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FULL PAPER

Preparation and characterization of copper/polysulfonamide complex immobilized on geraphene oxide as a novel catalyst for the synthesis of pyrimido[1,2-a]benzimidazoles

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Copper–polysulfonamide complex immobilized on geraphene oxide as a novel heterogeneous catalyst (GO@PSA-Cu) was synthesized and the structure and morphology of catalyst were characterized with various analytical techniques such as Fourier-transform infrared spectroscopy, scanning electron microscopy, energy-dispersive X-ray, N_2 isotherms, elemental mapping, inductively coupled plasma–MS, and thermogravimetric analysis. The GO@PSA-Cu catalyst demonstrated good to excellent yields for the synthesis new derivatives of pyrimido[1,2-a]benzimidazoles via one-pot three-component condensation reaction of various aromatic aldehydes, 2-aminobenzimidazole, and ethyl acetoacetate in ethanol. The method presented herein has several prominent advantages such as cost-effectiveness, operational simplicity, short reaction times, high yields, and reusability of the catalyst even after six consecutive runs.

KEYWORDS

copper, geraphene oxide, heterogeneous, pyrimido[1,2-a]benzimidazoles, sulfonamide

1 | INTRODUCTION

Multiple component reactions (MCRs) can synthesize complex molecules in one pot with good atom economy, high selectivity, high yields, and providing a quick access to new organic molecules. MCRs offer remarkable advantages such as convergence; operational simplicity; and reduction in the number of workups, extraction and purification processes. In this sense, the synthesis of the compounds can be achieved with less waste, time, and cost without the isolation of intermediates. Recently, studies on MCRs have emphasized their significant applications in organic and medicinal chemistry. In MCRs, the required activation energy will be altered by the catalyst.[1,2] In this sense, it is worth mentioning that homogeneous catalysts show greater catalytic activity in comparison to the heterogeneous catalysts due to their molecular-level dispersions. It is worth noting that separation, purification, and reusability of homogeneous catalysts have been considered as time-consuming processes.[3] However, when considering heterogeneous catalysts, one can point to their easy separation and consecutive reusability, which are economical. Undesirably, the applicability of heterogeneous catalysts is hindered by the lack of catalytic activity and selectivity toward desired products.[4] In this regard, low cost, high catalytic activity, high stability, easy recovery, and excellent reusability are the most fundamental features for designing new catalysts. Accordingly, it is very significant to design a new catalyst with excellent catalytic activity—just like that of the homogeneous catalysts—and also with easy recyclability—like the heterogeneous ones.

During recent years, researchers have paid significant attention to the novel fabricated composite structures

which apply geraphene oxide (GO) and polymers. In this sense, GO supports as compared with other supports can be regarded as excellent candidates to design catalysts. The most significant advantages of the GO are as follows: they possess many active sites and pores; have high stability with good selectivity; contain abundant oxygen functional groups; and also, they are reusable, economic, and ecofriendly.

Researchers have paid great attention to the GO which can be applied to immobilize polymers.[5] Ligands having sulfonamide groups are excellent in the stabilization of metal species.[6] In this work, our goal has been to synthesize a novel geraphene oxide@polysulfonamide composite as a substrate for the stabilization of copper (GO@PSA-Cu). The van der Waals interaction between Cu and GO@PSA is very important in the stabilization of Cu species. The development of organic–inorganic nanocomposite with high loading and a good surface area can provide interesting applications as catalyst for the synthesis of heterocyclic compounds.

Of these heterocyclic compounds, pyrimido[1,2-a]benzimidazoles have attracted immense attention because of their valuable pharmacological properties and clinical applications.[7] The one-pot three-component condensation reaction between β-dicarbonyl compounds, aldehydes, and 2-amino-1*H*-benzimidazole is a well-known technique for the preparation of pyrimido[1,2-a]benzimidazoles. These methods employed diverse catalysts such as silica-supported sulfuric acid,[8] poly(vinylpyrrolidonium)perchlorate,[9] L-proline,[10] magnesium oxide,[11] and *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide (TBBDA).[12] Many of the recent reported protocols have interesting merits, but some suffer from one or more disadvantages such as harsh reaction conditions, tedious workup procedures, long reaction times, and emission of hazardous materials into environment. Therefore, there remains room to develop greener, milder, and simpler protocols based on application of retrievable catalysts or green solvents to avoid the emission of hazardous substances into environment and run the synthesis of pyrimido[1,2-a]benzimidazole ring systems efficiently.

In continuation of our interest in exploring catalytic methodologies,[13] we have synthesized Cu–PSA complex immobilized on GO and then investigated its performance as a novel acidic nanocatalyst for the synthesis of pyrimido[1,2-a]benzimidazoles. To the best of our knowledge, there are no reports on the use of Cu–PSA complex immobilized on GO as a catalyst for the synthesis of pyrimido[1,2-a]benzimidazoles via MCRs (Figure 1).

