

Surface modification of graphene oxide by citric acid and its application as a heterogeneous nanocatalyst in organic condensation reaction

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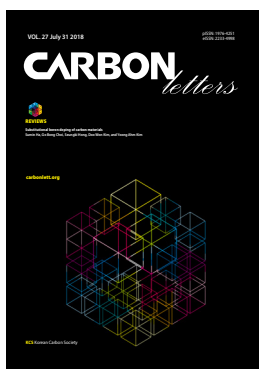
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Abstract

A citric acid functionalized graphene oxide nanocomposite was successfully synthesized and the structure and morphology of the nanocatalyst were comprehensively characterized by Fourier transform infrared spectroscopy, energy-dispersive X-ray analysis, X-ray diffraction patterns, atomic force microscopy images, scanning electron microscopy images, transmission electron microscopy images, and thermogravimetric analysis. The application of this nanocatalyst was exemplified in an important condensation reaction to give imidazole derivatives in high yields and short reaction times at room temperature. The catalyst shows high catalytic activity and could be reused after simple work up and easy purification for at least six cycles without significant loss of activity, which indicates efficient immobilizing of citrate groups on the surface of graphene oxide sheets.

Key words: graphene oxide, citric acid, heterogeneous catalyst, nanocomposite, imidazole

1. Introduction

The design and use of eco-friendly catalysts having superior features, including high activity, high surface-to-volume ratio, excellent selectivity, high stability, low preparation cost, and good recyclability, are urgently needed [1]. Nanocatalysts including the advantages of both heterogeneous and homogeneous catalysts have received considerable attention in recent decades. To meet the needs of technology in the field of synthesis of organic and biologically important compounds, the design and the synthesis of new environmentally benign catalysis systems are of prime importance. In this regard, nanocomposites with properties of high surface-to-volume ratio, good thermal stability, and mechanical strength are good candidates [2].

In recent decades, organocatalysts have won attention in the development of catalytic chemical technology [3]. However, there are some drawbacks that limit their applications such as the use of harmful organic solvents, difficulty in catalyst separation from the reaction media, toxicity of reagents, and tedious work-up in some of these methods. One of the most promising solutions to these problems is the immobilization of the catalysts over chemically stable substrates that have high surface-to-volume area. These immobilized insoluble catalysts can be separated easily and reused several times. Citric acid (CA) is an eco-friendly and low-cost small organic acid with a carboxylic group rich structure. Some papers recently demonstrated that CA plays a similar role to that of common catalysts used in various organic transformations [4]. In addition, CA has been used in the modification of activated carbon for copper adsorption [5], magnetic graphene oxide (GO) for the elimination of methylene blue [6] and magnetic nanoparticles as a catalyst [7].

Due to its unique two-dimension planar structure, graphene and GO are considered good candidates to immobilize organocatalysts [8]. GO is mainly produced through Hummers' method and modified versions of it by using strong mineral acids and oxidizing agents. GO

