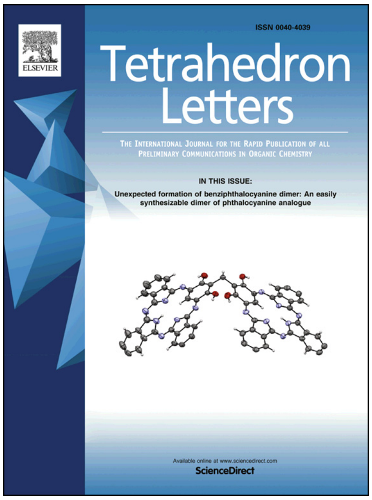

Graphene-supported ZnO nanoparticles: an efficient heterogeneous catalyst for the Claisen-Schmidt condensation reaction without additional base

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Graphene-supported ZnO nanoparticles: an efficient heterogeneous catalyst for the Claisen-Schmidt condensation reaction without additional base

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ABSTRACT

ZnO nanoparticles supported on reduced graphene oxide (ZnO/RGO) were prepared by the hydrothermal method and characterized by TEM, XPS, XRD, and Raman spectroscopy. As a green catalyst, ZnO/RGO was applied to the Claisen-Schmidt condensation reaction of aryl aldehydes and aryl ketones under microwave irradiation. Therein, chalcone products could be efficiently synthesized and easily separated from the heterogeneous catalysis system. The catalyst could be recycled four times without significant loss of catalytic activity.

Introduction

In recent years, reduced graphene oxide (RGO) has received extensive attention on account of its unique sp^2 hybrid structural characteristics, large specific surface area, and stable chemical structure, as well as excellent mechanical, physical and other properties.[1-4] Therefore, RGO has been applied in the catalyst carrier,[5] solar cell,[6] and super capacitor[7] fields. So far, a large number of groups have reported various metal oxides, including TiO_2,[8] CuO,[9] ZnO,[10] and SnO_2,[11] supported on RGO as catalysts. With advantages including plentiful raw material availability, low cost, non-toxicity, good thermal stability, chemical stability and easy availability;[12] ZnO as a catalyst has become a research hotspot. ZnO nanoparticles dispersed on a RGO layer can not only avoid the phenomenon of agglomeration, but also produce synergistic effects and good catalytic activity. These materials are typically used as photocatalysts in photodegradation reactions. Bai and co-workers[13] reported that graphene/ZnO hybrids showed excellent photocatalytic activity in the photodegradation of deoxynivalenol under UV light, while Xu and co-workers[14] reported the photocatalytic activities of ZnO-graphene in the degradation of methyl orange and water splitting under visible light. However, little attention has been paid to organic synthesis reactions catalyzed by ZnO nanocomposites supported on RGO. Rajesh and co-workers[15] reported RGO/ZnO nanocomposites as a catalyst for the synthesis of 3-substituted indoles in water.

Chalcone derivatives are found in many natural products, and are also important synthetic intermediates for the formation of flavonoids and isoflavones.[16, 17] The various bioactivities of chalcones mainly depend on the number and position of substituents on the two benzene rings. The flexible structures of chalcones and the ability to interact with different receptors leads to a wide range of biological activities, such as anti-tumor, antibacterial, antiallergic, antiviral, and antimalarial properties.[17-20] Therefore, many synthetic methods have been developed for the synthesis of these compounds. Since the 1970s, one of the most important tools has been the use of a strong base or Lewis acid to catalyze the Claisen-Schmidt reaction;[21] however, this method is, to a certain extent, not environmentally friendly. A way to overcome this problem is the use of a heterogeneous catalyst instead of a base or Lewis acid. So far, numerous heterogeneous catalysts, such as hydroxyapatite, activated carbon, ZSM-5 zeolite, and magnesium oxide hollow spheres, have been developed.[22-25] However, these methods also have some limitations and shortcomings in terms of cost, environmental pollution or other aspects.

