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## Introduction

Nowadays, there is an intense focus on using heterogeneous catalysts for the promotion of various chemical transformations.<sup>1,2</sup> In addition, heterogeneous catalysis is a very interesting tool that facilitates many organic reactions.<sup>3-9</sup> In this context, the application of heterogeneous nanocatalysts with particular activities has also attracted the attention of numerous scientists. After the synthesis and application of heterogeneous nanocatalysts, their recovery and reusability as one of the essential aspects of green chemistry are more important. A literature review shows that a combination system of heterogeneous nanocatalysts with various magnetic materials could be a prominent choice for the above mentioned strategy. The magnetic nanocatalysts are easily separated from the reaction mixture using an external magnetic field and facilitate the recovery of the examined catalyst systems.<sup>10-12</sup> In spite of this, however, due to high surface energy and attraction of magnetic cores, nanoparticles of magnetic materials have a high tendency for aggregation.13-15

Graphene oxide (GO) as a multi-functional carbon material and possessing huge surface area is commonly used for protecting magnetic nanoparticles (MNPs), particularly  $Fe_3O_4$ .<sup>16,17</sup> By the *in situ* immobilization of  $Fe_3O_4$  MNPs on the surface or interlamellar spaces of graphene oxide, the nanocomposite of



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In this study, a nanocomposite of  $Fe_3O_4@GO@Zn-Ni-Fe$ -layered double hydroxide was synthesized as a novel and efficient mesoporous magnetic nanocatalyst. The synthesis was carried out *via* the immobilization of  $Fe_3O_4$  MNPs (magnetic nanoparticles) on graphene oxide and then the layering of Zn-Ni-Fe-layered double hydroxide moieties on the constituents of  $Fe_3O_4@GO$ . The magnetic graphene oxide/layered double hydroxide system was then characterized using SEM, EDX, FTIR, XRD, TEM and VSM analyses. The catalytic activity of the prepared composite system was further studied towards one-pot Knoevenagel-Michael reaction of aromatic aldehydes with 4-hydroxycoumarin in water. All reactions were carried out under reflux conditions giving biscoumarin materials in 87-95% yields within 3-40 min. This method has noteworthy advantages in terms of mild reaction conditions, short reaction times, utilizing water as an environmental friendly solvent and applying a magnetically separable catalyst system.

Fe<sub>3</sub>O<sub>4</sub>@GO is prepared. This composite system prevents the aggregation of magnetic nuclei effectively. A literature survey shows that graphene oxide, because of its unique characteristics, has been widely used in the fields of sensors, nanofiltration, solar cells, electrodialysis, electronics and nanocatalysts for chemical transformations.<sup>18-25</sup> In addition, the presence of carboxylic acids and epoxy functionalities in the basal planes of graphene oxide boosts its propagation in water. Moreover, they can operate as active sites for the functionalization and hybridization of graphene oxide with other nanomaterials.<sup>26,27</sup> On the other hand, layered double hydroxides (LDHs) have a two-dimensional structure and belong to the category of anionic clay minerals.<sup>28</sup> They are defined as environmentally friendly materials and exhibit attractive chemical and physical properties.<sup>29,30</sup> LDHs are naturally occurring and therefore can be easily prepared by routine procedures. Based on the unique characteristics of graphene oxide and LDH materials, nowadays, the focus on the combination systems of GO and LDHs has gained considerable interest.

Coumarin and biscoumarin derivatives are heterocyclic components of various synthetic and natural organic compounds. Coumarins show several applications in fragrance and pharmaceutical industries.<sup>31</sup> In addition, biscoumarin materials represent a wide range of biological activities including antibiotics, anticancer, anticoagulants, insecticidal, antifungal and HIV protease inhibition.<sup>32–34</sup> Because of these great potentialities, the synthesis of biscoumarin materials was carried out using Pechmann, Reformatsky, Perkin, Wittig and Knoevenagel reactions. Among these, application of the Knoevenagel condensation reaction



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#### Paper

using different catalyst/promoter systems is more investigated.<sup>35–40</sup> Although most of the reported methods have their own merits, they generally suffer from some limitations. Therefore, the development of simple synthetic procedures utilizing recyclable green catalyst systems<sup>41–45</sup> is still demanded for the preparation of biscoumarin materials. In line with the outlined strategies, herein, we wish to report the synthesis of nanostructured Fe<sub>3</sub>O<sub>4</sub>@GO@Zn–Ni–Fe-LDH composite system as a novel heterogeneous and highly efficient mesoporous catalyst towards the Knoevenagel–Michael reaction of 4-hydroxycoumarin with aromatic aldehydes in refluxing H<sub>2</sub>O to afford biscoumarin materials in high yields.

