Sonosynthesis of pyranochromenes and biscoumarins catalyzed by Co$_3$O$_4$/NiO@GQDs@SO$_3$H nanocomposite

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ABSTRACT

Co$_3$O$_4$/NiO@GQDs@SO$_3$H nanocatalyst has been used as an effective catalyst for the preparation of dihydropyrano[3,2-c]chromenes and biscoumarins under ultrasonic irradiations in ethanol. The catalyst has been characterized by FT-IR, XRD, SEM, EDS, BET, TGA, XPS and VSM. Atom economy, reusable catalyst, low catalyst loading, applicability to a wide range of substrates, high yields of products, and applying the sonochemical methodology as an efficient method and innocuous means of activation in synthetic chemistry for the preparation of medicinally privileged heterocyclic molecules are some of the substantial features of this method. The present catalytic procedure is extensible to a wide diversity of substrates for the synthesis of a variety-oriented library of pyranochromene and biscoumarins. The ultrasound approach decreases times, increases yields of products by creating the activation energy in micro surroundings. Meanwhile, this recoverable catalyst will provide a regular platform for heterogeneous catalysis, green chemistry, and environmentally benign protocols in the near future.

GRAPHICAL ABSTRACT

ARTICLE HISTORY

Received 22 January 2020
Accepted 25 May 2020

KEYWORDS

Nanocomposite; one-pot; ultrasonic; chromene; biscoumarins; nanoanalysis

Introduction

Pyranochromenes and biscoumarins indicate biological activities including anticoagulant [1], anticancer [2], anti-Alzheimer [3], anti-Parkinson [4] and anti-HIV [5]. These attributes make pyranochromenes and biscoumarins notable targets in organic preparation for future consideration. A number of procedures have been developed for the preparation of pyranochromenes and biscoumarins using ruthenium(III) chloride hydrate [6], H$_6$P$_2$W$_{18}$O$_{62}$.18H$_2$O [7], tetrabutylammonium bromide (TBAB) [8] and DBU [9]. Each of these methods has their own advantages but also suffer from certain disadvantages containing prolonged reaction time, tedious work-up processes, low yield, high temperature and hazardous reaction conditions. Despite the availability of these ways, there remains enough choice for a capable and reusable catalyst with high catalytic activity for the preparation of pyranochromenes and biscoumarins.

Ideally, utilizing environmental and green catalysts which can be easily recycled at the end of reactions has obtained great attention in recent years. Nanocomposites have emerged as a suitable group of heterogeneous catalysts owing to their numerous applications in synthesis and catalysis [10, 11]. Since, these nanocomposites are often recovered simply by easy workup, which prevents contamination of products, they may be considered as a promising safe and reusable catalysts as well as greener compared to traditional catalysts [12, 13]. Graphene quantum dots (GQDs) are a novel
member of carbon nanostructures that have quasi-spherical structures. GQDs have gained intensive attention owing to the remarkable features containing biological [14], biomedical [15], therapeutic applications [16], photocatalysts [17], surfactants [18], electrochemical biosensing [19], electrocatalytic activity [20], Li-ion battery [21], solar cells [22], photoluminescence [23, 24], bioimaging properties [25], and catalytic activity [26]. Potential applications of N-graphene quantum dots were recently reviewed on the basis of experimental and theoretical studies [27–30]. Synthesis of highly efficient nanocomposite catalysts for the synthesis of organic compounds is still an attractive challenge. To obtain larger surface area and more active sites, nanocatalysts are functionalized by active groups [31–33]. It has been demonstrated that the decoration of the nanocatalyst with GQDs prevents the aggregation of fine particles and thus increases the effective surface area and number of reactive sites for an efficient catalytic reaction. The chemical groups on a GQD are able to catalyze chemical reactions. The -COOH and -SO3H groups can serve as acid catalysts for many reactions [26–34]. Herein, we reported the use of Co3O4/NiO@GQDs@SO3H nanocomposite as a new efficient catalyst for the preparation of pyranochromenes and biscoumarins under ultrasonic irradiations in ethanol (Scheme 1). The ultrasound approach decreases times, increases yields of products by creating the activation energy in micro surroundings [35, 36]. We found that Co3O4/NiO@GQDs@SO3H nanocomposite produce our desired compounds in high yields (86–95%) with excellent recovery and simple work-up procedure. In addition, Co3O4/NiO@GQDs@SO3H nanocomposite has a good recycling properties and this advantage is important from economic point of view.