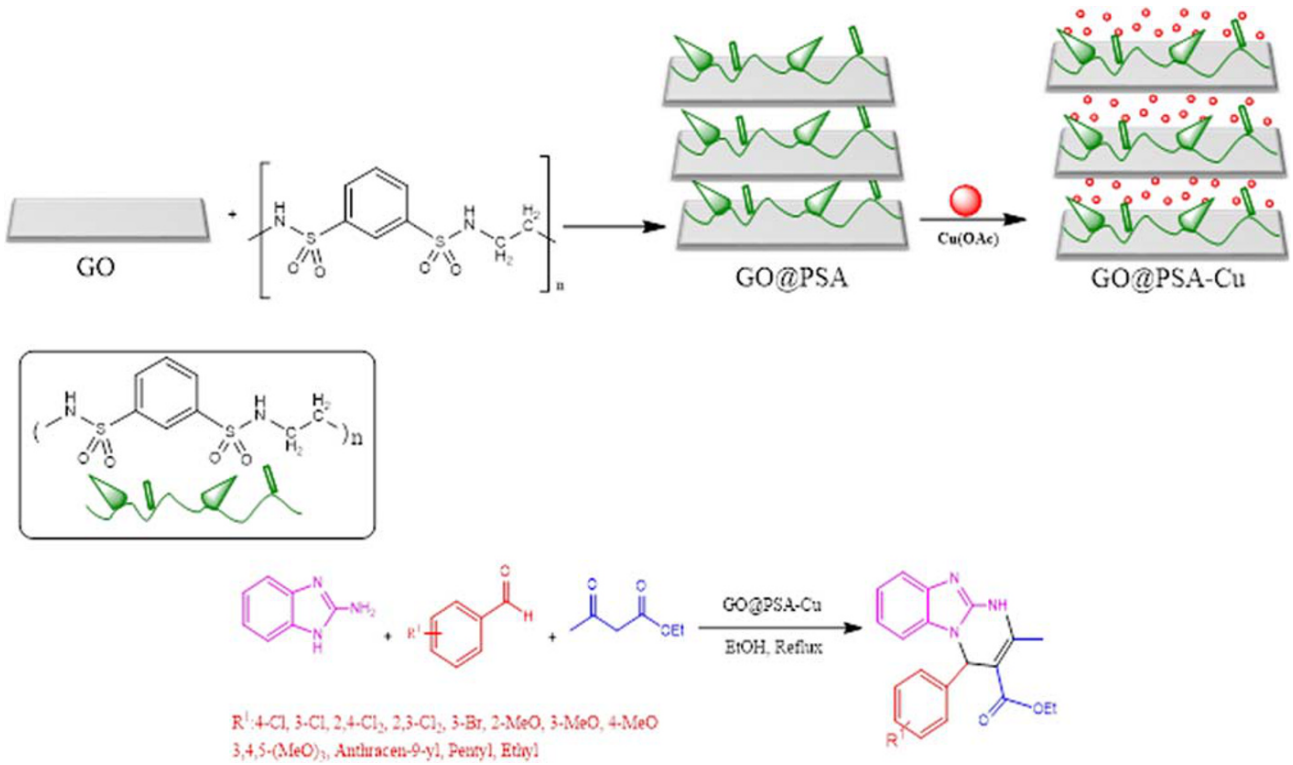


FIGURE 1 One-pot synthesis of pyrimido[1,2-a]benzimidazole derivatives in the presence of GO@PSA-Cu. GO, geraphene oxide; PSA, polysulfonamide

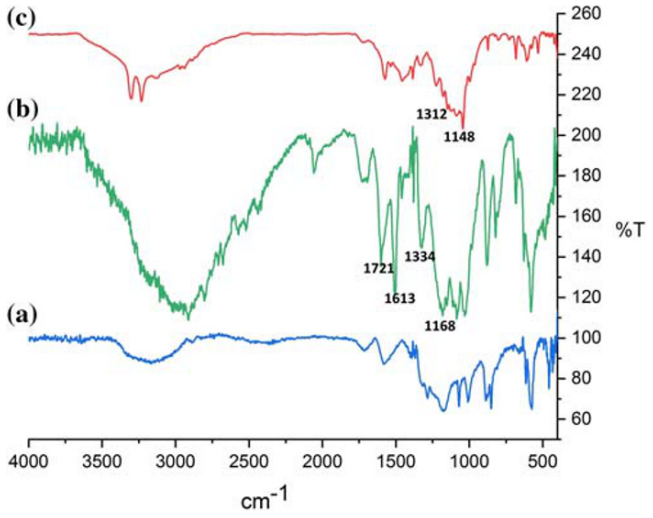


FIGURE 2 Fourier-transform infrared of (a) geraphene oxide (GO), (b) GO@PSA, (c) GO@PSA-Cu. GO, geraphene oxide; PSA, polysulfonamide

