1. FTIR-Spectrum of GO

Fig. 1 displays the FTIR spectrum of GO, showing stretching vibrational frequencies of phenolic, aliphatic, and carboxylic acid hydroxyl groups above 3000 cm⁻¹ [29]. Stretching vibrational frequencies of aliphatic CH moieties were found at 2854 cm⁻¹ and 2938 cm⁻¹ [30]. Additionally, stretching vibrations of C=O were

observed at 1722 cm⁻¹ [31], and for C=C aromatic rings, they were determined at 1578 cm⁻¹ [32]. Vibrations of C-O bonds were also detected at 1177 cm⁻¹ [33].

Fig. 2a shows the FTIR spectrum of GO@THMAM in which carboxylic acid vibrations were detected at 3427 cm⁻¹ [34], and vibrations of

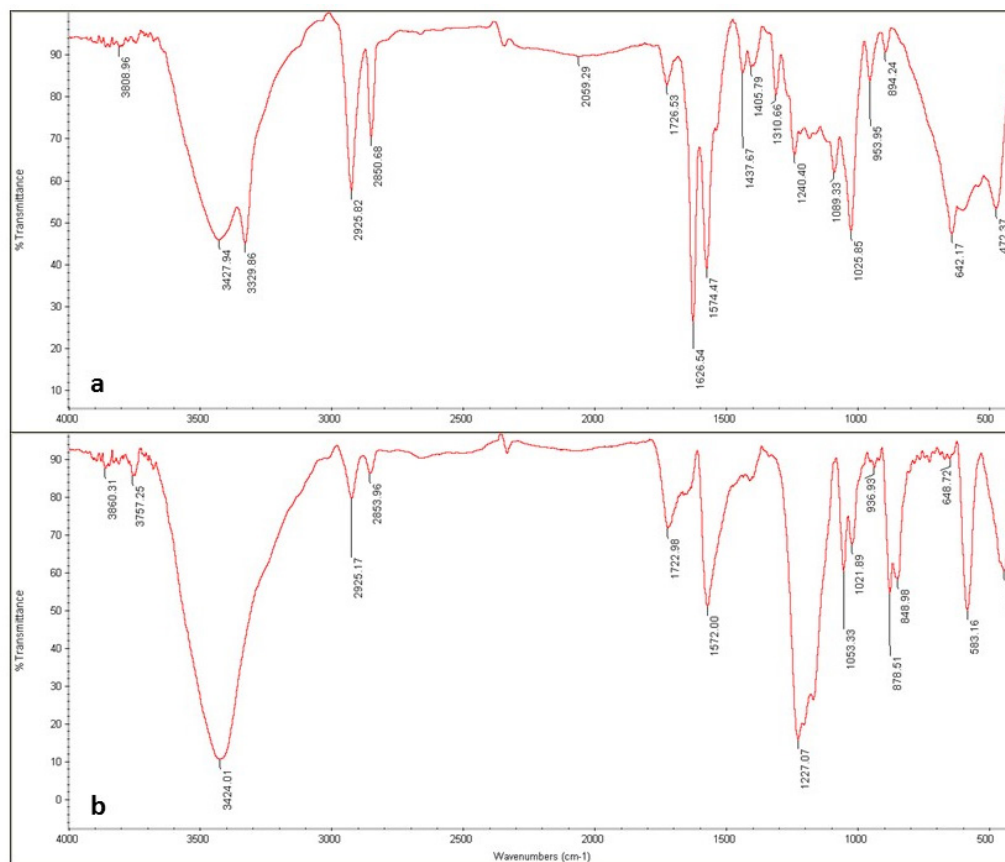


Fig. 2. FT-IR spectra of (a) GO@THMAM and (b) catalyst (GO@THMAM-SO₃H)