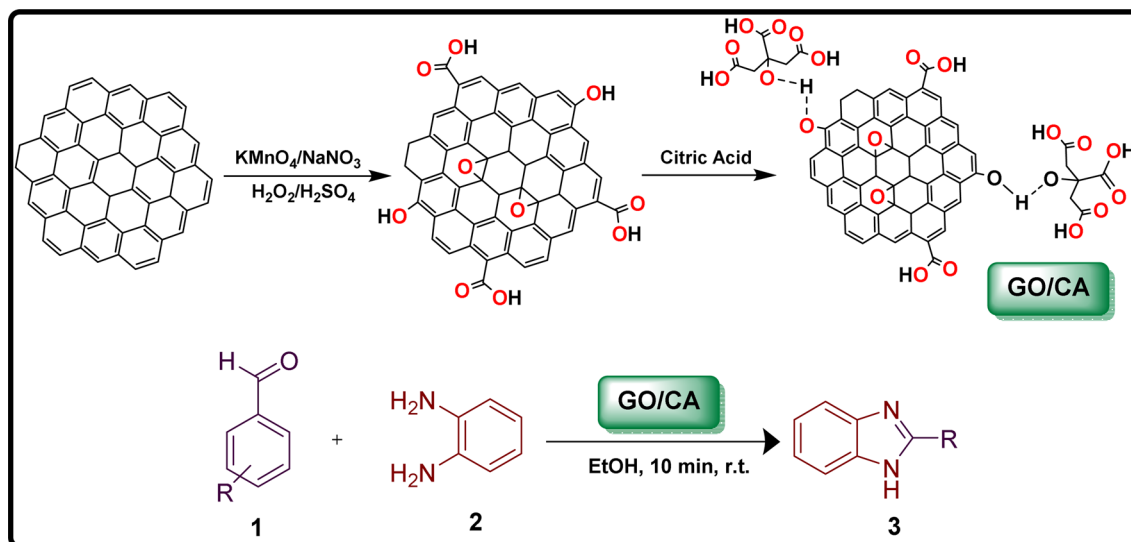


Fig. 1. Preparation of GO/CA and catalytic application in the reaction of benzaldehydes with *o*-phenylenediamine.

has a high surface area and abundant hydroxyl and epoxy groups with highest concentrations in the basal plane and carboxylic acid groups around the periphery of the sheets. The groups are key chemical skeletons that can be used to anchor active catalytic sites [9-11].

Imidazole derivatives diverse nitrogen-containing heterocyclic compounds with unique pharmaceutical and biological activities. Due to the importance of imidazole derivatives, many synthetic methods have been reported with different catalysts such as cellulose sulfuric acid [12], silica sulfuric acid [13], PEG-400 [14], GO-chitosan [15], and heteropolyacids [16]. Despite advantages, most of the previously reported methods accompany some drawbacks such as using harmful solvents, difficulties in separating the catalyst and affording a pure product, the requirement of long reaction times and high temperatures, and low yields. Keeping these considerations in mind and in continuation of our research on the introduction of new recoverable nanocatalysts in organic synthesis, herein we report the synthesis and characterization of a novel GO/CA nanocomposite as a heterogeneous catalyst and its application in the effective synthesis of imidazole derivatives 3a-n via the reaction of benzaldehyde 1 and *o*-phenylenediamine 2 in an eco-friendly ethanol media at room temperature (r.t.) (Fig. 1). To the best of our knowledge, this is the first report on the synthesis and application of a GO/CA nanocomposite as an efficient and eco-friendly catalyst in organic synthesis such as imidazole derivatives.

2. Experimental

2.1. General

All the solvents, chemicals, and reagents were purchased from Merck and have been used without any further purification. Melting points were measured on an Electrothermal 9100 apparatus. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellet. ^1H NMR

(nuclear magnetic resonance) and ^{13}C NMR spectra were recorded with a Bruker DRX-500 Avance spectrometer (USA) at 500 and 125 MHz, respectively. The morphology and the structure of the nanocatalyst were examined by a scanning electron microscope (SEM; Hitachi S-4800, Japan) and a transmission electron microscope (TEM; Philips CM200). An energy dispersive X-ray (EDX) analysis was conducted to show the elemental composition of the nanocatalyst. The tip radii were obtained from direct atomic force microscopy (AFM) measurements of the tip apex region in tapping mode by Nano System Pars Co., Iran (NAMA AFM model). The shell surface was mounted on the AFM stage and a Triboscope recording unit with transducers and a leveling device was placed on the top of a NanoScope III E 164 | 164 mm² XY piezo scan base. X-ray diffraction (XRD) patterns of the solid powders were recorded with an X' Pert Pro X-ray diffractometer operating at 40 mA, 40 kV. A thermogravimetric analysis (TGA) was carried out using a Bahr-STA 504 instrument.

2.2. Synthesis of catalyst

2.2.1. Synthesis of graphene oxide nanosheets

GO nanosheets were synthesized via a modified version of Hummer's method [17]. Typically, 4 g of graphite and 2 g of NaNO_3 were added to a flask containing 95 mL of sulfuric acid 98%. The mixture was then sonicated for 30 min at 60°C and stirred for 1 h at 20°C. Then, 12 g of KMnO_4 was added under sonication. The mixture was sonicated for 30 min at 80°C and stirred for 1 h at 95°C. The resulting mixture was dispensed into 250 mL of distilled water. The mixture was heated at 100°C for 1 h in an oven to give a brown mixture. The mixture was subsequently poured into 500 mL of distilled water and H_2O_2 5% was added dropwise until a yellow brown solution yielded. This was followed by adding HCl 5% until the pH was adjusted to 6. The mixture was then stirred for 10 min and filtered. To evaluate the removal of Cl^- and manganese ions, 5 mL of H_2O_2 30% and 0.1 mL of AgNO_3 were added to the filtrate solution. Finally, the obtained dark brown powder was dried for 24 h at 60°C in a vacuum oven.