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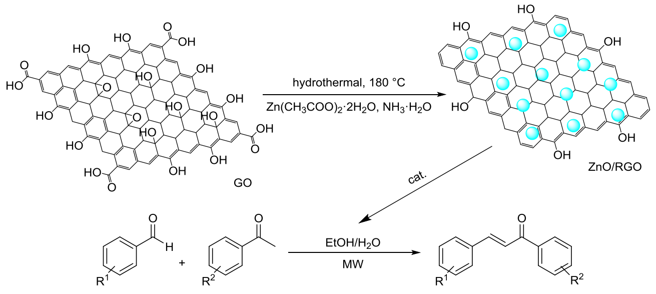
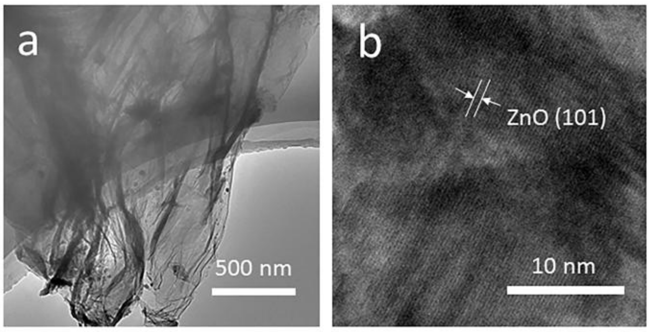
Our team has previously studied the use of metals supported on RGO composites, such as Pd@PdO-NDG,[26] Cu NPs@RGO[27] and WO_3/RGO,[28] to catalyse organic synthesis reactions. Based on these publications, we proposed ZnO nanocomposites supported on RGO (ZnO/RGO) by the hydrothermal method, to catalyze the Claisen-Schmidt condensation reaction.



Scheme 1. Synthesis and application of the ZnO/RGO catalyst.

Results and Discussion

As shown in Figure 1, the morphology and particle size of ZnO/RGO could be observed by transmission electron microscopy (TEM). The representative crinkles of graphene were present, and the ZnO nanoparticles were dispersed on the surface of graphene without aggregation (Fig. 1a). It could also be seen that the ZnO nanoparticles were successfully anchored on RGO; after centrifugation and sonication, the nanoparticles still existed, indicating a strong bond between the two materials. The high-resolution transmission electron microscopy (HRTEM) image showed the lattice fringe was 0.248 nm, corresponding to the (101) crystal plane of the wurtzite ZnO crystal (Fig. 1b).[29]



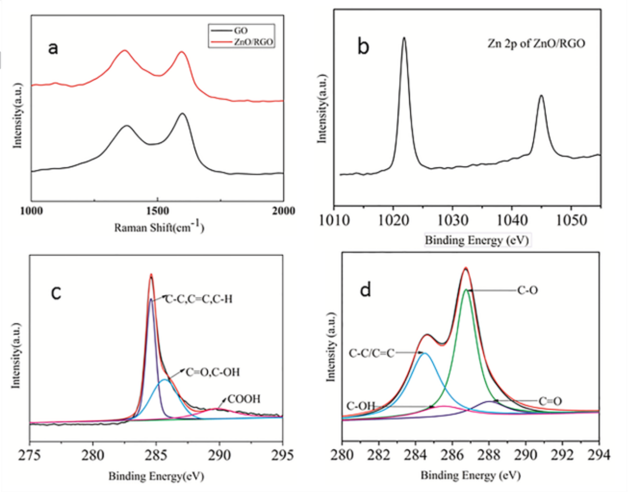


Figure 1. (a) TEM and HRTEM (b) images of ZnO/RGO.

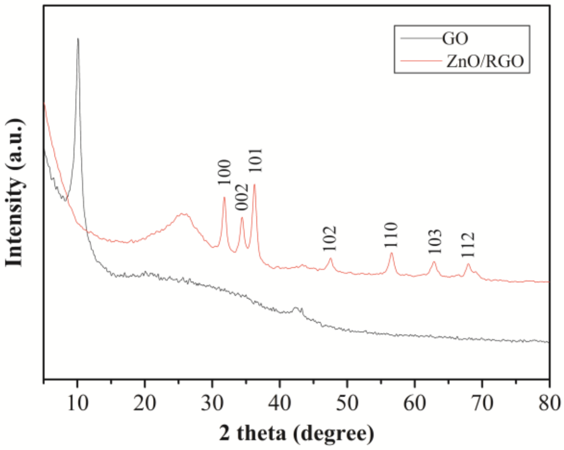


Figure 2. XRD pattern of GO and ZnO/RGO.

Figure 2 depicts the XRD pattern of the ZnO/RGO composite. The diffraction peaks at 31.5°, 34.1°, 36.3°, 47.6°, 56.7°, 62.7°, and 68.1° were consistent with those of (100), (002), (101), (102), (110), (103), and (112), respectively,[29] indicating that ZnO was hexagonal wurtzite. The diffraction peak around 25°, which could be seen as a broad absorption peak, is the typical absorption peak for graphene. However, there was no strong absorption at the diffraction peak of 10°, which proved that the graphene oxide is fully transformed into graphene during the reduction process.

