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ARTICLE

A novel ternary GO@SiO$_2$-HPW nanocomposite as an efficient heterogeneous catalyst for the synthesis of benzazoles in aqueous media

Setareh Habibzadeh[1] | Ghasem Firouzzadeh Pasha[2] | Mahmood Tajbakhsh[2] |
Nasim Amiri Andi[1] | Ehsan Alaee[3]

[1]Department of Chemistry, Babol Noshirvani University of Technology, Babol, Iran
[2]Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
[3]Neonatal and Children's Health Research Center, Golestan University of Medical Sciences, Gorgan, Iran

Correspondence
Setareh Habibzadeh, Department of Chemistry, Babol Noshirvani University of Technology, Babol 47148-71167, Iran.
Email: habibzadeh@nit.ac.ir

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Babol Noshirvani University of Technology, Babol, Iran

A new solid acid catalyst, consisting of 12-phosphotungstic heteropoly acid (HPW) supported on graphene oxide/silica nanocomposite (GO@SiO$_2$), has been developed via immobilizing HPW onto an amine-functionalized GO/SiO$_2$ surface through coordination interaction (GO@SiO$_2$-HPW). The GO@SiO$_2$-HPW nanocomposite was characterized by Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and powder X-ray diffraction (XRD). The prepared nanocomposite could be dispersed homogeneously in water and further used as a heterogeneous, reusable, and efficient catalyst for the synthesis of benzimidazoles and benzothiazoles by the reaction of 1,2-phenelynediamine or 2-aminothiophenol with different aldehydes.

KEYWORDS
benzimidazole, benzothiozole, graphene oxide, heterogeneous catalyst, heteropoly acid

1 | INTRODUCTION

Benzazoles such as benzimidazoles and benzothiazoles are considered an important class of heterocyclic compounds possessing interesting biological and pharmacological properties such as antifungal,[1] antioxidant,[2] anti-inflammatory,[3] antibacterial,[4] antiviral[5] and anticancer activity.[6] Up to now, several methods have been employed for the synthesis of these heterocyclic moieties. The conventional synthetic method for the preparation of benzimidazoles or benzothiazoles is based on the condensation of *o*-substituted aminoaromatics with carboxylic acids or their derivatives (nitriles, amidates, orthoesters) in the presence of a strong acid as catalyst. However, the most attractive method for the synthesis of benzimidazoles is the reaction of 1,2-phenelynediamine with aldehydes.[7] Similarly, benzothiazoles are also synthesized by reacting 2-aminothiophenol with aldehydes.

The recently reported methods mostly employed homogeneous catalysts that require special work-up and separation techniques for the recovery and recycling from the reaction environment. Some other catalysts such as mesoporous titania-iron(III) oxide,[8] CuO/silica,[9] β-cyclodextrin,[10] Pt-TiO$_2$,[11] α-MoO$_3$ nanobelts,[12] Fe$_3$O$_4$/SiO$_2$/(CH$_2$)$_3$N$^+$Me$_3$Br$^-{}_3$ core–shell nanoparticles,[13] and Fe$_3$O$_4$-SiO$_2$-(NH$_4$)$_6$Mo$_7$O$_{24}$ magnetic core–shell nanocomposite[14] were also used in alleviating some of the limitations. Most of these methods suffer from some drawbacks, such as the use of highly toxic or expensive reagent, long reaction times, tedious work-up procedures, low yields of products, and, in some cases, harsh reaction conditions. In view of these drawbacks, the development of an efficient and convenient method for the synthesis of benzazoles would be valuable.

Heteropoly acids (HPAs), especially 12-phosphotungstic heteropoly acid (HPW), have attracted extensive interest in the last decade as a solid acid catalyst. The main disadvantage of HPAs as catalysts is their low specific surface area (1–10 m^2/g), which hinders accessibility of the reactants to the acidic sites. Consequently, it becomes necessary to disperse HPAs on supports that possess large surface area. HPAs have been reported to catalyze the reaction of aldehydes with *o*-substituted aminoaromatics[15–17] Rafiee and co-workers compared the catalytic activity of a supported HPA (γ-Fe_2O_3@SiO_2-PW) catalyst and several other catalysts for this reaction and found that supported HPA is more active than others, substantially due to its stronger acidity.[18]

In recent years, graphene oxide (GO), also termed as "carbocatalyst," has been widely used as a support for heterogeneous nanocatalysts due to its intrinsic properties such as the large surface area, abundant functional sites, high chemical stability, low toxicity, and facile hybridization with other functional nanomaterials.[19] Nanocomposites of GO and nonmetallic oxide particles (such as GO/SiO_2) have superior properties compared to GO and nonmetallic oxide particles, which is attributed to the synergistic effect of the pristine materials.

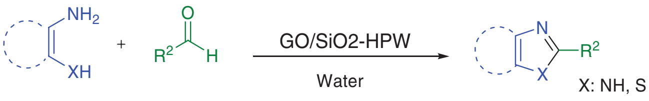
As far as we know, in spite of the development of GO/SiO_2-supported catalysts, GO/SiO_2-supported HPW nanocomposite (GO@SiO_2-HPW) has still not been reported. In this paper, we report a simple, green, and efficient method for the synthesis of benzimidazoles and benzothiazoles using GO@SiO_2-HPW in water (Scheme 1).

