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FULL PAPER

Synthesis of graphene oxide supported copper–cobalt ferrite material functionalized by arginine amino acid as a new high–performance catalyst

Rahim Ghadari[1] | Hassan Namazi[1] | Mohammad Aghazadeh[2]

[1] Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran

[2] Microbiology Department, Faculty of Medicine, Tabriz University of Medical Sciences, Tabriz, Iran

Correspondence
Rahim Ghadari, Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran.
Email: r-ghadari@tabrizu.ac.ir

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A novel $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalytic system was successfully prepared by immobilization of copper substituted cobalt ferrite nanoparticles on arginine–grafted graphene oxide nanosheets, in which ferrite moiety acts as an oxidation catalyst and arginine has the role of base catalyst. Also, arginine amino acid was used to modify the surface of graphene oxide nanosheets which the prepared support can improve dispersion and uniform loading of nanoparticles. The prepared nanocomposite was characterized by flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectrometer (ICP–OES), energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT–IR), ultraviolet–visible spectroscopy (UV–vis), Raman spectroscopy, thermogravimetric analysis (TGA), x–ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analysis. The prepared $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was used as an efficient catalyst for one–pot tandem oxidative synthesis of 2–phenylbenzimidazole derivatives in good yields.

KEYWORDS
arginine, copper substituted cobalt ferrite nanoparticles, graphene oxide, oxidative synthesis

1 | INTRODUCTION

Fe_3O_4 ferrite (it occurs in nature as the mineral magnetite as one of the major iron ores found in the earth's crust) was made from iron and oxygen *via* chemical combination of iron(II) oxide with iron(III) oxide. Spinel ferrites can chemically modify with different transition metal ions to produce metal ferrites with variable application. Ferrites as attractive inorganic materials with excellent physical and chemical properties can catalyze various kinds of the organic transformation. Several kinds of ferrites nanomaterials have been utilized in different catalytic processes based on their transition metal.[1–5] Spinel ferrite nanoparticles such as cobalt substituted spinel ferrite ($CoFe_2O_4$) [6–8] and copper substituted spinel ferrite ($CuFe_2O_4$) [9–11] are two groups of important magnetic materials in catalysis applications due to their excellent chemical stability, high thermal stability, and high catalytic activity. It is reported that the catalytic activity of spinel ferrites containing transition metal ions is often enhanced by means of rapid electron exchange between their tetrahedral and octahedral sites.[12] The catalytic performance of spinel ferrite nanoparticles will be increased by keeping the size of the nanoparticles as small as possible.[13] The use of suitable supports with high surface area can provide high loading, uniform dispersion, and keeping the size of ferrite nanoparticles. Graphene, the one–atom–thick two–dimensional (2D) layer of sp^2–bonded carbon, has become the focus of considerable interest for this purpose due to its unique electronic properties and large specific surface area.[14,15]

Graphene oxide (GO), as one of the most important derivatives of graphene, contains a large number of oxygen–containing functional groups (hydroxyl, carboxyl, epoxy group, etc.) bearing on its basal planes and edges.[16–19] The large specific surface area and the oxygen–containing functional groups of GO provide it suitable for the immobilization of large amount of catalytically active nanoparticles with uniform dispersion.[20] In recent years, modified graphene oxide nanosheets have received a lot of attention as support for immobilization of catalytic nanoparticles. The surface of graphene oxide nanosheets coated by a suitable modifier has a strong interaction with nanoparticles which modified GO inhibits the aggregation of nanoparticles in liquid and increases the chemical stability of them. Therefore, combining nanometer–sized and nanostructured graphene oxide with suitable modifier can produce the appropriate support for catalytic applications.[17] The large number of oxygenated functional groups of graphene oxide can act as favorable anchoring centers and nucleation sites for chemical modifiers.[21] Because of oxygen–containing functional groups on the basal planes and edges of GO, it can easily functionalized with small molecules chemically by using the nucleophilic substitution reactions. So, some α–amino acids contain free $-NH_2$ functional groups can be used as green, biodegradable, renewable modifiers for chemical modification of GO.[22]

Amino acids, as biologically important organic compounds, are green, inexpensive, and nontoxic materials containing amine and carboxyl functional groups along with a side–chain specific to each amino acid. Amino acids with free $-NH_2$ functional groups can be used as good candidates to improve the nanoparticle loading property of GO.[22] The basic groups (primary amines) on side–chain of amino acids also provide an active base–catalyst for an enormous variety of synthetic applications.

