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Nickel-substituted cobalt ferrite nanoparticles supported on arginine-modified graphene oxide nanosheets: Synthesis and catalytic activity

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The amino acid arginine was used to modify the surface of graphene oxide nanosheets and then nickel-substituted cobalt ferrite nanoparticles were supported on those arginine-grafted graphene oxide nanosheets ($Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO). The prepared $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO was characterized using flame atomic absorption spectroscopy, inductively coupled plasma optical emission spectrometry, energy-dispersive spectroscopy, Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, Raman spectroscopy, X-ray diffraction, thermogravimetric analysis, scanning electron microscopy and transmission electron microscopy. The application of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO as a catalyst was examined in a one-pot tandem oxidative cyclization of primary alcohols with *o*-phenylenediamine to benzimidazoles under aerobic oxidation conditions. The results showed that 2-phenylbenzimidazole derivatives were successfully achieved using $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite catalyst via the one-pot tandem oxidative cyclization strategy.

KEYWORDS
arginine, graphene oxide, nickel-substituted cobalt ferrite nanoparticles

1 | INTRODUCTION

Graphene is an atomically thin two-dimensional carbonaceous material with exceptional electronic, electrical and mechanical properties which has attracted tremendous attention in the scientific community.[1] Due to the exceptional properties of graphene, this two-dimensional material has attracted increasing attention as a promising new nanomaterial for a variety of unique applications.[2–4] Graphene oxide (GO) as heavily oxygenated graphene can readily exfoliate in water. Exfoliation of GO in water yields stable dispersions of single-layer sheets, this property making GO a potential material for green applications. Due to the unique and fascinating behaviour of GO as a support in catalytic applications, this carbonaceous material can be used beneficially where supports with high surface area, high mechanical strength and electrical conductivity, intrinsic low mass, high water dispersibility, easy surface modification and oxygen-carrying functionalities are employed to immobilize catalytically active metal or metal oxide nanoparticles with high loadings and high dispersion by keeping the size of the nanoparticles as small as possible.

Due to the good coordinative interaction of amino acids and metal ions or metal/metal oxide nanoparticles on the one hand and the green nature of them on the other hand, preparation of amino acid-grafted GO as a support to immobilize catalytic active metal or metal oxide nanoparticles can be introduced as a good protocol to improve the catalytic performance of active sites.[5] The appropriate functional groups on the amino acids which are selected to modify the surface of GO can well control the morphology, distribution and loading of catalytically active sites on the support. Therefore, an enhanced catalytic performance was achieved for catalytically active sites supported on modified

GO compared to the unmodified GO support.[5] The structures of some α-amino acids have free ─NH_2 functional groups which can accelerate base-assisted reactions; by using these α-amino acids as modifiers for the preparation of a support to immobilize catalytically active sites, high performance can be achieved for designed reactions which need both basic and catalytic systems. Also the presence of side-chain groups on amino acids helps them to bind the GO surface. Among the common α-amino acids, arginine has a unique structure which contains guanidine functional groups on its side chain. Due to the presence of ─NH_2 and guanidine functional groups in arginine, this amino acid is capable of binding to various compounds chemically by using nucleophilic substitution reactions and it can be used as an organic base.

Spinel ferrites, especially cobalt ferrite ($CoFe_2O_4$) and nickel ferrite ($NiFe_2O_4$) nanoparticles, have been intensively studied because of their unique magnetic and catalytic properties as well as their considerable chemical and mechanical stability.[6] Due to the unique chemical features of nanosized cobalt ferrite (as the most technologically important ferrite), $CoFe_2O_4$ nanoparticles can be used as an attractive candidate for a wide range of advanced catalytic applications. Also, $NiFe_2O_4$ as an important magnetic ferrite has extensive uses in diverse areas such as catalysis, sensing, photomagnetic materials, drug delivery, magnetic resonance imaging, etc.[6]

Synthesis of mixed metal ferrites is a common approach for increasing and improving the catalytic properties of the mentioned materials[7–9] because of the synergy effect between metals in the structure of spinel ferrite. Substitution of metal ferrite by another appropriate transition metal can optimize the catalytic activity and provide both an active and selective catalyst. Therefore, in order to modify the catalytic properties of $CoFe_2O_4$ nanoparticles, substitution of nanosized cobalt ferrite by nickel was selected as preferred transition metal due to considerable catalytic properties of nickel ferrite.[10]

Nanosized particles have unique chemical and physical properties compared to their bulk counterparts due to their nanodimension.[11] Agglomeration and aggregation of nanoparticles is one of the main constraints in the synthesis of nanosized ferrite[11] because the transfer rate of reactants to the nanosized ferrite within the solvent in the reaction medium is inversely proportional to the size of the nanoparticles. To overcome this drawback, modified GO nanosheets with high surface area and suitable functional groups as support can be used to isolate the nanoparticles. On the other hand, a hybrid combining GO and nanosized metal oxide particles could have the properties and features of both GO (as a fascinating paper-shape material) and metal oxide nanoparticles, so the use of GO as a nanoscale substrate for the formation of nanocomposites with metal oxides is technically considerable.

