Iranian Journal of Catalysis 8(3), 2018, 189-194

IRANIAN JOURNAL OF CATALYSIS

Graphene–ZnO@SiO_2 hybrid: An efficient and solid acid catalyst for synthesis of azlactones under ultrasound irradiation

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Received 1 July 2017; received in revised form 6 January 2018; accepted 4 March 2018

ABSTRACT

The central theme of this article is how to explore a novel route to fabricate graphene– ZnO@SiO_2 hybrid by a covalent process. The synthesis procedure consists of three-steps: (1) synthesis of ZnO nanoparticles, (2) ZnO nanoparticles modification by tetraethyl orthosilicate and (3-aminopropyl) triethoxysilane after introduction of amino groups on its surface, (3) the covalent attachment of ZnO@SiO_2 onto the graphene surface by the amidation reaction between amino group of ZnO@SiO_2 and carboxylic group of graphene. This hybrid was then used as a catalyst for the synthesis of azlactones obtained by Erlenmeyer synthesis from aromatic aldehydes and hippuric acid under the ultrasonic irradiation. The protocol offers advantages in terms of higher yields, short reaction times, mild reaction conditions, and reusability of the catalyst.

***Keywords**: Graphene– ZnO@SiO_2 hybrid, Ultrasound irradiation, Hippuric acid, Aldehydes.*

1. Introduction

Azlactones, or 2,4-substituted oxazolin-5-ones, are interesting intermediates for the synthesis of a variety of bioactive compounds, including aminoacids, peptides, heterocycles, biosensors and antitumor or anticancer compounds [1]. The most important route for their preparation is the Erlenmeyer–Plöchl reaction comprising condensation of an aldehyde with hippuric acid and acetic anhydride as dehydrating agent in the presence of a catalyst [2]. A variety of methods utilizing different catalysts have been reported for the synthesis of azalactones by Erlenmeyer Plöchl reaction, including the use of sodium acetate [3], anhydrous zinc chloride [4], alumina [5], KPO_4 [6], calcium acetate [7], basic ionic liquid [bmIm]OH [8].

Graphene, a novel carbon-based material, possesses many unique features such as two-dimensional plane structure coupled with one-atom thickness, large surface area, and also extraordinary electrical, thermal, and mechanical properties [9]. Hybrids containing graphene oxide (GO) and nanoparticles are widely applicable in fabrication of heterogeneous catalysts.

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Nanoparticles could be attached to the graphene by physical absorption or electrostatic interaction. In these cases, they may easily leach out of the graphene during application, so precise control of the loading amount of nanoparticles and the properties of the resultant hybrids could not be done. An effective way to solve the problems is the attachment of nanoparticles to graphene by covalent bonding [9].

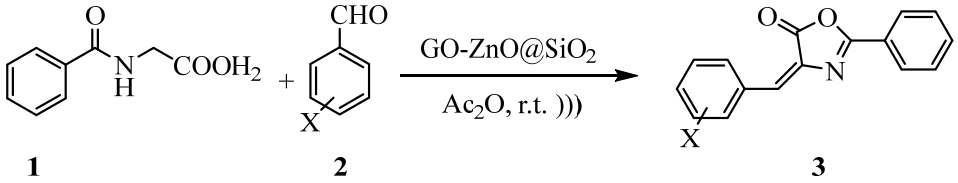
Ultrasonic-assisted organic synthesis as a green synthetic approach is a powerful technique that is being used more and more to accelerate the organic reactions [10]. The advantages of ultrasound procedures, such as good yields short reaction times and mild reaction conditions, are well documented [11].

This paper presents a novel route to produce GO–ZnO@SiO_2 hybrid using a covalent process. The prepared hybrid was then used as a catalyst in the Erlenmeyer–Plöchl reaction for the synthesis of azlactones under ultrasonic irradiation (Scheme 1).

2. Experimental

2.1. Chemicals and apparatus

All the chemicals were obtained from Merck Company and used as received.



Scheme 1. The Erlenmeyer–Plöchl reaction for the synthesis of azlactones under ultrasonic irradiation.