The Raman spectrum of GO and ZnO/RGO composites are shown in Figure 3a. Two strong absorption peaks at 1368 cm^{-1} and 1600 cm^{-1}, for the G band and D band, respectively, are clearly observed. The G band corresponded to the sp^2 hybridized carbon, while the D band was mainly caused by defects or disordered carbon. The I_D and I_G intensity ratios indicate the structural regularity of the graphitic carbon; when the I_D/I_G values are closer to zero, the regularity is higher. In Figure 3a, the I_D/I_G value of the graphene oxide was 0.83, whereas the value of the ZnO/RGO nanocatalyst was 1.02. The reason why the value increased was that a large amount of the functional groups on GO (such as carboxyl and hydroxyl) are anchored as reaction sites for Zn^{2+} demonstrating ZnO/RGO nanocomposites are obtained,[30] which was consistent with the TEM results. It also indicated that the structure of the carbon was destroyed and the degree of crystallinity decreases during reduction of the graphene oxide.

Figure 3. (a) Raman spectra of ZnO/RGO and GO. (b) Zn 2p XPS spectra of ZnO/RGO catalyst. (c) C1s XPS spectra of ZnO/RGO. (d) C1s XPS spectra of GO.

The XPS spectra of the ZnO/RGO composites are shown in Figure 3b. The binding energies at 1021.8 and 1044.9 eV, which were assigned to $Zn2p_{3/2}$ and $Zn2p_{1/2}$, respectively, indicated that zinc was present in the form of ZnO.[31] These results indicate that there are no impurities within the sample.[32] Figure 3c depicts the C 1s fitting spectrum of the composites. The peak at 284.5 eV corresponded to the sp^2 carbon atom, whereas the deconvoluted peaks at 285.7 eV and 289.8 eV were attributed to C-OH, C=O and COOH oxygen-containing carbonaceous bands, respectively.[29] The C 1s spectrum of ZnO/RGO is consistent with the C 1s absorption peak spectrum of graphene oxide (Fig. 3d). According to the comparison of Fig. 3c and Fig. 3d, the decrease of oxygen-containing functional groups in theZnO/RGO nanocomposite proves that the graphene oxide is reduced to graphene.

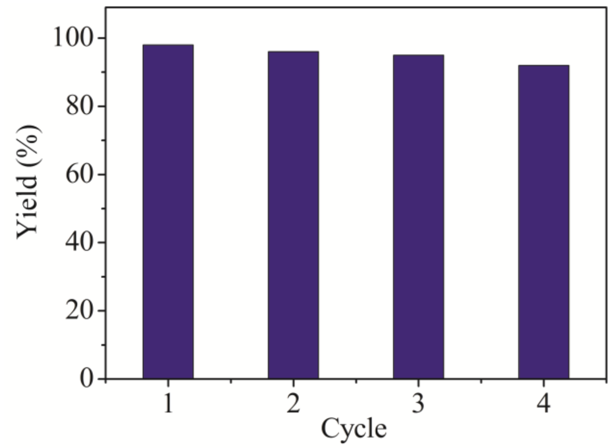
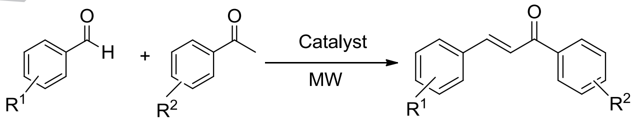


Figure 4. ZnO/RGO catalyst recycling.

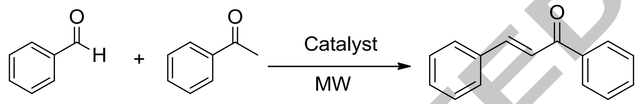
Next, benzaldehyde and acetophenone were examined as model substrates, and the reaction conditions for the ZnO/RGO catalyzed Claisen-Schmidt condensation were optimized by screening the solvent, temperature and time (Table 1).

Initially, various solvents, including water, ethanol, tetrahydrofuran, *N*,*N*-dimethylformamide, and ethanol/water were examined. The yields only reached 30% and 50% in water and ethanol, respectively (Entries 1-2), while yields of 20% were obtained in THF and DMF (Entries 3-4). When different ratios of ethanol and water were utilised, a yield of 98% was obtained in 2:1 ethanol/water (Entries 5-7). Note that the addition of ethanol could increase the substrate solubility and the dispersibility of the catalyst.



Subsequently, it was found that microwave irradiation for 15 minutes was the optimal reaction time (Entries 6 and 8-9). The reaction yield was only 15% when the reaction was heated at 80 °C without microwave irradiation (Entry 10). It was also found that ZnO/RGO was a better catalyst than ZnO (Entries 6 and 11). Without the catalyst, the reaction did not occur (Entry 12), Finally, ZnO/RGO (10 mol%) was found to be the optimum catalyst loading (Entries 6 and 13-14).

