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#### ARTICLE



# Cu(II)-supported graphene quantum dots modified NiFe<sub>2</sub>O<sub>4</sub>: A green and efficient catalyst for the synthesis of 4H-pyrimido[2,1-b]benzothiazoles in water

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#### Abstract

NiFe<sub>2</sub>O<sub>4</sub> nanoparticles are modified by graphene quantum dots (GQDs) and utilized to stabilize the Cu(II) nanoparticles as a novel magnetically retrievable catalytic system (Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>) for green formation of 4H-pyrimido[2,1-b]benzothiazoles. The prepared catalyst can be isolated assisted by an outer magnet and recovered for five courses without significant reduction in its efficiency. The as-prepared magnetic heterogeneous nanocomposite was characterized by UV–Vis, FT-IR, XRD, EDS, VSM, TEM, and ICP. Performing the reactions in environmentally friendly and affordable conditions (water), the low catalyst percentage, high yield of products, short reaction times, and easy workup are the merits of this protocol.

#### K E Y W O R D S

4H-pyrimido[2,1-b]benzothiazoles, graphene quantum dots, nanocatalyst, NiFe<sub>2</sub>O<sub>4</sub>

## **1** | INTRODUCTION

Graphene quantum dots (GODs) are the zerodimension nanographenes with special characteristics like small size, chemical inertness, photoluminescence, ease to be functionalized with biomolecules and biocompatibility have received a lot of attention in the nanotechnology research studies.<sup>[1]</sup> Nevertheless, the diverse uses of GQD, little consideration has been given for applying GQD as a solid support or catalyst in the reactions.<sup>[2]</sup> Preparation of high-performing nanocatalysts for organic reactions remains a major challenging task. To achieve greater specific area and more effective sites, nanocatalysts should be functionalized by activated moieties. It is proved that the modification of the nanocatalyst with GQDs avoids the aggregation of fine particles and therefore enhances the active specific area for an effective catalytic reaction.<sup>[3]</sup> Magnetic nanoparticles have been the

focus of attention to researchers for consecutive years.<sup>[4]</sup> Many works have been published and also indicated that the importance of magnetic catalysts.<sup>[5]</sup> Among them, NiFe<sub>2</sub>O<sub>4</sub> has been getting more consideration, owing to its strong coercive power, appropriate magnetic induction, and high permanence.<sup>[6]</sup> Several research studies verify the outlooks of using NiFe<sub>2</sub>O<sub>4</sub> as an effective nanocatalyst.<sup>[7]</sup> The immobilization of nano-NiFe<sub>2</sub>O<sub>4</sub> on GQDs will lead to a multi-purpose nanoscaffold for efficient catalytic activity.<sup>[8]</sup> Benzothiazoles and their condensed system make a wider category of nitrogen and sulfur-comprising compounds with an extensive biological activity.<sup>[9]</sup> Among fused benzothiazoles, pyrimido[2,1-b]benzothiazoles have fascinated significant attention due to their effective pharmaceutical actions. An overview of the literature indicated that pyrimido[2,1-b]benzothiazoles show several biological operations such as anti-tumoral agents,<sup>[10]</sup> anti-allergic,<sup>[11]</sup> antimicrobial,<sup>[12]</sup> and

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anticonvulsant.<sup>[13]</sup> Given the significance of pyrimido [2,1-b]benzothiazoles, the advancement of efficient policies for the synthesis of these condensed heterocycles will be noteworthy in both medicinal and organic chemistry. Three component linkage of 2-amino benzothiazole, b-ketoesters, and aldehydes is a conventional synthetic way to pyrimido[2,1-b]benzothiazole derivatives.<sup>[14]</sup> Formerly, this procedure has been catalyzed by acetic acid,<sup>[10b]</sup> Chitosan,<sup>[15]</sup> tetrabutylammonium hydrogen sulfate,<sup>[14c]</sup> aluminum chloride,<sup>[16]</sup> and N-sulfonic acid-modified poly(styrene-maleic anhydride).<sup>[17]</sup> Nevertheless, some of these procedures have impediments that must be considered. Therefore, the application of newer and greener approaches is remaining necessary. Herein, the preparation of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> by the way of an easy co-sedimentation of NiFe2O4 nanoparticles on GQDs is described and its identification by diverse methods was investigated. The catalyst synthesis process is illustrated in Scheme 1. Upon full identification, the catalyst performance was investigated in preparation of pyrimido[2,1-b]benzothiazole derivatives. The overall reaction is shown in Scheme 2.