2 | EXPERIMENTAL

2.1 | Materials and methods

All reagents and solvents were purchased from Merck, Fluka, and Aldrich chemical companies and used without further purification. Double-distilled, deionized (DI) water was used throughout the studies.

Fourier transform infrared (FT-IR) spectra were recorded on a Broker Vector spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a TGA (model 951, Dupont) apparatus at the heating rate of 10°C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) pattern was recorded using Cu Kα radiation source on a Philips PW 1830 diffractometer. Scanning electron microscopy (SEM) studies were performed using a Vega Tescan-XMU microscope. The progress of reactions were checked by thin-layer chromatography (TLC) on precoated plates (Merck silica gel 60, F254) using UV light as a visualizing agent. Melting points of the products were determined on an Electrothermal model 9100 apparatus using open glass capillary: the reported values are uncorrected. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance spectrometer at 400.13 and 100.61 MHz, respectively, with TMS as internal standard.



SCHEME 1 One-pot synthesis of benzazoles catalyzed by GO/SiO_2-HPW in water

2.2 | Catalyst preparation

2.2.1 | Preparation of GO

GO was prepared from natural graphite by using a modified Hummers' method.[20] Typically, 1.0 g of graphite was added to a mixture of concentrated H_2SO_4 (125 mL) and H_3PO_4 (15 mL) and stirred for 12 hr at room temperature. Subsequently, 3.0 g of $KMnO_4$ was added, and the obtained mixture was oxidized for 3 hr. Then, 200 mL of DI water and 6 mL H_2O_2 (30%) were added slowly to the reaction mixture and stirred for 30 min at 5°C. Finally, the GO was collected by centrifugation at 8,000 rpm for 10 min and washed twice with 25 mL of 10% HCl and twice with 25 mL DI water.

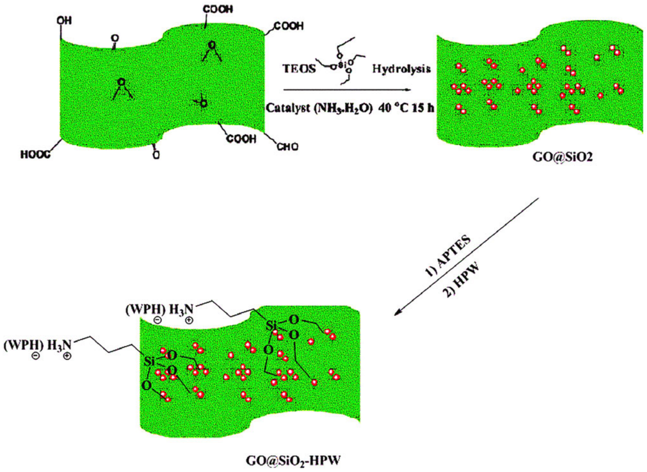


FIGURE 1 Schematic diagram of the preparation of GO@SiO_2-HPW

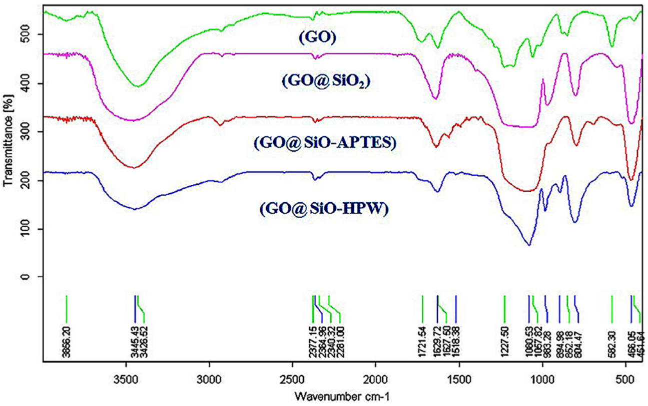


FIGURE 2 FT-IR of spectra of GO, GO@SiO_2, GO@SiO_2-APTES, and fresh GO@SiO_2-HPW catalyst

2.2.2 | Preparation of GO@SiO_2

A mixture of GO (0.5 g), tetraethylorthosilicate (TEOS, 7 mL), and ammonium hydroxide (1 mL) in ethanol (40 mL) was stirred at room temperature. After 15 hr, the obtained solid mixture was filtered and washed with DI water (2 × 5 mL) and ethanol (2 × 5 mL) alternately and dried at 60°C for 12 hr to give GO@SiO_2.