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Time (min)	Yield (%)[b]
1	ZnO/RGO (10mol%)	H_2O	15	30
2	ZnO/RGO (10mol%)	EtOH	15	50
3	ZnO/RGO (10mol%)	THF	15	20
4	ZnO/RGO (10mol%)	DMF	15	20
5	ZnO/RGO (10mol%)	EtOH/H_2O (3:1)	15	93
6	ZnO/RGO (10mol%)	EtOH /H_2O (2:1)	15	98
7	ZnO/RGO (10mol%)	EtOH /H_2O (1:1)	15	90
8	ZnO/RGO (10mol%)	EtOH /H_2O (2:1)	20	98
9	ZnO/RGO (10mol%)	EtOH /H_2O (2:1)	10	80
10	ZnO/RGO (10mol%)	EtOH /H_2O (2:1)	60	15[c]
11	ZnO	EtOH /H_2O (2:1)	15	30
12	None	EtOH /H_2O (2:1)	15	-
13	ZnO/RGO (5mol%)	EtOH /H_2O (2:1)	15	78
14	ZnO/RGO (15mol%)	EtOH /H_2O (2:1)	15	97

[a] Reagents and conditions: aryl aldehyde (0.05 mol), aryl ketone (0.05 mol), catalyst (10 mol%), solvent (6 mL), MW (120W, reflux). [b] Isolated yield. [c] Without microwave irradiation at 80°C.

Therefore, the optimum reaction conditions were as follows: benzaldehyde and the substituted acetophenone as substrates, ZnO/RGO as catalyst, EtOH/H_2O (2:1) as solvent under microwave irradiation for 15 minutes. Using these conditions, high yields and low by-product formation was observed, as well as simple catalyst separation.

Under the optimized reaction conditions, we broadened the range of substrates to various aryl aldehydes and aryl ketones to investigate their electronic and steric hindrance characteristics in the Claisen-Schmidt condensation (Table 2).

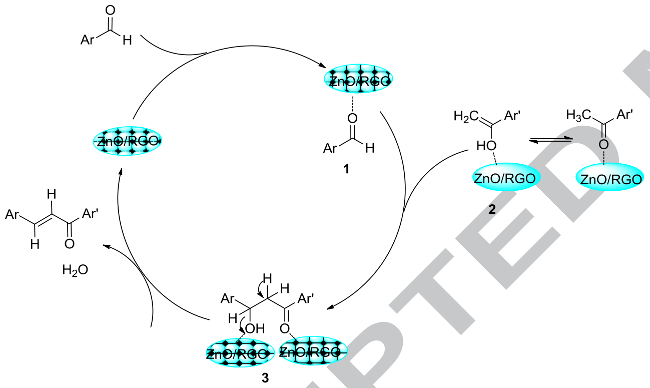
Firstly, the reactions of acetophenone with different aryl aldehydes were studied. *para*-Substituted aryl aldehydes with electron-withdrawing groups ($–NO_2$, –Cl and –Br) or electron-donating groups ($–OCH_3$ and $–CH_3$), gave the corresponding chalcone product in over 90% yield (Entries 1-6). It could be seen that electron-withdrawing groups were beneficial to the reaction. Moreover, 4-nitrobenzaldehyde gave a yield of 94% (Entry 4), while 2-nitrobenzaldehyde did not give the product (Entry 7); this could be due to steric hindrance. Moreover, hydroxyl chalcones were synthesized in 90-91% yields (Entries 8-10). Furthermore, acetophenones with different groups at various positions were investigated; these acetophenones all gave high yields (Entries 11-22). When furfural was used as substrate, the corresponding product was obtained in 90% yield (Entries 17-18), indicating that the catalyst system was also effective for heterocyclic aromatic aldehydes.

Table 2. Substrate scope of the ZnO/RGO-catalyzed Claisen-Schmidt condensation reaction.[a]

Entry	R^1	R^2	Yield (%)[b]
1	H	H	98
2	4-OCH_3	H	91
3	4- CH_3	H	90
4	4-NO_2	H	94
5	4- Cl	H	93
6	4- Br	H	94
7	2-NO_2	H	Trace
8	H	2-OH	90
9	4-OCH_3	2-OH	91
10	4-Br	2-OH	91
11	4-Cl	3-Br	90
12	H	3-Br	95
13	H	4-OCH_3	96
14	4-OCH_3	4-OCH_3	92
15	4-Br	4-OCH_3	93
16	4-Cl	4-OCH_3	92
17	furfural	4-OCH_3	90
18	furfural	4-CH_3	90
19	H	4-CH_3	96
20	4-OCH_3	4-CH_3	91
21	4-Br	4-CH_3	94
22	4-Cl	4-CH_3	93

[a] Reagents and conditions: aryl aldehyde (0.05 mol), aryl ketone (0.05 mol), ZnO/RGO (10 mol%), EtOH/H_2O (6 mL, 2:1), MW (120W, reflux).[b] Isolated yield.