## Results and discussion

# Synthesis and characterization of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system

The study was started by the synthesis of a nanostructured  $Fe_3O_4$ @GO@Zn–Ni–Fe-LDH composite system *via* a four step procedure (Fig. 1). Primarily, the synthetic process was carried out with the transformation of graphite to graphene oxide. Next, the magnetic nanoparticles of  $Fe_3O_4$  were immobilized on the surface or interlamellar spaces of graphene oxide *via* a chemical co-precipitation method. Zn–Ni–Fe-layered double hydroxide was then prepared and after that it was immobilized on the surface of the  $Fe_3O_4$ @GO constituents. Structural elucidation of the prepared nanocomposite system was then carried out using SEM, EDX, FTIR, XRD, TEM and VSM analyses.

The scanning electron microscopy technique as a primary tool was utilized to determine the size distribution of the nanoparticles as well as the surface-morphology of the Fe<sub>3</sub>O<sub>4</sub>(a)GO(a)Zn–Ni–Fe-LDH composite system. The illustrated SEM images (Fig. 2) show that the surface of the composite system is extremely porous and constructed from rough/irregular nanoparticles. The images also represent that the agglomeration of nanoparticles led to



Fig. 2 Scanning electron microscopy images of the  $Fe_3O_4@GO@Zn-Ni-Fe-LDH$  system.

the formation of small segments with the size distribution ranging from 25 to 39 nm.

Next, the elemental composition of the composite system was determined using the energy-dispersive X-ray spectroscopy technique. Fig. 3 represents the elemental contents and EDX spectrum of the nanostructured Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system. The analysis clearly shows that the elements of Fe,



Fig. 1 Synthesis of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system.



O, C, Zn and Ni exist in the structure of the nanocomposite system.

The existence of functional groups in graphene oxide,  $Fe_3O_4$ , Fe<sub>3</sub>O<sub>4</sub>(a)GO, Zn-Ni-Fe-LDH and Fe<sub>3</sub>O<sub>4</sub>(a)GO(a)Zn-Ni-Fe-LDH was also elucidated using Fourier transformed infrared spectroscopy (Fig. 4). The FTIR spectrum of graphene oxide shows a strong absorption peak at 3416 cm<sup>-1</sup> corresponding to the stretching vibration of O-H bonds. This absorption clearly verifies the existence of OH or COOH groups in the structure of graphene oxide. In addition, the symmetric and asymmetric stretching vibrations of C-H bonds (2927 and 2962 cm<sup>-1</sup>), the stretching vibration of C=O bonds (1724 cm<sup>-1</sup>) and C=C from the unoxidized graphitic domain (1627  $\text{cm}^{-1}$ ), deformation of O-H bonds (1373 cm<sup>-1</sup>), and stretching vibration of C-O bonds in the epoxy groups (1221 cm<sup>-1</sup>) and C-O bonds in the alkoxy groups (1050 cm<sup>-1</sup>) are also observable in the spectrum of graphene oxide. In this context, the FTIR spectrum of Fe<sub>3</sub>O<sub>4</sub> shows a strong absorption peak at 575 cm<sup>-1</sup> attributed to the vibration of Fe-O bonds in iron oxide. The absorption peaks at 1625 and 3400 cm<sup>-1</sup> are also assigned to the O-H deformation and stretching vibrations of OH groups on the surface or the adsorbed water in Fe<sub>3</sub>O<sub>4</sub>, respectively. Consequently, the FTIR spectrum of the Fe<sub>3</sub>O<sub>4</sub>(a)GO system represents that the spectrum contains the characteristics peaks of Fe<sub>3</sub>O<sub>4</sub> and GO constituents. This verifies that the magnetic nanoparticles of Fe<sub>3</sub>O<sub>4</sub> were successfully immobilized on the surface and interlamellar spaces of GO. In the cases of FTIR spectra of Zn-Ni-Fe-LDH and Fe<sub>3</sub>O<sub>4</sub>(a)GO(a)Zn-Ni-Fe-LDH systems, the presence of a strong absorption peak at 3435 cm<sup>-1</sup> is attributed to the stretching vibrations of OH groups in metal-OH groups as well as hydrogen bonding from the adsorbed water. Deformation of OH groups exhibits an additional absorption peak at 1630 cm<sup>-1</sup>. In addition, asymmetric stretching of  $CO_3^{2-}$  is observed around 1360 cm<sup>-1</sup>. The lattice vibration modes of M-OH and M-O also exist between 1000 and 500  $\text{cm}^{-1}$ .