2.2.2. Preparation of GO/CA

Initially, 0.02 g of GO was added to a beaker containing 100 mL of distilled water and sonicated for 1 h. Then, 10 mL of CA solution (5 M) was added dropwise and stirred for 3 h at room temperature. The obtained product was washed several times with distilled water to remove excess CA and dried in a vacuum oven at 100°C overnight.

2.3. General procedure for the synthesis of imidazole derivatives 3a-n

o-Phenylenediamine (1 mmol, 0.181 g), benzaldehyde (1 mmol, 0.104 g), and GO/CA (0.05 g) were mixed in ethanol. The mixture was stirred at room temperature for 10 min. After completion of the reaction (monitored by TLC), the catalyst was separated by filtration. Recrystallization in ethanol yielded pure crystalline products.

3. Results and Discussion

In this work, GO/CA as a heterogeneous acidic nanocatalyst was synthesized for the first time and applied to organic reactions under mild conditions and short reaction times. GO nanosheets were synthesized via a modified Hummers method and subsequently the CA groups were covalently bonded to GO sheets. The nanocomposite was characterized by several analyses, which are discussed in the following.

3.1. Characterization of GO/CA catalyst

3.1.1. FT-IR spectroscopy

In order to investigate the interface bonding in the GO/CA nanocomposite, the FT-IR spectrum of sample composite was obtained. Fig. 2 shows the FT-IR spectra of GO and GO/CA. The presence of several characteristic peaks of GO confirms the successful oxidation of graphite. In detail, C=O (1735 cm^{-1}), aromatic C=C (1626 cm^{-1}), and alkoxy C-O (1074 cm^{-1}) stretching vibrations were observed and were in good agreement with previous studies [18,19]. The FT-IR spectrum of GO/CA differs from that of GO. The peak at 3392 cm^{-1} in the GO spectrum is related to O-H. This peak is reduced in broadness and shifts to 3431 cm^{-1} due to the aliphatic carboxylic groups of CA. The ab-

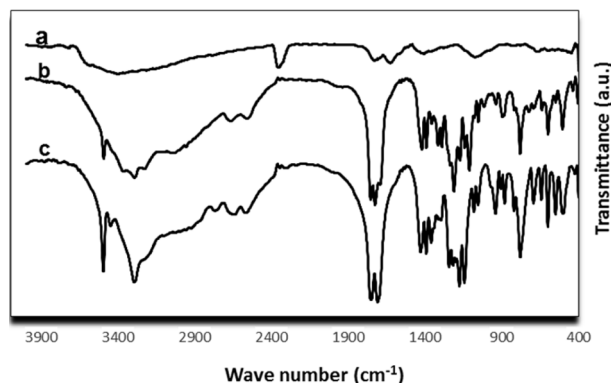


Fig. 2. FT-IR spectra of (a) GO, (b) CA, and (c) GO/CA catalyst.

sorption band at 1740 cm^{-1} in the GO/CA spectrum is attributed to the ester and the upcoming new bands at 2927 cm^{-1} are assigned to CH_2 groups of CA. The signals of C=O in the carboxylic acids of CA are observed at 1694 and 1647 cm^{-1} [5]. Also, to verify the stability of the catalyst in green solvents such as ethanol and water, the catalyst was stirred for 1 h in these solvents and the related FT-IR were obtained (Supplementary Materials), which verified the stability of the catalyst in solvents.

3.1.2. Scanning electron microscopy

SEM images of the nanocatalyst were used to observe the surface morphology and size details of the GO/CA composite. As can be seen in Fig. 3, the nanocatalyst has uniform shape with an average size of 32.44 ± 6 nm. As a result, the SEM images confirm the functionalizing GO sheets with CA groups.

3.1.3. Transmission electron microscopy

A TEM micrograph of the GO/CA nanocomposite is presented in Fig. 4. It clearly shows considerable exfoliation of GO after being functionalized by CA by nearly monodisperse in grain color. This analysis confirms the successful synthesis of the GO/CA nanocomposite.