aliphatic hydroxyl groups were observed at 3329 cm⁻¹ [35]. Additionally, aliphatic CH vibrations were detected at 2850 cm⁻¹ and 2925 cm⁻¹ [30], and the stretching vibration band of carbonyl (C=O) was identified at 1726 cm⁻¹ [31]. The vibrational band of C=C was determined at 1626 cm⁻¹ and that of C=C was detected at 1574 cm⁻¹ [32]. The vibrational bands at 1437 cm⁻¹ and 1405 cm⁻¹ show C-H moieties [36]. Vibrations of O-H were determined at 1310 cm⁻¹ [37], and bands of C-O and N-H were observed at 1240 cm⁻¹ [38]. Vibrations of C-O were determined at 1089 cm⁻¹, and that of C-H deformation was observed at 1025 cm⁻¹ [39]. Additionally, vibrations of C-O-C were detected at 953 cm⁻¹ [40], and that of C-H was determined at 642 cm⁻¹ [41].

The FTIR spectrum of GO@THMAM-SO₃H (Fig. 2b) shows the vibrational frequencies of carboxylic acid, sulfonic acid hydroxyls, and NH groups at approximately 3424 cm⁻¹ [42,43].

Vibrations of CH groups were detected at 2925 cm⁻¹ and 2853 cm⁻¹ [30]. Carbonyl moieties vibrations were observed at 1722 cm⁻¹ [31], and vibrations of the aromatic carbon-carbon double bond (C=C) can be determined at 1572 cm⁻¹ [32]. Frequency vibrations of etheric and sulfonic acid moieties were detected at 1227 cm⁻¹ [44], and vibrations of the sulfone moiety can be observed at 1053 cm⁻¹ [45]. Additionally, the frequency vibration at 878 cm⁻¹ can be assigned to C-H aromatic out-of-plane deformation [46].

XRD patterns of graphene oxide, GO@THMAM, and GO@THMAM-SO₃H catalyst are shown in Fig. 3. In these patterns, the peak of graphene oxide at 11° [47] disappeared, and a broad peak around 20° appeared due to reduced graphene oxide (rGO) resulting from functionalization and sulfonation in the carbon backbone [48].

Fig. 4 displays the FESEM images of GO@THMAM and the catalyst. The images reveal the structure of reduced graphene oxide in the GO@

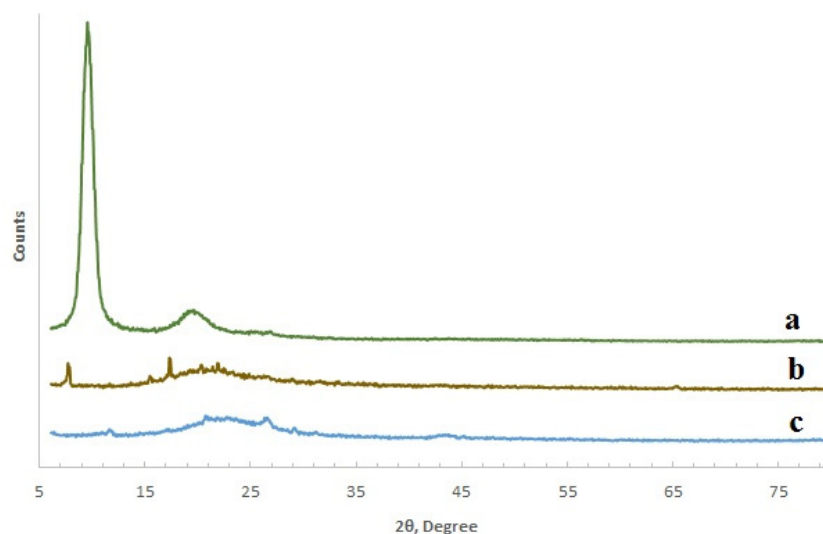


Fig. 3. XRD spectra of (a) GO, (b) GO@THMAM and (c) catalyst (GO@THMAM-SO₃H)