In continuation, the phase purity and crystalline character of the Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@GO@Zn–Ni–Fe-LDH composite system were studied using X-ray diffraction analysis (Fig. 5). The XRD diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> (Fig. 5a) shows the reflection planes at  $2\theta = 30.2^{\circ}$  (0 2 2),  $35.5^{\circ}$  (1 1 3),  $43.3^{\circ}$  (0 0 4),  $53.7^{\circ}$  (2 2 4),  $57.2^{\circ}$ (1 1 5) and  $62.9^{\circ}$  (0 4 4) corresponding to the standard one of



Fig. 4 FTIR spectra of graphene oxide,  $Fe_3O_4$ ,  $Fe_3O_4@GO$ , Zn-Ni-Fe-LDH and  $Fe_3O_4@GO@Zn-Ni-Fe-LDH$ .



Fig. 5 X-ray diffraction patterns of (a)  $Fe_3O_4$  and (b) the  $Fe_3O_4@GO@Zn-Ni-Fe-LDH$  system.

the cubic spinel structure of Fe<sub>3</sub>O<sub>4</sub> with a high phase purity and crystallinity (JCPDS 65-3107).46,47 In the XRD pattern of the Fe<sub>3</sub>O<sub>4</sub>(a)GO(a)Zn-Ni-Fe-LDH system, consequently, the corresponding reflection planes at  $2\theta = 11.4^{\circ}$  (0 0 3),  $23.0^{\circ}$  (0 0 6), 34.6° (0 1 2), 39.0° (0 1 5), 46.3° (0 1 8), 60.2° (1 1 0) and 61.5° (1 1 3) represent the characteristic signals for the layered double hydroxide moiety (Fig. 5b). The nanocomposite has a rhombohedral crystalline structure and exhibits the ICSD reference pattern of 01-089-7111 for nickel oxide hydroxide. The reflection planes of (0 0 3), (0 0 6), (1 1 0) and (1 1 3) are the particular characteristics of LDH-like materials.<sup>48</sup> The literature review shows that graphene oxide has the reflection planes at  $2\theta = 10.6^{\circ} (0 \ 0 \ 1), 22.5^{\circ} (0 \ 0 \ 2), 43.2^{\circ} (1 \ 0 \ 1) \text{ and } 50.9^{\circ} (1 \ 0 \ 2).$ the case of the XRD pattern of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system, the relevant peaks of graphene oxide were overlapped or influenced by the reflection planes of LDH and Fe<sub>3</sub>O<sub>4</sub> constituents.

Structural elucidation of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH composite system was further investigated using the transmission electron microscopy (TEM) technique. The depicted images in Fig. 6 clearly represent that the nanocomposite was constructed from the layering of LDH over Fe<sub>3</sub>O<sub>4</sub>@GO constituents. In addition, the nanoparticles are agglomerated to some extent to afford bigger segments.

The magnetic behavior and value of the Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>(a) GO(a)Zn–Ni–Fe-LDH system were also studied using vibrating sample magnetometer (VSM) analysis. The depicted graphs in Fig. 7 show the non-linear and reversible magnetic property for Fe<sub>3</sub>O<sub>4</sub> (curve a) and Fe<sub>3</sub>O<sub>4</sub>(a)GO(a)Zn–Ni–Fe-LDH (curve b). The saturation magnetization ( $M_s$ ) values of Fe<sub>3</sub>O<sub>4</sub> and the Fe<sub>3</sub>O<sub>4</sub>(a) GO(a)Zn–Ni–Fe-LDH system are respectively 70 emu g<sup>-1</sup> and 16 emu g<sup>-1</sup>. It is clear that when a layer of non-magnetic LDH surrounds the magnetic graphene oxide species, the saturation magnetization value of Fe<sub>3</sub>O<sub>4</sub> was intensively decreased. Nevertheless, the magnetization value is still enough for any magnetic separation.

## Preparation of biscoumarin materials

After the successful synthesis and characterization of the nanostructured Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system, in continuation, it was prompted that the catalytic activity of the prepared nanocomposite system was studied towards one-pot Knoevenagel-Michael reaction of aromatic aldehydes with 4-hydroxycoumarin. In this context, the condensation reaction of benzaldehyde with 4-hydroxycoumarin was selected as a model reaction and therefore the influence of the amount of nanocatalyst, temperature and solvent was studied therein. The results of this investigation are summarized in Table 1. Investigation of the results exhibited that the progress of the condensation reaction in the absence of the nanocatalyst led to poor to moderate yield of the product. By examining the title reaction in DMF, CH<sub>3</sub>CN, EtOAc, MeOH, EtOH, H<sub>2</sub>O-EtOH and H<sub>2</sub>O with 20-40 mg of the Fe<sub>3</sub>O<sub>4</sub>(a) GO@Zn-Ni-Fe-LDH system, it was concluded that H<sub>2</sub>O as a green solvent was the best solvent of choice and 30 mg of the nanocatalyst was an adequate amount to promote the condensation reaction perfectly. Moreover, using reflux conditions completed the



Fig. 6 TEM images of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system.

condensation reaction within 3 min. Therefore, the conditions mentioned in entry 14 (Table 1) were selected as the requirements to carry out the condensation reaction of benzaldehyde with 4-hydroxycoumarin efficiently.