2.2.3 | Preparation of GO@SiO_2-HPW

GO@SiO_2 (1.5 g) and 3-aminopropyl triethoxy silane (APTES; 6 mL) were stirred in 10 mL of an aqueous ethanol solution (80% ethanol +20% DI water, by volume) at 80 °C for 24 hr. The resultant mixture was filtered and washed with ethanol (4 × 5 mL) and dried at 60°C for 12 hr to obtain GO@SiO_2-APTES. In the next step, 0.5 g of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) was dissolved in 25 mL of DI water, and then 1.0 g of GO@SiO_2-APTES was added to the solution with vigorous stirring under ambient temperature for 12 hr. The final GO@SiO_2-HPW product was obtained by similar steps of filtering, washing, and drying. A schematic diagram of the synthesis approach for the preparation of GO@SiO_2-HPW is shown in Figure 1.

2.3 | General procedure for the synthesis benzazoles

A mixture of aldehyde (1 mmol), amine (1 mmol), and GO@SiO_2-HPW (0.01 g) as a catalyst in a 25-mL round-bottom flask equipped with a condenser was stirred at 100 °C for an appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethanol and subsequently centrifuged to get the catalyst. Evaporation of the solvent of the filtrate under reduced pressure gave the crude product. The pure product was obtained by recrystallization in ethanol. All products were characterized by spectroscopy (^1H NMR and ^{13}C NMR spectra) and melting points.

Spectral data for the selected compounds:

2-(4-Chlorophenyl)-1H-benzimidazole (Table 2, entry 1)

White solid, m.p. = 290–292°C; ^1H NMR (400 MHz, DMSO-d_6): δ_H 13.1 (br, 1H, NH), 8.19 (d, $J = 8.8$ Hz, 2H), 7.61–7.64 (m, 4H, Ar), 7.19–7.24 (m, 2H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 150.6, 135.0, 129.5, 129.5, 128.6, 122.8.

4-(1H-Benzimidazol-2-yl)benzonitrile (Table 2, entry 4)

White solid, m.p. = 260–262°C; ^1H NMR (400 MHz, DMSO-d_6): δ_H 13.2 (s, 1H, NH), 8.34 (dd, $^3J = 6.8$ Hz, $^4J = 1.6$ Hz, 2H), 8.03 (dd, $^3J = 6.8$ Hz, $^4J = 1.6$ Hz, 2H), 7.72 (d, $J = 8$ Hz, 1H), 7.58 (d, $J = 8$ Hz, 1H), 7.22–7.30 (m, 2H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 133.5, 127.4, 123.9, 122.7, 119.8, 119.1, 112.3, 112.2, 112.1.

2-Phenyl-1,3-benzothiazole (Table 4, entry 1)

White solid, m.p. = 112–114°C; ^1H NMR (400 MHz, DMSO-d_6): δ_H 8.24–8.25 (m, 1H, Ar), 8.16–8.18 (m, 1H, Ar), 8.05–8.10 (m, 2H, Ar), 7.77–7.79 (m, 1H, Ar), 7.47–7.59 (m, 4H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 165.9, 153.8, 135.4, 135.1, 134.5, 132.1, 129.6, 127.3, 126.9, 126.4, 123.6, 123.0, 122.9.

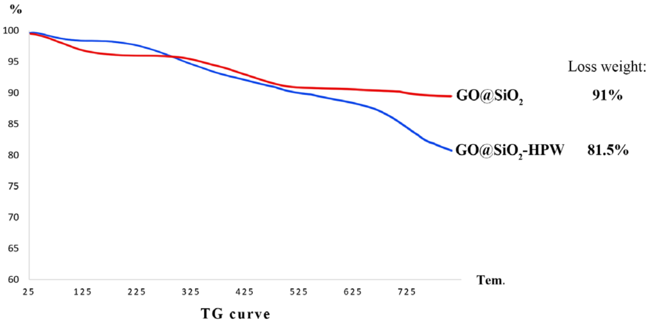


FIGURE 3 TGA curves of GO@SiO_2 and GO@SiO_2-HPW

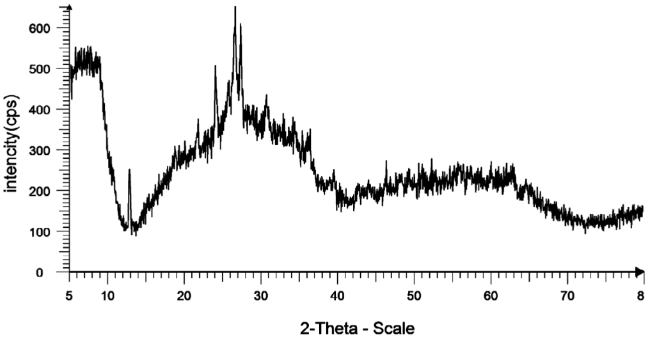


FIGURE 4 XRD pattern of GO@SiO_2-HPW

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

FT-IR spectra of GO, GO@SiO_2, GO@SiO_2-APTES, and fresh GO@SiO_2-HPW catalyst are compared in Figure 2. The bare GO gave five intense peaks at 3,422, 1,721, 1,627, 1,227, and 1,057 cm^{-1}, corresponding to the stretching vibrations of the O–H, C=O, C=C, C–OH, and C–O groups