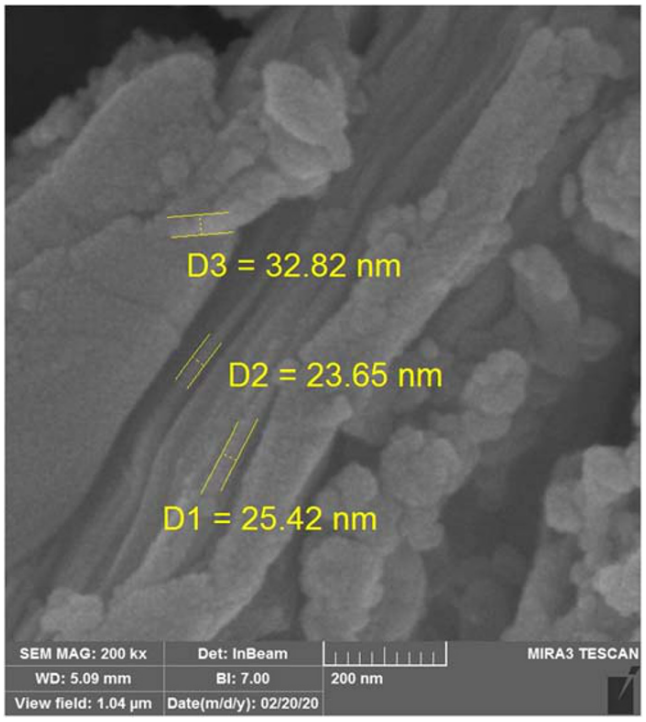


FIGURE 3 Field emission scanning electron microscopy image of the synthesized catalyst

2 | EXPERIMENTAL

2.1 | Materials and methods

All commercially available chemicals were obtained from Merck and FLUKA companies, and used without further purification otherwise stated. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on Bruker AVANCE spectrometers 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR using tetramethylsilane as an internal standard; chemical shifts were expressed in parts per million (ppm). Infrared (IR) spectroscopy was conducted on a Perkin Elmer GX Fourier-transform infrared (FT-IR) spectrometer. Mass spectra were recorded on a Shimadzu QP 1100 BX mass spectrometer. Melting points were determined on a Stuart Scientific SMP3 apparatus. Thermo-gravimetric analysis (TGA) was performed on a PYRIS Diamond instrument (London, UK). Energy-dispersive X-ray analysis of the prepared catalyst was performed on an field emission scanning electron microscopy (FESEM; SIGMA, Zeiss, Germany) instrument. Scanning electron microscopy (SEM) was performed on with China KYKY- EM3200 instrument operated at 30-kV accelerating voltage. Prior to the surface area analysis, the samples were activated in high vacuum at 80 °C for 12 h. Adsorption and desorption measurements were

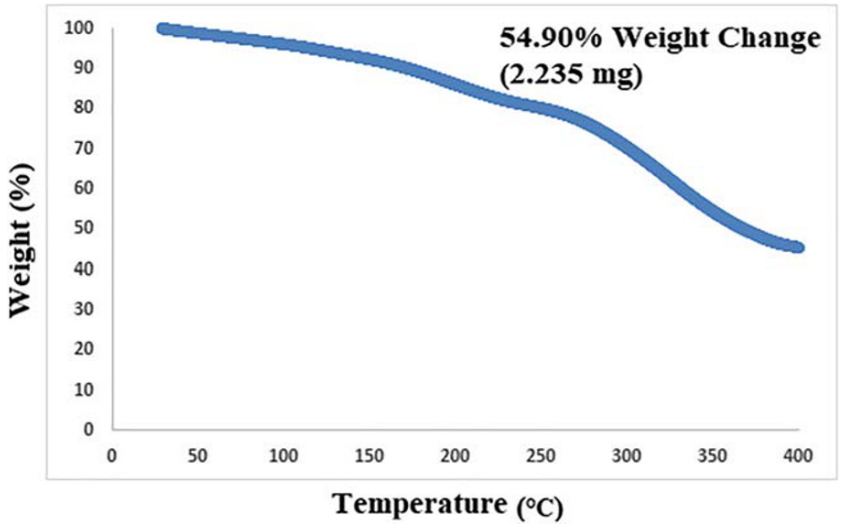


FIGURE 4 Thermogravimetric analysis curve of the synthesized GO@PSA-Cu nanocomposite. GO, geraphene oxide; PSA, polysulfonamide

