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Research Article

Fabrication of novel Co_3O_4@GO/La_2O_3 nanocomposites as efficient, innovative and recyclable nanocatalysts for the synthesis of quinazolinone derivatives under solvent-free conditions

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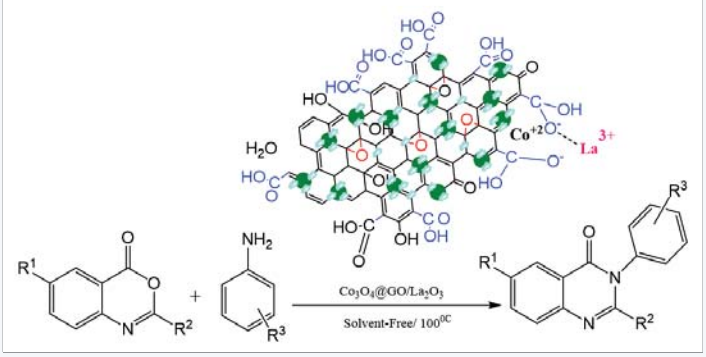
Abstract

For the first time, this research has developed an efficient and novel approach to high to excellent yields for synthesizing Quinazolinone derivatives. Also, the synthesis of Quinazolinone derivatives has been carried out in the presence of Co_3O_4@GO/La_2O_3 nanocomposite as a novel heterogeneous catalyst and a green under solvent-free conditions and in a short time and excellent yields for the first time. Various structural and morphological characteristics of the nanocatalyst were employed for the catalyst characterization, such as FT-IR, XRD, FE-SEM, EDX and VSM analyses. All characterization data were checked with each other so that the structure of the nanocatalyst was exactly characterized. The reactions were carried out in the presence of a low amount of nanocatalyst at 100 °C under solvent-free conditions for a short period of time. The proposed nanocomposite exhibits excellent catalytic activity. One of the most important advantages of this method is easy magnetic nanocatalyst separation, green condition, excellent recoverability and easy workup.



More Information

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Keywords: Quinazolinone derivatives; Heterogeneous; Lanthanum; Magnetic nanocomposite

Introduction

In recent years, one of the main challenges facing scientists is to make the materials they utilize as environmentally friendly as possible. Therefore, the idea of green chemistry is raised [1].

Graphene, the thinnest and strongest material in the world, was discovered in 2004 [2]. Graphene has a two-dimensional (2D) structure of a honeycomb lattice layer of carbon atoms due to unique properties such as adjustable surface properties, high thermal stability, and excellent electronic conductivity. Graphene is an excellent candidate for catalysts. One of the most important derivatives of graphene is graphene oxide (GO), which contains hydroxyl and epoxide groups and carboxyl groups that organic molecules can modify and metal oxide nanoparticles with magnetic properties [2,3]. Graphene

oxide (GO) was attention as an excellent carrier for transition metal ions with high conductivity, high mechanical and wide specific surface area [4].

Recently, cobalt oxide nanoparticles (Co_3O_4) are an important p-type magnetic semiconductor due to their properties such as low cost, good electrical conductivity, environmental compatibility, simple preparation, and high chemical and physical stability. It has been increasingly considered a catalyst in various reactions [5].

Lanthanides were discovered in 1794 [6]. Lanthanum oxide (La_2O_3), due to its properties such as unique electronic and basic structure, excellent paramagnetic sensitivity, saturated magnetization, and the largest band gap, can be an excellent candidate for improving catalytic activity [3,6,7].

Recently, Quinazolinones have attracted the attention of chemists due to their unique properties, such as antifungal, antimalarial, antihypertensive, anticonvulsant and antiparkinson [8,9].

In this work, we report a simple and efficient method for synthesizing quinazolinone derivatives in the presence of Co_3O_4/GO/La_2O_3 nanocomposite as a novel nanocatalyst under solvent-free conditions at 100 °C.