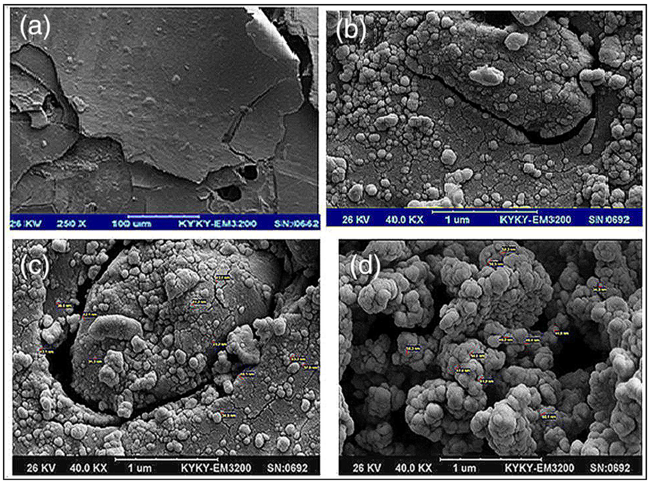
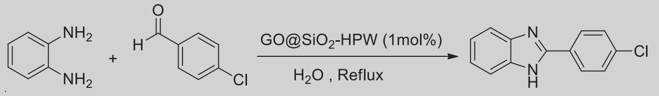


FIGURE 5 SEM images of (a) GO, (b) GO@SiO_2, (c) fresh GO@SiO_2-HPW, and (d) used GO@SiO_2-HPW catalysts

TABLE 1 Optimization of the reaction conditions



Entry	Amount of catalyst (Mol %)	Solvent	Time (min)	Temp. (°C)	Yield (%)[a]
1	1	Toluene	90	Reflux	75
2	1	Acetonitrile	90	Reflux	65
3	1	DMF	90	Reflux	92
4	1	Ethanol	90	Reflux	80
5	1	Ethanol/water (1:1 v/v)	90	Reflux	88
6	1	No solvent	90	Reflux	60
7	1	Water	90	Reflux	96
8	0.5	Water	90	Reflux	80
9	2	Water	85	Reflux	96
10	3	Water	90	Reflux	90

[a] Isolated yields.

TABLE 2 Synthesis of benzimidazoles using GO@SiO_2-HPW in water[a]

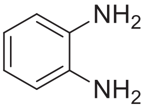
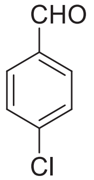
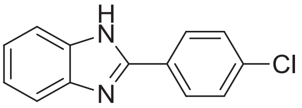
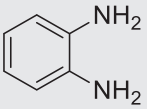
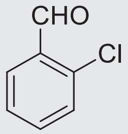
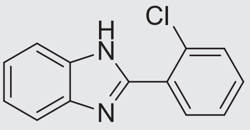
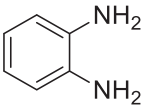
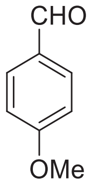
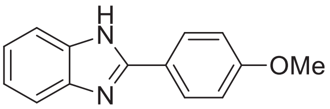
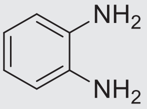
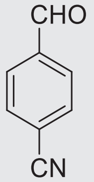
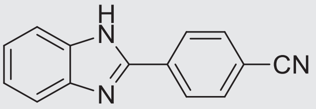
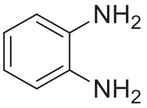
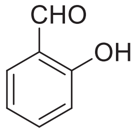
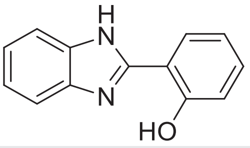
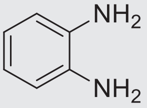
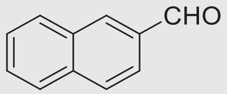
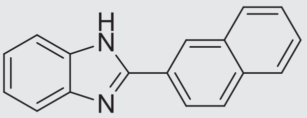
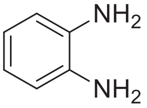
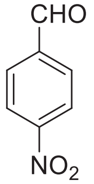
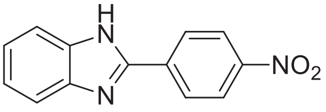
Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)[b] [ref.]
1				90	96 [24]
2				90	90 [25]
3				120	85 [26]
4				70	96 [26]
5				120	87 [27]
6				110	94 [24]
7				70	95 [25]

TABLE 2 (Continued)

