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Introduction

Metal-organic frameworks (MOFs) are ordered porous crystalline materials constituted by metal ion nodes and organic molecule linkers in a specific coordination number and geometry.1 Because of their large surface area, high porosity, and precisely controllable structure and functionality, MOFs have attracted enormous interest in heterogeneous catalysis recently.2 Until now, they have been extensively used in a wide range of chemical transformations, such as acid or base catalysis,^{3,4} selective oxidation,⁵ asymmetric organic synthesis⁶ and photocatalysis.7 In this context, one of the most promising applications is the use of MOFs as solid catalysts for multistep synthesis because the versatilities in component and morphology of MOFs allow for an extensive tunability in the composition, configuration and dispersion of varied active species.8 Obviously, these systems offer significant benefits to chemical synthesis owing to the increased process intensification and sustainability, and the reduction of costs and wastes.9

A functionalized graphene oxide and nano-zeolitic imidazolate framework composite as a highly active and reusable catalyst for [3 + 3] formal cycloaddition reactions[†]

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We report a facile coordination-induced growth approach to fabricate a SO₃H-functionalized graphene oxide and nanosized zeolitic imidazolate framework composite (ZIF-8@SO₃H-GO) under mild conditions. The interactions between the functional groups on the sheets of GO with Zn(II) ions of the ZIF-8 precursor initiated the nucleation and growth of ZIF-8 on the GO and meanwhile nanosized ZIF-8 particles were well dispersed on the sheets of GO. Owing to the co-existing basic imidazole moieties from ZIF-8 and the SO₃⁻⁻ and CO₂⁻⁻-functional groups on the sheets and Zn²⁺ ions from ZIF-8 in this Lewis acid rich composite, it exhibited high catalytic reactivity and selectivity in [3 + 3] formal cycloaddition reactions that consist of two-step Knoevenagel-type condensation and electrocyclic ring-closure to give various synthetically valuable pyranyl heterocycles. Interestingly, it was especially advantageous for the large sized reactants. The results indicated that it displayed 2 times higher reactivity compared to ZIF-8 nanoparticles due to the newly formed mesopores in the junctions between GO sheets and ZIF-8 nanoparticles. More importantly, it could be conveniently recovered and recycled 10 times without the loss of activity.

To date, some MOFs have been developed for various multistep reactions in different acid/base, oxidation/reduction, and metal–organic combination ways, including pristine MOFs,¹⁰ organic-functionalized MOFs¹¹ and metal particle loaded MOFs.¹² However, the existence of diffusion limitation caused by the relatively small pores in most of these reported MOFs impedes their practical usefulness in multiple chemical transformations. Moreover, these above-mentioned MOFs have rarely been adopted to construct synthetically useful and complex molecules.¹³ Therefore, the design of the novel MOF-based solid catalyst with high reactivity and stability for multistep synthesis still remains a big challenge.

Recently, graphene oxide (GO) with a two-dimensional sheetlike structure and abundant functional groups has provided a novel platform for the nucleation and subsequent growth of MOFs, resulting in the generation of a series of MOF@GO hybrid nanocomposites.¹⁴ Interestingly, these functional materials exhibited remarkably enhanced properties compared to the individual corresponding MOFs or GO in adsorption applications such as CO₂ capture and reactive adsorption of toxic gas, due to the additional pores existing at the MOF@GO interface and the increased dispersive interactions.¹⁵ In spite of these recent advances, there has been relatively little exploration in heterogeneous catalysis by using MOF@GO nanocomposites, especially for multistep reactions.¹⁶ Herein we report for the first time the synthesis of a functionalized

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graphene oxide and nano-ZIF-8 composite (ZIF-8@SO₃H-GO) by a facile coordination-induced growth approach. Owing to the co-existing basic imidazoles and abundant Lewis acidic species including the SO_3^- and CO_2^- -functional groups on the sheets and Zn^{2+} ions, it showed excellent catalytic reactivity and selectivity in [3 + 3] formal cycloaddition reactions that comprise two-step Knoevenagel-type condensation and electrocyclic ring-closure to give a variety of synthetically valuable pyranyl heterocycles. It is noteworthy that it was especially advantageous for the large size molecules due to the newly formed mesopores in the junctions between GO sheets and ZIF-8 nanoparticles. Meanwhile, it was also easily isolated by simple filtration and reused ten times without significant degradation in catalytic activity.