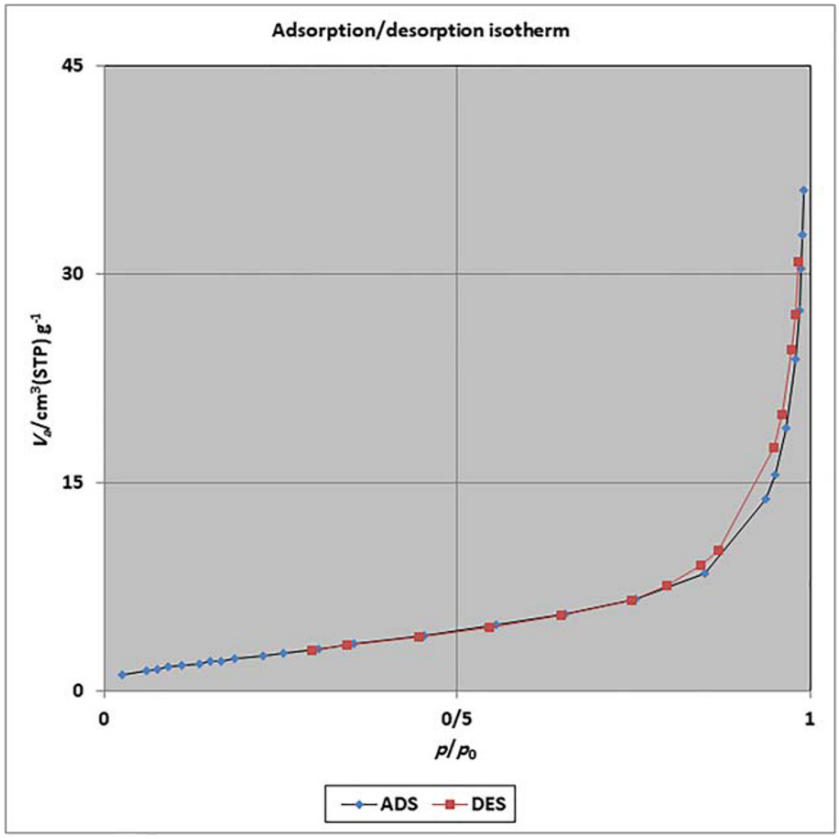


FIGURE 5 N_2 adsorption–desorption isotherms of GO@PSA-Cu. GO, geraphene oxide; PSA, polysulfonamide

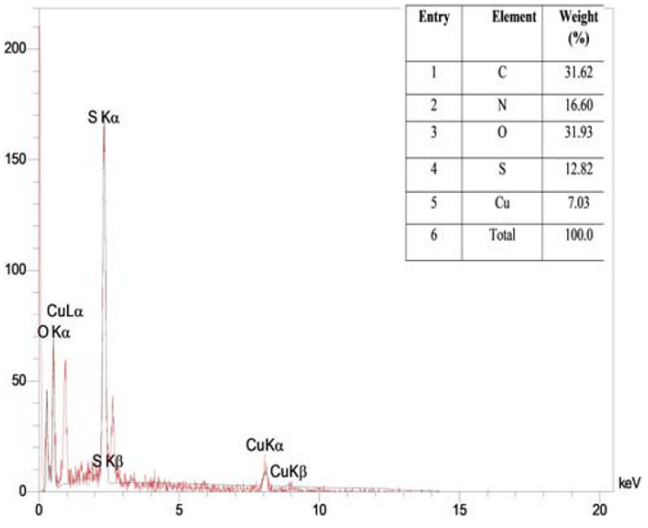
performed on a Micromeritics TriStar 3020 version 3.02 (N_2) system and measured at 77 K. The data were analyzed using the TriStar II 3020 version 1.03 software (Micromeritics, Norcross, GA, USA). Wavelength-dispersive X-ray spectroscopy (WDX) was performed using a TESCAN MIRA3.

2.2 | Synthesis of geraphene oxide@polysulfonamide-Cu (GO@PSA-Cu)

In this research, GO was prepared from graphite powder using a modified Hummer's method.[14] Then, 1 g of polybenzene-1,3-disulfonylamide and CH_3CN (20 mL) were slowly added to the GO (1 g) and magnetically stirred at 60 °C. After completion of the reaction, the obtained black GO@PSA were separated from the reaction medium by centrifusion, and then washed with CH_3CN three times. The obtained GO@PSA were dried for 120 min at 90 °C. To prepare the GO@PSA–Cu nanosheet, the obtained GO@PSA (1 g) was dispersed in 50 mL EtOH by sonication for 30 min, and then 0.5 g of $Cu(OAc)_2$ was added to the aforesaid mixture. A brown suspension was formed that was refluxed with vigorous stirring for 24 h. The catalyst (GO@PSA-Cu) was separated from the solution by centrifusion, washed with deionized water several times, and dried in an oven overnight.

2.3 | General procedure for the synthesis of pyrimido[1,2-a]benzimidazole using GO@PSA-Cu

To a 5-mL flask, various aldehydes (1.0 mmol), ethyl acetoacetate (1 mmol, 0.130 g), 1*H*-benzimidazole-2-amine (1 mmol, 0133 g), GO@PSA-Cu (0.05 g), and EtOH (2 mL) were added and the reaction was stirred



Entry	Element	Weight (%)
1	C	31.62
2	N	16.60
3	O	31.93
4	S	12.82
5	Cu	7.03
6	Total	100.0

FIGURE 6 Energy-dispersive X-ray spectrum of the GO@PSA-Cu nanocomposite. GO, geraphene oxide; PSA, polysulfonamide