The usefulness and catalytic activity of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn–Ni–Fe-LDH system was further studied toward one-pot Knoevenagel–Michael reaction of structurally diverse aromatic aldehydes with 4-hydroxycoumarin at the optimized reaction conditions (Table 2). Reviewing the results shows that all the condensation reactions were carried out successfully within 3–40 min to



Fig. 7 Magnetization curves of (a) Fe<sub>3</sub>O<sub>4</sub> and (b) the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system.

afford the corresponding biscoumarin materials in 87-95% yields. In addition, an examination for gram-scale synthesis of biscoumarin materials with the present protocol represents that the condensation reaction of 4-hydroxycoumarin (3 mmol) and benzaldehyde (1.5 mmol) in the presence of Fe<sub>3</sub>O<sub>4</sub>(a) GO@Zn-Ni-Fe-LDH (90 mg) was carried out successfully under reflux conditions to afford 3,3'-benzylidenebis(4-hydroxycoumarin) in 94% yield (1.16 g) within 10 min.

Next, the suitability of this synthetic method was highlighted by the comparison of the obtained result for the  $Fe_3O_4$ GO@Zn-Ni-Fe-LDH system with those reported for other protocols. Table 3 represents that in terms of the yield, reaction time and reusability of the nanocatalysts, the present work exhibited a more outstanding result than the previous systems.

Although the exact mechanism of this synthetic protocol is not known, the depicted mechanism in Fig. 8 exhibits the role of Fe<sub>3</sub>O<sub>4</sub>(a)GO(a)Zn-Ni-Fe-LDH in the catalysis of the Knoevenagel-Michael reaction of 4-hydroxycoumarin with aromatic aldehydes. The figure shows that through the activation of aldehyde by the nanocatalyst, the nucleophilic attack of 4-hydroxycoumarin took place. Subsequently, the Michael reaction of another molecule of 4-hydroxycoumarin with the prepared intermediate of benzylidenecoumarin affords the final biscoumarin material.

### Reusability of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system

The economic and green aspect of the Knoevenagel-Michael reaction of benzaldehyde with 4-hydroxycoumarin in the presence of the Fe3O4@GO@Zn-Ni-Fe-LDH system was further studied by examining the reusability of the nanocomposite at the optimized reaction conditions. In this context once the condensation reaction was completed, the nanocatalyst was magnetically separated from the reaction mixture, washed with EtOAc and then dried under air atmosphere. The reaction vessel was again charged with fresh benzaldehyde, 4-hydroxycoumarin and the recycled nanocatalyst to run the reaction for a second time. Fig. 9 shows that the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system can be reused for 5 consecutive cycles with a small loss in the yield from 95% to 87%. In this context, the FTIR spectrum (Fig. S1, ESI<sup>†</sup>), SEM (Fig. S2, ESI<sup>†</sup>) and EDX analysis (Fig. S3, ESI<sup>†</sup>) of the first recycling step of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system represent that during the progress of the condensation reaction, the morphology and elemental composition of the

Table 1 Optimization experiments for the Knoevenagel-Michael reaction of benzaldehyde with 4-hydroxycoumarin catalyzed by the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH system<sup>4</sup>

	CHO + 2 0H	_Fe <sub>3</sub> O <sub>4</sub> @GO@Zn-Ni-Fe-LDH ►		OH COH	
Entry	Fe <sub>3</sub> O <sub>4</sub> @GO@Zn-Ni-Fe-LDH (mg)	Solvent (2 mL)	Temp. (°C)	Time (min)	Conversion (%)
1	_	H <sub>2</sub> O	r.t.	600	70
2	_	H <sub>2</sub> O	Reflux	70	60
3	—	Solvent-free	100	90	Trace
4	30	Solvent-free	70	30	50
5	30	$H_2O$	70	15	100
6	30	$H_2O$	r.t.	360	60
7	30	$H_2O-EtOH(1:1)$	Reflux	60	90
8	30	EtOH	70	30	50
9	30	MeOH	70	30	30
10	30	EtOAc	70	30	40
11	30	CH <sub>3</sub> CN	70	30	60
12	30	DMF	70	30	70
13	30	$H_2O$	r.t.	60	70
14	30	$H_2O$	Reflux	3	100
15	20	$H_2O$	Reflux	15	100
16	40	$H_2O$	Reflux	1	100

<sup>a</sup> All reactions were carried out with the molar ratio of 1:0.5 for 4-hydroxycoumarin and benzaldehyde in 2 mL of solvent. Conversions less than 100% were determined on the basis of the recovered 4-hydroxycoumarin.