Experimental section

1. Sample preparation

1.1 Synthesis of sulfonated graphene oxide (SO₃H-GO). Graphene oxide (GO) was first prepared by the conventional Hummers method. In a typical procedure, the mixture of 1.0 g natural graphite powder and 1.0 g anhydrous NaNO3 was added slowly into 40 mL concentrated H₂SO₄ (98%) in an ice bath. After continuous stirring for 2.0 h, 5.0 g KMnO₄ was gradually added into the mixture. Next, the mixture temperature was increased to 35 °C and allowed to stir for another 24 h. Then, after the temperature was adjusted to 60 °C, 100 mL 0.50 mol L^{-1} H₂SO₄ aqueous solution was added. After stirring for 2.0 h, the temperature was increased to 95 °C. Subsequently, 100 mL 30% H₂O₂ aqueous solution and 1000 mL H₂O were successively added into the mixture. After stirring for 0.5 h, the solid sample was thoroughly washed with 0.50 mol L^{-1} HCl aqueous solution and water five times. The obtained graphene oxide was collected by centrifugation and vacuum drying at 60 °C for 12 h. After that, 0.50 g GO was introduced into 10 mL chlorosulfonic acid (HSO₃Cl) under a nitrogen atmosphere and then sonicated for 0.5 h. After stirring for 12 h, the mixture was added into 500 mL deionized water and allowed to stir for 1.0 h. The obtained product was separated by centrifugation, washed with ethanol and water, and dried in a vacuum at 80 °C for 10 h.

1.2 Fabrication of the graphene oxide-nano-zeolitic imidazolate framework composite (ZIF-8@SO₃H-GO). First, a certain amount of GO was dispersed into 10 mL 2-methylimidazole aqueous solution ($3.5 \text{ mol } L^{-1}$) at 30 °C and sonicated for 0.5 h. Then, 1.0 mL Zn(NO₃)₂ aqueous solution (0.50 mol L^{-1}) was added dropwise into the mixture under magnetic stirring and afterward continuously stirred for 12 h. After centrifugation, the solid sample was washed with imidazole buffer solution and ethanol three times to thoroughly remove the uncoordinated Zn ion and 2-methylimidazole. Finally, the product was dried at 80 °C in a vacuum for 12 h. The final catalyst could be defined as ZIF-8@SO₃H-GO-1, ZIF-8@SO₃H-GO-2 and ZIF-8@SO₃H-GO-3, corresponding to 50 mg, 100 mg and 200 mg GO used in the initial mixture, respectively.

1.3 Synthesis of nano-zeolitic imidazolate frameworks (ZIF-8). 1.0 mL $Zn(NO_3)_2$ aqueous solution (0.50 mol L⁻¹) was added dropwise into 10 mL 2-methylimidazole aqueous

solution (3.5 mol L^{-1}) at 30 °C under magnetic stirring. After stirring for 12 h, the white powder was collected by centrifugation and washed with deionized water and ethanol three times, dried in a vacuum at 80 °C for 6.0 h.

2. Characterization

The nitrogen, carbon and sulfur contents were calculated with a Vario EL III Elemental analysis analyzer. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All the binding energy values were calibrated by using $C_{1S} = 284.6$ eV as a reference. X-Ray diffractions (XRD) were performed on a Rigaku D/MAX B diffraction system with Cu K α radiation. N₂ adsorption–desorption isotherms were obtained on a Micromeritics ASAP2020 analyzer. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM2011 electron microscope.

3. Activity test

In a typical procedure of the [3 + 3] formal cycloaddition reaction, 1.0 mmol 1,3-cyclohexanedione, 1.0 mmol 3-methyl-2butenal, 50 mg solid catalyst and 5.0 mL CH₂Cl₂ were mixed and allowed to stir at 20 °C for 24 h. The product was extracted with ethyl acetate, followed by analysis on a high performance liquid chromatography analyzer (HPLC, Agilent 6410 series Triple Quad) equipped with an Agilent C18 column. The reaction conversion was calculated based on the consumption of 3methyl-2-butenal and the selectivity was determined by the yield of the achieved pyranyl heterocycle product.

In order to determine the catalyst recyclability, ZIF-8 $(3SO_3H-GO-2)$ was centrifuged after each run of the [3 + 3] formal cycloaddition reaction with 1,3-cyclohexanedione and 3-methyl-2-butenal as the reactants and the clear supernatant liquid was decanted slowly. The residual solid catalyst was washed thoroughly with toluene and dichloromethane, followed by vacuum drying at 80 °C for 6.0 h. Then, the catalyst was re-used with a fresh charge of solvent and reactants for subsequent recycle runs under the same reaction conditions.