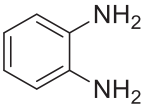
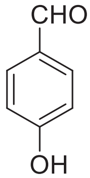
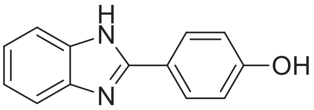
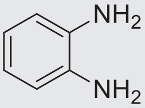
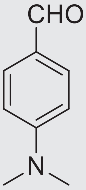
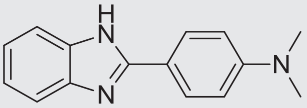
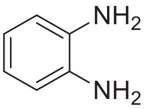
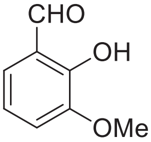
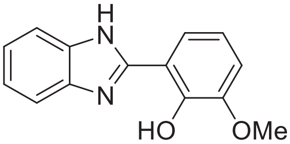
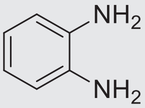
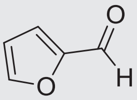
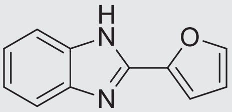
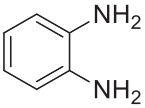
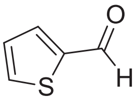
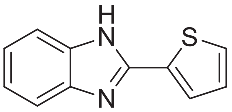
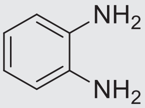
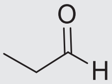
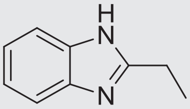
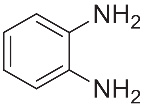
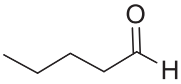
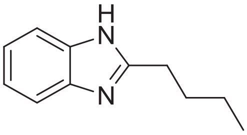
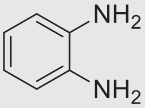
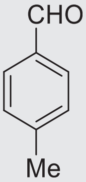
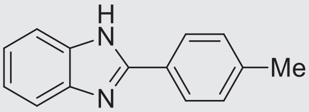
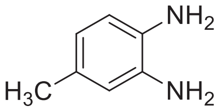
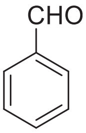
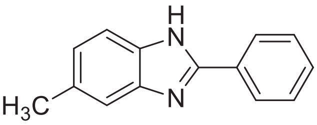
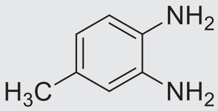
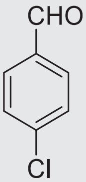
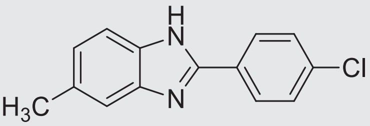
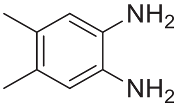
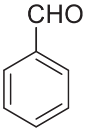
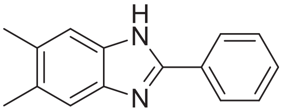
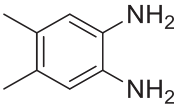
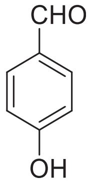
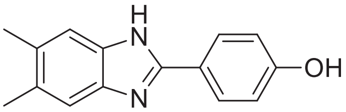
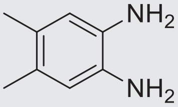
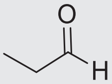
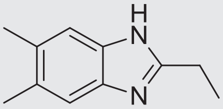
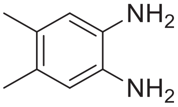
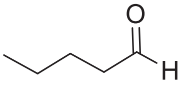
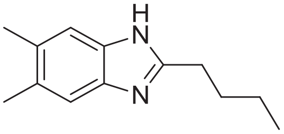
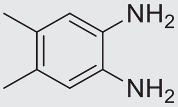
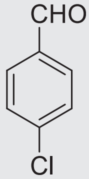
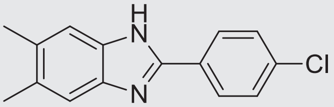
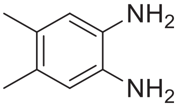
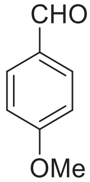
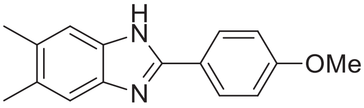
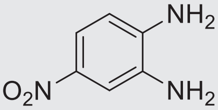
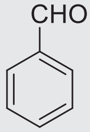
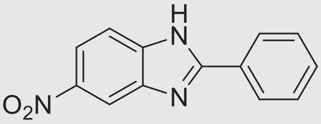
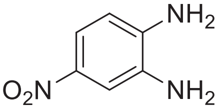
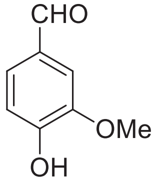
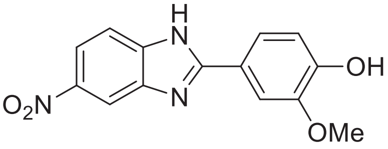
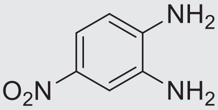
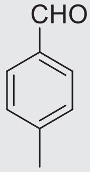
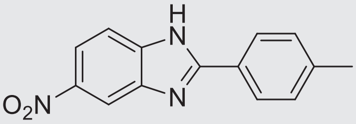
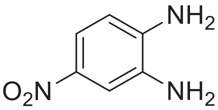
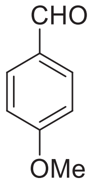
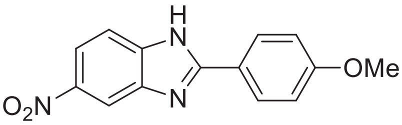
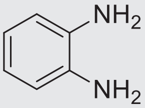
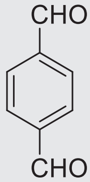
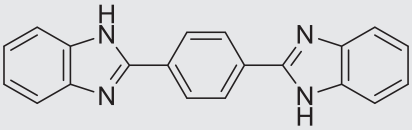
Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)[b] [ref.]
8				95	85 [25]
9				130	80 [28]
10				100	85 [25]
11				130	80 [29]
12				160	70 [30]
13				150	85 [31]
14				150	82 [31]
15				80	95 [25]
16				90	92 [32]
17				80	95 [33]
18				120	87 [32]