## $\label{eq:constraint} \mbox{Table 2} \quad \mbox{Synthesis of biscoumarin materials by the $Fe_3O_4@GO@Zn-Ni-Fe-LDH$ system}^a$

	R	+ 2 0H Fe <sub>3</sub> O <sub>4</sub> @	9GO@Zn-Ni-Fe-LDH H₂O, Reflux		OH OH	
					M.p. (°C)	
Entry	R	Product	Time (min)	Yield <sup><math>b</math></sup> (%)	Found	Reported <sup>ref.</sup>
1	н		3	95	230-232	229–231 <sup>36</sup>
2	4-Me		20	90	267-269	266–269 <sup>36</sup>
3	4-OMe		20	91	249-251	250-252 <sup>36</sup>
4	2-OMe		25	89	190–193	_
5	4-Cl		10	91	257-259	261-263 <sup>36</sup>
6	2-Cl		5	89	200-202	201–203 <sup>36</sup>
7	4-NO <sub>2</sub>		4	93	231-233	233-235 <sup>36</sup>
8	3-NO <sub>2</sub>		10	91	215-217	214–215 <sup>36</sup>

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<sup>*a*</sup> All reactions were carried out with the molar ratio of 1:0.5 for 4-hydroxycoumarin and aromatic aldehydes in the presence of 30 mg of the nanocatalyst under refluxing  $H_2O$  (2 mL). In the case of entry (14), 4-hydroxycoumarin (2 mmol) was used. <sup>*b*</sup> Yield refers to isolated pure product.

nanocatalyst remained intact. However after five recycling steps, yield-losing of the product could be attributed to the leaching of

active species and/or collapse of the mesopores on the surface or within the interlamellar spaces of the nanocomposite system.

Entry

Reusability

Ref.

## Table 3 Comparison of the synthesis of 3,3'-benzylidenebis(4-hydroxycoumarin) with Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH and other reported systems



1	Fe <sub>3</sub> O <sub>4</sub> @GO@Zn-Ni-Fe-LDH	Reflux/H <sub>2</sub> O	3	95	5	а
2	$RuCl_3 \cdot nH_2O$	80 °C/H <sub>2</sub> O	25	84	6	35
3	$[MIM(CH_2)_4SO_3H][HSO_4]$	80 °C/solvent-free	30	92	3	36
4	Phosphotungstic acid	80 °C/H <sub>2</sub> O	20	93	5	37
5	(H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ])/SiO <sub>2</sub>	r.t./EtOH	30	92	3	38
6	CuO-CeO <sub>2</sub>	Reflux/H <sub>2</sub> O	12	94	5	39
7	SiO <sub>2</sub> –OSO <sub>3</sub> H NPs	80 °C/EtOH	20	93	3	40

<sup>*a*</sup> Present work.

Catalyst



Fig. 8 A proposed mechanism for the Knoevenagel-Michael reaction of aromatic aldehydes with 4-hydroxycoumarin catalyzed by the Fe<sub>3</sub>O<sub>4</sub>@ GO@Zn-Ni-Fe-LDH system.

# Conclusions

In this study, through the combination system of magnetic graphene oxide and Zn-Ni-Fe-layered double hydroxide constituents, the nanocomposite of Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH was synthesized. The prepared magnetic GO-LDH system was

then characterized using SEM, EDX, FTIR, XRD, TEM and VSM analyses. Next, the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH (30 mg) was further investigated towards the Knoevenagel-Michael reaction of 4-hydroxycoumarin (1 mmol) with structurally diverse aromatic aldehydes (0.5 mmol). All reactions were carried out in refluxing H2O to afford biscoumarins in 87-95% yields

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Fig. 9 Reusability of the Fe $_3O_4@GO@Zn-Ni-Fe-LDH$  system in the synthesis of 3.3'-benzylidenebis(4-hydroxycoumarin) material.

within 3–40 min. Moreover, this synthetic protocol was successfully utilized for the gram-scale synthesis of 3,3'-benzylidenebis(4hydroxycoumarin) material. The prepared nanocatalyst system was reused for 5 consecutive cycles with a small decrease in the yield. This synthetic method represents the advantages in terms of preparing the novel magnetic graphene oxide-LDH composite system, high yield of biscoumarin materials, short reaction times and applying water as a green solvent as well as the magnetic separation of the nanocatalyst system.