According to the literature,[33] a possible mechanism for the ZnO/RGO catalyzed Clasien-Schmit condensation was proposed (Scheme 2). The ZnO/RGO catalyst can both activate the aldehyde carbonyl group to form transition complex **1** and also promote formation of the active enol form **2** of the ketone. The addition product **3** is then generated by nucleophilic addition. Finally an elimination reaction gives the chalcone product with the loss of H_2O.



Scheme 2. Possible mechanism for the Clasien-Schmit condensation.

In order to demonstrate the reusability of ZnO/RGO, four cycles of experiments were conducted (Fig. 4). The catalyst retained considerable activity after four cycles; the yield of chalcone was always greater than 90%, although it gradually decreased. This also indicated that the catalyst had good stability and activity.

Using benzaldehyde and acetophenone as representative substrates, the catalytic system was compared with earlier reports. The protocol had good catalytic performance with lower reaction times and higher yields (Entries 1-4). Therefore, the heterogeneous ZnO/RGO catalytic system is more desirable and efficient than previous methods.

Table 3. Comparisons of optimal protocol with earlier reports.

Entry	Catalyst	Temperature	Time	Yield	Reference
1	Fe_3O_4@MOF	110 °C	24 h	96	21
2	hydroxyapatite	MW (700W)	1 h	80	22
3	flower-like MgO	110	2 h	99	25
4	NAFAP	r.t.	24 h	90	17
5	ZnO/RGO	MW (120W)	0.25 h	98	This work

In conclusion, ZnO nanoparticles supported on RGO were prepared by the hydrothermal method and utilised to efficiently catalyze the Claisen-Schmidt condensation of aromatic aldehydes and ketones under microwave irradiation without additional base. The catalytic system could be recycled four times without a dramatic loss of activity. The heterogeneous catalytic system had high catalytic efficiency and good functional group tolerance.

Acknowledgments

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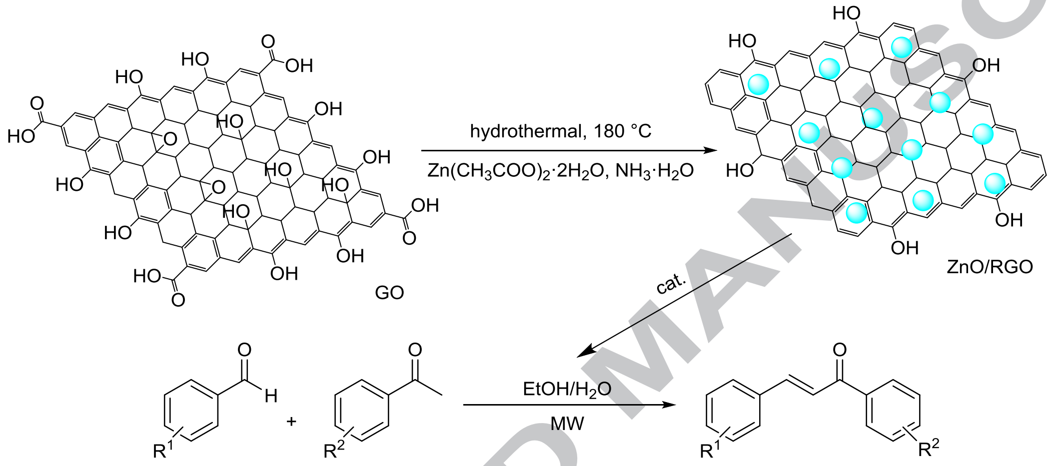
Graphical Abstract

Graphene-supported ZnO nanoparticles: an efficient catalyst for the heterogeneous catalysis Claisen-Schmidt condensation reaction without additional base

Zhuofei Li, Hongyan Zhao, Huatao Han, Yang Liu, Jinyi Song, Weihao Guo, Wenyi Chu∗ and Zhizhong Sun*



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Highlights

1. ZnO nanoparticles supported on reduced graphene oxide were prepared.
2. ZnO/RGO as catalyst was applied to the Claisen-Schmidt condensation.
3. A new catalytic system was developed under microwave conditions.
4. ZnO/RGO could be recycled without obvious losses of catalytic activity.