Melting points were measured using a Barnstead Electrothermal melting point apparatus. X-ray diffraction (XRD) measurements of the catalyst powder were recorded by a Philips PW 1800 diffractometer. IR spectra were recorded with a Brucker Vector 22 spectrometer using KBr disks. The size and morphology of the obtained nanoparticles were observed by scanning electron microscopy (SEM, LEO1455VP).The core-shell morphology of the ZnO@SiO_2 nanoparticles was examined using transmission electron microscopy (TEM, Philips EM208S at 100KV) and the morphology of the GO–ZnO@SiO_2 hybrid was tested by field emission scanning electron microscopy (FESEM, ZEISS). The ultrasound apparatus was a cleaning bath Wiseclear 770W (Seoul, Korea). The operating frequency was 40 kHz and the output power was 200 W.

2.2. Synthesis of ZnO nanoparticles

To prepare ZnO nanoparticles, 250ml of the solution (0.1 M) of zinc acetate ($Zn(Ac)_2.2H_2O$) in EtOH was posited in an ultrasonic bath, then into this solution, 100 ml of NaOH solution (0.1 M) was added dropwise. After the reaction for 1 h, 0.015 mmol of citric acid was added to the solution and sonicated at room temperature for another 1 h. The as-prepared dispersion was centrifugally filtered and washed with ethanol and distilled water for several times, followed by drying in an oven at 50 ◦C for 4 h. To form ZnO powders, the obtained precipitates were heated at 400 °C in a furnace for 4 h.

2.3. Preparation of APTES modified ZnO@SiO_2 nanoparticles

0.2 g ZnO nanoparticle was dispersed in 14mLwater and 16 mL ethanol, under continuous mechanical stirring, as 0.5 mL ammonia solution (30 wt%) was added. In order to obtain ZnO@SiO_2 nanoparticles, the precursor of tetraethyl orthosilicate (TEOS) (0.5 mL) was added to the reaction mixture, the reaction was allowed to proceed at 40 °C for 24 h. Then, (3-aminopropyl) triethoxysilane (APTES) (0.5 mL) was added to the reaction mixture and the mixture was stirred for another 24 h at 40 °C. The as-prepared dispersion was centrifugally filtered and washed with ethanol for 4 times and with water for 4 times.

2.4. Synthesis of graphene oxide

The synthesis of GO was prepared by the Hummers method described in the previous report with a slight modification [12]. In brief, 1.0 g of graphite powder, 13 mL H_3PO_4, and 120 mL H_2SO_4 were mixed by constant stirring at 50 °C. Then, 6 g of $KMnO_4$ was gradually added to the mixture and stirred for 8 h while the temperature was kept at 50 °C. When the color of the solution turned to deep brown, the flask was placed into an ice bath. Then, 200 mL of deionized water was added to the solution and stirred for another 30 min followed by the addition of 2 mL of H_2O_2 30% slowly with stirring to reduce the residual $KMnO_4$ until no gas was produced and the color of the solution changed to light brown. The obtained product was washed three times with HCl solution (5% wt) and five times with water and then dried at 60 °C in an oven.

2.5. Preparation of GO– ZnO@SiO_2 hybrid

20 mg of GO in 60 ml of water was ultrasonicated for 30 min, and then 20 mg of *N,N'*-dicyclohexylcarbodiimide (DCC) was added to this solution. The reaction mixture was stirred for 30 min and then ultrasonicated for 30 min. Next, 20 mg of APTES modified ZnO@SiO_2 nanoparticles were added to the suspension and the mixture was subjected to ultrasonication for 30 min. The reaction was carried out at 80 °C for 1 h under stirring. The as-prepared dispersion was centrifugally filtered and washed with acetone, ethanol and acetonitrile, and finally rinsed.

2.6. Catalytic reaction

A mixture of hippuric acid **1** (1 mmol), aldehyde **2** (1 mmol), acetic anhydride (3 mmol) and GO– ZnO@SiO_2 powder (3 mg) was irradiated in the water bath of an ultrasonic at 25-30 °C for 10 min. After completion of the reaction, the resulting suspension was centrifuged to remove the catalyst. The filtrate was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate and concentrated under the reduced pressure to afford the crude product; it was recrystallized from ethanol. All products were known and characterized by comparison of their physical and spectra data with those already reported [7,8].