## Experimental

### Materials and methods

All materials and reagents were purchased from commercial sources and they were used without further purifications. FT-IR and <sup>1</sup>H NMR spectra were recorded on Thermo Nicolet Nexus 670 and Bruker Avance 300 MHz spectrometers, respectively. The obtained products were characterized using physical and spectral data followed by a comparison with authentic data. The purity of the chemicals and also the progress of the reactions were monitored by TLC over silica gel 60 F254 aluminum sheet. X-ray diffractions were recorded by an X'PertPro Panalytical diffractometer at 40 kV (30 mA, CuK $\alpha$  radiation source,  $\lambda = 1.5418$  Å) at  $2\theta = 10^{\circ} - 80^{\circ}$ . The size and morphology of the particles were determined using SEM images from an FESEM ZEISS-Sigma VP instrument. Magnetic properties of the nanocatalysts were measured by vibrating sample magnetometer (Meghnatis Daghigh, Iran) under magnetic fields up to 20 kOe. The irradiation of ultrasound was carried out on SOLTEC SONICA 2400MH S3 (305 W).

#### Synthesis of graphene oxide

The synthesis of graphene oxide was carried out *via* the modified Hummers procedure.<sup>50,51</sup> In a round-bottom flask containing concentrated sulfuric acid (46 mL) and under vigorous stirring, graphite (1.0 g) was added. After the addition of NaNO<sub>3</sub> (1.0 g), stirring of the reaction mixture was continued for 30 min. To the prepared mixture, KMnO<sub>4</sub> (6.0 g) was gradually added and the reaction mixture was stirred for 2 h at 0 °C and an additional 2 h at 35 °C. In continuation, distilled water (46 mL) was added in a

drop-wise manner and the reaction mixture was stirred at 98  $^{\circ}$ C for 15 min. Next, the addition of distilled water (100 mL) and H<sub>2</sub>O<sub>2</sub> (20 mL, 30%) to the reaction mixture was also carried out. The solid residue was filtered and washed twice by an aqueous solution of HCl (5%). The prepared graphene oxide was then dried in an oven at 50  $^{\circ}$ C.

### Synthesis of the magnetic graphene oxide composite system

The composite of magnetic graphene oxide was prepared by a chemical co-precipitation method.52 Accordingly in a roundbottom flask containing a solution of distilled water (100 mL) and glacial acetic acid (3 mL), FeCl<sub>2</sub>·4H<sub>2</sub>O (1.29 g, 0.0065 mol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (3.51 g, 0.013 mol) were added under vigorous stirring. In another vessel, a mixture of graphene oxide (50 mg) in distilled water (15 mL) was sonicated for 2 h. After that, the solution of iron chlorides and suspension of graphene oxide were mixed together and the prepared mixture was stirred at 80 °C. Next, aqueous ammonia (20 mL, 25 wt%) was added rapidly and the resulting mixture was stirred for 20 min. During the addition of ammonia, nanoparticles of Fe<sub>3</sub>O<sub>4</sub> were successfully immobilized on the surface or within the interlamellar spaces of graphene oxide. Finally, the prepared composite of Fe<sub>3</sub>O<sub>4</sub>@GO was magnetically separated and washed twice with ethanol and distilled water and left to dry in an oven at 50 °C.

### Synthesis of the Zn-Ni-Fe-LDH system

The layered double hydroxide system of Zn–Ni–Fe was prepared by the *in situ* growth of Zn<sup>2+</sup>, Ni<sup>2+</sup> and Fe<sup>3+</sup> cations. In this context, a solution of sodium carbonate (1.060 g, 0.01 mol) and sodium hydroxide (0.160 g, 0.004 mol) in distilled water (30 mL) was prepared. In another vessel, a solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.785 g, 0.006 mol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.617 g, 0.009 mol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (1.352 g, 0.005 mol) in distilled water (30 mL) was also prepared. Both of the solutions were sonicated for 30 min and at the same time were added to a vessel containing distilled water (30 mL) under vigorous stirring. The pH of the reaction mixture was adjusted at the value of 11. The prepared slurry was stirred for 30 min at ambient temperature and then stored at 80 °C for 24 h. After cooling and filtration, finally, the prepared Zn–Ni–Fe-LDH system was dried in an oven at 150 °C.

# Preparation of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn-Ni-Fe-LDH composite system

The nanocomposite of the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn–Ni–Fe-LDH system was prepared through a solvothermal method. For this, in a roundbottom flask containing distilled water (40 mL), Fe<sub>3</sub>O<sub>4</sub>@GO (0.30 g) and Zn–Ni–Fe-LDH (0.8 g) were added and the resulting mixture was sonicated for 20 min. After stirring the mixture for 2 h, the resulting slurry was stored at 90 °C for 24 h. The solid residue was then filtered and dried in an oven at 100 °C to afford the Fe<sub>3</sub>O<sub>4</sub>@GO@Zn–Ni–Fe-LDH composite system.