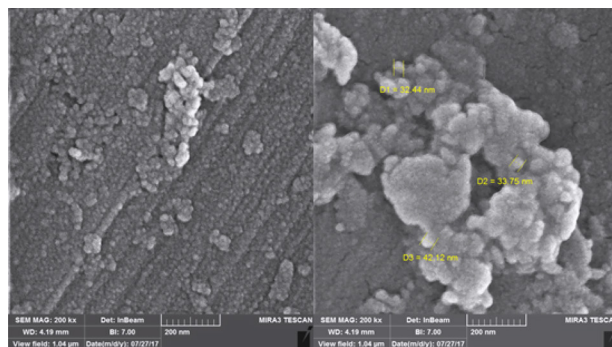


Fig. 3. SEM images of GO/CA nanocomposite.

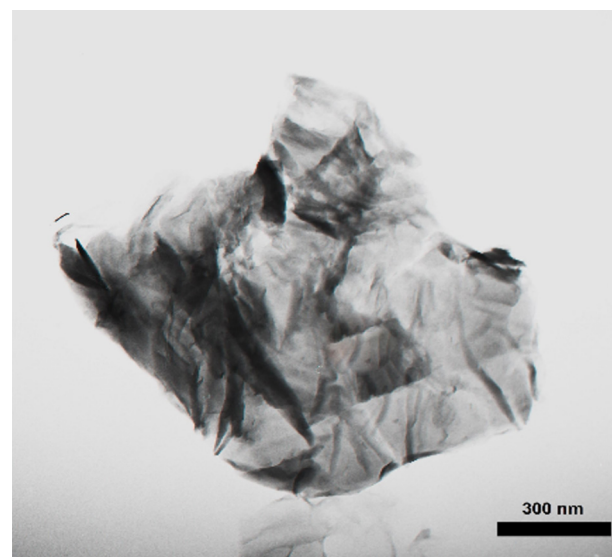


Fig. 4. TEM image of GO/CA nanocomposite.

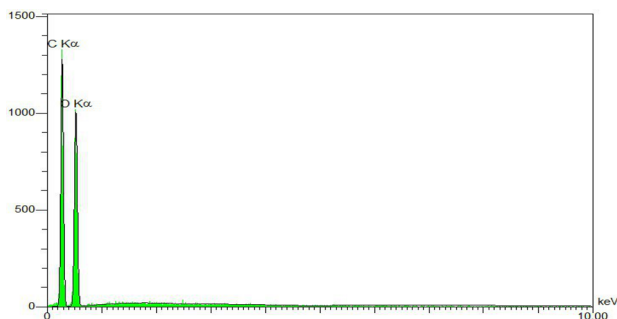


Fig. 5. EDX analysis of the GO/CA nanocomposite.

3.1.4. Energy-dispersive X-ray

The EDX analysis of the GO/CA nanocomposite (Fig. 5) revealed the existence of C and O elements, which indicated that the catalyst was free of impurities.

3.1.5. Atomic force microscopy

The nanostructured surface of the GO/CA catalyst was confirmed by AFM (Fig. 6). As indicated in the scale bar of the AFM image, the average size distribution of the GO/CA nanosheets was measured to be about 50 nm. Also, based on a previous study on single layer GO where the distance between graphene sheets was predicted to be 1.0–1.4 nm [20], we can assume the presence of CA groups on the graphene sheets.

3.1.6. X-ray diffraction

The XRD patterns of GO/CA are shown in Fig. 7. All of the observed peaks for the CA are similar to the characteristic data of CA (JCPDS card No. 00-001-0251) [21]. Crystalline peaks were observed at diffraction angles (2θ) of 13.82, 16.40, 17.94, 19.40, 21.65, 23.83, 26.03, 28.77, 31.24, 33.66, 35.16, 36.19, 37.12, 39.13, 40.99, 43.25, and 51.59.