3. Results and Discussion

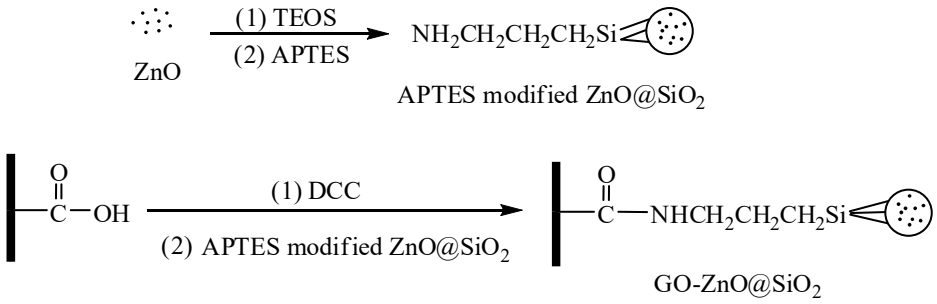
The synthesis process of GO–ZnO@SiO_2 hybrid is illustrated in Scheme 2. The procedure consists of three-steps: (1) synthesis of ZnO nanoparticles, (2) ZnO nanoparticles were modified by TEOS and APTES after introduction of amino groups on its surface, (3) the covalent attachment of ZnO@SiO_2 onto GO surface by the amidation reaction between amino group of ZnO@SiO_2 and carboxylic group of GO.

3.1. Characterization of catalyst

The XRD pattern of resulting ZnO nanoparticles is shown in Fig. 1. All the peaks in the diffraction diagram could be assigned to the hexagonal phase ZnO. The crystallographic phase is in good agreement with the standard data form JCPDS card No. 001-1136.

The SEM image of the synthesized ZnO nanoparticles (Fig. 2) shows well-defined spherical shapes of the nanoparticles having a narrow size and shape distribution over the relevant size range 30-40 nm.

TEM micrograph of the synthesized APTES modified ZnO@SiO_2 nanoparticles is shown in Fig. 3b. A higher magnification image of the shell and core structure is shown in Fig. 3a. It can clearly be seen that the shell structure is amorphous and much less dense than the core structure.



Scheme 2. The fabrication of GO– ZnO@SiO_2 hybrid.

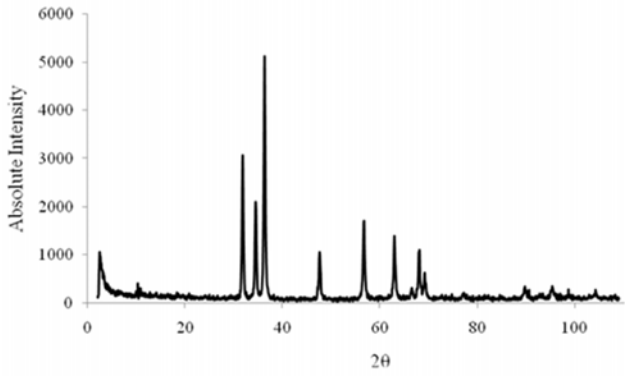


Fig. 1. XRD patterns of ZnO nanoparticles.

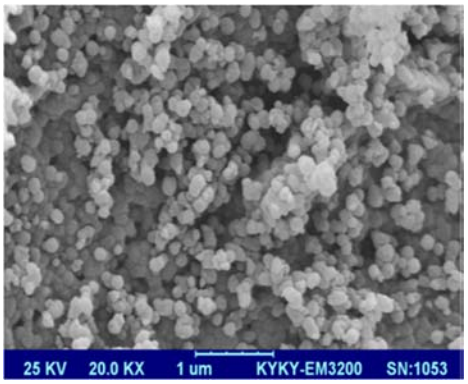


Fig. 2. SEM images of ZnO nanoparticles.

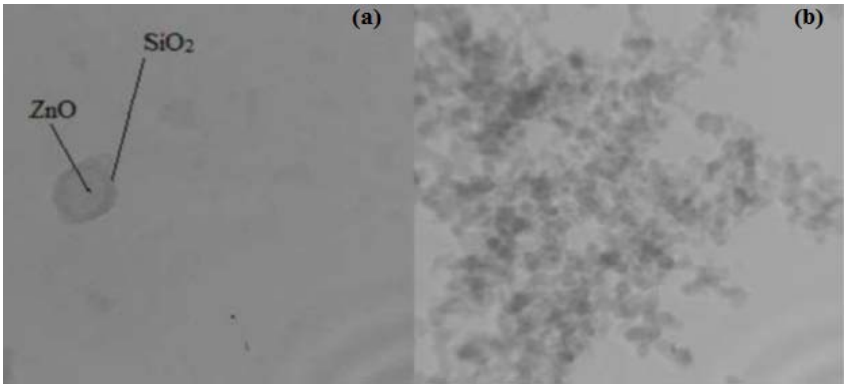


Fig. 3. TEM micrograph of the APTES modified ZnO@SiO_2 nanoparticles. (a) A higher magnification image, (b) Overview.