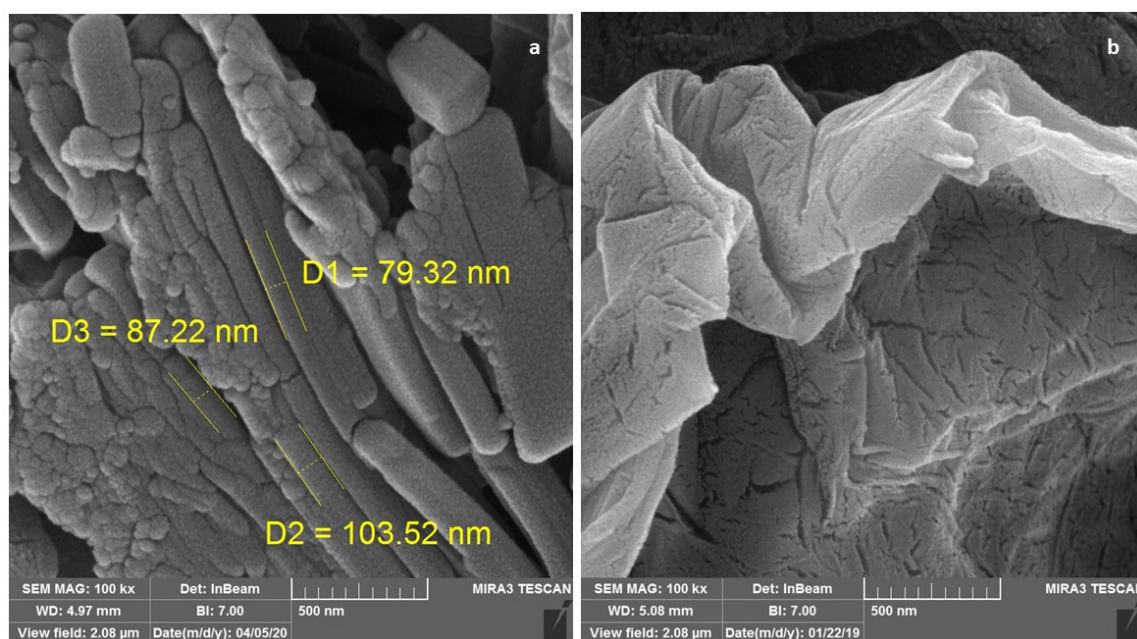


Fig. 4. FE-SEM images of (a) GO@THMAM and (b) catalyst (GO@THMAM-SO₃H)

THMAM and catalyst structures as curved plates [49].

Fig. 5 illustrates the EDAX analysis of the catalyst, showing carbon, nitrogen, oxygen, and sulfur ions, indicating the successful functionalization of graphene oxide with amine and sulfonic acid [50].

Thermogravimetric analysis of the GO@THMAM-SO₃H catalyst (Fig. 6) was conducted under an argon atmosphere in the range of

30 °C to 500 °C at a heating rate of 10 °C/min. There are two main steps for the degradation of the catalyst. The first degradation step occurred around 100 °C, likely due to the evaporation of water and low boiling point solvents [51]. The second, and main, weight loss occurred from 170 to 270 °C, probably due to the isolation of high molecular weight physically adsorbed chemicals or functional groups [52]. The total weight change