Experimental

Materials and characterization

Powder X-ray diffraction was taken on a Philips diffractometer of X’pert Company with monochromatized Cu Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) spectra were determined on an ESCA-3000 electron spectrometer. Microscopic morphology of nanocatalyst was performed by SEM (MIRA3). The thermogravimetric analysis (TGA) curves are gained by V5.1A DUPONT 2000. The magnetic measurement of samples was registered in a vibrating sample magnetometer (VSM) (Iran, Kashan Kavir). Surface area was carried out using nitrogen adsorption measurement (Micrometrics ASAP-2000).

Preparation of Co3O4/NiO nanoparticles

Co(NO3)3 and of NiCl2 with 3:1 molar ratio were dissolved in ethylene glycol. Afterward, the appropriate amount of aqueous ammonia solution (28 wt%) was added to the above solution until the pH value reached 10. Then, transparent solution was placed in autoclave at 150°C for 4 h. The obtained precipitate was washed twice with methanol and dry at 60°C for 8 h. Finally, the product was calcined at 500°C for 2 h.

Preparation of Co3O4/NiO@N-GQDs nanocomposite

1 g citric acid and was dissolved into 20 mL deionized water, and stirred to form a clear solution. After that, 0.3 mL ethylenediamine was added to the above solution and mixed to obtain a clear solution. Then, 0.1 g Co3O4/NiO nanoparticles were added to mixture. The mixture was stirred at room temperature within 5 min. Then the solution was transferred into a 50 mL Teflon lined stainless autoclave. The sealed autoclave was heated to 180°C for 12 h in an electric oven. Finally, as-prepared nanostructured Co3O4/NiO@GQDs was obtained, washed several times with deionized water and ethanol, and then dried in an oven until constant weight was achieved.

Preparation of Co3O4/NiO@GQDs@SO3H nanocomposite

1g of Co3O4/NiO@N-GQDs nanocomposite was dispersed in dry CH2Cl2 (10 mL) and sonicated for 5 min. Then, chlorosulfonic acid (0.8 mL in dry CH2Cl2) was added drop-wise to a cooled (ice-bath) mixture of Co3O4/NiO@N-GQDs, during a period of 30 min under N2 with vigorous stirring. The mixture was stirred for 120 min, while the residual HCl was removed by suction. The resulted Co3O4/
NiO@GQDs@SO3H nanocomposite was separated, washed several times with dried CH2Cl2 before being dried under vacuum at 60°C.

**General procedure for the synthesis of pyranochromenes and biscoumarins**

A mixture of benzaldehydes (1.0 mmol), 4-hydroxy-coumarin (1.0 mmol), ethyl cyanoacetate (1.0 mmol) and Co3O4/NiO@GQDs@SO3H nanocatalyst (4 mg) in 5 mL of ethanol was sonicated at 40 W power for the appropriate times. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature. The solution was filtered and the heterogeneous catalyst was recovered. Water was added, and the precipitate was collected by filtration and washed with water. The crude product was recrystallized or washed with ethanol to give the pure product. Also, we prepared biscoumarins via reaction of aldehyde (1 mmol) and 4-hydroxy-coumarin (2 mmol) using Co3O4/NiO@GQDs@SO3H nanocatalyst (4 mg) at the same as above conditions.

Spectra data **4a** and **5e** compounds are presented:

2-Amino-4-(4-chlorophenyl)-3-carboethoxy-4H,5H pyrano[3,2-c]chromene-5-one (**4a**): White powder; mp 192–194°C, IR (KBr, cm⁻¹): \( \nu_{\text{max}} \) 3423, 3352, 3094, 2894, 1698, 1608, 1567, 1494, 1450, 1196, \(^1\)H NMR (400 MHz, CDCl3): \( \delta \) 1.16 (3H, t, \( J = 7.3 \) Hz, CH3), 4.07 (2H, q, \( J = 7.3 \) Hz, CH2), 5.05 (1H, s, CH), 6.57 (2H, s, NH3), 7.28 (2H, d, \( J = 7.2 \) Hz), 7.39–7.48 (m, 3H), 7.88 (1H, d, \( J = 8.0 \) Hz), 8.17 (2H, d, \( J = 7.2 \) Hz) ppm; \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)): \( \delta \) 14.3, 39.0, 61.8, 74.8, 105.2, 117.4, 121.6, 125.7, 125.9, 126.5, 128.6, 128.9, 129.5, 130.8, 131.5, 140.2, 150.4, 160.6, 162.7, 168.8 ppm. Anal. Calcd. for C21H16ClNO5: C 63.40, H 4.05, N 3.52, Found: C 63.35, H 4.08, N 3.41.