Experimental

Sigma Aldrich and Merck prepared all solvents and reagents used in this work with excellent purity. Melting point (m.p) was operated by Electro-Thermal 9200 and FT-IR analysis was obtained by PerkinElmer 1600 FTIR spectrometer. Bruker confirmed 1 H and 13 C Nuclear Magnetic Resonance (NMR) spectroscopy at 300 and 75 MHz, respectively (in DMSO, internal reference: TMS). Philips-X'pertpro, an X-ray diffractometer utilizing Ni-filtered Cu Kα radiation, was used for operating X-ray Diffraction (XRD) analysis at a scanning speed of 2 min1 from 10 to 100 (2Θ). Magnetic properties were characterized by a Vibrating Sample Magnetometer (VSM, Taban laboratory, Tehran, Iran) at room temperature. In addition, the morphology and size of samples were investigated by the Scanning Electron Microscope (SEM) and Energy-Dispersive Spectroscopy (EDS, EDX).

Preparation of Co_3O_4 nanoparticles

According to previous literature, Co_3O_4 NPs were synthesized was reported to be successful [10]. At the first step, in a round bottom flask, about 8.60 g of cobalt (II) nitrate was dissolved in 100 ml of Ethanol for about half a min. After this step, about 2.14 g of Ethane dioic acid was slowly added, and the reaction mixture was stirred for 120 min at 45 °C. The precipitate obtained containing cobalt oxalate (II) (CoC_2O_4) powder was collected by centrifuge followed by calcined at 400 °C for 120 min to generate Co_3O_4 nanoparticles.

Preparation of Co_3O_4@GO

Co_3O_4@GO nanocomposite was fabricated by dispersing about 0.5 g of Co_3O_4 in 25 mL deionized water that was added 0.1 g wise into GO (50 mL, aq.) by the Hummer method [11]. After that, the reaction mixture was stirred for 60 min at 60 °C. In the final stage, the nanocomposite was separated by an external magnet, washed three times with deionized water and dried [3].

Procedure for the preparation of Co_3O_4@GO/La_2O_3

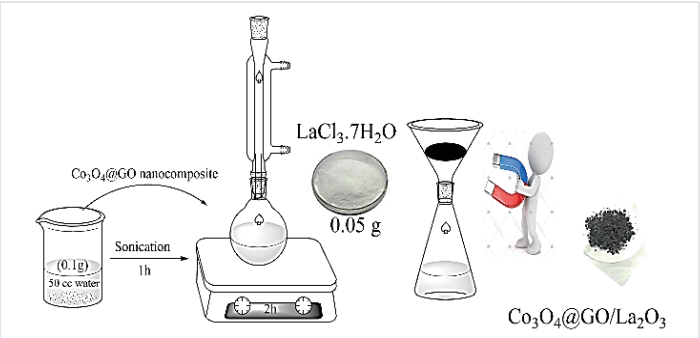
According to previous literature, Co_3O_4@GO/La_2O_3 nanocomposites were synthesized. Nanocomposites were synthesized [3,7] -approximately 0.1 g Co_3O_4@GO nanocomposites in 50 mL deionized water and sonicated for 60 min. About 0.05 g of $LaCl_3.7H_2O$ was added and the reaction mixture was stirred under reflux conditions for 120 min. Fabricated nanocomposites were collected through an external magnet and then washed thrice with distilled water Scheme 1.

General procedure for the synthesis of quinazolinone

Typically, 1,3-benzoxazine-4-one derivatives (0.001 mol), aniline derivatives (0.001mol) and Co_3O_4@GO/La_2O_3 (0.05 g) were added to the tube and prepared in an oil bath at 100°C. The reaction mixture was stirred using a magnetic stirrer continuously. The thin-layer chromatography technique checked the reaction mixture and then the catalyst was separated by an external magnet. Finally, the product was recrystallized with hot ethanol to obtain a pure product (Figure 1). All products were investigated by Melting Point (m. p), ^{1}H NMR, ^{13}C NMR and FTIR. The spectral data of all are provided.

Results and discussion

The FT-IR spectra are utilized to analyze the prepared nanocrystals. FTIR spectra of the Co_3O_4 NPs and Co_3O_4@



Scheme 1: Preparation of Co_3O_4@GO/La_2O_3.