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#### 2 | RESULTS AND DISCUSSION

The catalyst (Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>) was synthesized as specified by the procedure outlined in Scheme 1, by means of GQDs and NiFe2O4 nanoparticles produced in accord with literature.<sup>[2c,6,8,18]</sup> To verify synthesis of the nanocatalyst, it was completely identified using diverse methods comprising UV–vis and fluorescence spectroscopy, FT-IR spectroscopy, XRD, EDS, TEM, VSM, and ICP spectroscopy.

The light-conducting characteristics of the prepared graphene quantum dots were examined by UV–Visible and fluorescence spectroscopy. The absorbing spectrum of graphene quantum dots give not any peak as illustrated in Figure 1a. The fluorescence spectra of graphene quantum dots could be observed in Figure 1b. The graphene quantum dots were excited at wavelengths of 360, 380, and 400 nm and the proper fluorescence emission peaks were found at 454, 463, and 469 nm, respectively. The emission peaks indicate a gentle red shift with a raising in the excitation wavelengths (360–400 nm). It has been observed that the color of the GQDs aqueous



SCHEME 1 Method for synthesis of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>

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**FIGURE1** (a) UV–Vis absorbance spectrum of GQDs. (b) Fluorescence spectra of GQDs. Inset indicates images of GQDs solution taken under visible light (weak yellow) and 365 nm excitation (blue)

solution is weak yellow under visible light, but when excited by UV light at 365 nm, it seems blue, as indicated in inside of Figure 1b. Changes in fluorescence intensity after the synthesis of GQDs/NiFe<sub>2</sub>O<sub>4</sub> were also examined. The fluorescence spectra of GQDs/NiFe<sub>2</sub>O<sub>4</sub>, excited at 360, 380, and 400 nm are indicated in Figure 2. The fluorescence emission peaks were found at 486, 483, and 480 nm respectively. It has been found that with increasing excitation wavelengths, a slight blue shift is observed in emission peaks. This differentiation in the fluorescence properties in comparison to the graphene quantum dots demonstrate the change in the chemical surface of the GQDs/NiFe<sub>2</sub>O<sub>4</sub> implying a probable linkage of graphene quantum dots on the nickel ferrite nanoparticles, leading to a change in the surface characteristics of graphene quantum dots.



FIGURE 2 Fluorescence spectra of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>

FT-IR spectroscopy was accomplished to validate the exterior framework of the nanocatalyst. The FT-IR spectrum has been displayed in Figure 3 for Cu(II)/GODs/ NiFe<sub>2</sub>O<sub>4</sub>. The wide peak at 3,362.97 cm<sup>-1</sup> is assigned to the hydroxyl (O-H) bond, showing the absorption of water by the Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>. The bands located at 2,981  $\text{cm}^{-1}$  and 1,450  $\text{cm}^{-1}$  are related to the C–H bond vibrational stretching from remaining citric acid, implying the partial citric acid carbonization.<sup>[19]</sup> The peak located at 1,001.35 cm<sup>-1</sup> is related to the vibrational stretching of the C-O-C bond. The peaks located at 1,415.34 and 1,594.81  $\text{cm}^{-1}$  would be the result of skeletal vibrations of aromatic rings in graphene quantum dots.<sup>[20]</sup> The presence of NiFe<sub>2</sub>O<sub>4</sub> is validated by absorption bands located at 550.64 and 685.24 cm<sup>-1</sup>, which are correlated to Ni-O and Fe-O bonds vibrations, respectively.<sup>[21]</sup> The outcomes of this analysis confirm successful synthesis of magnetic nanocatalyst.