3-((4-methoxyphenyl)-(4-hydroxy-2H-chromen-3-yl)methyl)-4-hydroxy-2H-chromen-2-one (**5e**): White powder, mp 245–247°C, IR (KBr, cm⁻¹): \( \nu_{\text{max}} \) 3423, 3352, 3094, 2894, 1679, 1608, 1567, 1494, 1450, 1196, \(^1\)H NMR (400 MHz, CDCl3): \( \delta \) 4.14 (OCH3, s, 3H), 6.04 (s, 1H), 7.18 (2H, d, \( J = 8.0 \) Hz), 7.29 (2H, d, \( J = 8.0 \) Hz), 7.39–7.48 (4H, m), 7.69 (2H, \( J = 7.6 \) Hz), 8.04 (1H, d, \( J = 7.2 \) Hz), 8.08–8.12 (1H, m), 11.38 (2H, s, OH, br s) ppm; \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)): \( \delta \) 32.98, 55.51, 104.80, 110.94, 115.91, 117.54, 118.85, 123.60, 123.93, 128.29, 131.64, 150.98, 157.34, 163.63, 163.99 ppm. Anal. Calcd. for C26H18O7: C 70.65, H 4.03.

**Results and discussion**

In the beginning, we prepared Co3O4/NiO nanoparticles by easy techniques. A facile hydrothermal method was used for the preparation of N-GQDs [37]. Sulfonated graphene quantum dots were prepared using chlorosulfonic acid [38]. XRD pattern of Co3O4/NiO, Co3O4/NiO@N-GQDs and Co3O4/NiO@GQDs @ SO3H nanocomposite, is shown in Figure 1. XRD pattern confirms presence of both NiO (JCPDS No.22-1189) and Co3O4 (JCPDS No 65-3103).
In order to investigate the particle size and morphology of nanoparticles, SEM image of Co$_3$O$_4$/NiO and Co$_3$O$_4$/NiO@GQDs@SO$_3$H nanocomposite is indicated in Figure 2. SEM images of the Co$_3$O$_4$/NiO@GQDs@SO$_3$H nanocomposite showed the formation of uniform particles, and the energy-dispersive X-ray spectrum (EDS) confirmed the presence of Co, Ni, O, S and C species in the structure of the nanocomposite (Figure 3).

Magnetic properties of nanocomposites before and after their being decorated with GQDs were tested by vibrating-sample magnetometer (VSM) (Figure 4). The lower magnetism of the as-synthesized Co$_3$O$_4$/NiO@GQDs@SO$_3$H compared with the Co$_3$O$_4$/NiO was ascribed to the antiferromagnetic behavior of GQDs as a dopant. These results demonstrate that the magnetization property decreases by coating and functionalization [39, 40].

FT-IR spectra of Co$_3$O$_4$/NiO, Co$_3$O$_4$/NiO@N-GQDs and Co$_3$O$_4$/NiO@GQDs@SO$_3$H nanocomposite are shown in Figure 5. The absorption peak at 3335 cm$^{-1}$ related to the stretching vibrational absorptions of OH.
The peaks at 461.4, 568.4, 657.1 cm\(^{-1}\) corresponded to the Ni-O, Co\(^{2+}\)-O and Co\(^{3+}\)-O respectively. The characteristic peaks at 3440 cm\(^{-1}\) (O-H stretching vibration), 1705 cm\(^{-1}\) (C=O stretching vibration), 1125 cm\(^{-1}\) (C-O-C stretching vibration) appear in the spectrum of Figure 5b. The peak at approximately 1475–1580 cm\(^{-1}\) is attributed to C=C bonds. The presence of sulfonyl group is also verified by the peaks appeared at 1215 and 1120 cm\(^{-1}\). The broad peak at 3350 cm\(^{-1}\) related to the stretching vibrational absorptions of OH (SO\(_3\)H) (Figure 5c).

The BET specific surface area of Co\(_3\)O\(_4\)/NiO and Co\(_3\)O\(_4\)/NiO@GQDs@SO\(_3\)H nanocomposites was determined by the nitrogen gas adsorption-desorption isotherms (Figure 6). The results presented that the BET specific surface area of Co\(_3\)O\(_4\)/NiO was...
improved from 12.25 to 32.43 m²/g after modification with GQDs, therefore more active sites were introduced on Co₃O₄/NiO@GQDs@SO₃H surface.