Nitrogen containing five membered heterocyclic aromatic compounds, as important structures in pharmacological researches, are found in natural and synthetic compounds. Among nitrogenous five membered heteroaromatics, benzazoles are crucial core structures with significant biological and pharmacological activities. Benzimidazoles, as nitrogen containing benzazoles, are considered as important building blocks for pharmaceuticals and bioactive molecules in the field of medicinal chemistry. Traditionally, benzimidazoles were prepared using condensation of carboxylic acid derivatives such as acids, acyl chlorides, esters, nitriles, and amides with *o*–phenylenediamines.[23] Due to harsh conditions (high temperatures, strong dehydrating reagents, etc.) needed for the mentioned methods, oxidative condensation of aldehydes with *o*–phenylenediamines were developed later.[23] Oxidative condensation of aldehydes with *o*–phenylenediamines had inherent drawbacks such as the utilization of reactive and toxic reagents and transition–metal catalysts, therefore, improved methods have been developed for the synthesis of benzimidazoles using greener, cheaper, and more readily available substrates and catalysts. Alcohols are readily available chemicals feedstock which are used for the preparation of benzimidazoles using various catalysts or reagents, recently.[23–29]

In order to the developing new heterogeneous catalyst for organic transformations, the synthesis and catalytic application of copper substituted cobalt ferrite nanoparticles supported on arginine–grafted graphene oxide nanosheets ($Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO) are investigated. The activity of the obtained $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst was studied in the one–pot tandem oxidative synthesis of 2–phenylbenzimidazole derivatives. The prepared novel $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite has both $Cu_{0.5}Co_{0.5}Fe_2O_4$ and arginine moieties which can be not only used to oxidation reactions but also applied in organic base catalysis.

2 | EXPERIMENTAL

Arginine was used to modify the graphene oxide nanosheets surfaces due to inertness property of graphene oxide for immobilization of ferrite nanoparticles and good coordination interaction between $-NH_2$ group of arginine and ferrite nanoparticles. Use of $Cu_{0.5}Co_{0.5}Fe_2O_4$ ferrite nanoparticles and arginine for the synthesis of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocatalyst gave double nature to the prepared nanocomposite because of oxidation capability of ferrite moiety and basic property of arginine moiety. The mentioned double nature of the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite made it usable in the both oxidation and synthetic sections of the one–pot tandem oxidative synthesis of 2–phenylbenzimidazole derivatives. $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocatalyst was prepared as Figure 1.

2.1 | Synthesis of arginine–grafted graphene oxide nanosheets (Arg–GO)

The modified Hummers method was used to synthesize the graphene oxide.[30,31] The graphite powder (2.0 g) was treated with 1.0 g of $K_2S_2O_8$ and 1.0 g of P_2O_5 in the 6.0 ml of concentrated sulfuric acid. The reaction media was magnetically stirred at 80 °C for 6 h. In continue, the mixture of reaction was cooled to room temperature and diluted with deionized water (DI water, 200 ml) and