X-ray diffraction technique was employed to acquire information about the crystallinity of the nanocatalyst. XRD pattern of GQDs/NiFe<sub>2</sub>O<sub>4</sub> is displayed in Figure 4. The GQDs/NiFe<sub>2</sub>O<sub>4</sub> diffraction pattern agrees well with



FIGURE 3 FT-IR spectrum of

Cu(II)/GQDs/NiFe2O4

the standard NiFe<sub>2</sub>O<sub>4</sub> (JCPDS 10-0325) and exhibits the important diffraction lines at  $2\theta = 17.15^{\circ}$ ,  $30.59^{\circ}$ ,  $35.76^{\circ}$ , 37.30°, 43.43°, 53.84°, 57.34°, and 63.01°, which may be attributed to the (220), (311), (222), (400), (422), (511), and (440) planes of NiFe2O4, respectively. The diffraction peak of graphene quantum dots (004) (JCPDS 26-1080) is not recognizable, may have been due to their high dispersals, and low crystallization degree of graphene quantum dots in GQDs/NiFe<sub>2</sub>O<sub>4</sub>.<sup>[6,22]</sup>

The EDS was employed as an influential method to identify the chemical constitution of the produced nanocatalyst. The EDS analysis verifies the existence of envisaged elements comprising nickel, iron, oxygen, carbon, and copper in the catalyst structure (Figure 5).

The morphology and structural characteristics of the synthesized nanocatalyst was observed under TEM technique (Figure 6). It is revealed that the darker region in Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> image, is related to agglomeration of NiFe2O4 nanoparticles on GQDs. Also, the TEM micrograph of the nanocatalyst indicates that the mean sizes of Cu(II)/GQDs/NiFe2O4 nanoparticles are approximately not more than 40 nm.

The magnetic characteristic of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> was studied by VSM. As evidenced in Figure 7, the value of the saturation magnetization of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> (60.82 emu.g<sup>-1</sup>), almost equal to Fe<sub>3</sub>O<sub>4</sub> nanoparticles  $(61.60 \text{ emu.g}^{-1})$  which indicates that the nanocatalyst has magnetic properties and their magnetic characteristics are so high that they could be isolated by a typical magnet.

The quantity of Cu loading onto the nanocatalyst was determined by the ICP technique, which was obtained to be 0.94 mmol  $g^{-1}$ .

After validating the successful synthesis of nanocatalyst by various techniques, its catalytic capability was examined in the synthesis of 4H-pyrimido[2,1-b]benzothiazoles. To achieve this goal, 4-nitrobenzaldehyde, ethyl acetoacetate, and 2-aminobenzothizole were used



**FIGURE 5** EDS pattern of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>





**FIGURE 7** Magnetization curve of  $Cu(II)/GQDs/NiFe_2O_4$ 

 $\label{eq:FIGURE6} FIGURE6 \quad \text{TEM image of Cu(II)/GQDs/NiFe}_{2}O_{4}$ 

as model substrates for optimizing the reaction elements including solvent, nanocatalyst amount, and temperature. At the beginning, the above reaction was also conducted without and in the presence of various quantities of the nanocatalyst (Table 1). The outcomes revealed that the reaction did not progress in the lack of nanocatalyst in some polar and non-polar solvents and solvent-free state, even after 24 hr (Entries 1-7). In the presence of nanocatalyst, the best results were achieved in EtOH and water (Entries 8-15). Enhancing the nanocatalyst dosage to 10 mg raised the reaction efficiency (Entries 15-16). Increasing the amount of catalyst more than this did not increase the efficiency of the reaction (Entry 17). Lastly, the greatest efficiency was achieved when the model reaction was performed in H<sub>2</sub>O in the presence of 10 mg of nanocatalyst at room temperature (Entry 16). To illustrate the role of copper in the reaction progress, the function of other components of the nanocatalyst like NiFe<sub>2</sub>O<sub>4</sub>, GQDs, and GQDs/NiFe<sub>2</sub>O<sub>4</sub> was also examined