In order to develop a new heterogeneous catalyst for organic transformations, the synthesis of nickel-substituted cobalt ferrite nanoparticles supported on arginine-grafted GO nanosheets ($Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO) was studied. Reduction and oxidation reactions are among the most important transformations in synthetic chemistry, such redox reactions providing key methodologies to introduce and modify functional groups.[12–14] Therefore the catalytic activity of the synthesized $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was investigated in the one-pot tandem oxidative synthesis of 2-phenylbenzimidazole derivatives. The obtained novel $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite has both arginine and $Ni_{0.5}Co_{0.5}Fe_2O_4$ moieties which can be used not only in organic base catalysis but also applied in oxidation reactions.

2 | EXPERIMENTAL

Since GO has inertness for immobilization of ferrite nanoparticles, arginine was used to modify the GO surface. The selection of the arginine for modification of the surface of GO nanosheets was made because of good coordination interaction between ─NH_2 group of arginine and ferrite nanoparticles. Also, use of arginine for the synthesis of the catalyst gave a double nature to the prepared catalyst (oxidation capability of ferrite moiety and basic property of arginine moiety of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite) which made it possible for us to use the same catalyst in the oxidation and synthetic parts of the one-pot tandem oxidative synthesis of 2-phenylbenzimidazole derivatives. The $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocatalyst was prepared as shown in Figure 1.

2.1 | Synthesis of arginine-grafted GO Nanosheets (Arg–GO)

The synthesis of GO was done using a modified Hummers method.[15,16] Graphite powder (1.0 g) was added to a round-bottom flask containing the mixture of $K_2S_2O_8$ (1.0 g) and P_2O_5 (1.0 g) in concentrated H_2SO_4 and the resulting mixture was stirred with a magnetic bar at 80 °C. After 6 h, the reaction medium was cooled to room temperature and diluted by addition of 200 ml of deionized (DI) water. The stirring of the reaction medium was continued overnight while keeping at room temperature. Finally, the preoxidized graphite was obtained by filtration of the reaction mixture and washing the residue using DI water. The preoxidized graphite was dried at room temperature. The obtained powder was added to a round-bottom flask containing concentrated H_2SO_4 (50 ml) at 0 °C. Under vigorous stirring, $KMnO_4$ (6.0 g) was added slowly and the resulting mixture was stirred for 4 h while the temperature was kept below 25 °C. Then, the reaction vessel was kept in an ice bath

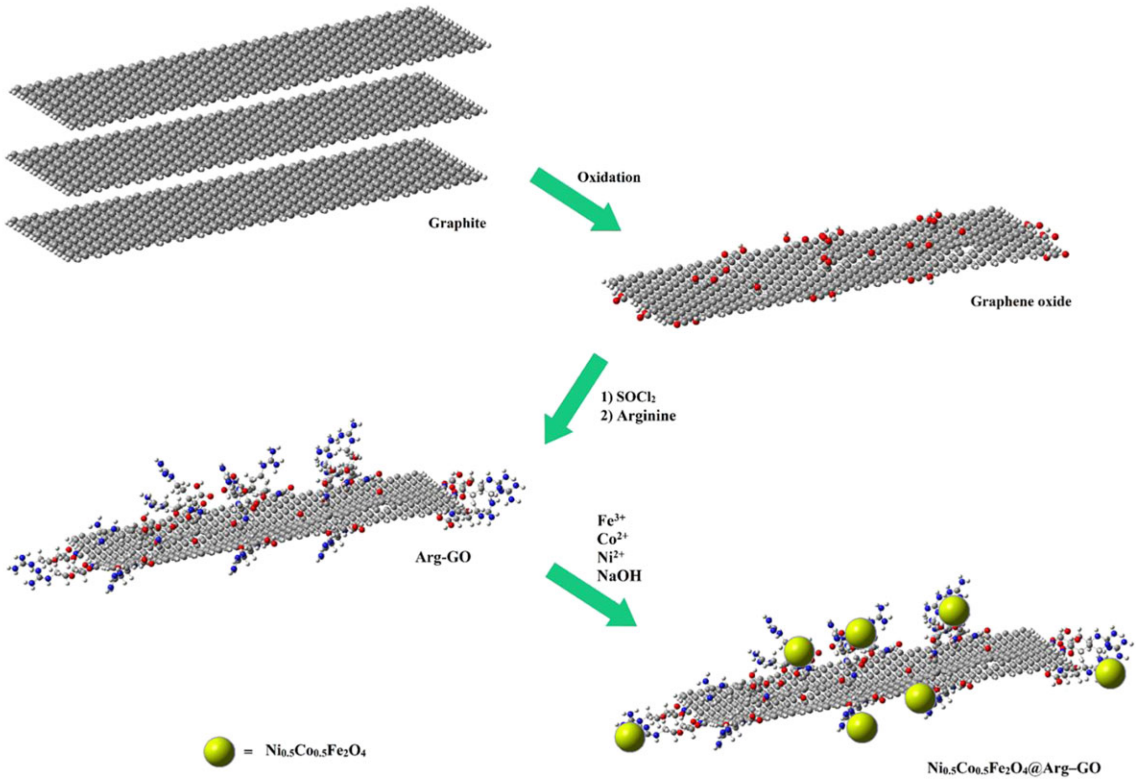


FIGURE 1 Preparation of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocatalyst

and DI water in two steps (at first 100 ml and, after 2 h, 300 ml) was added slowly to the reaction mixture and the solution was stirred for 30 min. Next, hydrogen peroxide (30%) was added dropwise to the mixture until the colour changed from black to golden yellow. The resulting precipitate was centrifuged and washed repeatedly with HCl (0.1 M, 300 ml) and DI water and dried in air at room temperature. The GO was obtained as a brown powder.

For the grafting reaction of arginine and GO nanosheets, GO (0.3 g), $SOCl_2$ (20 ml) and dimethylformamide (DMF; 0.5 ml) were added to a round-bottom flask and the reaction medium was stirred at 70 °C for 24 h under nitrogen atmosphere. Then, the excess solvent was evaporated at 100 °C. The residue was washed with dry tetrahydrofuran for at least five times. To the obtained acylated product in a round-bottom flask, dry DMF (20 ml) and arginine (2.0 mmol, 0.1 g) were added. The reaction mixture was stirred at 90 °C for 12 h. Then, the reaction mixture was subjected to centrifugation and thorough washing with DI water and ethanol successively, followed by drying at 50 °C under vacuum. The Arg–GO product was obtained as a black powder.

2.2 | Synthesis of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO

For the synthesis of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO, a mixture of Arg–GO (1.0 g) in DI water (200 ml) was dispersed by ultrasonication for 30 min. To the as-prepared dispersed Arg–GO mixture, $FeCl_3{\cdot}6H_2O$ (1.6 mmol), $CoCl_2{\cdot}6H_2O$ (0.4 mmol) and $NiCl_2{\cdot}6H_2O$ (0.4 mmol) were added. The prepared mixture was sonicated at room temperature for 1 h. After that, the temperature of the reaction mixture was raised to 80 °C. Magnetic stirring of the mixture was done continuously for 30 min while keeping the temperature at 80 °C. By dropwise addition of NaOH solution (0.1 M) to the reaction medium during 20 min, the pH was raised to 10. After stirring of the obtained mixture for 30 min, the temperature was decreased to room temperature and stirring continued for 6 h. Finally, the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was separated (by centrifuging), washed (with DI water and EtOH) and dried (at room temperature).

2.3 | General procedure for catalytic reactions

In a two-necked flask containing a solution of diamine (1.0 mmol) and alcohol (1.2 mmol) in CH_3CN (7.0 ml), $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (0.06 g) was added. The reaction mixture was stirred magnetically under air blowing (air was bubbled into the reaction mixture at a rate of 5 ml min^{-1}) and reflux conditions (at 80 °C). The progress of the reaction was monitored by GC and TLC. After reaction completion, filtration of reaction mixture was done to separate the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite and the separated catalyst was washed with EtOH. Finally, the organic solvents were removed and the crude product was separated on a silica gel column to afford 2-phenylbenzimidazole derivatives. (The final products were identified using ^1H NMR spectroscopy and quantified by isolated yield; selected ^{1}H NMR spectra are included in the supporting information.)

3 | RESULTS AND DISCUSSION

The characterization of the prepared $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was done using flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), energy dispersive spectroscopy (EDS), Fourier transform infrared (FT-IR) spectroscopy, UV–visible spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The amounts of nickel, cobalt and iron of the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite were calculated using FAAS. The $Ni_{0.5}Co_{0.5}Fe_2O_4$ content in the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was determined as 9.04 wt%. ICP-OES analysis was also used to determine the amounts of nickel, cobalt and iron in the prepared nanocomposite, the obtained result corroborating the determined nickel, cobalt and iron content in the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite. The obtained results from FAAS and ICP-OES analyses showed that the composition of the prepared specimen is corroborated within the composition of predicted $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite. Also, determination of the chemical composition of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was done using EDS analysis. As is clear from Figure 2, the EDS analysis confirmed the presence of carbon, nitrogen, oxygen, nickel, cobalt and iron in the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite.