Thermal Analysis TGA (Thermogravimetric analysis) determines the thermal stability of the Co₃O₄/NiO@GQDs@SO₃H nanocomposite (Figure 7). The curve indicates a weight loss about 14.06% from 150 to 500°C, are attributed to the oxidation and degradation of GQD.

X-ray photoelectron spectroscopy (XPS) analysis of Co₃O₄/NiO@GQDs@SO₃H nanocomposite was indicated in Figure 8. In the wide-scan spectrum of nanocatalyst, the predominant components are Ni 2p₃/2 (873.4 eV), Ni 2p₁/2 (854.4 eV), Co 2p₃/2 (792.6 eV), Co 2p₁/2 (780.4 eV), O 1s (529.8 eV), N 1s (400 eV), C 1s (284.5 eV) and S 2p (164.3 eV).

Initially, we carried out three-component reaction of 4-chlorobenzaldehyde (1.0 mmol), 4-hydroxycoumarin (1.0 mmol) and ethyl cyanoacetate (1.0 mmol).

Table 1. Optimization of reaction condition using different catalysts.

| Entry | Catalyst (amount) | Solvent | Time (min) | Yield (%) b |
|-------|------------------|---------|------------|-------------|
| 1     | None             | EtOH (reflux) | 400        | NR          |
| 2     | Et₃N (5 mol%)    | EtOH (reflux) | 250        | 42          |
| 3     | NaHSO₄ (4 mol%)  | EtOH (reflux) | 250        | 38          |
| 4     | ZrO₂ (4 mol%)    | EtOH (reflux) | 140        | 50          |
| 5     | pTSA (5 mol%)    | EtOH (reflux) | 120        | 56          |
| 6     | Nano-Co₃O₄ (5 mol%) | EtOH (reflux) | 150        | 43          |
| 7     | Nano-NiO (5 mol%) | EtOH (reflux) | 150        | 52          |
| 8     | Co₃O₄/NiO@GQDs nanocomposite (7 mg) | EtOH (reflux) | 120        | 62          |
| 9     | Co₃O₄/NiO@GQDs nanocomposite (7 mg) | EtOH (reflux) | 120        | 72          |
| 10    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (5 mg) | EtOH (reflux) | 80         | 80          |
| 11    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (7 mg) | EtOH (reflux) | 80         | 85          |
| 12    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (9 mg) | EtOH (reflux) | 80         | 85          |
| 13    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | EtOH (US: 30 W) | 10       | 82          |
| 14    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (2 mg) | EtOH (US: 40 W) | 10       | 87          |
| 15    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | EtOH (US: 40 W) | 10       | 94          |
| 16    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (6 mg) | EtOH (US: 40 W) | 10       | 94          |
| 17    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | EtOH (US: 50 W) | 10       | 92          |
| 18    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | H₂O (US: 40 W) | 15       | 69          |
| 19    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | DMF (US: 40 W) | 15       | 75          |
| 20    | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | CH₃CN (US: 40 W) | 10     | 82          |

*aReaction conditions: 4-chlorobenzaldehyde (1.0 mmol), 4-hydroxycoumarin (1.0 mmol) and ethyl cyanoacetate (1.0 mmol).

bIsolated yield.

Conditions for the best results are indicated in bold.
(1.0 mmol) and ethyl cyanoacetate (1.0 mmol) as a model reaction. The model reaction was performed by Et3N, NaHSO4, ZrO2, p-TSA, NiO, Co3O4, Co3O4/NiO, Co3O4/NiO@GQDs and Co3O4/NiO@GQDs@SO3H nanocomposite. The reactions were tested using diverse solvents containing ethanol, acetonitrile, water and dimethylformamide. The best results were gained in EtOH and we found that the reaction gave convincing results in the presence of Co3O4/NiO@GQDs@SO3H nanocomposite (4 mg) under ultrasonic irradiation (Table 1). We also determined recycling of Co3O4/NiO@GQDs@SO3H nanocomposite for the model reaction under ultrasonic irradiation in ethanol. The results showed that nanocomposite can be reused several times without noticeable loss of catalytic activity (Yields 94 to 92%).