3.1.7. Thermogravimetric analysis

TGA analysis was utilized to assess the thermal stability of the nanocomposite (Fig. 8). The observed loss weight in the TGA analysis is about 70% at around 200°C and is related

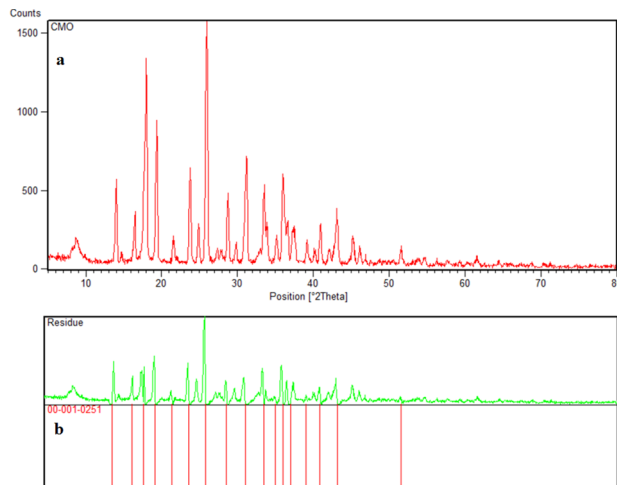


Fig. 7. XRD pattern of (a) GO/CA and (b) the reference CA.

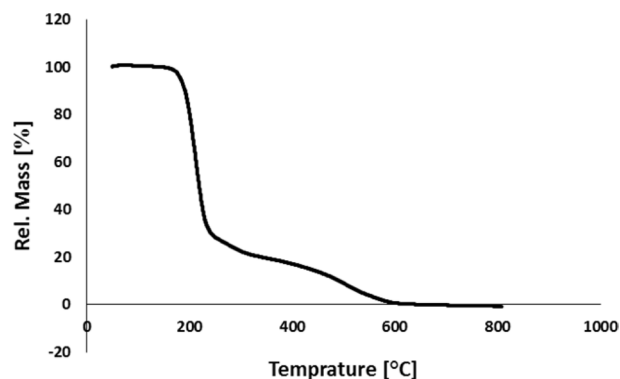


Fig. 8. TGA curve of GO/CA nanocomposite.

to decomposition of oxygen-containing functional groups to CO, CO₂, and H₂O on both the GO and CA structures. According to previous research [22] decomposition of GO at the same temperature is around 40%. This result successfully confirms the grafting of CA to GO sheets. Also, at higher temperatures, all of the decomposition is related to the GO

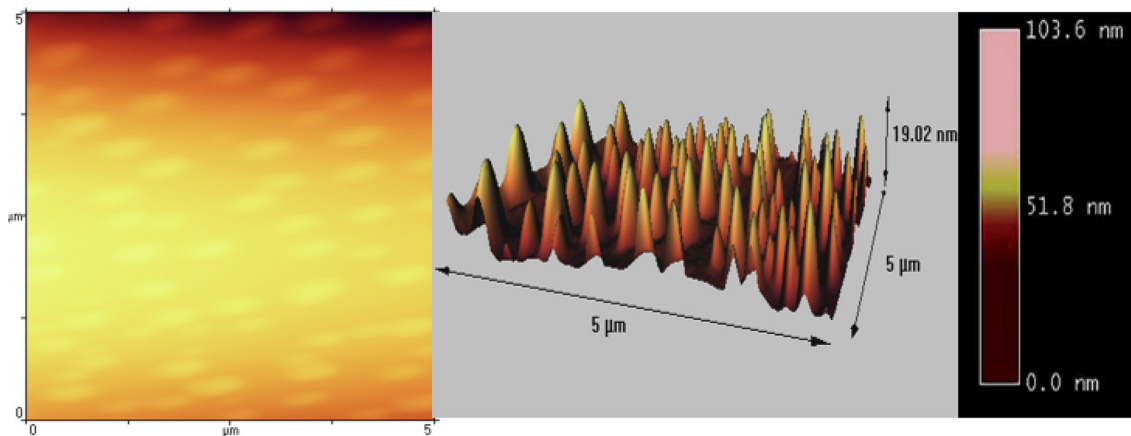


Fig. 6. AFM images of GO/CA nanosheets.

Table 1. Optimization of different parameters in the model reaction^{a)}

Entry	Solvent	Catalyst (g)	Temperature (°C)	Time (min)	Yield (%) ^{b)}
1	-	GO/CA (0.05)	r.t.	30	Trace
2	H ₂ O	GO/CA (0.05)	r.t.	30	Trace
3	CH ₂ Cl ₂	GO/CA (0.05)	r.t.	30	45
4	EtOH	GO/CA (0.05)	r.t.	10	95
5	EtOH	-	r.t.	30	Trace
6	EtOH	GO	r.t.	30	40
7	EtOH	GO/CA (0.01)	r.t.	10	60
8	EtOH	GO/CA (0.02)	r.t.	10	78
9	EtOH	GO/CA (0.04)	r.t.	10	86

^{a)}Reaction condition: benzaldehyde (1 mmol, 0.104 g), *o*-phenylenediamine (1 mmol, 0.181g).