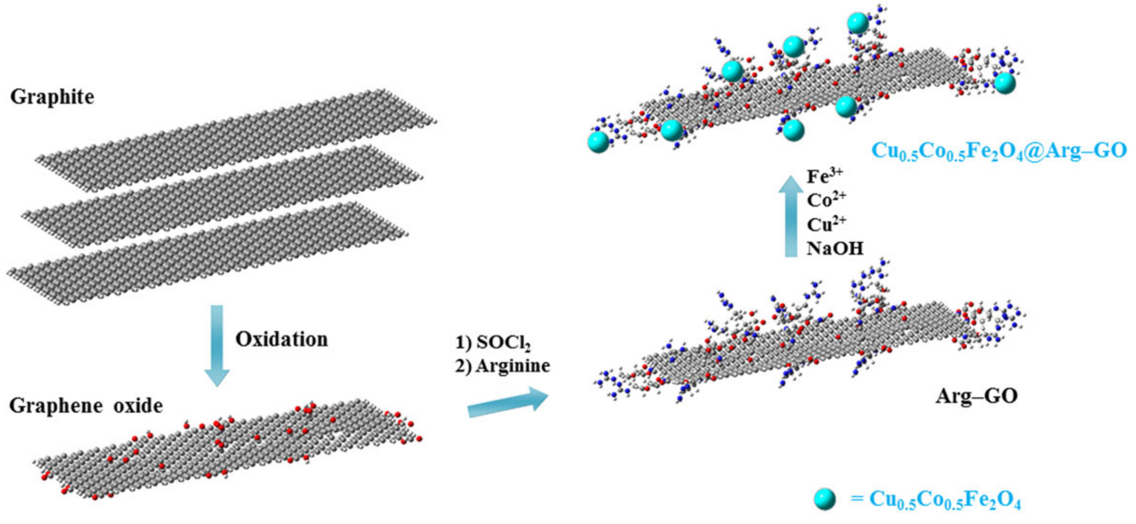

FIGURE 1 Preparation of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite

left overnight. After that, the mixture was filtered and the residue was washed with DI water to remove the residual acid. The obtained product was dried under ambient conditions overnight to give the preoxidized graphite. The obtained preoxidized graphite powder was put into cold concentrated H_2SO_4 (50 ml) at 0 °C. The $KMnO_4$ (6.0 g) was added gradually under stirring while keeping the temperature at 0 °C. The mixture was stirred at room temperature for 4 h. In continue, the mixture was diluted with DI water in two steps (at first, 100 ml and after 2 h, 300 ml) while the reaction vessel was kept in the ice bath. After adding all of the 400 ml DI water, the mixture was stirred at room temperature for 2 h. Finally, hydrogen peroxide (30%) was drop–wise added to the mixture until the color of the reaction media was changed from black to the golden yellow. The mixture was filtered and washed by HCl (0.1 M, 300 ml) and DI water to remove metal ions and residual acid. The resulting GO solid was dried in air, at room temperature. To synthesize the acylated graphene oxide, 0.3 g of as–synthesized GO was added into the solution containing 20 ml of thionyl chloride and 0.5 ml of dimethylformamide, and then treated at 70 °C for 24 h under nitrogen atmosphere. Then, the reaction solvent was evaporated. After evaporation of the excess solvent from the reaction mixture at 100 °C, the residue was washed with dry tetrahydrofuran at least five times. The obtained acylated GO, arginine (2.0 mmol, 0.1 g), and dry DMF (20 ml) were added to the round flask and the reaction mixture was stirred at 90 °C. After magnetic stirring for 12 h, the obtained product was centrifuged and washed with DI water and ethanol successively and dried at 50 °C under vacuum. Finally, the arginine attached graphene oxide product was obtained as a black powder.

2.2 | Copper substituted cobalt ferrite nanoparticles supported on arginine–grafted graphene oxide nanosheets ($Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO)

The as–prepared Arg–GO (1.0 g) was added to DI water (200 ml) and sonicated until a dispersed mixture was obtained. To a magnetically stirred mixture of as–prepared dispersed Arg–GO, $FeCl_3.6H_2O$ (1.6 mmol), $CoCl_2.6H_2O$ (0.4 mmol), and $CuCl_2.2H_2O$ (0.4 mmol) were added at room temperature. The prepared mixture was sonicated for 1 h and then, the temperature is raised to 80 °C. The stirring of reaction media is continued at this temperature for about 30 minutes. NaOH solution (0.1 M) was drop–wise added to the reaction media during 20 minutes until the pH of the mixture solution was raised to 10. The obtained mixture was magnetically stirred for 30 minutes and then, the temperature of mixture was decreased to room temperature and stirred for 6 h. Finally, the mixture was centrifuged and the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was washed with DI water and EtOH in sequence and dried at room temperature.

2.3 | General procedure for catalytic test

A mixture of diamine (1.0 mmol), alcohol (1.2 mmol), and dispersed $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (0.07 g) in 7.0 ml of acetonitrile was prepared in a two–necked flask equipped with an air bubbling tube and reflux condenser. The mixture of the reaction was stirred under reflux conditions (at 80 °C) while air was bubbled into the reaction mixture at a rate of 5 ml min^{-1}. The reaction progress was monitored by thin–layer chromatography (TLC) and gas chromatography (GC) methods. After that, the mixture was cooled to room temperature. After separation of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite and evaporation of the filtrate solvent under vacuum, the crude product was separated on a silica gel column to give 2–phenylbenzimidazole derivatives. (The final products were identified using ^1H NMR spectroscopy and quantified by isolated yield; selected ^1H NMR spectra are included in the supporting information.)

3 | RESULTS AND DISCUSSION

The prepared $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was characterized by flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectrometer (ICP–OES), energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT–IR), ultraviolet–visible spectroscopy (UV–vis), Raman spectroscopy, thermogravimetric analysis (TGA), x–ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analysis. The FAAS method has been applied to determine the elements of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite including copper, cobalt, and iron metals. The determination of copper, cobalt, and iron contents of the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite using FAAS method showed that the amount of $Cu_{0.5}Co_{0.5}Fe_2O_4$ in the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst is 8.21 weight percent. ICP–AES, an analytical technique used for the detection of trace metals, was used to provide the data about $Cu_{0.5}Co_{0.5}Fe_2O_4$ content in the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite. The analysis of elements of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO using ICP–AES method corroborates the previously determined amount of copper, cobalt, and iron in the mentioned nanocomposite which the determined composition of the prepared specimen was conformed within the composition of predicted $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO product. The EDS analytical technique was applied for the elemental analysis and chemical characterization of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite which the obtained results proves the presence of carbon, nitrogen, oxygen, copper, cobalt, and iron in the mentioned nanocomposite (Figure 2).