XRD analysis as an effective method for characterizing the interlayer change and degree of crystallinity of graphene-based materials and was employed to further investigate the structure of graphite, GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite (Figure 3). The spacing between two layers gives structural information of parent graphite and GO nanosheets. The parent graphite shows a characteristic diffraction peak at 26.7° related to an interlayer spacing of 0.33 nm (Bragg equation). The XRD pattern of GO nanosheets shows a diffraction peak at $2\theta = 11.3°$ that indicates an interlayer spacing of 0.78 nm. The increased interlayer spacing is mainly due to a large amount of oxygen-containing functional groups produced during oxidation of graphite. The appearance of the GO peak at 11.3° and the disappearance of the graphite peak at 26.7° confirmed that the prepared GO nanosheets were completely oxidized. The XRD pattern of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO indicates characteristic diffraction peaks at 2θ values of 30.2°, 32.7°, 35.6°, 43.3°, 57.3° and 62.9° which agree with those reported in the literature for $Ni_{0.5}Co_{0.5}Fe_2O_4$.[7,10,17] These reflection peaks, which demonstrate the formation of $Ni_{0.5}Co_{0.5}Fe_2O_4$, correspond to the characteristic inter-planar spacing between (220), (222), (311), (400), (511) and (440) planes of spinel ferrite with cubic symmetry.[7,10,17] In the XRD pattern of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO, the characteristic diffraction peaks of Arg–GO were not observed because the diffraction peaks of the ferrite moiety are stronger than the diffraction peaks of Arg–GO. The mentioned characteristic peaks related to $Ni_{0.5}Co_{0.5}Fe_2O_4$ confirm the successful preparation of the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalytic system.

Raman spectroscopy is used to investigate the electronic and phonon structure of graphene-based materials. So, Raman spectroscopy as a useful tool was applied to study the prepared $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite (Figure 4). The Raman spectrum of GO indicates two prominent peaks at 1584 cm^{-1} (G-band) and 1317 cm^{-1} (D-band). G-band is the result of the first-order E_{2g} mode from sp^2 carbon domains and D-band is characteristic of a breathing mode for k-point. For the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite, the characteristic D-band and G-band are observable at around 1313 and 1588 cm^{-1}, respectively, which show the Raman lines of GO.

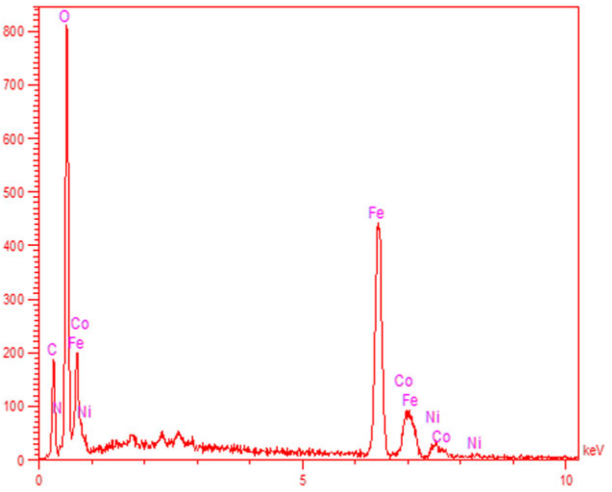


FIGURE 2 SEM-EDS result for $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite

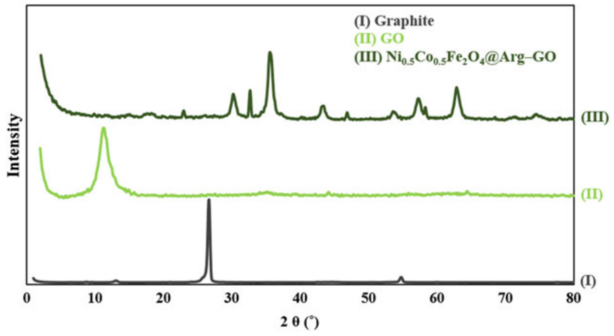


FIGURE 3 XRD patterns of graphite (I), GO (II) and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (III)

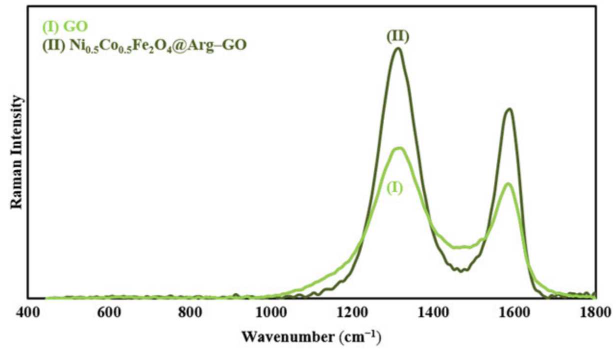


FIGURE 4 Raman spectra of GO (I) and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (II)

The UV–visible spectral analysis of GO, Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite is presented in Figure 5. These spectra were obtained with GO, Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO dissolved in concentrated HCl and diluted with DI water.