^{b)}Isolated yield.

Table 2. Comparison of the efficiency of synthesized nanocatalyst with other reported works

Entry	Catalyst	Cat. (%)	Solvent	Temperature (°C)	Time (min)	Yield (%) ^{a)}	Reference
1	Zeolite	0.25	Dioxane	100	180	82	[23]
2	[BiPy](HSO ₃) ₂ Cl ₂	0.01	EtOH	r.t.	15	98	[24]
3	Nano Ni/Zeolite	0.02	Solvent-free	100	6	92	[25]
4	Fe ₃ O ₄ @Collagen	0.05	EtOH	r.t.	15	78	[26]
5	GO/CA	0.05	EtOH	r.t.	10	98	This work

^{a)}Isolated yield.

structure. As a result, the thermal decomposition of the nano-composite exhibited the remarkable thermal stability of GO/CA.

3.1.8. Back titration of GO/CA in aqueous media

Acidity ([H⁺]) of the synthesized GO/CA nanocatalyst was investigated by the back titration method. The pH value of the GO/CA nanocatalyst was obtained as 1.77 after calculation. In detail, GO/CA (0.5 g), NaCl (0.5 g), and NaOH (10 mL, 0.1 M) were added to distilled water (35 mL) and stirred with a magnetic stirrer for 24 h. To this mixture, a few drops of phenolphthalein were added and the color of the mixture changed to pink. Finally, to reach neutral pH, the mixture was titrated by a solution of HCl (0.1 M).

3.2 Optimization of different parameters in the synthesis of imidazole derivatives

At the onset of this research, we investigated the model one-pot two-component cyclocondensation reaction between benzaldehyde (1 mmol, 0.104 g) and *o*-phenylenediamine (1 mmol, 0.181 g) under mechanical stirring to optimize the reaction parameters. First, we investigated the reaction without using any solvent in the presence of the catalyst, and trace yield was taken (Table 1, entry 1). We then investigated the reaction in the pres-

ence of different solvents. Based on the results obtained in different solvents (Table 1, entries 2-4), ethanol showed the highest yield as a solvent. To improve the yield and optimize the reaction conditions, the effects of the catalyst and amount of catalyst were studied (Table 1, entries 4-9).

3.3 Comparison the efficiency of synthesized nanocatalyst

To investigate the efficiency of GO/CA with some other reported works on the synthesis of imidazole derivatives, the model reaction of benzaldehyde and *o*-phenylenediamine was compared with the results of other previous reports. Most recent reports have disadvantages such as high temperature, long time reaction, and the use of toxic solvents, as can be seen in Table 2 [22-26], whereas the results of the present work are more reliable than previous ones.

In order to demonstrate the repeatability of this strategy, a broad variety of aromatic aldehydes possessing electron-withdrawing and electron-releasing substitutions were employed and a variety of products were synthesized under the optimized conditions at room temperature. As can be seen in the results summarized in Table 3 [27-32], all the utilized aldehydes supplied the desired products in high yields and short reaction times.

Table 3. Synthesis of imidazole derivatives 3a-n in optimal conditions^{a)}

Entry	R	Product	Yield (%) ^{b)}	Mp (°C)	
				Found	Reported
1	C ₆ H ₅	3a	98	291-292	293 [27]
2	3-NO ₂ -C ₆ H ₄	3b	95	185-187	185-187 [28]
3	4-NO ₂ -C ₆ H ₄	3c	93	308-309	310 [29]
4	2-NO ₂ -C ₆ H ₄	3d	82	264	261-263 [29]
5	4-CN-C ₆ H ₄	3e	93	246-247	247-249 [30]
6	4-Br-C ₆ H ₄	3f	90	257-259	255-257 [30]
7	4-Cl-C ₆ H ₄	3g	88	267-269	268-270 [30]
8	4-MeO-C ₆ H ₄	3h	90	222-224	223-226 [27]
9	3-OH-C ₆ H ₄	3i	91	245-246	245-247 [31]
10	4-OH-C ₆ H ₄	3j	90	273-275	275 [27]
11	4-Me-C ₆ H ₄	3k	88	272-273	271 [27]
13	2,4-(Cl) ₂ -C ₆ H ₃	3l	88	271-273	273-275 [30]
14	2,6-(Cl) ₂ -C ₆ H ₃	3m	86	272	273-275 [32]
15	4-(CH ₃) ₂ N-C ₆ H ₄	3n	90	290-292	292-294 [28]

^{a)}Reaction condition: benzaldehyde (1 mmol, 0.104 g), *o*-phenylenediamine (1 mmol, 0.181 g), and GO/CA composite (0.05 g) at room temperature in 5 mL of ethanol.