The UV–vis analysis of GO, Arg–GO, and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite is carried out in the solution of the mentioned specimens dissolved in the concentrated HCl and diluted with DI water. The obtained results are presented in the Figure 1S (see Electronic Supplementary Material). As can be seen, GO and Arg–GO does not show significant characteristic bands in the region 200–800 nm. The UV–visible spectrum of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite shows a broad band due to the presence of ferrite moiety. The maximum ultraviolet absorbance of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was found to be approximately 335 nm.

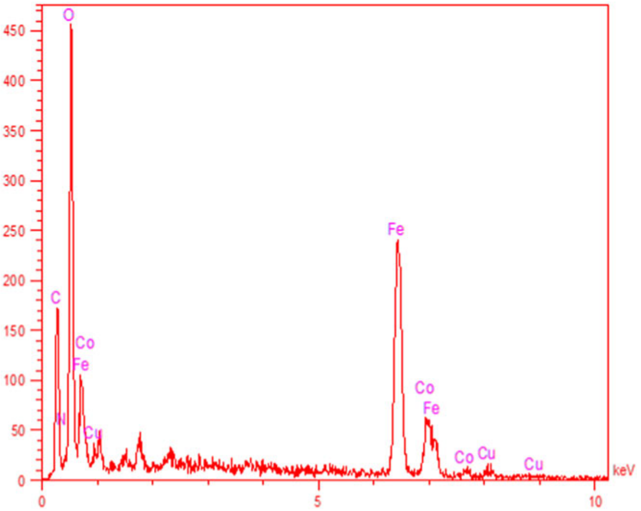

FIGURE 2 SEM–EDS result for $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite

Two main peaks in the Raman spectrum of graphene–based materials is observable due to the first order E_{2g} mode from sp^2 carbon domains (G–band) and characteristic of a breathing mode for k–point (D–band). Therefore, Raman spectroscopy was used for investigating the electronic and phonon structure of the prepared GO and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO. The Raman spectra of prepared GO and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO are shown in Figure 3. The characteristic D and G bands of GO are observed around 1308 and 1584 cm^{-1}, respectively. Also, Raman spectrum of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite in Figure 3 shows two prominent peaks at 1585 and 1313 cm^{-1} related to G–band and D–band, respectively.

The XRD patterns of graphite, GO and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite were employed to further investigate the structure of the synthetic materials (Figure 4). The XRD patterns of graphite, GO, and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite are shown

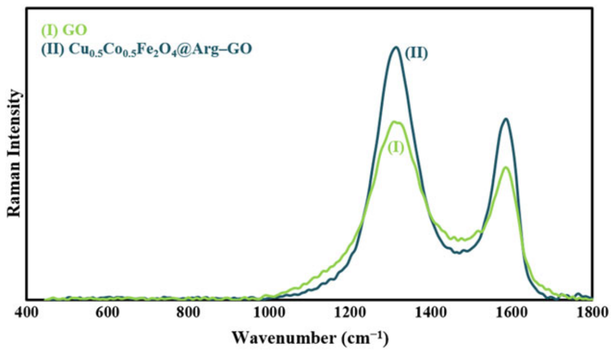

FIGURE 3 Raman spectra of GO (I) and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (II)

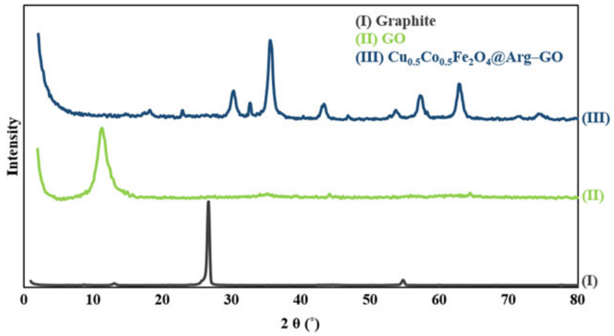

FIGURE 4 XRD patterns of graphite (I), GO (II), and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (III)

in Figure 4. The parent graphite exhibits a characteristic sharp peak at 26.7° related to the plane with an interlayer spacing equal to 0.33 nm. After oxidation of graphite to graphene oxide, the obtained GO shows the diffraction peak at $2\theta = 11.3°$ with an interlayer spacing value at 0.78 nm which has been assigned to the intercalation of the large amount of oxygen containing functional groups between the layers of the graphite. The completely oxidation of the parent graphite to graphene oxide nanosheets is confirmed by the disappearance of the graphite peak at 26.7° in the XRD pattern of GO. The diffraction characteristic peaks related to the $Cu_{0.5}Co_{0.5}Fe_2O_4$ is observable at $2\theta = 30.3°$, 32.6°, 35.6°, 43.3°, 57.3°, and 62.8° which corroborate to the reported ones in the literature[32–34] and confirm the successful preparation of the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalytic system.