TABLE 2 (Continued)

Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)^b [ref.]
19				130	85 [34]
20				150	88 [31]
21				150	84 [31]
22				110	90 [32]
23				110	88 [32]
24				160	70 [34]
25				180	44 [30]
26				160	65 [34]
27				160	50 [34]
28^c				100	85 [35]

[a] *Reaction conditions*: 1,2-phenylenediamine (1 mmol), aldehyde (1 mmol), GO@SiO_2-HPW (1 mol%).
[b] Isolated yields.
[c] *Reaction conditions*: 1,2-phenylenediamine (1 mmol), aldehyde (2 mmol), GO@SiO_2-HPW (1 mol%).

of GO, respectively.[21] For the GO@SiO_2 sample, the new peak at 1,081 cm^{-1} was assigned to the Si–O–C stretching vibration.[22] GO@SiO_2-APTES showed the characteristic stretching vibration of the CH_2 groups of the aminopropyl moieties at 2,936 cm^{-1}.

The formation of the GO@SiO_2-HPW catalyst was confirmed by the new peaks at 805 and 1,080 cm^{-1} attributed to the stretching vibrations of W–O and P–O bonds of the HPW Keggin anions, respectively.[23]

TGA was used to evaluate the thermal stability of GO@SiO_2 and GO@SiO_2-HPW. The TGA curves in Figure 3 demonstrate a weight loss around 100 °C, which was related to the loss of absorbed water molecules. The weight loss of GO@SiO_2-HPW below 100 °C (1.0%) was lower compared to that of GO@SiO_2 (3.0%), which indicates that the hydrophilic feature of GO@SiO_2 was reduced after modification with the hydrophobic APTES functional group.[24] Moreover, the pronounced weight loss in the temperature range 250–600°C (10.0%) can be attributed to the degradation of APTES (Figure 3). The content of APTES on the GO@SiO_2-HPW surface was calculated based on TGA as 1.7 mmol/g. These results proved that GO@SiO_2-HPW could endure about 250°C, which was much higher than the reaction temperature (100°C) in the following catalytic experiments.

The XRD pattern of GO@SiO_2-HPW showed characteristic diffraction peak at $2\theta = 11.8°$, confirming the formation of graphite oxide upon graphite oxidation by the Hummer's method (Figure 4). In addition, the amorphous SiO_2 in GO@SiO_2-HPW was identified from the broad peak at $2\theta = 5–10°$. The peaks at $2\theta = 35.8°$, 58.2°, and 62.8° can be attributed to HPW.

The surface morphologies and particle sizes of GO, GO@SiO_2, and fresh and used GO@SiO_2-HPW catalysts were investigated using SEM. As shown in Figure 5a, GO sheets showed smooth surfaces and layered structures. The SEM image of GO@SiO_2 in Figure 5b indicates that the SiO_2 particles are nearly spherical with particle sizes in the range 30–40 nm. The SEM image of fresh GO@SiO_2-HPW catalyst (Figure 5c) also showed morphology similar to that of GO@SiO_2. The used GO@SiO_2-HPW catalyst indicated agglomeration of particles with size up to 100 nm (Figure 5d).

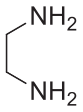
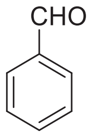
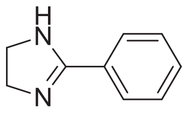
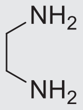
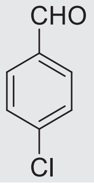
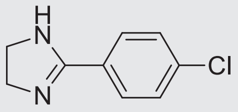
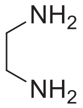
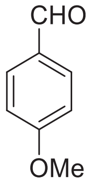
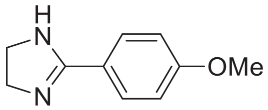
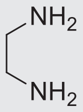
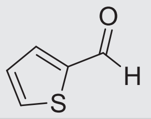
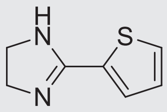
3.2 | Catalyst activity

To optimize the reaction conditions, we selected the reaction of 1,2-diaminobenzene with 4-chlorobenzaldehyde as a model reaction.

As shown in Table 1, water and various organic solvents such as toluene, acetonitrile, *N*,*N*-dimethyl formamide (DMF), ethanol, and ethanol/water mixture (1:1 v/v) were investigated using 1 mol% of catalyst, and it was found that water was the best solvent for this transformation.