| Entry | Product | Aldehydes | Time (min) | Yield (%) | MP [Ref] °C |
|-------|---------|-----------|------------|-----------|-------------|
| 1     | 4a      | 4-Cl-C6H4 | 10         | 94        | 192–194     |
| 2     | 4b      | 4-NO2-C6H4| 10         | 95        | 240–242     |
| 3     | 4c      | 4-F-C6H4  | 10         | 93        | 223–225     |
| 4     | 4d      | 4-OMe-C6H4| 15         | 90        | 160–162     |
| 5     | 4e      | 2,4,6-C6H4| 10         | 95        | 200–201     |
| 6     | 5a      | C6H5      | 10         | 90        | 229–231     |
| 7     | 5b      | 4-Cl-C6H4 | 10         | 92        | 254–256     |
| 8     | 5c      | 4-NO2-C6H4| 10         | 93        | 236–237     |
| 9     | 5d      | 4-F-C6H4  | 10         | 92        | 267–269     |
| 10    | 5e      | 4-OMe-C6H4| 15         | 86        | 245–247     |

*Isolated yield.

Table 2. Synthesis of pyranochromenes and biscoumarins using Co3O4/NiO@GQDs@SO3H nanocomposite (4 mg).

Scheme 2. Proposed mechanism for the synthesis of pyranochromenes and biscoumarins.
A plausible mechanism for the preparation of chromenes using Co₃O₄/NiO@GQDs@SO₃H nanocomposites is shown in Scheme 2. Firstly, we assumed that the reaction occurs via a condensation between ethyl cyanoacetate and aldehyde, to form the intermediate I on the active sites of Co₃O₄/NiO@GQDs@SO₃H nanocatalyst. Then, 4-hydroxycoumarin added to intermediate I to give the intermediate II. The intermediate III is formed by intra-molecular cyclization reaction. The migration of the hydrogen atom will provide the final product (Scheme 2). Meanwhile, a plausible mechanism for the preparation of biscoumarins using Co₃O₄/NiO@GQDs@SO₃H nanocomposites is shown in Scheme 2. In this mechanism the surface atoms of Co₃O₄/NiO@GQDs@SO₃H activate the C=O and C=N groups for better reaction with nucleophiles. Co₃O₄/NiO@GQDs@SO₃H nanocomposite has the Lewis and Bronsted acid properties. The combination of active Lewis and Bronsted acidic sites increase the activity of catalyst.

To compare the efficiency of Co₃O₄/NiO@GQDs@SO₃H nanocomposite with the reported catalysts for the synthesis of chromenes and coumarins, we have tabulated the results in Table 3. Our study has some advantages in compare with other mention studies including high yield of synthetic compound, reasonable time reaction and easy catalyst recovery.

In this study, Co₃O₄/NiO@GQDs@SO₃H nanocomposite has been used as an effective catalyst for the preparation of dihydropyrano[3,2-c]chromenes and biscoumarins under ultrasonic irradiations in ethanol. The catalyst has been characterized by FT-IR, XRD, SEM, EDS, BET, TGA, XPS and VSM. The present catalytic procedure is extensible to a wide diversity of substrates for the synthesis of a variety-oriented library of pyranochromene and biscoumarins. The ultrasound approach decreases times, increases yields of products by creating the activation energy in micro surroundings. The results showed that nanocomposite can be reused several times without noticeable loss of catalytic activity. Thus, these results indicated that the nanocomposite was stable and could tolerate the MCR (multicomponent reactions) conditions.

Table 3. Comparison of catalytic activity of Co₃O₄/NiO@GQDs@SO₃H nanocomposite with other reported catalysts.

| Entry | Catalyst (condition) | Time (min) | Yield, % | [Ref] |
|-------|----------------------|------------|----------|-------|
| 1     | RuCl₃ (5 mol%)       | 30         | 85       | [6]   |
| 2     | H₂[PMo₉V₃O₄₀] (3 mol%) | 120       | 75       | [7]   |
| 3     | Tetraethylammonium bromide (10 mol%) | 60 | 91 | [8] |
| 4     | DBU (10 mol%)        | 60         | 90       | [9]   |
| 5     | Co₃O₄/NiO@GQDs@SO₃H nanocomposite (4 mg) | 10 | 94 | This work |

*Isolated yield.

Conclusion

In this study, we described the preparation of pyranochromenes and biscoumarins using Co₃O₄/NiO@GQDs@SO₃H nanocomposite as a superior catalyst under ultrasonic irradiation. The current method provides obvious positive points containing environmental friendliness, significantly shorter reaction time, reusability of the catalyst, low catalyst loading and simple workup procedure.

Acknowledgment

The authors are grateful to the University of Kashan for supporting this work under grant no. 159148/XII.

Disclosure statement

The authors declare that they have no conflict of interest.

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