in the reaction under optimal conditions. The outcomes are displayed in Table 1 (Entries 18–20). As illustrated, no progress was detected in the model reaction when applying the other components of nanocatalyst in the absence of Copper, verifying that the existence of copper is vital for catalyzing the reaction.

After creating optimal reaction conditions, Cu(II)/ GQDs/NiFe<sub>2</sub>O<sub>4</sub> the range of the reaction was expanded to diverse 4H-pyrimido[2,1-b]benzothiazoles. In accord with the outcomes presented in Table 2, the electronic influence did not have extraordinary affection on outcome of the reaction, thus all 4H-pyrimido[2,1-b]benzothiazoles with electron-withdrawing or electronreleasing groups and heterocyclic moiety provided similar yields (30–90 min).

In accord with literature,<sup>[17,25]</sup> a plausible catalytic mechanism for the preparation of 4H-pyrimido[2,1-b] benzothiazoles by Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> is suggested in Scheme 3 in which Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> could perform as a Lewis acid to actuate the carbonyl groups. It looks benzaldehyde as an electrophile and  $\beta$ -ketoester as active

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Entry	Condition	Catalyst (mg)	Temp. (°C)	Time (hr)	Yield (%) <sup>a</sup>
1	Toluene	—	rt	24	Trace
2	$CH_2Cl_2$	—	rt	24	Trace
3	EtOH	—	rt	24	Trace
4	n-Hexane	—	rt	24	Trace
5	CH <sub>3</sub> CN	—	rt	24	Trace
6	Solvent-free	—	rt	24	Trace
7	H <sub>2</sub> O	—	rt	24	Trace
8	Toluene (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	Trace
9	n-Hexane (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	Trace
10	CH <sub>3</sub> CN (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	15
11	Solvent-free (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	Trace
12	Solvent-free (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	70	5	20
13	CH <sub>2</sub> Cl <sub>2</sub> (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	Trace
14	EtOH (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	30
15	H <sub>2</sub> O (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	5	rt	5	60
16	H <sub>2</sub> O (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	10	rt	0.5	98
17	H <sub>2</sub> O (Cu/GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	0.15	rt	0.5	98
18	$H_2O$ (NiFe <sub>2</sub> O <sub>4</sub> )	10	rt	1.0	None
19	H <sub>2</sub> O (GQDs)	10	rt	1.0	None
20	H <sub>2</sub> O (GQDs/NiFe <sub>2</sub> O <sub>4</sub> )	10	rt	1.0	None

TABLE 1 Optimization of solvent, temperature, and nanocatalyst dosage

<sup>a</sup>On the basis of isolated yield.

					Melting point (°C)	
Entry	Ar	<b>Product</b> <sup>b</sup>	Time (min)	Yield (%) <sup>c</sup>	Found	Reported
1	Ph	4a	40	98	177–180	177–179 <sup>[11]</sup>
2	4-NO <sub>2</sub> Ph	4b	30	98	171	170-172 <sup>[16]</sup>
3	4-Br Ph	4c	30	92	112	110-114 <sup>[14b]</sup>
4	4-Cl Ph	4d	30	95	86	86-88 <sup>[17]</sup>
5	4-OCH <sub>3</sub> Ph	4e	35	98	130-132	130-132 <sup>[15]</sup>
6	4-OH Ph	4f	45	95	212	210-212 <sup>[16]</sup>
7	3-NO <sub>2</sub> Ph	4g	40	91	222-224	222-224 <sup>[17]</sup>
8	3-OH Ph	4h	45	93	260-262	260-263 <sup>[23]</sup>
9	2-NO <sub>2</sub> Ph	4i	40	89	122-125	122-125 <sup>[23]</sup>
10	2-Cl Ph	4j	30	88	125–127	125-127 <sup>[14c]</sup>
11	2,4-(Cl) <sub>2</sub> Ph	4k	30	90	133–134	133-135 <sup>[14c]</sup>
12	2,4-(OCH <sub>3</sub> ) <sub>2</sub> Ph	41	60	96	165	164-166 <sup>[23]</sup>
13	3,4-(OH) <sub>2</sub> Ph	4m	60	92	224-226	225-227 <sup>[23]</sup>
14	Tiophenyl	4n	90	97	180-182	180-182 <sup>[24]</sup>