## Typical procedure for the synthesis of biscoumarin materials

In a round-bottom flask, a mixture of benzaldehyde (0.053 g, 0.5 mmol) and 4-hydroxycoumarin (0.162 g, 1 mmol) in water (2 mL) was prepared.  $Fe_3O_4@GO@Zn-Ni-Fe-LDH$  (30 mg) was

then added and the mixture was stirred for 3 min under reflux conditions. Once the reaction was completed (monitored by TLC, *n*-hexane/EtOAc: 4/2), the mixture was cooled to room temperature. The nanocatalyst was magnetically separated from the reaction mixture. EtOAc (5 mL) was then added and the reaction mixture was stirred for an additional 10 min. The organic layer was separated and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The evaporation of the solvent under reduced pressure affords pure 3,3'-benzylidenebis(4-hydroxycoumarin) in 95% yield (Table 2, entry 1). FT-IR (KBr,  $\nu \text{ cm}^{-1}$ ) 3065, 2737, 1659, 1609, 1564, 1336, 1090, 755; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.12 (s, 1H, CH), 7.23–8.07 (m, 13H, ArH), 11.32 (s, 1H, OH), 11.55 (s, 1H, OH).

# Conflicts of interest

There are no conflicts to declare.

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# References

- 1 A. Corma, H. Garcia and F. X. Llabres i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- 2 N. Mizuno and M. Misono, Chem. Rev., 1998, 98, 199.
- 3 M. Gilanizadeh and B. Zeynizadeh, *New J. Chem.*, 2018, **42**, 8553.
- 4 M. Gilanizadeh and B. Zeynizadeh, *Res. Chem. Intermed.*, 2018, 44, 6053.
- 5 M. Gilanizadeh and B. Zeynizadeh, *J. Iran. Chem. Soc.*, 2018, **15**, 2821.
- 6 B. Zeynizadeh, E. Gholamiyan and M. Gilanizadeh, *Curr. Chem. Lett.*, 2018, 7, 121.
- 7 M. Gilanizadeh, B. Zeynizadeh and E. Gholamiyan, *Iran. J. Sci. Technol., Trans. A: Sci.*, 2019, **43**, 819.
- 8 M. Gilanizadeh and B. Zeynizadeh, *Res. Chem. Intermed.*, 2019, 45, 2811.
- 9 M. Gilanizadeh and B. Zeynizadeh, *Polycyclic Aromat. Compd.*, 2019, DOI: 10.1080/10406638.2019.1567560.
- 10 R. Abu-Reziq, H. Alper, D. Wang and M. L. Post, *J. Am. Chem. Soc.*, 2006, **128**, 5279.
- 11 A. H. Lu, E. L. Salabas and F. Schuth, Angew. Chem., Int. Ed., 2007, 46, 1222.
- 12 M. B. Gawande, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.*, 2013, **42**, 3371.
- B. Feng, R. Y. Hong, L. S. Wang, L. Guo, H. Z. Li, J. Ding,
  Y. Zheng and D. G. Wei, *Colloids Surf.*, A, 2008, 328, 52.
- 14 W. Wu, Q. He, H. Chen, J. Tang and L. Nie, *Nanotechnology*, 2007, 18, 145609.
- 15 Y. J. Chen, F. Zhang, G. G. Zhao, X. Y. Fang, H. B. Jin, P. Gao, C. L. Zhu, M. S. Cao and G. Xiao, *J. Phys. Chem. C*, 2010, 114, 9239.