Results and discussion

The synthesis of the graphene oxide and nano-zeolitic imidazolate framework composite (ZIF-8@SO₃H-GO) is illustrated in Scheme 1. Briefly, GO was prepared according to the previously reported Hummers method.¹⁷ Then, chlorosulfuric acid (HSO₃Cl) was chosen to react with GO to afford SO₃H-functionalized GO (SO₃H-GO). Next, SO₃H-GO was added into a mixture of 2-methylimidazole and Zn(NO₃)₂ aqueous solution. The coordination interactions of the SO₃⁻ and COO⁻ ions on the sheets of GO with Zn ions initiated the growth of ZIF-8 nanoparticles, leading to the formation of the ZIF-8@SO₃H-GO nanocomposite. In parallel, ZIF-8 nanoparticles were also synthesized in aqueous solution by using the same precursors.

Elemental analysis revealed that the sulfur content in the GO sample was only 0.105 wt% (Table S1†). Also, the S2p XPS spectrum (Fig. S1†) revealed that no apparent signal of the sulfur element could be detected, confirming the negligible

Scheme 1 Schematic synthesis of ZIF-8@SO3H-GO composites.

sulfur species in the GO sample due to the efficient washing work-up treatment.18 For comparison, the amount of sulfur was found to be 1.75 wt% in SO₃H-GO (Table S1[†]). FTIR spectra (Fig. S2[†]) showed that SO₃H-GO exhibited an additional peak at 1090 cm⁻¹ characteristic of the stretching vibration of the S=O bond in comparison with GO.19 In addition, the S2p XPS spectrum (Fig. 1a) of SO₃H-GO displayed an obvious peak at 168.6 eV associated with the S-O bond.20a These results indicated the successful modification of SO₃H groups on the GO. Moreover, the C1s spectrum of SO₃H-GO (Fig. 1b) revealed that the peak at 286.9 eV characteristic of C-OH and C-O-C moieties almost completely disappeared while the peaks at 284.7 and 289.1 eV corresponding to sp² C-C bonding and the carboxylic acid group remained almost the same with GO,20b suggesting the incorporation of SO₃H-groups on the GO via a possible esterification reaction between the surface hydroxyl groups (OH-) and HSO₃Cl.^{19a} Furthermore, the FTIR spectrum of the representative ZIF-8@SO3H-GO-2 (Fig. S2⁺) exhibited the typical ZIF-8 absorption peaks at 990, 1585 and 2960 cm⁻¹ corresponding to C-N stretch, C=N stretch and aliphatic C-H stretch of imidazole groups, respectively.21 In addition, the N1s XPS spectrum of ZIF-8@SO₃H-GO-2 (Fig. 1c) displayed almost the same peak at 398.7 eV indicative of imidazole moieties with ZIF-8 nanoparticles,²² demonstrating the effective nucleation and growth of ZIF-8 on the GO. Interestingly, the S2p XPS spectrum (Fig. 1a) revealed the complete disappearance of the S-O bond signal for the ZIF-8@SO₃H-GO-2 composite. Also, the C1s XPS spectrum of ZIF-8@SO₃H-GO-2 (Fig. 1b) showed that the peak at 289.1 eV attributed to the carboxylic acid group also disappeared. This phenomenon suggested that both SO_3^{-} and COO⁻ ions initiated the growth of ZIF-8 on the sheets of GO, thereby these functional groups were covered by ZIF-8 after the formation of the ZIF-8@SO₃H-GO composite.

XRD spectra (Fig. 2a) showed that the major diffraction peak at $2\theta = 10.2^{\circ}$ assigned to the (001) plane in GO almost completely disappeared and changed to a broad peak in SO₃H-GO. In combination with its TEM image (Fig. S3†), these results revealed that the sheets of SO₃H-GO were efficiently exfoliated with single or several layers, providing a suitable two-dimensional support to attach the nanoparticles on its sheets.²³ Accordingly, XRD spectra of these ZIF-8@SO₃H-GO composites exhibited similar well resolved diffraction peaks to those of ZIF-8 nanoparticles, evidently identifying the generation of ZIF-8 with a crystalline size on the nanoscale.²⁴ The intensities of diffraction peaks were gradually decreased with the increase in amounts of GO in the initial solution, which was maybe attributed to the reduced ZIF-8 size and the increased amount of low crystallinity GO. Additionally, N₂ sorption isotherms of