The TGA thermograms of GO and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalytic system are showed in Figure 2S (see Electronic Supplementary Material). The relatively high thermal stability of the GO and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO in air is observable from Figure 2S (see Electronic Supplementary Material). As it is clear from Figure 2S (see Electronic Supplementary Material), in the TGA curve of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite, three stages could be observed. In the low temperature range, removal of adsorbed water on the surface of the mentioned catalyst is occurred. In the range of 148–499 °C and 499–715 °C, a large weight loss was occurred in two stages related to the decomposition of GO and arginine.

FT–IR spectroscopy was used to confirm the chemical attachment of arginine to the graphene oxide nanosheets and immobilization of the $Cu_{0.5}Co_{0.5}Fe_2O_4$ on arginine–grafted graphene oxide nanosheets (Figure3S, Electronic Supplementary Material). The GO exhibits various prominent bands at 3408, 1713, 1600, 1391, 1229, and 1093 cm^{-1} which have been assigned to: –OH, –C = O present in COOH, aromatic –C = C–, carboxyl –C–O, epoxy –C–O, and alkoxy –C–O functional groups, respectively.[35] In the IR spectrum of Arg–GO, the new bands appeared at 1624 cm^{-1} and 1408 cm^{-1} corresponds to the –C = N and –C–N stretches, respectively, due to the chemical attachment of arginine to the GO.[22] The characteristic bands at 621 cm^{-1} and 428 cm^{-1} (attributed to stretching vibrations of tetrahedral and octahedral complexes, respectively) in the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite also is appeared due to the metal – O stretching vibrations.[33]

The morphological characterization of the obtained GO, Arg–GO, and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was conducted by SEM. SEM images of GO, Arg–GO, and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite are shown in Figure 5. The SEM image of Arg–GO comparing to the SEM image of GO was confirmed that the formation of arginine–grafted graphene oxide nanosheets was done without a large change in the morphology of GO. SEM images of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO show it to be a nanocomposite structure having the uniform dispersion of $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles on the arginine–grafted graphene oxide nanosheets surfaces.

The microstructure and morphology of the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite is characterized by means of TEM, as well. As is seen in representative TEM micrographs, Figure 6a,b compares the morphologies of GO and Arg–GO. The micrographs of GO and Arg–GO possess similar sheet morphology which confirmed that arginine was grafted on GO surface without a large change in the morphology of GO. TEM image of copper substituted cobalt ferrite nanoparticles on arginine–grafted graphene oxide nanosheets shows the uniform dispersion and the size distribution of the supported $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles on the Arg–GO (Figure 6c). As Figure 6c shows, the surface of Arg–GO is covered with good dispersion of $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles.

In order to achieve suitable reaction conditions for the oxidative synthesis of 2–phenylbenzimidazole derivatives, a mixture of *o*–phenylenediamine (**1a**) and benzyl alcohol (**2a**) in acetonitrile was stirred at 80 °C for 24 h under air blowing. The obtained result showed that the formation of 2–phenylbenzimidazole (**3a)** product was not observed in the absence of catalyst (Table 1, Entry 1). Also, the mentioned reaction did not proceed in the presence of the Arg–GO (Entry 2), which excluded the contribution of arginine–grafted graphene oxide itself as a catalyst. Another reaction carried out to test the possibility of the oxidative synthesis of 2–phenylbenzimidazole derivatives by $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles (Entry 3). Therefore, $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles as catalytic system was added to the reaction media. To our surprise, 2–phenylbenzimidazole product was obtained in 32% yield (Entry 3) which confirmed the role of $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles in the oxidative synthesis of 2–phenylbenzimidazole derivatives. Since the π–π

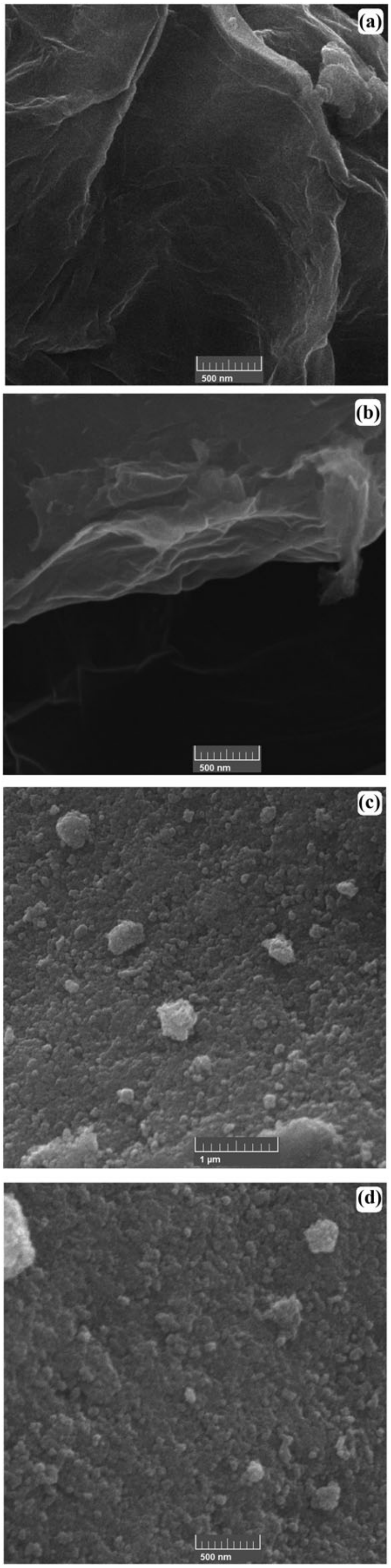

FIGURE 5 SEM images of GO (a), Arg–GO (b), and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (c,d)