- 16 N. Ye, Y. Xie, P. Shi, T. Gao and J. Ma, *Mater. Sci. Eng.*, C, 2014, 45, 8.
- 17 X. Huang, X. Qi, F. Boey and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 666.
- 18 S. Khodabakhshi, B. Karami, K. Eskandari, S. J. Hoseini and A. Rashidi, *RSC Adv.*, 2014, 4, 17891.
- 19 S. Khodabakhshi, F. Marahel, A. Rashidi and M. Khaleghi Abbasabadi, *J. Chin. Chem. Soc.*, 2015, **62**, 389.
- 20 W. C. Hou and Y. S. Wang, ACS Sustainable Chem. Eng., 2017, 5, 2994.
- 21 M. Singh, A. Sahu, S. Mahata, P. K. Singh, V. K. Rai and A. Rai, *New J. Chem.*, 2019, **43**, 14972.
- 22 F. Fei, L. Cseri, G. Szekely and C. F. Blanford, ACS Appl. Mater. Interfaces, 2018, **10**, 16140.
- M. V. Prabhagar, M. P. Kumar, C. Takahashi, S. Kundu, T. N. Narayanan and D. K. Pattanayak, *New J. Chem.*, 2019, 43, 14313.
- 24 L. Cseri, J. Baugh, A. Alabi, A. AlHajaj, L. Zou, R. A. W. Dryfe, P. M. Budd and G. Szekely, *J. Mater. Chem. A*, 2018, 6, 24728.
- 25 N. Mitoma, Y. Yano, H. Ito, Y. Miyauchi and K. Itami, ACS Appl. Nano Mater., 2019, 2, 4825.
- 26 X. Guo, B. Du, Q. Wei, J. Yang, L. Hu, L. Yan and W. Xu, *J. Hazard. Mater.*, 2014, **278**, 211.
- 27 L. L. Li, L. L. Fan, M. Sun, H. M. Qiu, X. J. Li, H. M. Duan and C. N. Luo, *Colloids Surf.*, B, 2013, **107**, 76.
- 28 L. Xiao, W. Ma, M. Han and Z. Cheng, J. Hazard. Mater., 2011, 186, 690.
- 29 X. Wu, X. Tan, S. Yang, T. Wen, H. Guo, X. Wang and A. Xu, *Water Res.*, 2013, 47, 4159.
- 30 X. Cheng, X. Huang, X. Wang, B. Zhao, A. Chen and D. Sun, *J. Hazard. Mater.*, 2009, **169**, 958.
- 31 T. Takemura, T. Kamo, E. Sakuno, S. Hiradate and Y. Fujii, J. Tropical Forest Science, 2013, 25, 268.
- 32 I. Manolov, C. Maichle-Moessmer, I. Nicolova and N. Danchev, *Arch. Pharm.*, 2006, **339**, 319.
- 33 K. M. Khan, S. Iqbal, M. A. Lodhi, G. M. Maharvi, Z. Ullah, M. I. Choudhary, A. U. Rahman and S. Perveen, *Bioorg. Med. Chem.*, 2004, **12**, 1963.
- 34 J. H. Lee, H. B. Bang, S. Y. Han and J. G. Jun, *Tetrahedron Lett.*, 2007, 48, 2889.
- 35 K. Tabatabaeian, H. Heidari, A. Khorshidi, M. Mamaghani and N. O. Mahmoodi, *J. Serb. Chem. Soc.*, 2012, 77, 407.
- 36 N. Tavakoli-Hoseini, M. M. Heravi, F. F. Bamoharram, A. Davoodnia and M. Ghassemzadeh, *J. Mol. Liq.*, 2011, **163**, 122.
- 37 P. Singh, P. Kumar, A. Katyal, R. Kalra, S. K. Dass, S. Prakash and R. Chandra, *Catal. Lett.*, 2010, **134**, 303.
- 38 M. M. Heravi, F. Nahavandi, S. Sadjadi, H. A. Oskooie and F. F. Bamoharram, *Synth. Commun.*, 2010, 40, 498.
- 39 J. Albadi, A. Mansournezhad and S. Salehnasab, *Res. Chem. Intermed.*, 2015, 41, 5713.
- 40 B. Sadeghi and T. Ziya, J. Chem., 2013, 179013.
- 41 Z. Lu, Z. Hetman, G. B. Hammond and B. Xu, *Green Chem.*, 2016, **18**, 5769.
- 42 P. Kisszekelyi, A. Alammar, J. Kupai, P. Huszthy, J. Barabas, T. Holtzl, L. Szente, C. Bawn, R. Adams and G. Szekely, *J. Catal.*, 2019, 371, 255.

- 43 Z. Sun, X. Yang, X. Huang, M. Zhang, G. Bian, Y. Qi, X. Yang and W. Zhang, *New J. Chem.*, 2019, **43**, 16676.
- 44 C. Didaskalou, J. Kupai, L. Cseri, J. Barabas, E. Vass, T. Holtzl and G. Szekely, *ACS Catal.*, 2018, **8**, 7430.
- 45 C. Ó. Dálaigh, S. A. Corr, Y. Gun'ko and S. J. Connon, *Angew. Chem., Int. Ed.*, 2007, **46**, 4329.
- 46 G. Y. Li, Y. R. Jiang, K. L. Huang, P. Ding and L. L. Yao, *Colloids Surf.*, A, 2008, 320, 11.
- 47 J. A. Lopez, F. González, F. A. Bonilla, G. Zambrano and M. E. Gómez, *Rev. LatinAm. Metal. Mat.*, 2010, 30, 60.
- 48 C. Busetto, G. D. Piero, G. Manara, F. Trifiro and A. Vaccari, *J. Catal.*, 1984, **85**, 260.
- 49 R. K. Gupta, Z. A. Alahmed and F. Yakuphanoglu, *Mater. Lett.*, 2013, **112**, 75.
- 50 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 51 X. X. Wang, Q. H. Fan, S. J. Yu, Z. S. Chen, Y. J. Ai and Y. B. Sun, *Chem. Eng. J.*, 2016, 287, 448.
- 52 E. Doustkhah and S. Rostamnia, J. Colloid Interface Sci., 2016, 478, 280.