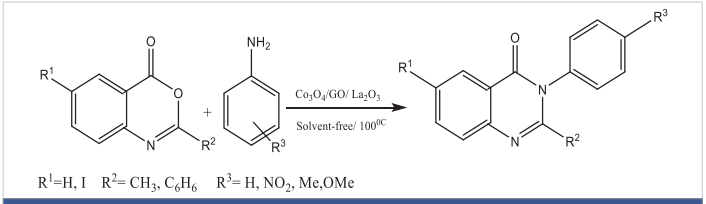


Figure 1: Synthesis of benzoxazine-4-one, aniline, in the presence of Co_3O_4/GO/La_2O_3 under solvent-free conditions and 100.

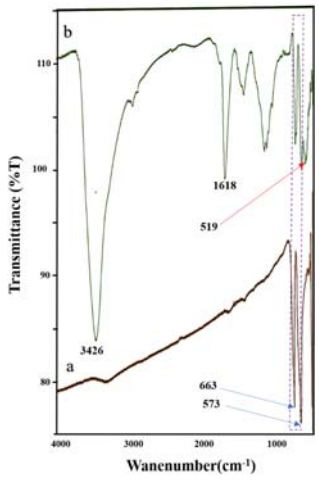


Figure 2: FT-IR spectra of Co_3O_4 NPs (a), Co_3O_4/GO/ La_2O_3 (b).

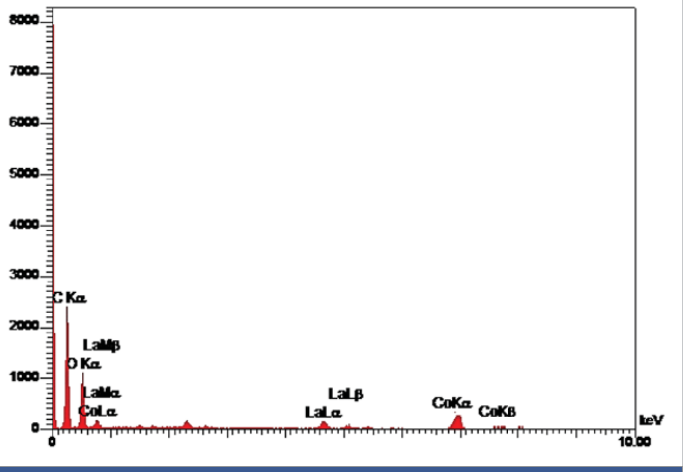


Figure 3: EDS spectrum of Co_3O_4/GO/ La_2O_3.

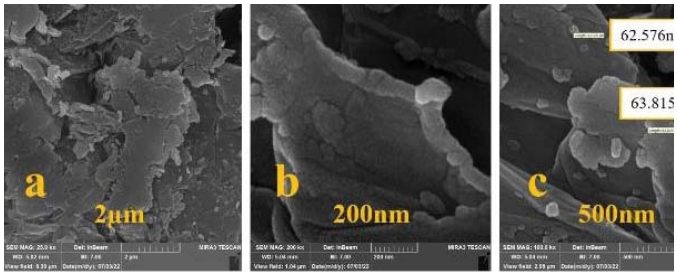


Figure 4: FESEM spectrum of Co_3O_4/GO/ La_2O_3 (a-c).

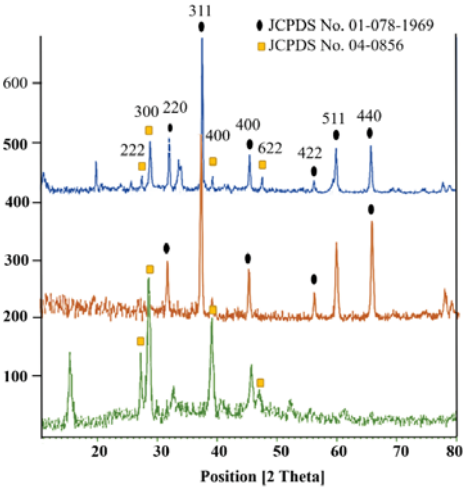


Figure 5: XRD patterns of a) La_2O_3 b) Co_3O_4 and c) Co_3O_4@GO/La_2O_3.