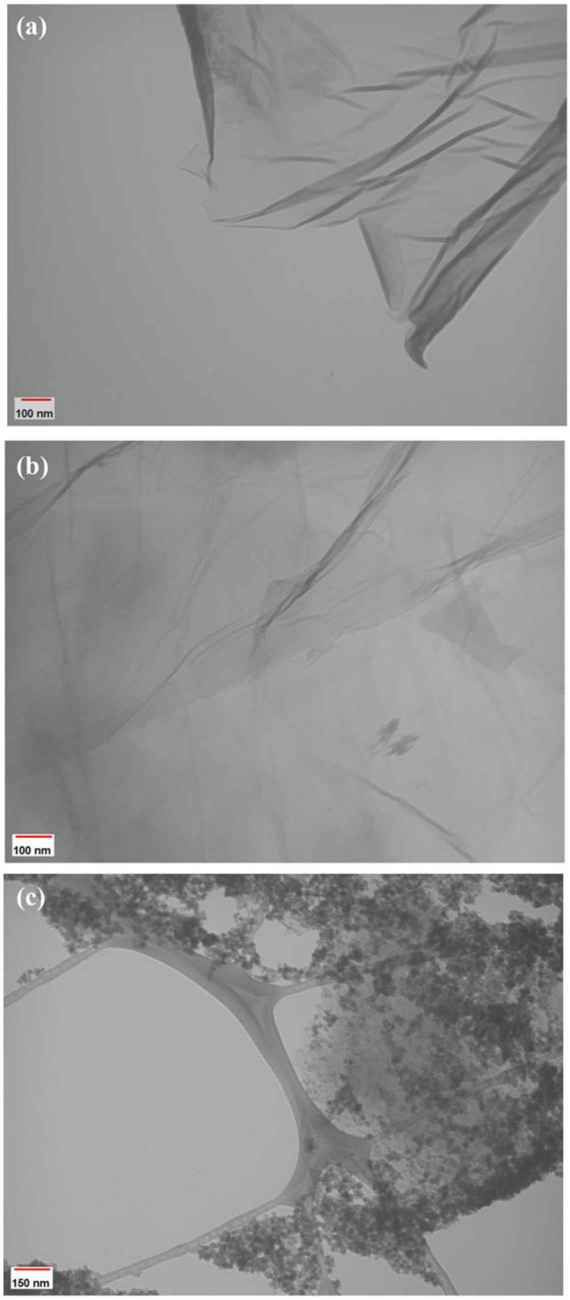

FIGURE 6 TEM images of GO (a), Arg–GO (b), and $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (c)

interaction between graphene support and benzene skeleton of the reactants can enhance the efficiency of graphene–supported nanoparticles compared to unsupported ones,[36,37] $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO as catalyst was added to the reaction media for the oxidative synthesis of 2–phenylbenzimidazole product. The obtained result showed that $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO has higher catalytic activity than unsupported $Cu_{0.5}Co_{0.5}Fe_2O_4$ which confirmed the adsorption of aromatic reactants on the surface of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite (Entry 4). The mentioned data proves the role of the arginine–grafted graphene oxide nanosheets as support

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

Entry	Catalyst	Amount of catalyst	Solvent	Time (h)	Temperature (°C)	Yield (%)[b]
1	–	–	CH_3CN	24	80	trace
2	Arg–GO	0.07	CH_3CN	24	80	trace
3	$Cu_{0.5}Co_{0.5}Fe_2O_4$	0.01	CH_3CN	5	80	32
4	**$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO**	**0.07**	**CH_3CN**	**5**	**80**	**82**
5[c]	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	trace
6	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.06	CH_3CN	5	80	49
7	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.05	CH_3CN	5	80	42
8	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	60	54
9	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	40	36
10	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	r.t.	13
11	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	toluene	5	80	49
12	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	*o*–xylene	5	80	75
13	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.07	DMF	5	80	20
14	$Cu_{0.5}Co_{0.5}Fe_2O_4$@GO	0.07	CH_3CN	5	80	35
15	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.09	CH_3CN	5	80	84
16	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	0.08	CH_3CN	5	80	84
17	$CuFe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	53
18	$CoFe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	61
19	$Cu_{0.2}Co_{0.8}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	78
20	$Cu_{0.4}Co_{0.6}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	83
21	$Cu_{0.6}Co_{0.4}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	89
22	$Cu_{0.8}Co_{0.2}Fe_2O_4$@Arg–GO	0.07	CH_3CN	5	80	70

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

[b] Isolated yield.