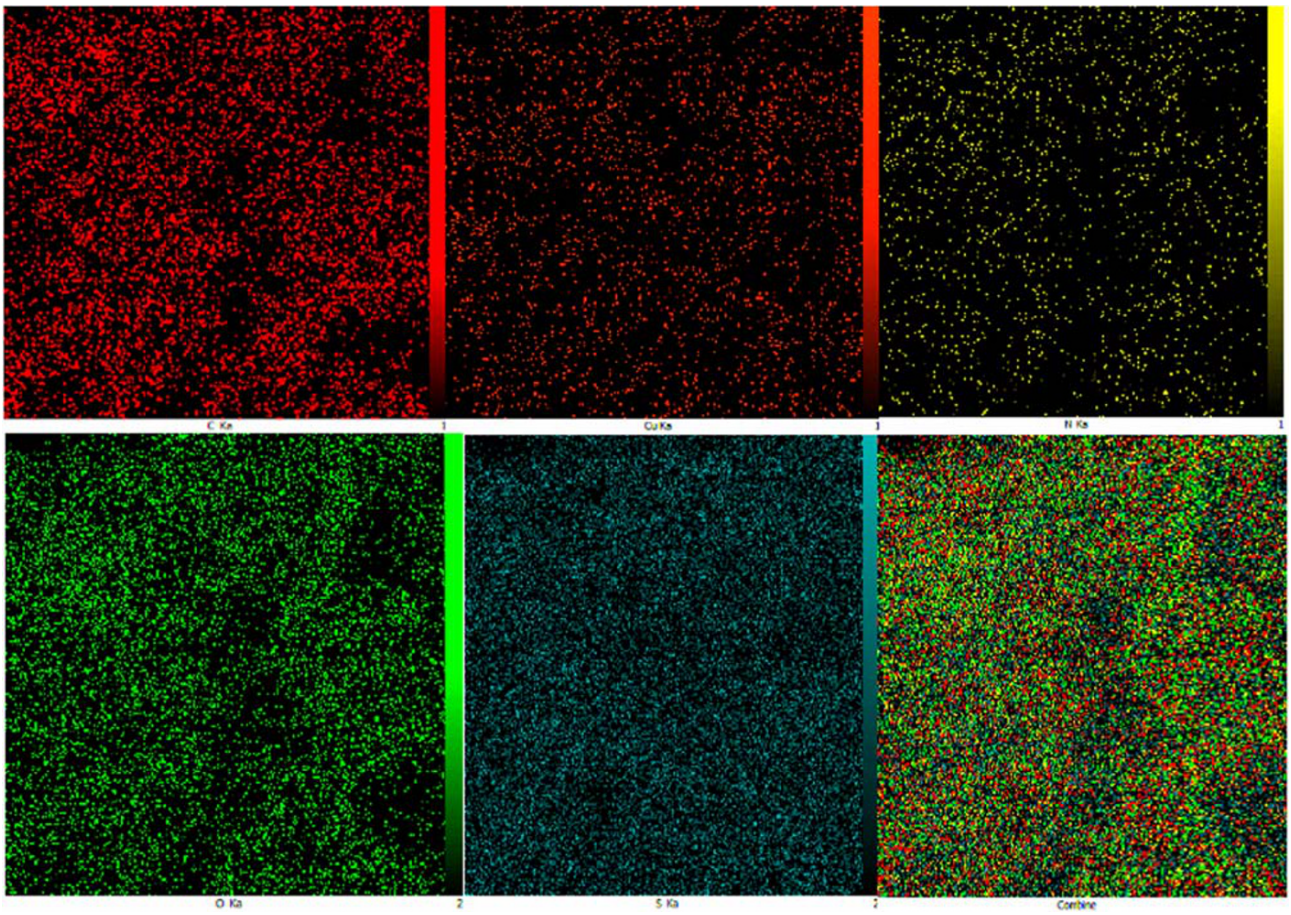


FIGURE 7 Elemental mapping of the GO@PSA-Cu nanocomposite. GO, geraphene oxide; PSA, polysulfonamide

for an appropriate reaction time under reflux condition. The progress of the reactions was monitored by thin-layer chromatography (*n*-hexan:EtOAc) (10:4). After completion of the reaction, the resulting mixture was filtered and the catalyst was separated from the product via centrifusion. The catalyst was washed with hot distilled H_2O (5 mL) and EtOH (3 mL) two times. The crude products were collected and recrystallized from EtOH if necessary.

Ethyl 4-(3-bromophenyl)-1,4-dihydro-2-methylpyrimido [1,2-a]benzimidazole-3-carboxylate (**4e**): melting point: 289–291 °C.[12] Light solid. IR (KBr): 3237, 1697, 1656, 1619, 1572, 1262, 1091, 731. ^{1}H-NMR (400 MHz): 1.17 (t, J = 7.2 Hz, Me); 2.47 (s, CH_3); 4.05 (q, J = 7.2 Hz, CH_2); 6.47 (s, CH); 6.98–7.62 (m, 8 ArH); 10.76 (s, NH). ^{13}C-NMR (100 MHz): 14.5; 19.1; 55.7; 59.9; 97.7; 110.3; 117.3; 120.8; 121.9; 122.4; 126.5; 130.4; 131.1; 131.2; 131.8; 142.7; 145.1; 145.8; 147.5; 165.4. Anal. Calc: C 58.26, H 4.40, N 10.19; found: C 57.80, H 4.08, N 10.02. All products were characterized on the basis of their spectroscopic data including ^{1}H NMR, ^{13}C NMR, and CHN that are given in the supporting information (Figures S1-S30).