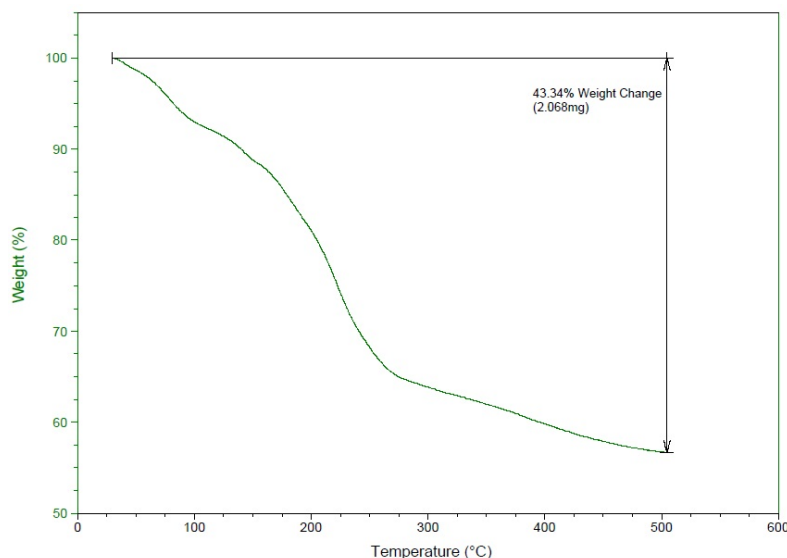


Fig. 6. TGA analysis of GO@THMAM-SO₃H catalyst

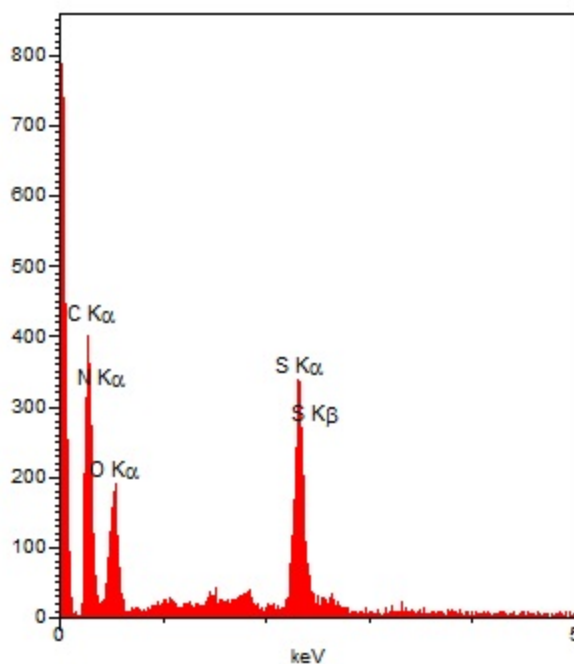


Fig. 5. EDS analysis of GO@THMAM-SO₃H catalyst

is 43.34%, with a char yield of 55%, indicating that the catalyst can be used up to 200 °C without a significant loss of activity.

3.2. Synthesis of pyrimido [2, 1-b] benzothiazoles using the catalyst

The catalyst was used to synthesize pyrimido [2,

1-b] benzothiazoles from 2-aminobenzothiazole, aldehydes, and ethylacetoacetate (Scheme 3). The reaction was enhanced by employing a solvent-free, one-pot, three-component approach. Optimized conditions were determined by analyzing three variables: temperature, catalyst, and solvent. The results indicated that no solvent was necessary.

Table 1: Optimized production of pyrimido [2, 1-b] benzothiazole (**4h**) utilized nanocatalyst