Next, the effect of catalyst loading was optimized by employing the reaction with 0.5, 1, 2, and 3 mol% of GO@SiO_2-HPW in water at reflux temperature (Table 1, entries 7–10). The best loading was found to be 1 mol%. A further increase in the amount of catalyst (up to 3 mol%) did not have any significant effect on the product yield or reaction time.

TABLE 3 Synthesis of imidazolines using GO@SiO_2-HPW in water

Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)[a] [ref.]
1				120	85 [36]
2				100	88 [36]
3				140	82 [36]
4				120	80 [37]

[a] Isolated yields.

[b] *Reaction conditions*: 1,2-ethylenediamine (1 mmol), aldehyde (1 mmol), GO@SiO_2-HPW (1 mol%).

TABLE 4 Synthesis of benzothiazoles using GO@SiO_2-HPW in water

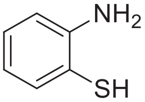
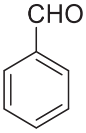
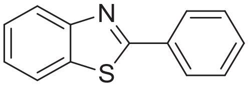
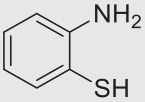
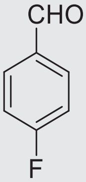
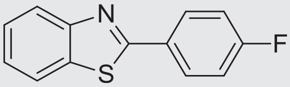
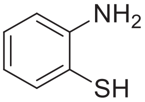
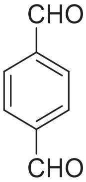
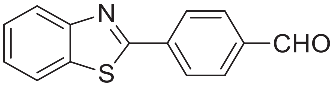
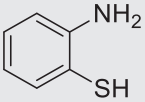
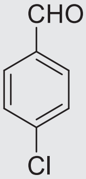
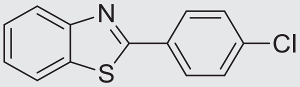
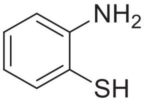
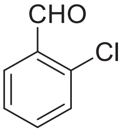
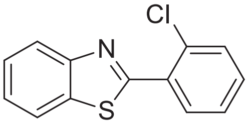
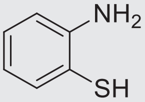
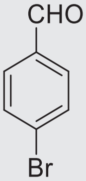
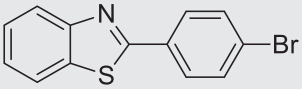
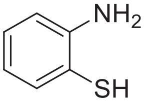
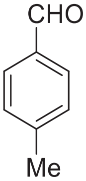
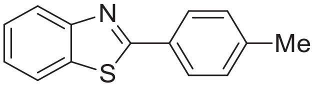
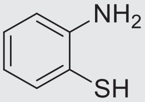
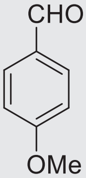
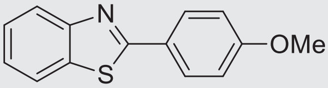
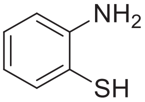
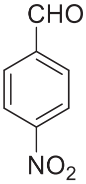
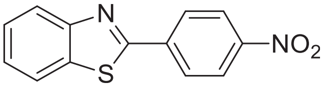
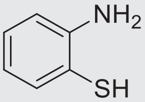
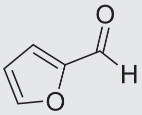
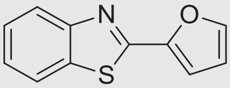
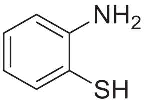
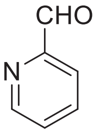
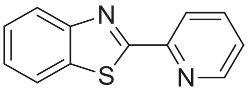
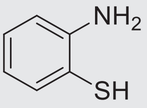
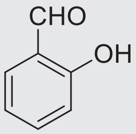
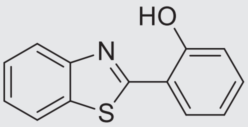
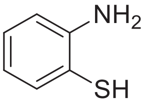
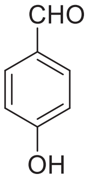
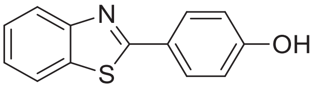
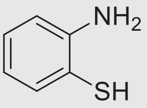
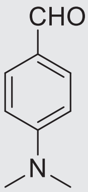
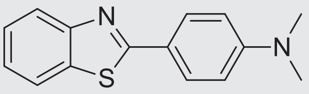
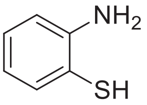
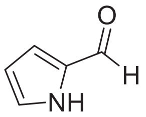
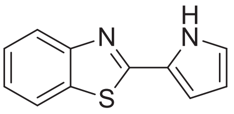
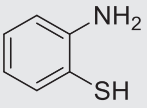
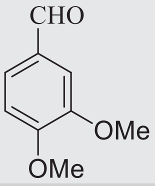
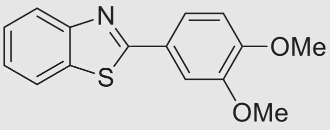
Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)[a] [ref.]
1				55	96 [38]
2				42	92 [38]
3				45	90 [39]
4				50	96 [38]
5				50	85 [40]
6				65	90 [41]
7				90	78 [42]
8				70	85 [38]
9				40	94 [43]
10				50	95 [42]

TABLE 4 (Continued)

Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)[a] [ref.]
11				80	78 [44]
12				75	80 [42]
13				80	80 [42]
14				80	85 [44]
15				45	80 [45]
16				85	75 [45]

[a] Isolated yields.