[c] The reaction in the absence of air oxidant.

for immobilization of $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles in the oxidative synthesis of 2–phenylbenzimidazole product (Entries 3, 4). Not surprisingly, without air blowing, the 2–phenylbenzimidazole product **3a** was not detected (Entry 5). In continue, the effect of various amounts of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was investigated in the mentioned reaction. 0.07 g of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst gave better yield (82%) as compared with lowering the amount of the catalyst which afforded the target molecule in <50% yield (Entries 4,6,7). Although the use of 60 °C, 40 °C, and room temperature of reaction resulted 2–phenylbenzimidazole product in 54%, 36%, and 13%, respectively (Entries 8–10), but improvement of the reaction yield was observed at 80 °C (Entry 4, 82%). The obtained results confirmed that heating at 80 °C is necessary to form the **3a** product in good yield. The reaction of *o*–phenylenediamine (**1a**) and benzyl alcohol (**2a**) in the presence of 0.07 g of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst was also tested in other solvents, e.g. toluene, *o*–xylene, and DMF (Entries 11–13), but all gave inferior results compared to that in acetonitrile. Therefore, acetonitrile was selected as preferred solvent for the oxidative synthesis of 2–phenylbenzimidazole derivatives by $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite. Since $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO has double nature due to oxidation capability of ferrite moiety and basic property of arginine moiety, the role of arginine in the synthesis of product **3a** was examined. For this purpose, copper substituted cobalt ferrite nanoparticles supported on graphene oxide nanosheets without use of arginine ($Cu_{0.5}Co_{0.5}Fe_2O_4$@GO) was applied in the same reaction conditions compared to Entry 4. The obtained result confirmed that arginine enhances the catalytic activity of the prepared $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO for the synthesis of product (Entries 4, 14) because of the basic property of the prepared catalytic system. As it is clear from the presented data in Table 1 (Entries 2–4, 14), double nature of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO promotes the catalytic activity of prepared nanocomposite because ferrite and arginine moieties of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO can catalyze aerobic oxidation and synthetic sections of the one–pot tandem oxidative synthesis of 2–phenylbenzimidazole product, as it has been designed. The effect of more amounts of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst than 0.07 g was tested in the oxidative synthesis of 2–phenylbenzimidazole product (Entries 15, 16). The obtained data are showing that increase of amount of catalyst will have no significant effect on its catalytic activity. Six $Cu_xCo_{1-x}Fe_2O_4$@Arg–GO ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) nanocomposites with different Cu/Co ratio were prepared to compare their activities with $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite (Entries 17–22). The obtained results showed that the order of the catalytic activity of $Cu_xCo_{1-x}Fe_2O_4$@Arg–GO nanocomposites can be regarded as $Cu_{0.6}Co_{0.4}Fe_2O_4$@Arg–GO > $Cu_{0.4}Co_{0.6}Fe_2O_4$@Arg–GO > $Cu_{0.2}Co_{0.8}Fe_2O_4$@Arg–GO > $Cu_{0.8}Co_{0.2}Fe_2O_4$@Arg–GO > $CoFe_2O_4$@Arg–GO > $CuFe_2O_4$@Arg–GO.

After examining the reaction profiles, the conditions of Entry 4 (0.07 g of $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst in acetonitrile at 80 °C under air blowing) was selected as the optimal conditions for further investigations of the substrate scope of the mentioned tandem oxidative reaction. Results for the reaction of *o*–phenylenediamine (**1a**) with a number of benzyl alcohols (**2**) using $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite and air