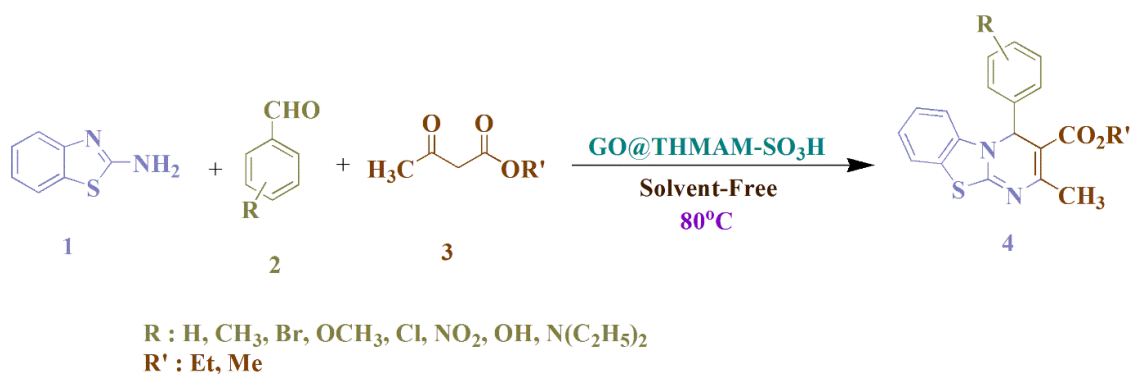
Entry	Solvent	Catalyst (g)	Temperature (°C)	Time/min	Yield (%) ^a
1	-	-	100	180	23
2	MeOH	0.03	Reflux	90	31
3	EtOH	0.03	Reflux	90	34
4	CH ₃ CN	0.03	Reflux	90	31
5	Isopropyl alcohol	0.03	100	90	38
6	H ₂ O	0.03	Reflux	90	44
7	DMF	0.03	90	90	49
8	Ethylene glycol	0.03	100	90	43
9	THF	0.03	Reflux	90	27
10	Solvent-free	0.005	110	90	55
11	Solvent-free	0.01	110	90	73
12	Solvent-free	0.01	120	100	81
13	Solvent-free	0.02	110	80	95
14	Solvent-free	0.02	100	80	95
15	Solvent-free	0.02	90	70	94
16	Solvent-free	0.02	80	70	94
17	Solvent-free	0.02	70	70	86
18	Solvent-free	0.03	80	60	89
19	Solvent-free	0.02 ^b	80	70	40
20	Solvent-free	0.02 ^c	80	70	47

^a Isolated yield, ^b GO was used as catalyst, ^c GO@THMAM was used as catalyst

Table 1 details the optimization conditions, which involved examining temperature, time, solvent, and catalyst loading. The optimal conditions are 0.02 g of nanocatalyst, a reaction time of 70 minutes at 80 °C in a solvent-free environment (Table 1, Entry 16). These optimized conditions were then used to investigate the effects of different functional groups, with the synthesized derivatives outlined in Table 2 (Scheme 3).

The effectiveness of the reported catalyst for the synthesis of pyrimido [2, 1-b] benzothiazoles was investigated using different aryl aldehydes, and the results are presented in Table 2. Higher product yields were achieved when utilizing

aldehydes with electron-withdrawing groups and halogens, while lower yields were observed with aldehydes containing electron-donating groups. The proposed mechanism suggests that electron-withdrawing groups and halogens increase the positive charge on the aldehyde carbon, making nucleophilic attack more favorable. This facilitates the removal of water and promotes the 1,4-addition in the subsequent step (refer to Fig. 7). Based on the outcomes of the reactions with various aldehydes, the GO@THMAM-SO₃H catalyst was proven to be sustainable and capable of efficiently driving the reaction without the need for a solvent, with short reaction times, high yields,



Scheme 3. Production of pyrimido [2, 1-b] benzothiazoles

Table 2: Production of pyrimido [2, 1-b] benzothiazoles utilized GO@THMAM-SO₃H catalyst

Entry	R ₁	R ₂	Product	Time/min	Yield ^a (%)	MP/ ^o C	
						Found	Reported [Ref.]
1	H	Et	4a	70	92	177-178	175-177[53]
2	4-HO	Et	4b	70	87	211-212	210-212[53]
3	2-Cl	Et	4c	60	92	125-126	124-126[54]
4	4-Cl	Et	4d	50	96	141-142	140-142[55]
5	4-NO ₂	Et	4e	50	94	173-174	155-157[53]
6	4-MeO	Et	4f	80	87	140-141	138-140[55]
7	2-NO ₂	Et	4g	60	90	123-124	122-125[54]
8	4-Br	Et	4h	70	94	113-114	107-109[53]
9	3-NO ₂	Et	4i	50	95	221-222	218-220[53]
10	2,4-Dichloro	Et	4j	60	91	134-135	133-135[54]
11	4-NMe ₂	Et	4k	70	84	177-178	175-178[56]
12	H	Me	4l	60	90	144-145	143-145[57]
13	4-OMe	Me	4m	60	89	151-152	150-153[57]
14	3-NO ₂	Me	4n	50	95	224-225	-