3 | RESULTS AND DISCUSSIONS

Cu–PSA complex supported on GO was prepared in three steps. At first, GO was synthesized using a modified Hummer's method.[14] Next, polybenzene-1,3-disulfonylamide was synthesized based on our previous work.[15] The method is based on the modification of GO by the chemical and physical interaction of polybenzene-1,3-disulfonylamide with surface functional groups on the GO. Finally, the GO@PSA was coordinated with $Cu(OAc)_2$ to generate Cu–PSA complex supported on GO. The synthesis steps of GO@PSA-Cu are depicted in Figure 1. The GO@PSA-Cu was characterized by various techniques such as FT-IR, TGA, FESEM, WDX, EDS, and N_2 adsorption–desorption. The FT-IR spectra of GO, GO@PSA, and GO@PSA-Cu are illustrated in Figure 2a–c. Wave numbers of the C–O–C bonds appear at 1047 cm^{-1}. The adsorption bands at 1613 and 1721 cm^{-1} were attributed to the C=C and C=O groups and the band at 3383 cm^{-1} corresponded to the broad OH groups on the surface of GO. In addition, in the FT-IR spectrum of GO, an adsorption band appears at 1047 cm^{-1} that is assigned to the C–O–C groups (Figure 2a). After grafting PSA, the peaks at

TABLE 1 Optimizing the reaction conditions for the synthesis of **4a** using GO@PSA-Cu as the catalyst[a]

Entry	Catalyst loading (g)	Conditions	Time (min)	Yield[b] (%)
1	0.05	EtOH (reflux)	10	95
2	0.05	CH_3CN (reflux)	10	88
3	0.05	CH_3Cl (reflux)	10	78
4	0.05	Toluene (reflux)	10	68
5	0.05	H_2O (reflux)	10	45
6	0.05	Solvent free (100 °C)	10	50
7	0.05	Solvent free (80 °C)	10	45
8	0.05	EtOH (room temperature)	30	55
9	0.01	EtOH (reflux)	10	61
10	0.03	EtOH (reflux)	10	81
11	0.07	EtOH (reflux)	10	95
12	0.05	EtOH (reflux)[c]	10	30

[a]Reaction condition: *p*-chlorobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), 1*H*-benzimidazole-2-amine (1 mmol), GO@PSA-Cu (0. 05 g), and EtOH (2 mL) were stirred under reflux condition.
[b]Isolated yield.
[c]*p*-Chlorobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), 1*H*-benzimidazole-2-amine (1 mmol), GO@PSA (0.05 g), and EtOH (2 mL) was stirred under reflux condition.

1168 and 1334 cm^{-1} can be assigned to the S=O stretching vibrations (Figure 2b). In addition, when copper coordinates with PSA, the S=O bonds shift to lower wave numbers (1148 and 1312 cm^{-1}; Figure 2b vs 2c).

Morphological characterizations of GO@PSA-Cu were investigated with the FESEM technique. FESEM images show that the particles are corrugated sheets with an average diameter of about 33–40 nm (Figure 3).

The thermal behavior of GO@PSA-Cu was studied by TGA with a heating rate of 10 °C min^{-1} within a temperature range of 0–400 °C (Figure 4). The composition ratio of the catalyst can be calculated from the residual mass percentage. As shown in Figure 4, the first weight loss stage at almost 100 °C was assigned to the evaporation of adsorbed water molecules. The second weight loss at 250–400 °C can be attributed to the removal of functional groups on the grafted polymer. According to the obtained results, PSA-Cu is well connected to the GO nanoparticles.

The Brunauer–Emmett–Teller (BET) surface areas were determined by N_2 adsorption (Figure 5). The surface areas for GO@PSA-Cu were found to be 50 m^2/g. Furthermore, according to Barrett–Joyner–Halenda (BJH) analysis, pore volume and pore diameter were 0.05 cm^3/g and 20.80 nm, respectively.

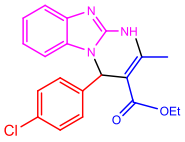
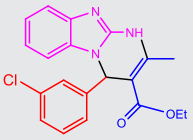
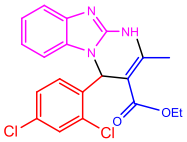
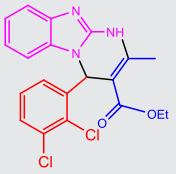
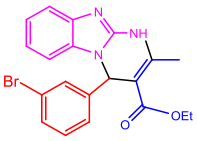
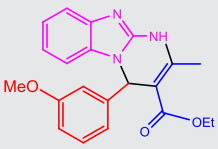
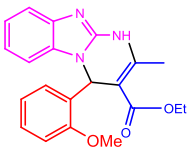
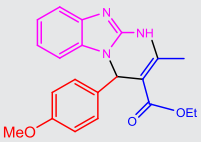
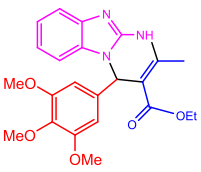
The EDS analysis of the synthesized catalyst is shown in Figure 6. As can be seen, the structure of the catalyst GO@PSA-Cu is composed of the expected elements, including oxygen, sulfur, nitrogen, carbon, and copper, which indicates that Cu has been correctly grafted to GO@PSA. Elemental mapping analysis suggested the homogeneous distribution of all elements (Figure 7). The concentration of copper in GO@PSA-Cu (8.17 wt%) was determined by inductively coupled plasma–optical emission spectrometry.