[b] *Reaction conditions*: 2-aminothiophenol (1 mmol), aldehyde (1 mmol), GO@SiO_2–HPW (1 mol%).

After finding the optimized reaction conditions, to evaluate the scope and limitations of this reaction, we studied the reactions of 1,2-phenylenediamines with various aldehydes (Table 2). Aliphatic and aromatic aldehydes containing either electron-donating or electron-withdrawing substituents reacted and afforded good to high yields of the products. It is worth noting that the reactions of aromatic aldehydes possessing electron-donating groups required longer reaction times compared to aromatic aldehydes with electron-withdrawing groups. The catalyst was also found to be very active for the preparation of benzimidazoles from a sterically hindered aldehyde such as naphthaldehyde (Table 2, entry 6).

Employing the same procedure given above but using 1,2-ethylenediamine instead of 1,2-phenylenediamine, the corresponding 2-substituted imidazolines were obtained in excellent yields with various substituents (Table 3).

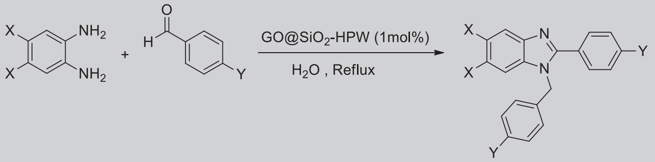
Encouraged by these results, the applicability of this protocol was further extended for the synthesis of benzothiazoles (Table 4). Aromatic aldehydes with electron-donating or electron-withdrawing substituents were used, and, as expected, gave good to excellent yield of the products. It can be seen that electron-donating and electron-withdrawing substituents do not show any difference in the reaction yields.

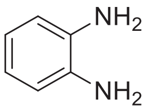
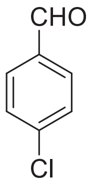
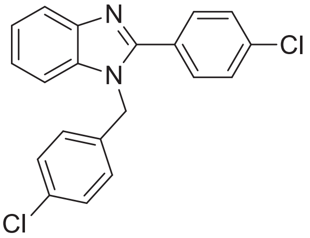
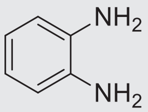
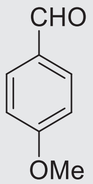
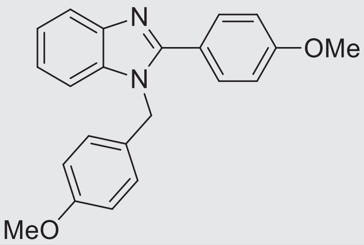
In the case of synthesis of benzimidazoles, the reaction of 1,2-phenylenediamine and aldehyde in 1:1 ratio gave only 2-substituted benzimidazoles, whereas when this ratio was changed to 1:3, then 1,2-disubstituted benzimidazole was obtained in good yield under same reaction conditions (Table 5). It is worth noting that most of the reported procedures generate mono-substituted benzimidazoles as a target product.

3.3 | Catalyst reusability

The recovery and reuse of a catalyst is highly desirable during its practical application. In this regard, the recyclability of GO@SiO_2-HPW was investigated in a model reaction of 1,2-diaminobenzene with 4-chlorobenzaldehyde under optimized reaction conditions. After the reaction was completed, the catalyst was separated by centrifugation. Then the catalyst was washed with methanol (3 × 5 mL) and

TABLE 5 Synthesis of 1,2-disubstituted benzimidazole using GO@SiO_2-HPW in water



Entry	Amine	Aldehyde	Product	Time (min)	Yield (%)[a] [ref.]
1				100	80 [45]
2				85	88 [45]

[a] Isolated yields.

[b] *Reaction conditions*: 1,2-phenylenediamine (1 mmol), aldehyde (3 mmol), GO@SiO_2–HPW (1 mol%).

TABLE 6 Reusability of GO@SiO_2-HPW catalyst

Entry	Reaction cycle	Time (min)	Yield (%)[a]
1	First	90	96
2	Second	90	95
3	Third	90	90
4	Fourth	90	87
5	Fifth	90	85

[a] Isolated yields.

subsequently dried in an oven at 60°C for 3 hr before being used in the next cycle. As shown in Table 6, GO@SiO_2-HPW could be reused in subsequent reactions without significant decrease in catalytic activity even after five runs.

4 | CONCLUSIONS

We have successfully developed an efficient, selective, and green methodology for the synthesis of benzimidazoles, benzothiazoles, and imidazolines using catalytic amounts of GO@SiO_2-HPW nanocomposite in water as an eco-friendly solvent. In addition, the catalyst could be easily separated from the reaction mixture by centrifugation and reused several times without any significant degradation in catalytic activity.

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ORCID

Setareh Habibzadeh https://orcid.org/0000-0002-5534-8210

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