Fig. 1 S2p XPS spectra (a) of SO₃H-GO and ZIF-8@SO₃H-GO-2, C1s XPS spectra (b) of GO, SO₃H-GO and ZIF-8@SO₃H-GO-2 and N1s XPS spectra (c) of ZIF-8 and ZIF-8@SO₃H-GO-2.

different samples are shown in Fig. 2b. Only a very low amount of N₂ molecules was adsorbed on the GO. Meanwhile, ZIF-8 displayed the type I adsorption-desorption isotherm, indicating its microporous structure.25 The shape of the isotherms for all the ZIF-8@SO₃H-GO composites was quite similar to ZIF-8. However, the additional small hysteresis loops at a high relative pressure around $p/p_0 = 0.47-1.0$ can be seen in ZIF-8(a)SO₃H-GO-1 and ZIF-8@SO₃H-GO-2. It was probably assigned to the formation of mesopores that existed in the junctions between ZIF-8 and GO surface for ZIF-8@SO₃H-GO composites.²⁶ As shown in Table 1, the average pore sizes of ZIF-8@SO3H-GO-1 and ZIF-8@SO3H-GO-2 calculated from their adsorption branches were 1.9 and 2.1 nm, further confirming the newly generated mesopores. Moreover, the specific surface areas and pore volumes of ZIF-8@SO3H-GO samples were gradually decreased with the increasing GO percentages in these composites (Table 1), which can be explained by the increasing proportion of nonporous GO in the composites.

The morphologies of ZIF-8@SO3H-GO composites were indicated by transmission electron microscopy (TEM). In the absence of GO, the as-made ZIF-8 nanoparticles displayed the approximate rhombohedral shape with a particle size in the range of 80 to 100 nm (Fig. 3a). In comparison, ZIF-8 particles with around 100 nm size were randomly distributed on the GO layers in ZIF-8@SO₃H-GO-1 (Fig. 3b). However, for ZIF-8@SO₃H-GO-2, most of ZIF-8 particles with about 80 nm size and some smaller particles with 20-30 nm size were densely laid on the surface (Fig. 3c). However, ZIF-8 particles with ca. 80 nm size were sporadically dispersed in the stacked interlays of ZIF-8@SO₃H-GO-3 (Fig. 3d). The drastic morphological differences highlighted the critical role of GO as a novel support for mediating the growth of ZIF-8. It is also important to note that the decreased amount of GO (50 mg) caused the bigger ZIF-8 size probably due to the less coordination sites while the increased amount of GO (200 mg) induced the irregular



Fig. 2 XRD spectra (a) and N_2 adsorption-desorption isotherm (b) of different samples.

distribution maybe owing to the serious accumulation of GO sheets.^{14b,h}

The [3 + 3] formal cycloaddition reaction is the important tool for constructing the piperidine ring, which is one of the most common structural subunits in natural products and biologically active compounds. It consists of a Knoevenagel-type condensation followed by a reversible 6π -electron electrocyclic ring-closure.²⁷ In this regard, we first employed a [3 + 3] formal cycloaddition reaction between 1,3-cyclohexanedione and 3methyl-2-butenal as a model reaction to evaluate the catalytic efficiencies of ZIF-8@SO₃H-GO composites. As summarized in Table 2, the blank experiment could not give any products and

Table 1 Textural parameters of different samples						
Sample	BET $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore size (nm)			
GO	58 ± 4	0.05	_			
SO ₃ H-GO	60 ± 5	0.07	_			
ZIF-8	1315 ± 39	0.76	_			
ZIF-8@SO3H-GO-1	842 ± 26	0.52	1.9			
ZIF-8@SO ₃ H-GO-2	643 ± 21	0.43	2.1			
ZIF-8@SO ₃ H-GO-3	242 ± 8	0.18	—			





Fig. 3 TEM images of ZIF-8 (a) and ZIF-8@SO₃H-GO (b−d) composites.

SO₃H-GO also showed low conversion (40%). ZIF-8 nanoparticles obtained good conversion with 81%. It is worth mentioning that all the ZIF-8@SO3H-GO composites promoted this reaction with the enhanced catalytic reactivity and ZIF-8@SO₃H-GO-2 gave the excellent result with 94% conversion. This phenomenon suggested that the basic imidazole moieties and the SO_3^- and CO_2^- -functional groups and Zn^{2+} ions in these Lewis acid rich composites cooperatively catalyzed this reaction.13 The inferior reactivity of ZIF-8@SO3H-GO-1 could be attributed to the bigger ZIF-8 particle size and the lowest catalytic efficiency of ZIF-8@SO₃H-GO-3 could be assigned to the reduced accessible active sites. Interestingly, the physical mixture of SO₃H-GO and ZIF-8 still achieved the unsatisfactory yield (76%), probably due to the increased mass transfer resistance between two different solid catalysts, especially in stirring reaction conditions. Moreover, the commonly used homogeneous Lewis acid AlCl3 was chosen for comparison.28 It displayed the similar conversion (97%) with ZIF-8@SO₃H-GO-2, further confirming the excellent catalytic performances of the ZIF-8@SO₃H-GO composite.