3.1 | Catalytic activity

We next investigated the catalytic effect of GO@PSA-Cu nanocomposite on the synthesis of ethyl 4-(4-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate **4a** as a model compound (Table 1). First, the reaction was carried out by refluxing the reaction mixture in different solvents such as EtOH, H_2O, $CHCl_3$, CH_3CN, and toluene (Table 1, Entries 1–5); under solvent-free conditions (Table 1, Entries 6 and 7), and at room temperature (Table 1, Entry 8). The experimental results in Table 1 revealed that refluxing in EtOH presented the optimum values of reaction variables (Table 1, Entry 1), whereas using H_2O, $CHCl_3$, CH_3CN, and toluene as solvent resulted in reduced yields. A study of the catalyst content (Table 1, Entries 9–11) showed that 50 mg of catalyst is the optimal value for this reaction (Table 1, Entry 1); importantly, catalyst content less than 50 mg resulted in a low reaction yield (Table 1, Entries 9 and 10), and the yield of the product did not increase by increasing the catalyst content to more than 50 mg (Table 1, Entry 11). Further increasing the temperature to 100 °C did not have a significant effect on the yield (Entry 6). We also observed that the product yield was decreased in the presence of GO@PSA in comparison with GO@PSA-Cu (Table 1, Entry 12).

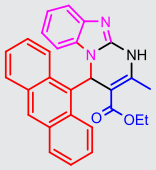
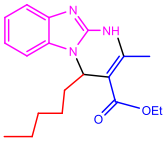
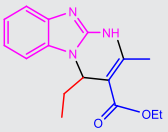
These results motivated us to examine the generality of this approach for different aromatic aldehydes and anilines under optimized conditions. According to Table 2, a broad substrate scope is observed for both electron-donating and electron-withdrawing substituents and aliphatic aldehydes. Different types of aldehydes such as *p*-Cl, *m*-Br, *m*-methoxy, *o*-methoxy, *m*-Cl, *p*-methoxy, 2,4-Cl_2, 2,3-Cl_2, 3,4,5-$(MeO)_3$, anthracen-9-yl, or aliphatic groups such as hexanaldehyde and propanaldehyde were used to synthesize diverse structurally functionalized pyrimido[1,2-a]benzimidazole derivatives. These results indicate that different types of aldehydes efficiently participated in the studied reactions, which lead to the

TABLE 2 Synthesis of pyrimido[1,2-a]benzimidazoles using GO@PSA-Cu as catalyst[a]

Compound	Product	Time (min)	Yield (%)[b]	MP (°C)
4a		10	95	302–303[12]
4b		10	92	250–252[12]
4c		12	95	300–302[12]
4d		12	90	289–290[12]
4e		20	95	266–268[12]
4f		30	91	211–212[12]
4g		30	90	265–269[12]
4h		25	93	223–225[12]
4i		35	90	198–199[12]

(Continues)

TABLE 2 (Continued)

Compound	Product	Time (min)	Yield (%)[b]	MP (°C)
4j		45	90	295–298[12]
4k		60	91	157–158[12]
4l		60	93	180–182[12]

[a]Reaction condition: benzaldehyde derivatives (1 mmol), ethyl acetoacetate (1 mmol), 1*H*-benzimidazole-2-amine (1 mmol), GO@PSA-Cu (0.05 g), and EtOH (2 mL) were stirred under reflux condition.
[b]Isolated yield.

formation of desired products at acceptable times with good to excellent yields. In addition, the nature and electronic properties of the substituents had negligible effect on the velocity and reaction yields. All products were fully characterized on the basis of their SPECTRONIC data including FT-IR, ^{1}H NMR, ^{13}C NMR, and CHN.

In the next step, the reusability of GO@PSA-Cu was also evaluated in the synthesis of **4a** under the optimized reaction conditions. For this purpose, after the completion of the reaction, the mixture was filtered off. Then the solvent was removed under vacuum up to 70 °C and the obtained catalyst was washed with ethanol for better purification and dried. These results show that, even after six sequential runs, the catalytic activity of the catalyst remained approximately unchanged in the preparation of **4a** (95%, 95%, 93%, 91%, 89%, 88%; Figure 8).

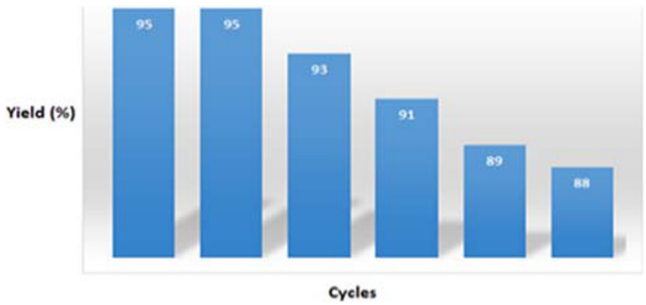


FIGURE 8 Recyclability of the GO@PSA-Cu nanocomposite. GO, geraphene oxide; PSA, polysulfonamide

The filtration test for the reaction between 3-methoxybenzaldehyde, ethyl acetoacetate, and 1*H*-benzimidazole-2-amine using GO@PSA-Cu as a catalyst was performed to investigate the leaching of copper during the reaction. A catalytic run was started as for a standard reaction, and after 15 min (the reaction was completed in 30 min), corresponding to 50% conversion, the mixing of reaction mixtures was stopped and the contents were centrifuged to obtain afford a clear filtrate. Then, the mixture without the solid catalyst was subjected to a standard catalytic run for another 15 min, but no significant conversion occurred. The results