Representative FESEM image of the obtained GO–ZnO@SiO_2 hybrids showed that the GO surface was coated with ZnO@SiO_2 nanoparticles (Fig. 4).

The functionalization of GO with magnetic ZnO@SiO_2 nanoparticles was further confirmed by the FTIR spectra presented in Fig 5. The as-prepared GO showed peaks at 1725 and 3415 cm^{-1}, indicating the presence of carbonyl (C=O) and hydroxyl group (–OH) from water molecules and carboxylic groups [13,14] (Fig. 1a). After the amidation reaction, the carbonyl stretching frequency disappeared and a new band of the amide carbonyl group for GO–ZnO@SiO_2 hybrid at 1653 (–CONH), 1593 (–NH), and 1472 cm^{-1} (C–N) appeared implying that ZnO@SiO_2 nanoparticles were linked to GO surface by the covalent bonding [15-17].

3.2. Catalytic reaction

First, the mixture of benzaldehyde and hippuric acid in acetic anhydride was chosen as the model reaction to detect if the use of GO–ZnO@SiO_2 catalyst was efficient. The mixture was irradiated by ultrasound at room temperature for 15 min. This reaction successfully afforded the desired product **3** in 95% yield. Without GO–ZnO@SiO_2 catalyst, the same reaction generated only 35% of **3** over the same period of time. To investigate the role of ultrasonic irradiation in this method, the reactions were carried out in the presence of the same amount of catalyst under the stirring condition at room temperature (Table 1). It is clear that the reaction carried out under ultrasonic irradiation afforded the desired product **3** in higher yield and shorter reaction time.

The generality of this process was demonstrated by the wide range of substituted aldehydes to synthesize the corresponding products in good to excellent yields (Table 2).

The catalyst was also found to be reusable, although a gradual decline of activity was observed. GO–ZnO@SiO_2 maintained its structure during the reactions, this matter was confirmed by examining their IR spectra (Fig. 6).

To show the merit of this method, the reaction of benzaldehyde with hippuric acid was selected as a model reaction. The yield of model reaction in the presence of GO–ZnO@SiO_2 catalyst under ultrasonic irradiation was compared to those with various catalysts and conditions, reported in the previous works (Table 3) [7,8,18,19]. It is clear that GO–ZnO@SiO_2 catalyst can catalyze the synthesis of azlactones with higher yields in shorter reaction times. In comparison with the microwave and ultrasound irradiations for the above reaction, we observed that this heterocyclic compound could be prepared under ultrasound irradiation with some improvement in the yield (Table 3).

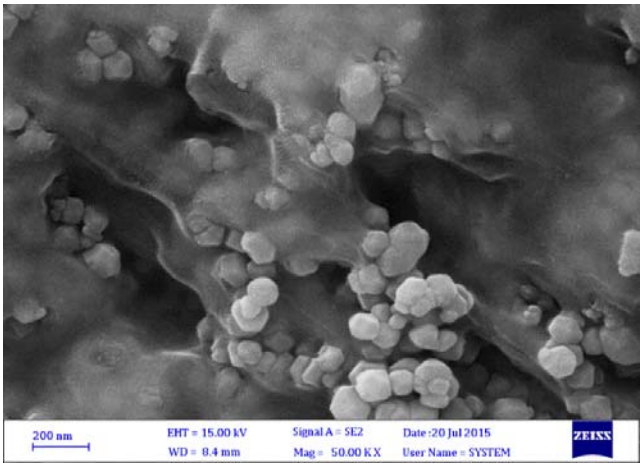


Fig. 4. FESEM image of GO–ZnO@SiO_2 hybrid.