Chemical attachment of arginine to the GO nanosheets and immobilization $Ni_{0.5}Co_{0.5}Fe_2O_4$ on Arg–GO were confirmed using FT-IR spectroscopy (Figure 6). The successful synthesis of GO nanosheets was corroborated from the FT-IR spectrum of GO which reveals characteristic bands at 3408 (—OH), 1713 (carboxyl —C=O), 1600 (aromatic —C=C—), 1391 (carboxyl —C—O), 1229 (epoxy —C—O) and 1093 cm^{-1} (alkoxy —C—O).[18] The new bands at 1624 cm^{-1} (—C=N stretch) and 1408 cm^{-1} (—C—N stretch) are associated with the presence of arginine moiety in Arg–GO.[5] The amount of arginine amino acid grafted to GO nanosheets was 12 wt% according to elemental analysis. In the case of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO, the characteristic bands at 617 and 436 cm^{-1} can be attributed to metal—O stretching vibrations.[19] The presence of characteristic bands of Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles in the FT-IR spectrum of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO indicates the successful preparation of the nanohybrid.

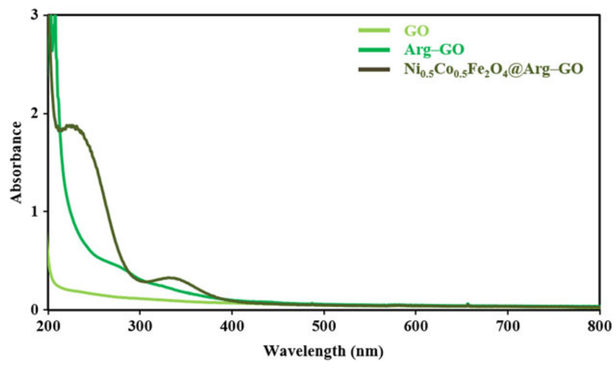


FIGURE 5 UV–visible spectra of GO, Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO in H_2O–HCl (10:1)

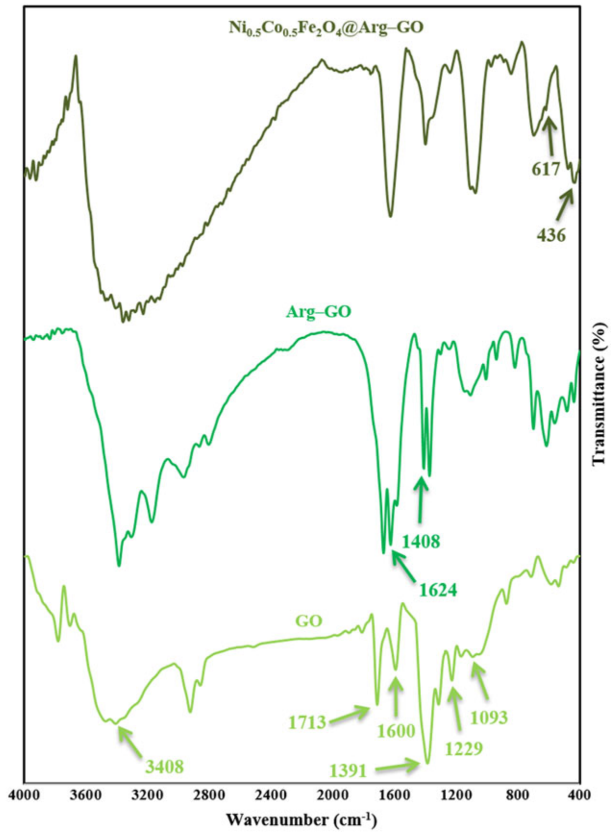


FIGURE 6 FT-IR spectra of GO, Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO

SEM analysis was used to characterize the morphology of the obtained GO, Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO. The SEM image of Arg–GO (Figure 7b) indicated that arginine was grafted on GO nanosheet surface without a large change in the morphology of GO. The presence and good dispersion of $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles on the Arg–GO nanosheet surface are observable in Figure 7(c,d).

TEM images of GO (Figure 8a), Arg–GO (Figure 8b) and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanoparticles (Figure 8c) confirm the uniform dispersion and the size distribution of the $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles supported on the Arg–GO surface.

The relatively high thermal stability of the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite in air was confirmed using TGA. The thermograms of GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO are shown in Figure 9. TGA curve of the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite indicated three stages: the low-temperature range (up to 156 °C, related to the removal of adsorbed water on the surface of the nanocomposite) and 156–503 and 503–710 °C ranges (attributed to the decomposition of GO and arginine).

In order to develop a suitable catalytic system using the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite, optimization studies were conducted with *o*-phenylenediamine (**1a**) and benzyl alcohol (**2a**) as model substrates using various amounts of catalyst, solvents and temperatures (Table 1). Initially, the effect of various amounts of