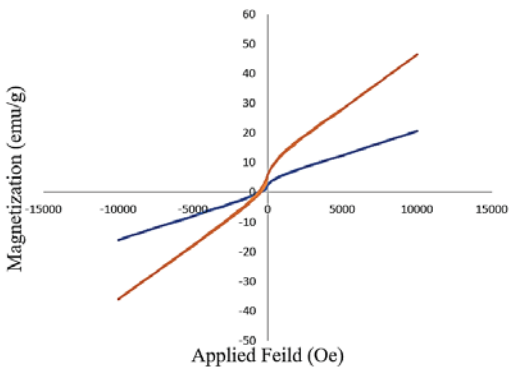


Figure 6: VSM (a) Co_3O_4, (b) Co_3O_4@GO/La_2O_3 nanocomposites.

GO/La_2O_3 are shown in Figure 2. Two strong characteristic absorptions at 573 and 663 cm^{-1} belong to the Co-O (Figure 2a,b). The absorption at 1618 cm^{-1} (aromatic C=C) can belong to skeletal vibrations of graphitic domains. Also, the peaks around 3426 cm^{-1} ascribe to the OH group bands in GO (Figure 2b) [11]. The characteristic absorptions showed at 519 cm^{-1} belong to the formation of La_2O_3, in which the range between 400 and 660 cm^{-1} corresponds to the literature (Figure 2b) [12].

In the EDS spectrum observed in Figure 3, the presence of elements C, O, Co and La is determined according to the energy, demonstrating the product purity.

FESEM was utilized to measure the morphology, particle size and shape. The catalyst particle size was measured at about 62.5 nm. A uniform spherical shape was observed for Co_3O_4@GO/La_2O_3 nanocomposites (Figure 4).

The data relating to the XRD analysis is shown for samples La_2O_3, Co_3O_4 nanoparticles and Co_3O_4@GO/La_2O_3 nanocomposite in Figure 5(a-c). Characteristic peaks for Co_3O_4 are shown in the region at 2θ of 31.47°, 37.04°, 45.01°, 55.86°, 59.57° and 65.44°, which correspond to (220), (311), (400), (422), (511) and (440) respectively. The network parameters were in excellent agreement with JCPDS card number 01-078-1969 [13]. The broad diffraction peaks of GO indicate around 2θ= 10.26 ° and it is in good match with the previous reports [3,14]. Also, La_2O_3 NPs had peaks that are explained at 27.2912°, 28.3643°, 39.6213° and 48.1237° are related to La_2O_3, which correspond to (222), (300), (400) and (622) respectively (La_2O_3; JCPDS card no.04-0856) [15] Characteristic peaks for Co_3O_4 and La_2O_3 illustrate that the structure of both of them has not changed during the combination process.

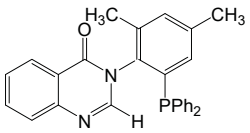
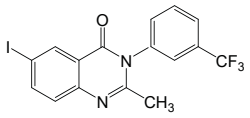
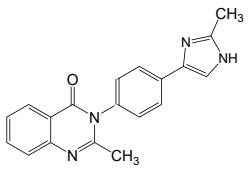
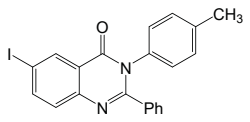
The magnetic behaviors of Co_3O_4 NPs and Co_3O_4@Cs/La_2O_3 were shown by a vibrating sample magnetometer (VSM) at room temperature (Figure 6). There is no hysteresis, coercivity, and remanence in bare Co_3O_4 NPs and Co_3O_4@Cs/La_2O_3 samples at room temperature that show their typical superparamagnetic behaviors. Co_3O_4 NPs and Co_3O_4@Cs/

Table 1: Synthesis of Quinazolinone Derivatives.