**TABLE 2** Synthesis of 4H-pyrimido[2,1-b]benzothiazoles **4a-n** using Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> as catalyst<sup>a</sup>

<sup>a</sup>Reaction conditions: aldehydes (1.0 mmol), 2-aminobenzothiazole (1.0 mmol), ethyl acetoacetate (1.0 mmol) and Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> (0.01 g) at room temperature in H<sub>2</sub>O.

<sup>b</sup>Known products identified by comparison of their melting points; some selected compounds identified by <sup>1</sup>H- NMR. <sup>c</sup>Isolated yields.



 $SCHEME~3 \qquad \mbox{Proposed mechanism for the synthesis of 4H-pyrimido[2,1-b] benzothiazoles in the presence of Cu(II)/GQDs/NiFe_2O_4} \label{eq:scheme}$ 

methylene compounds participate within an on-site Knoevenagel reaction and an alkene is initially produced. Subsequently, during the Michael addition reaction, 2-aminbenzothiazole, as a donor, attacks alkene during nucleophilic reaction, therefore, an iminium ion is produced. Afterward, with a proton exchange and an intra-molecular cyclization, 4H-pyrimido[2,1-b]benzothiazoles are produced.

The reusability of the catalyst (Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>) was examined in the sample reaction. For this goal, upon termination of the reaction, the nanocatalyst was separated with the aid of a magnet and washed with acetone and water to eliminate remaining product, dried, and reapplied in subsequent reactions. The outcomes revealed that the nanocatalyst could be successively retrieved without any considerable reduction in its performance (Figure 8).

To explore the leaking of copper, ICP study of the retrieved catalyst was additionally performed. In accord with the acquired outcomes, no considerable reduction was monitored in the Cu quantity. The Cu amount in the new nanocatalyst and the recovered one was 0.94 and 0.91 mmol g<sup>-1</sup>, respectively, which revealed the amount of leached Cu for this nanocatalyst is very slight. To investigate the heterogeneous character of the catalytic process, the hot filtration examination for the model reaction in attending Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> was studied. The model reaction was ceased after half the required reaction time and the nanocatalyst was fully isolated with



 $\label{eq:FIGURE8} FIGURE8 \quad \mbox{Reusability of Cu(II)/GQDs/NiFe}_{2}O_{4} \mbox{ in the model reaction}$ 

the aid of a magnet and allowed the reaction to progress for further time (30 min). The product generation was not detected as monitored by TLC, which proves the nanocatalyst is heterogeneous in character.

To validate the advantage of the present research, application of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> in producing of 4H-pyrimido[2,1-b]benzothiazole derivatives in comparison with other formerly reported heterogeneous catalysts is presented in Table 3. In accordance with the results, the introduced catalyst indicates more adequate catalytic performance quickly under environmentally friendly and affordable conditions (water).