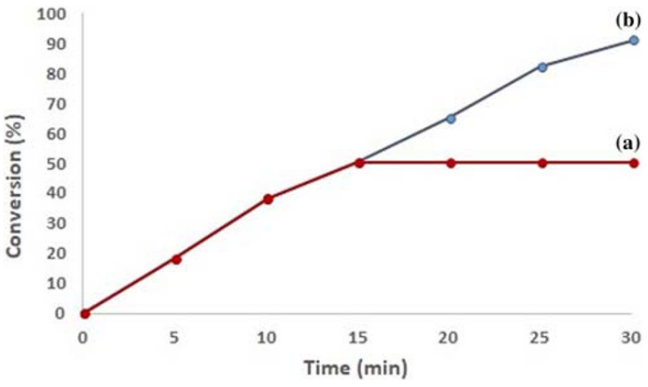
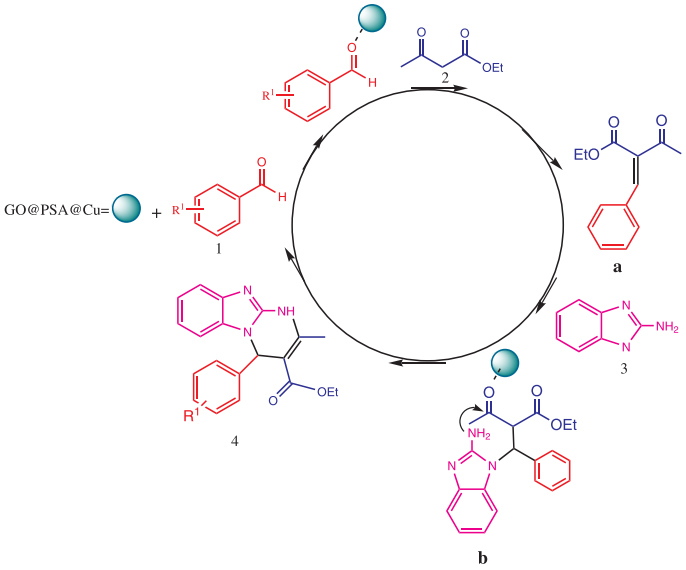


FIGURE 9 Reaction between 3-methoxybenzaldehyde, ethyl acetoacetate and 1*H*-benzimidazole-2-amine over GO@PSA-Cu: (a) Hot filtration test; (b) normal reaction. GO, geraphene oxide; PSA, polysulfonamide



SCHEME 1 One-pot synthesis of pyrimido[1,2-a]benzimidazole derivatives in the presence of GO@PSA-Cu

TABLE 3 Comparison of the present methodology with other reported catalysts for the synthesis of ethyl 4-(4-methoxyphenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate (4 h)

Entry	Catalyst	Condition	Time	Yield (%)	Reference
1	GO@PSA-Cu (3.5 mol%)	EtOH, reflux	25 min	93	This work
2	1,1,3,3-*N,N,N′,N′*-tetramethylguanidinium trifluoroacetate (30 mol%)	100 °C	5 h	67	[16]
3	L-Proline (20 mol%)	H_2O, reflux	2.5 h	88	[10]
4	Thiamine hydrochloride (5 mol%)	H_2O, reflux	3 h	85	[17]
5	α-Zirconium sulfophenylphosphonate (12 mol%)	90 °C	20 h	73	[18]

GO, geraphene oxide; PSA, polysulfonamide.

were compared with those of a standard catalytic run. Figure 9 clearly shows that after the removal of the heterogeneous catalyst, slow progression of the reaction occurred. This indicates that the prepared catalyst is stable and the leaching of copper species from the solid support is low.

The proposed mechanism of this reaction is shown in Scheme 1. According to this mechanism, at first, the carbonyl group of aldehyde 1 is activated with the copper species of the catalyst to make intermediate **a**. The Michael addition of **3** to the Knoevenagel product followed by cyclization and tautomerization generated the corresponding product.[12]

The efficiency of GO@PSA-Cu for the synthesis of 4-(4-methoxyphenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate (4 h) was compared with some other related reports (Table 3). In this work, using GO@PSA-Cu as a recyclable catalyst remarkably enhanced the product yield and shortened the reaction time.

4 | CONCLUSIONS

In conclusion, a novel and efficient complex (GO@PSA-Cu) has been developed as a highly active and recoverable heterogeneous catalyst for the synthesis of pyrimido[1,2-a]benzimidazoles via a multicomponent reaction of various benzaldehydes, ethyl acetoacetates, and 1*H*-benzimidazoles. The method offered several advantages, including excellent yields, recyclability of the catalyst, short reaction times, easy purification, and simple procedure.

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Shekarlab. N, Ghorbani-Vaghei. R, Alavinia. S, Preparation and characterization of copper/polysulfonamide complex immobilized on geraphene oxide as a novel

catalyst for the synthesis of pyrimido[1,2-a]benzimidazoles. Appl Organometal Chem. 2020, AOC-20-0608.

CONFLICTS OF INTEREST

The authors have no conflict of interest to declare.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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