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

Entry	Diamine	Alcohol	Product	Yield (%)[b]	Melting point Found	Melting point Reported
1	*o*–Phenylenediamine	Benzyl alcohol	**3a**	82	292–295	292–293 [38]
2	*o*–Phenylenediamine	2–Methylbenzyl alcohol	**3b**	85	223–225	223–224 [38]
3	*o*–Phenylenediamine	2–Methoxybenzyl alcohol	**3c**	91	157–158	156–158 [39]
4	*o*–Phenylenediamine	2–Nitrobenzyl alcohol	**3d**	92	234–235	232–235 [40]
5	*o*–Phenylenediamine	3–Methylbenzyl alcohol	**3e**	78	231–233	231–232 [38]
6	*o*–Phenylenediamine	3–Bromobenzyl alcohol	**3f**	84	222–223	223–224 [38]
7	*o*–Phenylenediamine	4–Methylbenzyl alcohol	**3 g**	92	276–277	275–276 [38]
8	*o*–Phenylenediamine	4–Bromobenzyl alcohol	**3 h**	88	256–257	255–256 [38]
9	*o*–Phenylenediamine	4–Methoxybenzyl alcohol	**3i**	90	219–220	218–219 [38]
10	*o*–Phenylenediamine	4–Chlorobenzyl alcohol	**3j**	90	288–290	287–289 [41]
11	*o*–Phenylenediamine	4–Nitrobenzyl alcohol	**3 k**	94	259–260	260–261 [38]
12	*o*–Phenylenediamine	3,4–Dimethoxybenzyl alcohol	**3 l**	95	183–184	181–182 [38]
13	4–Methyl–*o*–phenylenediamine	Benzyl alcohol	**3 m**	82	243–244	243–245 [41]
14	4–Methyl–*o*–phenylenediamine	2–Chlorobenzyl alcohol	**3n**	86	107–109	106–108 [42]

[a] Reaction conditions: diamine (1.0 mmol), alcohol (1.2 mmol), $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO (0.07 g), CH_3CN (7.0 ml), air as oxidant, 80 °C, 5 h.

[b] Isolated yield.

TABLE 3 Comparison of the results obtained using $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite and some other catalysts for the oxidative synthesis of 2–phenylbenzimidazole from *o*–phenylenediamine and benzyl alcohol

Entry	Catalyst	Reagent	Conditions	Molar ratio substrate to catalyst	Yield (%)	Reference
1	$Pt@TiO_2$	-	s.f./hν/N_2/30 °C/24 h	1:0.080	89	[24]
2	-	Propylphosphonic anhydride	DMSO/EtOAc/0–25 °C/4 h	-	90	[25]
3	FePc	-	Toluene/N_2/NaO*t*Bu/120 °C/36 h	1:0.010	84	[26]
4	CuCl	-	s.f./Bpy/TEMPO/Air/RT/12 h	1:0.050	95	[27]
5	$[RuCl(CO)(PPh_3)(PNS\text{-}Me)]$	-	Toluene/KOH/120 °C/24 h	1:0.005	93	[28]
6	$Fe_2(SO_4)_3$	-	s.f./TEMPO/Air/110 °C/24 h	1:0.100	88	[29]
7	*t*BuONa	-	xylene/O_2/130 °C/24 h	1:0.050	89	[23]
8	$Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO	-	CH_3CN/Air/80 °C/5 h	1:0.020	82	This work

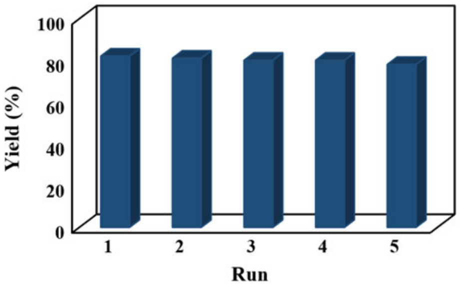

FIGURE 7 Successive use of the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite for the oxidative synthesis of 2–phenylbenzimidazole compound

oxidant are summarized in Table 2. The benzyl alcohols with both of electron donating and electron withdrawing substituents readily proceeded reaction.

In Table 3, the results of present study have been compared with previous reports of the catalytic oxidative synthesis of 2–phenylbenzimidazole from *o*–phenylenediamine and benzyl alcohol.[23–29]

Recyclability of the synthesized $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite was investigated in the oxidative synthesis of 2–phenylbenzimidazole compound. The separated catalyst from reaction media by centrifuging was washed with EtOH and dried under vacuum at 60 °C. The recovered catalyst was reused for five repetitive cycles in the mentioned reaction. The obtained results is showing in Figure 7 which confirmed the saving of catalytic activity of the $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite in a considerable amount during successive uses.

4 | CONCLUSION

Arginine–grafted graphene oxide nanosheets as a graphene–based support was produced by chemical attachment of arginine amino acid to the surface of acylated graphene oxide nanosheets. The prepared support was used for immobilization of copper substituted cobalt ferrite nanoparticles which the Arg–GO support led to produce a catalytic system with uniform dispersion of $Cu_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles. The prepared $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO nanocomposite had both oxidation capability and basic property due to the presence of $Cu_{0.5}Co_{0.5}Fe_2O_4$ ferrite and arginine moieties. In continue, a methodology for achieving a ferrite– and base–catalyzed one–pot tandem reaction for the construction of 2–phenylbenzimidazole derivatives has been developed using the readily available alcohols with *o*–phenylenediamines. The one–pot tandem oxidative synthesis of 2–phenylbenzimidazole derivatives was proceeded smoothly in the presence of the prepared $Cu_{0.5}Co_{0.5}Fe_2O_4$@Arg–GO catalyst due to its double nature of oxidation capability and basic property.

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