Entry	R^1	R^2	R^3	Time(min)	Yields%	Melting point
1	H	CH_3	NO_2	15	87	158 - 159
2	H	CH_3	CH_3	18	83	115 - 116
3	H	C_6H_5	NO_2	20	90	126 - 127
4	H	C_6H_5	CH_3	20	90	209 - 210
5	I	C_6H_5	CH_3	15	93	183 - 184
6	H	C_6H_5	OCH_3	17	87	222 - 223
7	I	C_6H_5	OCH_3	20	89	165 - 166
8	H	C_6H_5	H	15	70	172 - 173
9	I	C_6H_5	NO_2	20	80	150 - 151
10	I	C_6H_5	H	20	74	138 - 139

Reaction conditions: 1,3-benzoxazine-4-one derivatives (0.001 mol), aniline derivatives (0.001mol), Co_3O_4@GO/La_2O_3, at 100 °C under Solvent-Free conditions.

Table 2: Comparing the efficiency of Co_3O_4@GO/La_2O_3 with other reactions reported in the literature for the synthesis of quinazolinone.

Entry	Product	Catalyst[ref]	Condition	Yield%	Time(h)
1		Null [16]	Toluene/ Reflux	88	6
2		Null [17]	Reflux/ glacial acetic acid	92	3
3		γFe_2O_3@CPTMS–guanidine@SO_3H[18]	microwave irradiation/ Solvent-free	91	15
4		Co_3O_4@GO/La_2O_3	Solvent-free/ 100 °C	93	15

[a]**Reaction conditions:** 1,3-benzoxazine-4-one derivatives (0.001 mol), aniline derivatives (0.001mol), Co_3O_4@GO/La_2O_3, at 100 °C under Solvent-Free conditions.

La_2O_3 have superparamagnetic behavior, facilitating magnetic separation. The saturation magnetization value (Ms) Co_3O_4 NPs and Co_3O_4@Cs/La_2O_3 nanocomposites were 46.5 and 25.8 emu/g, respectively. Howbeit, the addition of the GO layer and La_2O_3 nanoparticles on the Co_3O_4 surface Caused decreased magnetic behaviors. Co_3O_4 NPs and Co_3O_4@Cs/La_2O_3 nanocomposite saturation magnetization was enough for a rapid magnetic separation by an external magnet.

As shown, Table 1 summarizes the results from the reaction of 1,3-(4H)-benzoxazine-4-one derivatives and aniline derivatives in the presence of Co_3O_4@GO/La_2O_3. A wide range of 1,3-(4H)-benzoxazine-4-one derivatives were successfully converted into Quinazolinone Derivatives with great yields within a short reaction time (Table 1, entries 1–10).

In Table 2, a vast comparison of catalytic activity Co_3O_4@GO/La_2O_3 was made with other conditions of reactions utilized in the preparation of quinazolinone (Table 2, entry 12-20). In conclusion, the catalyst has excellent results and offers a very gentle and green option.

XRD analysis of the Co_3O_4@GO/La_2O_3 nanocatalysts after five reuse cycles is indicated in Figure 7b. Characteristic peaks for Co_3O_4@GO/La_2O_3 are conserved, displaying that the nanocatalysts have been stable and pure.

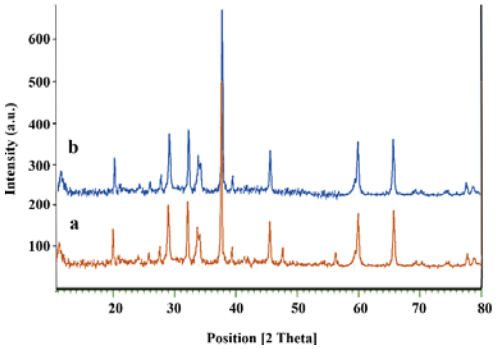


Figure 7: Comparison of XRD of the prepared Co_3O_4@GO/La_2O_3 (a) before and (b) after 5 runs.

Conclusion

Briefly, a highly efficient, powerful and green protocol was developed to synthesize 1,3-(4H)-benzoxazine-4-one derivatives and aniline derivatives under solvent-free conditions at 100 °C using novel Co_3O_4@GO/La_2O_3 nano-catalyst. The magnetically recoverable nanocatalyst was

characterized by FT-IR, FE-SEM, XRD, EDX and VSM analyses. This nanocatalyst has various advantages, such as being eco-friendly, having mild reaction conditions, low cost, high efficiency and being easily separated magnetically.

Supplementary materials: The ^{1}H-NMR and ^{13}C-NMR spectrums of compounds are available online.

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