^a Isolated yield

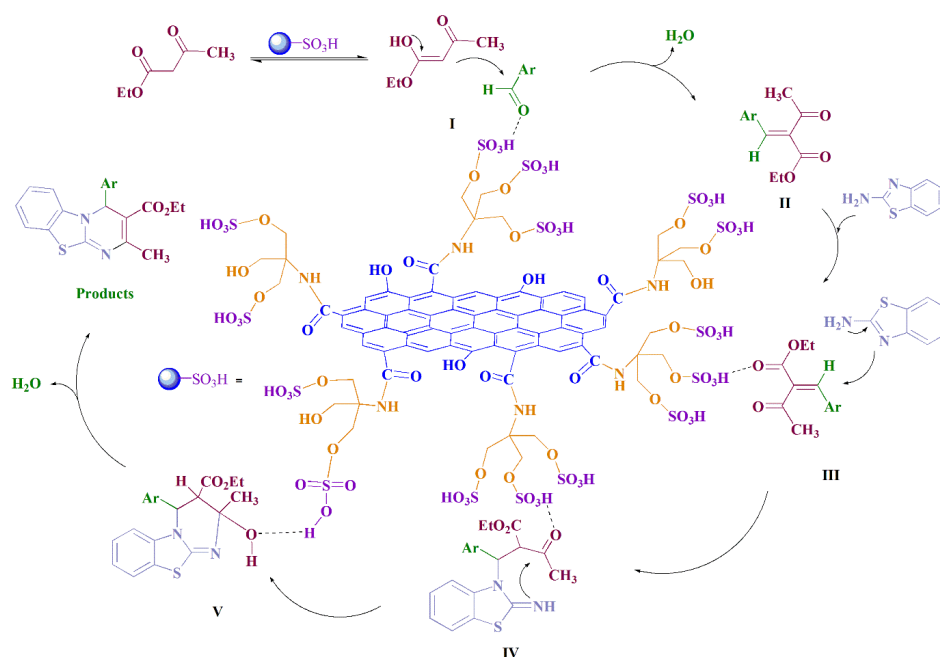


Fig. 7. Plausible mechanism for production of pyrimido [2, 1-b] benzothiazoles using GO@THMAM-SO₃H catalyst

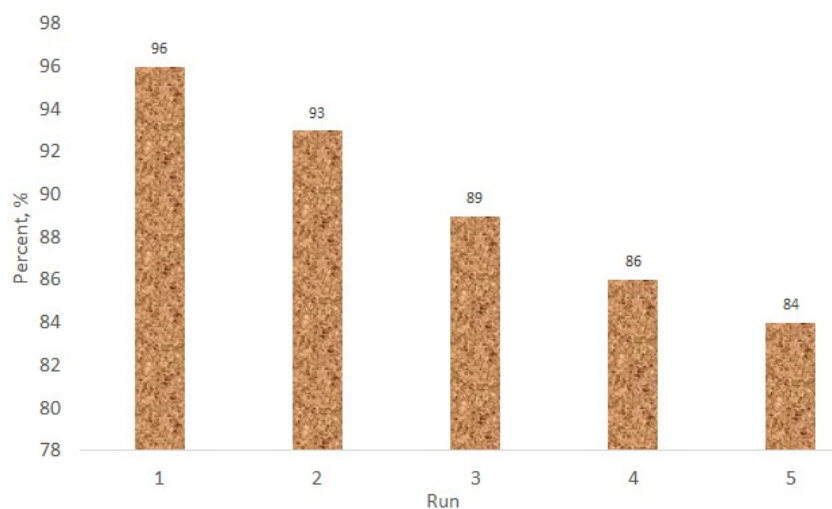


Fig. 8. Catalyst reuse for production of **4d**

and at room temperature. The structure of **4n**, a novel compound, was confirmed through NMR spectroscopy and elemental analysis.