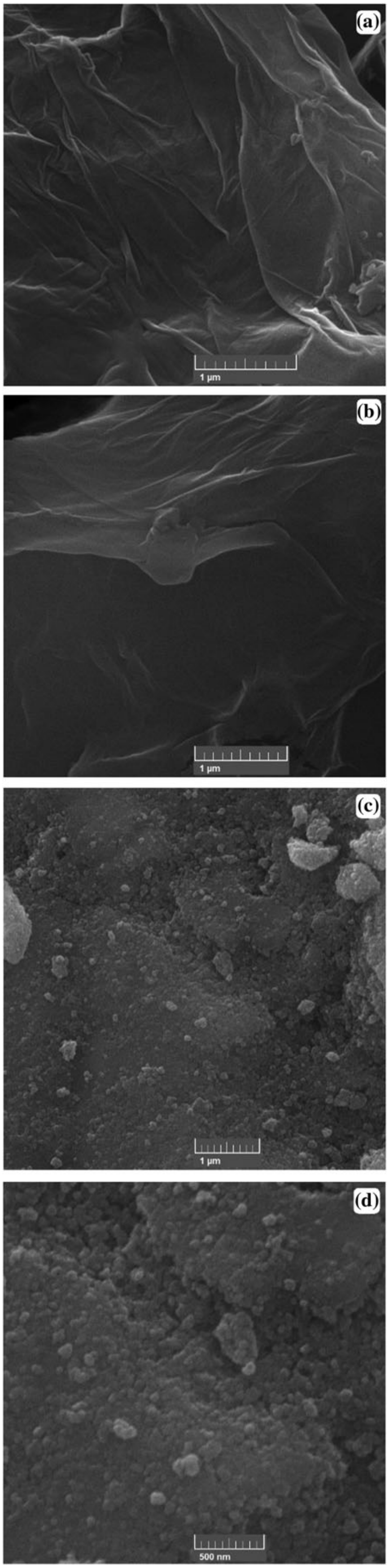


FIGURE 7 SEM images of GO (a), Arg–GO (b) and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (c, d)

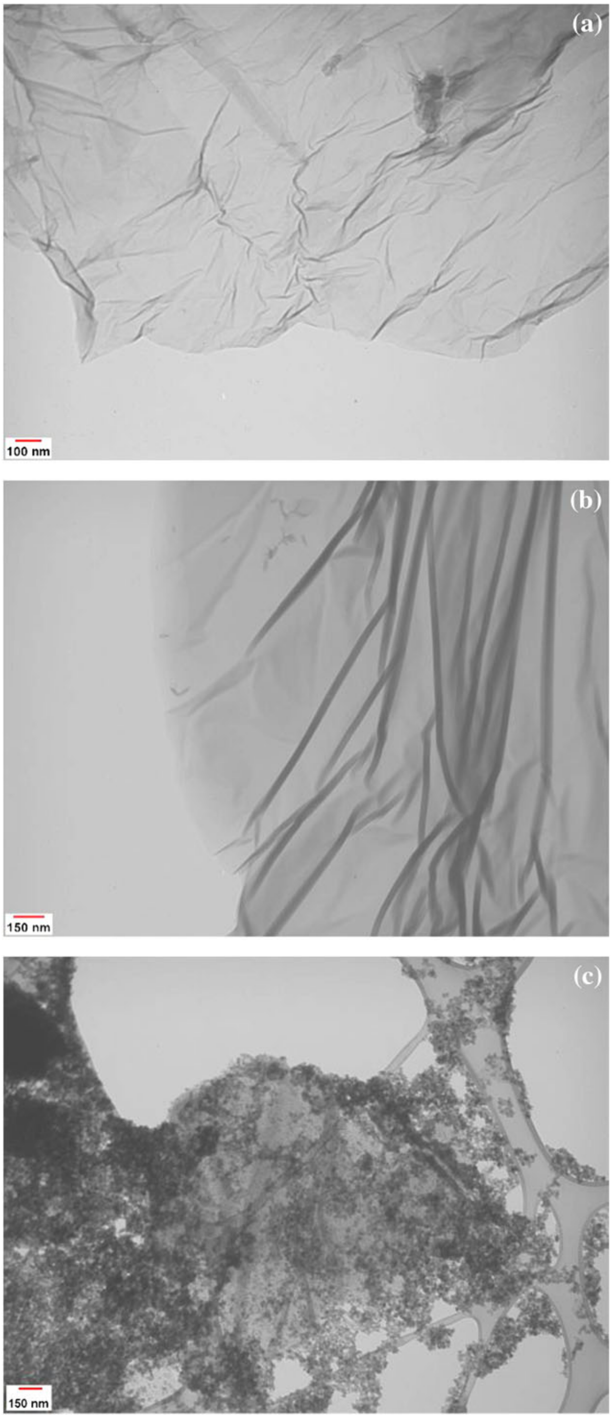


FIGURE 8 TEM images of GO (a), Arg–GO (b) and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (c)

$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was investigated. The obtained results confirmed that, in the absence of catalyst, the formation of **3a** was not observed (entry 1). The use of Arg–GO as catalyst failed to give 2-phenylbenzimidazole product, which excluded the contribution of Arg–GO itself as a catalyst (entry 2). Subsequent screening of various amounts of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite revealed that 0.06 g of catalyst exhibited the