^{b)}Isolated yield.

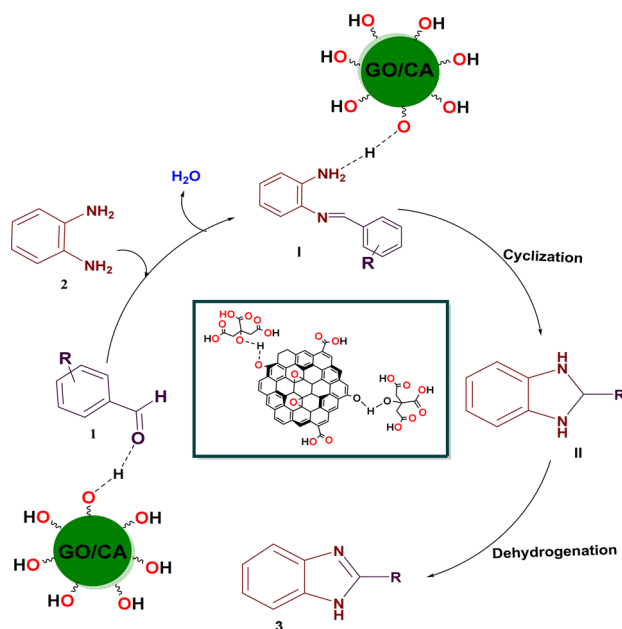


Fig. 9. Proposed mechanism for the synthesis of 3a-n by using GO/CA.

3.4. Mechanistic evaluation

A proposed mechanism for the formation of imidazole derivatives is presented in Fig. 9. In the first step, according to the literature [33], by the condensation reaction between an aro-

matic aldehyde and *o*-phenylenediamine in the presence of GO/CA, intermediate I was formed. GO/CA catalyst activated C=N of intermediate I to form intermediate II via cyclization. Finally, dehydrogenation of intermediate II yielded the products 3a-n.

3.5. Catalyst recyclability examination

The recovery and reusability of a catalyst is very important in industry. For this reason, after completion of the reaction, the catalyst was filtrated, washed with ethanol and water, and dried after each run, and then reused in the next runs under the same ratio of catalyst and other reaction conditions as for the model reaction. The results show that the catalyst does not undergo considerable reduction in activity within six cycles (Fig. 10).

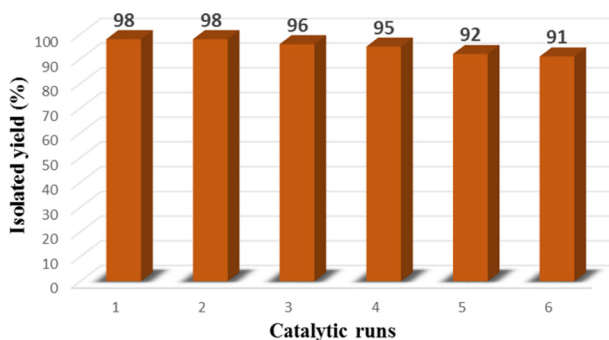


Fig. 10. Recycling diagram of GO/CA nanocatalyst in the synthesis of 3a.

4. Conclusions

In summary, we have demonstrated that CA immobilized on GO is an effective, green, and inexpensive nano-organocatalyst for the synthesis of chemically important imidazole derivatives. The nanocatalyst showed excellent catalytic activity and the organic products were obtained in high yields by using a variety of derivatives. The catalyst was chemically and mechanically stable and successfully characterized by FT-IR, SEM, EDX, AFM, TEM, TGA, and XRD analyses. The reusability of the GO/CA catalyst was high and was reused in six cycles without a noticeable decrease in its activity.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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Supplementary Material

Additional supporting information including spectroscopic characterization data of the recycled nanocatalyst, ^1H , and ^{13}C NMR of the products can be found in the online version of this article at the publisher's website.

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