3.3. Reaction mechanism

Fig. 7 illustrates the possible mechanism for the production of pyrimido [2, 1-b] benzothiazoles using the GO@THMAM-SO₃H catalyst. Initially, the aldehyde was protonated with the catalyst (I)

and attacked by ethylacetoacetate in its enol form to produce intermediate **II** after water removal. Subsequently, intermediate **II** was activated by the catalyst and attacked by 2-aminobenzothiazole to form **IV** through **III**. **IV** was further activated by the catalyst, and the ketone moiety was attacked by an imine to yield **V**, with water removal resulting in pyrimido [2, 1-b] benzothiazoles.

Table 3: Comparison with other catalysts and nanocomposites for production of **4h**

Entry	Catalyst	solvent	Temp. (°C)	Time (min.)	Yield (%)	Ref.
1	This work (0.02 g)	solvent-free	80	70	94	This work
2	Nano-kaolin/Ti4+/Fe3O4 (0.03g)	solvent-free	100	96	92	21
3	Trypsin	ethylene glycol	60	Two Days	64	14
4	Nano-TiCl2/cellulose (0.03g)	PEG-400	70	60	95	20
5	C/TiO2-SO3-SbCl2 (0.1g)	Solvent-free	90	120	92	15
6	Fe3O4@nano-cellulose-Sb (0.03 g)	Solvent-free	90	33	98	53
7	TMGTa (0.08 g)	H2O	100	300	61	52
8	Fe3O4@NCs-TiCl (0.03)	Solvent-free	70	40	97	56
9	nano-cellulose/BF3/Fe3O4 (0.06 g)	Solvent-free	100	50	97	11
10	Rose bengal/trypsin (0.03 g)	water	50	48h	43	11

^a 1,1,3,3-N,N,N',N'- tetramethylguanidinium trifluoroacetate

3.4. Reusability of catalyst

The stability and activity of the catalyst were investigated by synthesizing compound **4d** in five runs under the optimized conditions mentioned above. The catalyst recovered from each run was washed with ethyl acetate, dried, and reused in subsequent runs. Based on the results obtained, the loss of catalyst reactivity for the synthesis of compound **4d** was found to be insignificant (Fig. 8).

3.5. Comparison with previously reported catalysts and nanocomposites

The efficiency and capability of our nanocomposite for synthesizing **4h** were compared with other published procedures and are presented in Table 3. According to the table, our nanocomposite outperforms previously published catalysts in terms of sustainability, higher yields, moderate conditions, simple purification, and solvent-free conditions.

4. Conclusion

In this study, we present an efficient method

for producing pyrimido [2, 1-b] benzothiazoles using a newly synthesized catalyst without the need for a solvent. The catalyst, made from graphene oxide, tris(hydroxymethyl) aminomethane, and chlorosulfonic acid was used in a one-pot three-component reaction involving 2-aminobenzothiazole, ethyl acetoacetate, and aryl aldehydes successfully yield pyrimido [2, 1-b] benzothiazoles. The structural stability and catalytic activity of the catalyst were thoroughly examined for the production of these compounds. The catalyst was found to be reusable up to five times without and significant loss in activity. This demonstrates the sustainability and effectiveness of the catalyst in this reaction. This newly developed catalyst and procedure offer several advantages over previously published methods, including sustainability, mild reaction conditions, non-metal catalyst, cost-effectiveness, safety in handling, ease of purification, and high product yields. The catalyst shows promise for future studies in chemistry and material science.

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Conflicts of Interest

No conflicts of interests were reported by the authors

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