 $\label{eq:comparison} \begin{array}{l} TABLE \ 3 & Comparison \ of \ Cu(II)/GQDs/NiFe_2O_4 \ nanocatalyst \ with \ other \ heterogeneous \ catalysts \ in \ synthesis \ of \ 4H-pyrimido[2,1-b] \\ benzothiazole \ \textbf{4a} \end{array}$ 

Entry	Catalyst	Solvent	Temp. (°C)	Time (min.)	Yield (%) <sup>a</sup>	Ref.
1	Chitosan/HOAc	$H_2O$	60	100	92	[15]
2	N-sulfonic acid modified poly(styrene-maleic anhydride)	Solvent-free	100	180	72	[17]
3	Nano-TiCl <sub>2</sub> /cellulose	PEG 400	70	90	80	[25]
4	AlCl <sub>3</sub>	Solvent-free	60	72	79	[16]
5	Fe <sub>3</sub> O <sub>4</sub> @nano-cellulose/Cu(II)	Solvent-free	80	45	83	[26]
6	Cu(II)/GQDs/NiFe <sub>2</sub> O <sub>4</sub>	$H_2O$	rt	40	98	This study

<sup>a</sup>Isolated yield.

#### 3 | EXPERIMENTAL

#### 3.1 | General information

Citric acid, sodium hydroxide, nickel nitrate, Fe(III) nitrate, and Cu(II) acetate were purchased from Sigma. UV-vis absorption investigations were conducted by Hach DR 6000 UV-visible spectrophotometer. Fluorescence examinations were done on Jasco FP-6200 spectrofluorophotometer (Hitachi Japan). The phase crystallinity of the prepared nanocatalyst was studied by a diffractometer at a wavelength of 1.540 Å (Philips Company). Transmission electron microscopy (TEM) picture was captured by means of Zeiss electron microscope, LEO 912AB (120 kV), Germany. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker model 470 spectrophotometer. Magnetic characteristics were registered on a vibrating sample magnetometer apparatus (VSM, LDJ9600) at environment temperature. EDS spectroscopy study were conducted with 133 eV resolution (model 7,353, Oxford Instruments, United Kingdom). Copper determination was carried out by inductively coupled plasma (ICP) technique on a Varian VISTA-PRO. NMR spectra were registered in CDCl<sub>3</sub> on a Bruker Advance 300 MHz instrument. The melting points were measured on an Electrothermal Type 9100 device

#### 3.2 | Synthesis of NiFe<sub>2</sub>O<sub>4</sub> nanoparticles

Egg white (60 ml) was added to distilled water (40 ml) and was shaken hard to perfectly mix. Subsequently, 2.9081 g of nickel nitrate hexahydrate and 8.0800 g of Fe(III) nitrate nonahydrate were dissolved in the above solution and was stirred hard at ordinary temperature for 2 hr. Then, while the mixture was agitated, it was warmed to  $80^{\circ}$ C until dried. The

consequent powder was grinded and then heated at  $700^{\circ}$ C for 3 hr.<sup>[6]</sup>

#### 3.3 | Synthesis of GQDs

GQDs were made from thermally decomposed citric acid.<sup>[18]</sup> Concisely, citric acid (0.2 g) was melted and heated at 200°C for 5 min. Then, the subsequent yellowish liquid was added progressively into 20 ml of 0.25 M NaOH solution. Thereafter, the GQDs solution was dialyzed in a 1 kDa dialysis bag for 24 hr (dialysate was exchanged every 8 hr) to eliminate the unreacted chemicals. The produced graphene quantum dots solution was maintained in 4°C.

#### 3.4 | Synthesis of GQDs/NiFe<sub>2</sub>O<sub>4</sub>

NiFe<sub>2</sub>O<sub>4</sub> nanoparticles, 1 g, were dispersed in water (5 ml) for 15 min. Afterward, the GQDs suspension (20 ml) was added to the flask comprising the NiFe<sub>2</sub>O<sub>4</sub> nanoparticles and the resulting mixture was shaken for 48 hr at 60°C. The produced GQD-modified NiFe<sub>2</sub>O<sub>4</sub> was isolated through the use of a magnet and was washed with distilled water (3 × 20 ml) and ethanol (3 × 20 ml) and finally dried under low pressure.<sup>[8]</sup>