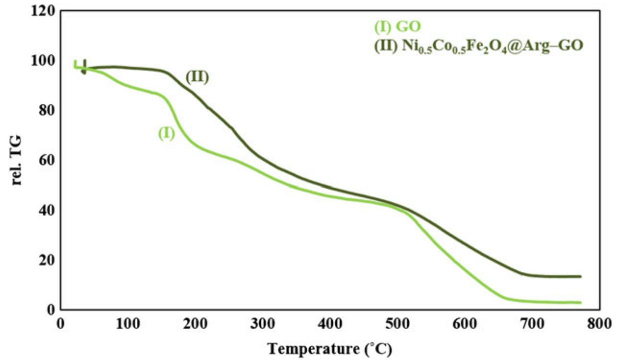
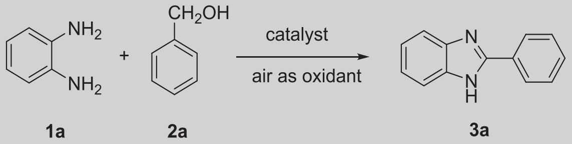


FIGURE 9 TGA curves of GO (I) and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (II) in air

best result, leading to **3a** in 79% yield, while lowering the amount of catalyst afforded the target product in less than 55% yield (entries 4–6). The obtained results related to the effect of solvent indicated that the use of acetonitrile as a solvent led to an increase the 2-phenylbenzimidazole product yield to 79%, whereas solvents such as *o*-xylene, DMF and toluene gave inferior results (entries 4, 7–9). The reaction took place to give product **3a** in 47% yield when the substrates were stirred in acetonitrile at 60 °C for 6 h (entry 10). The use of a reaction temperature of 40 °C led to a decrease in product yield to 20% (entry 11). The reaction at room temperature gave an inferior result (entry 12). To show the role of Arg–GO nanosheets as support in the oxidative synthesis of 2-phenylbenzimidazole product, the reaction was accomplished using $Ni_{0.5}Co_{0.5}Fe_2O_4$ and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO under the same reaction conditions. The obtained results (Table 1, entries 3 and 4) confirmed that $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO has higher catalytic activity than unsupported $Ni_{0.5}Co_{0.5}Fe_2O_4$. The adsorption of aromatic reactants on the surface of the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite because of the π–π interaction between graphene support and benzene skeleton of the reactants seems to enhance the efficiency of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO compared to unsupported $Ni_{0.5}Co_{0.5}Fe_2O_4$.[20,21] To examine the role of arginine in the synthesis of product **3a**, $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@GO (nickel-substituted cobalt ferrite nanoparticles supported on graphene oxide nanosheets without

TABLE 1 Optimization of reaction conditions for oxidative synthesis of 2-phenylbenzimidazole derivatives catalysed by $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite[a]



Entry	Catalyst	Amount of catalyst (g)	Solvent	Time (h)	Temperature (°C)	Yield (%)[b]
1	—	—	CH_3CN	24	80	Trace
2	Arg–GO	0.06	CH_3CN	24	80	Trace
3	$Ni_{0.5}Co_{0.5}Fe_2O_4$	0.01	CH_3CN	6	80	26
4	**$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO**	**0.06**	**CH_3CN**	**6**	**80**	**79**
5	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.05	CH_3CN	6	80	52
6	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.04	CH_3CN	6	80	41
7	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	*o*-Xylene	6	80	74
8	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	DMF	6	80	38
9	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	Toluene	6	80	60
10	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	CH_3CN	6	60	47
11	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	CH_3CN	6	40	20
12	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	CH_3CN	6	r.t.	11
13	$Ni_{0.5}Co_{0.5}Fe_2O_4$@GO	0.06	CH_3CN	6	80	49
14[c]	$Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	CH_3CN	6	80	Trace
15	$NiFe_2O_4$	0.01	CH_3CN	6	80	7
16	$CoFe_2O_4$	0.01	CH_3CN	6	80	12

[a] Reaction conditions: *o*-phenylenediamine (1.0 mmol), benzyl alcohol (1.2 mmol), solvent (7.0 ml), air as oxidant.

[b] Isolated yield.

[c] In the absence of air oxidant.

use of arginine) were applied in the reaction. The obtained results showed that arginine amino acid enhances the catalytic activity of the prepared system for the synthesis of product **3a**. In fact, use of arginine for the synthesis of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite gave a basic property to the prepared catalytic system by which it can catalyse the synthetic part of the one-pot tandem oxidative synthesis of 2-phenylbenzimidazole. From the data presented in Table 1 (entries 2, 4 and 13), it could be concluded that the double nature of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO led to the promotion of the catalytic activity of prepared nanocomposite in the oxidation and synthetic parts of the one-pot tandem oxidative synthesis of product **3a** due to the oxidation capability of ferrite moiety and basic property of arginine moiety of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO. The successful carrying out of the one-pot tandem oxidative synthesis of product **3a** confirmed the utility of the synthesized $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite for both aerobic oxidation and base catalysis, as it had been designed. It is important to note that the synthesis of 2-phenylbenzimidazole product did not proceed without air blowing (entry 14). A comparison was done of the catalytic activities of $NiFe_2O_4$, $CoFe_2O_4$, $Ni_{0.5}Co_{0.5}Fe_2O_4$, $Ni_{0.5}Co_{0.5}Fe_2O_4$@GO and $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalysts (entries 3, 4, 13, 15 and 16). The obtained results show that the substitution of cobalt ferrite nanoparticles by nickel transition metal and use of arginine amino acid give a more active catalytic system.