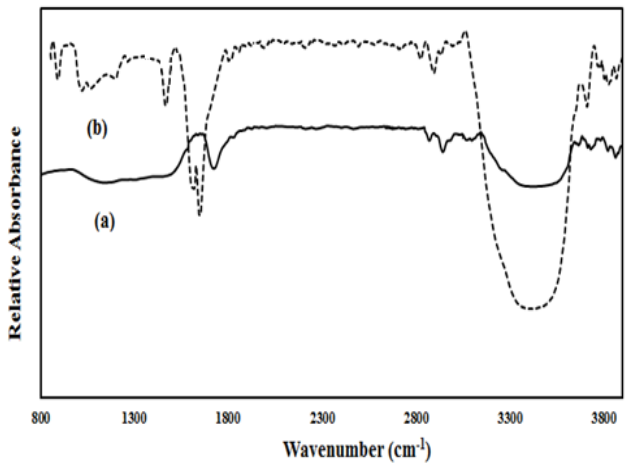


Fig. 5. FTIR spectra of (a) GO and GO–ZnO@SiO_2 hybrid.

Table 1. The reaction of benzaldehyde and hippuric acid in acetic anhydride under different reaction conditions.

Entry	Conditions	Catalyst	Time (min)	Yield (%)
1	Stirring (r.t.)	Without catalyst	45	12
2	Stirring (r.t.)	GO–ZnO@SiO_2	30	44
3	Ultrasound-assisted (r.t.)	Without catalyst	15	35
4	Ultrasound-assisted (r.t.)	GO–ZnO@SiO_2	15	95

Table 2. Erlenmeyer Plöchl reaction with different aldehydes.

Product	X	Time (min)	Yield (%)	m.p. (°C)[a]	
				Found	Reported
3a	H	10	95	168–170	170
3b	4-Br	10	98	204-206	204
3c	4-NO_2	10	98	240-241	241
3d	2- NO_2	15	94	164–165	166
3e	4-OMe	15	96	164–165	165
3f	4-Cl	15	91	199-200	197
3g	4-Me	15	93	143-144	145-146
3h	3,4-$(OMe)_2$	10	89	151-153	151-152
3i	3-NO_2	15	93	193-195	195-196

[a]From Ref. [7,8].

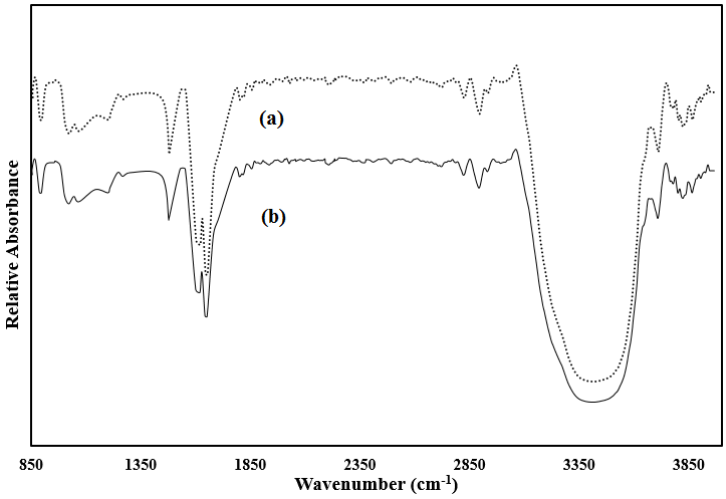


Fig. 6. FT-IR spectra of catalyst, before (a) and after (b) use.

Table 3. Comparison of the reported methods for the condensation of benzaldehyde with hippuric acid in different conditions.

Entry	Catalyst	Time	Conditions	Yield (%)[a]
1	Montmorillonite K10	6 h	Reflux	89
2	Bi(III) salts	1 h	Reflux	75
3	$CaCO_3$	5 min	MW (60–62 °C)	70
4	$Ca(OAc)_2$	5 min	MW (48–50 °C)	97
5	Ionic liquid [bmIm]OH	10 min	(r.t.)	91
6	ZnO	10 min	(r.t.)	90
7	Sm	5 min	MW	92
8	$RuCl_3$	3 min	MW	80
9	$H_3PW_{12}O_{40}$	3 min	MW	87
10	GO–ZnO@SiO_2	10 min	Ultrasound-assisted (r.t.)	95

[a]From Ref. [7,8,18,19].

4. Conclusions

This research work demonstrates a novel and highly efficient method for the synthesis of azlactones in the presence of GO–ZnO@SiO_2 catalyst under ultrasound irradiation. In addition to efficiency and simplicity, this protocol provides a very fast and low cost procedure for the synthesis of these products.

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