## 3.5 | Synthesis of Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub>

GQDs/NiFe<sub>2</sub>O<sub>4</sub> (0.5 g) was dispersed in acetone (25 ml) at ordinary temperature for 30 min. Afterward, 0.1 mmol copper(II) acetate (0.018 g) was added gently to the flask comprising GQDs/NiFe<sub>2</sub>O<sub>4</sub> nanocomposite. The consequent mixture was mechanically shaken for 48 hr at ambient temperature. Then, the solid was isolated with the aid of a magnet, washed with water (3 × 25 ml) and

ethanol  $(3 \times 25 \text{ ml})$ , and finally dried at  $60^{\circ}\text{C}$  overnight.<sup>[2c]</sup>

## 3.6 | Synthetic typical manner for 4Hpyrimido[2,1-b]benzothiazoles 4a-n

Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> catalyst (0.10 g) was added to a solution comprising 2-aminobenzothiazole (1.0 mmol), aldehyde (1.0 mmol), and ethyl acetoacetate in water under continuous stirring for 30-90 min at room temperature. The proceeding of the reaction was controlled using TLC (thin layer chromatography), whenever the reaction was completed, the reaction mixture was diluted with ethyl acetate and the nanocatalyst was isolated with the aid of a magnet, washed with acetone, and then dried on a night to be ready to react again. The organic layer was dried over anhydrate sodium sulfate and after that, evaporated to separate the solvent. The remaining part was recrystallized in ethanol to provide corresponding 4H-pyrimido[2,1-b]benzothiazole derivatives. All the products are known and were identified by comparison of their melting points, and spectroscopic data (<sup>1</sup>HNMR) with those of authentic samples. Selected spectral data of some synthesized compounds are given below.

## 3.7 | Ethyl-2-methyl-4-(4-nitrophenyl)-4H-pyrimido[2,1-b] [1,3] benzothiazole-3-carboxylate

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.30 (t, J = 7.29 Hz, 3H, CH3), 2.40 (s, 3H, CH<sub>3</sub>), 4.19 (q, J = 7.30 Hz, 2H, OCH<sub>2</sub>), 6.62 (s, 1H, CH), 7.02 (d, J = 8.20 Hz, 1H, Ar-H), 7.15 (t, J = 7.74 Hz, 1H, Ar-H), 7.25 (t, J = 7.74 Hz, 1H, Ar-H), 7.49 (d, J = 8.20 Hz, 1H, Ar-H), 7.60 (d, J = 8.20 Hz, 2H, Ar-H), 8.11 (d, J = 8.20 Hz, 2H, Ar-H) (Table 2, Entry 2).

#### 3.8 | Ethyl-2-methyl-4-(4-chlorophenyl)-4H-pyrimido[2,1-b][1,3] benzothiazole-3-carboxylate

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.23 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 4–4.1 (m, 2H, OCH<sub>2</sub>), 6.47 (s, 1H, CH), 7.16–7.21 (t, 1H, ArH), 7.27–7.49 (m, 6H, ArH), 7.74–7.76 (d, 1H, Ar-H) ppm (Table 2, Entry 4).

## 4 | CONCLUSIONS

We have successfully synthesized a copper heterogeneous catalyst on graphene quantum dots/NiFe $_2O_4$  nanomagnetic

particles as a very stable and recoverable nanocatalyst for the green production of 4H-pyrimido[2,1-b]benzothiazoles rapidly in aqueous media. The proposed reaction, in which the designed Cu(II)/GQDs/NiFe<sub>2</sub>O<sub>4</sub> was a recoverable catalyst, consistent with the principles of green chemistry owing to the following properties: no toxicity, great durability, recovery capability, shorter times of reaction, aqueous medium, and excellent products yields. Above all others, the nanocatalyst could be recovered five runs without any failure in its productivity. So, the nanomagnetic heterogeneous catalyst might be useful in related industries

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#### SUPPORTING INFORMATION

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