Having the optimal conditions in hand, the scope of the protocol was investigated for the synthesis of 2-phenylbenzimidazole derivatives using the reaction of a series of substituted benzyl alcohols with diamines (Table 2). As is clear from Table 2, electron-donating and electron-withdrawing substituents on benzyl alcohols readily promote the reaction.

The recyclability of the synthesized $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst was examined in the oxidative synthesis of 2-phenylbenzimidazole compound. After completion of the reaction, the catalyst was recovered from the reaction medium by centrifuging and was washed with EtOH. The recovered $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst was dried and then reused for five repeat cycles of the reaction (Figure 10). The obtained results indicated that the

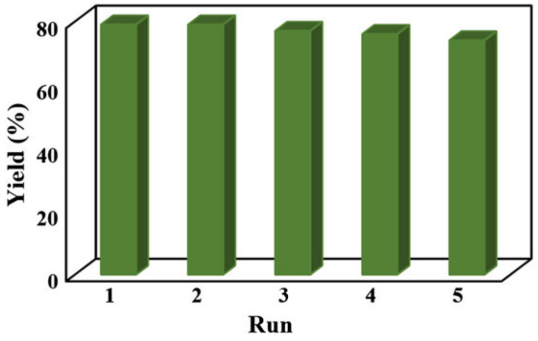
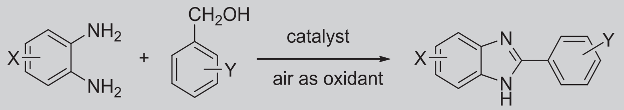


FIGURE 10 Successive use of $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst for oxidative synthesis of 2-phenylbenzimidazole

TABLE 2 Oxidative synthesis of 2-phenylbenzimidazole derivatives catalysed by $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite[a]



Entry	Diamine	Alcohol	Product	Yield (%)[b]	Melting point (°C)	
					Found	Reported
1	*o*-Phenylenediamine	Benzyl alcohol	**3a**	79	293–295	292–293[22]
2	*o*-Phenylenediamine	2-Methylbenzyl alcohol	**3b**	81	222–224	223–224[22]
3	*o*-Phenylenediamine	4-Methylbenzyl alcohol	**3c**	89	272–273	275–276[22]
4	*o*-Phenylenediamine	4-Bromobenzyl alcohol	**3d**	90	257–259	260–261[22]
5	*o*-Phenylenediamine	2-Methoxybenzyl alcohol	**3e**	88	159–160	156–158[23]
6	*o*-Phenylenediamine	4-Methoxybenzyl alcohol	**3f**	91	218–220	218–219[22]
7	*o*-Phenylenediamine	4-Chlorobenzyl alcohol	**3g**	87	288–289	287–289[24]
8	*o*-Phenylenediamine	2-Nitrobenzyl alcohol	**3h**	90	230–231	232–235[25]
9	*o*-Phenylenediamine	4-Nitrobenzyl alcohol	**3i**	93	256–258	255–256[22]
10	4-Methyl-*o*-phenylenediamine	Benzyl alcohol	**3j**	85	241–242	243–245[24]
11	4-Methyl-*o*-phenylenediamine	2-Chlorobenzyl alcohol	**3k**	81	105–106	106–108[26]

[a] Reaction conditions: diamine (1.0 mmol), alcohol (1.2 mmol), $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (0.06 g), CH_3CN (7.0 ml), air as oxidant, 80 °C.

[b] Isolated yield.

catalytic activity of the $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite is not altered by a considerable amount during successive uses.

4 | CONCLUSIONS

Modification of the surface of GO nanosheets was done using the amino acid arginine to produce arginine-grafted GO nanosheets as a support for immobilization of nickel-substituted cobalt ferrite nanoparticles. Functionalization of GO with arginine led to a catalytic system with uniform dispersion of $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles which has both oxidation capability of ferrite moiety and basic property of arginine moiety. The one-pot tandem oxidative reaction of readily available alcohols with *o*-phenylenediamines proceeds smoothly in the presence of the prepared $Ni_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst to afford substituted 2-phenylbenzimidazole derivatives. The use of arginine-grafted GO nanosheets to immobilize nickel-substituted cobalt ferrite nanoparticles enhances the catalytic activity of the prepared system. The use of a green and inexpensive catalytic system, air as green oxidant and readily available starting materials are significant practical advantages of the presented protocol.

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SUPPORTING INFORMATION

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