To further explore the advantage of ZIF-8@SO₃H-GO, we chose 3-(9-anthryl)acrylaldehyde with a very large molecular size as the reactant (Table 2). ZIF-8 exhibited a significantly decreased conversion (37%), because of its small micropore it was difficult to allow the effective diffusion for large molecules. Meanwhile, the other byproduct was formed due to the self-condensation of α , β -unsaturated aldehydes, leading to the reduced selectivity (90%).²⁹ Note that ZIF-8@SO₃H-GO-2 displayed good conversion (71%) and excellent selectivity (98%). As a result, the yield of ZIF-8@SO₃H-GO-2 was 2 times higher than that of ZIF-8. This remarkable enhancement could be explained by the fact that the newly formed mesopores in the junctions between GO sheets and ZIF-8 nanoparticles were readily accessible to the reactants with the decreased mass transfer resistance.³⁰

Encouraged by these promising results, we next investigated the capability of the ZIF-8 $(3SO_3H-GO-2)$ catalyst for the other heterocycle synthesis (Table 3). For 4-pyran-3,6-dione participating [3 + 3] formal cycloaddition reactions, similar benefits

Table 2 Catalytic properties of different catalysts in [3 + 3] formal cycloaddition reactions between 1,3-cyclohexanedione and α , β -unsaturated aldehydes^{*a*}



^{*a*} Reaction conditions: 50 mg ZIF-8@SO₃H-GO, ZIF-8 or SO₃H-GO, 1.0 mmol 1,3-cyclohexanedione, 1.0 mmol aldehyde, 5.0 mL of CH₂Cl₂, T = 20 °C and t = 24 h. ^{*b*} 30 mg GO + 20 mg ZIF-8. ^{*c*} 13.3 mg AlCl₃.

were also achieved with superior reactivity for ZIF-8 $(3SO_3H-GO-2)$. It displayed the higher catalytic efficiencies in all the α,β unsaturated aldehydes compared with ZIF-8. Note that it showed the same trend for the large size molecules. For example, for these aromatic aldehydes, it exhibited at least 2.0 times improved conversion compared to ZIF-8 nanoparticles.

Table 3 Catalytic properties of ZIF-8@SO₃H-GO-2 and ZIF-8 in [3 + 3] formal cycloaddition reactions between 4-pyran-3,6-dione and α , β -unsaturated aldehydes^{*a*}

R₂

0	+ 0=/=		R^1	
Catalyst	Aldehyde	Product	Conv. (%)	Sel. (%)
ZIF-8@SO ₃ H-GO-2 ZIF-8	0 ~~~	it to	72 54	99 99
ZIF-8@SO ₃ H-GO-2 ZIF-8	⁰≫>>>>>	Ļ.	63 41	99 99
ZIF-8@SO ₃ H-GO-2 ZIF-8	and	i Likad	51 26	99 99
ZIF-8@SO ₃ H-GO-2 ZIF-8		Å.	40 21	99 99
ZIF-8@SO ₃ H-GO-2 ZIF-8	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Bet	31 15	93 91

^{*a*} Reaction conditions: 50 mg ZIF-8@SO₃H-GO-2 or ZIF-8, 1.0 mmol 4pyran-3,6-dione, 1.0 mmol aldehyde, 5.0 mL of CH₂Cl₂, T = 20 °C and t = 24 h.



Scheme 2 A possible cooperative catalytic mechanism of ZIF- $8@SO_3H$ -GO for the [3 + 3] formal cycloaddition reaction.

These results clearly demonstrated the generality of the strategy for the use of ZIF-8@SO₃H-GO nanocomposites for the multistep synthesis of structurally diverse and functionalized molecules. On the basis of these results, a plausible cooperative mechanism for the ZIF-8@SO₃H-GO catalyzed [3 + 3] formal cycloaddition reaction was proposed (Scheme 2). The SO₃⁻ and CO_2^- -functional groups on the sheets and Zn^{2+} ions from ZIF-8 in this Lewis acid rich composite activated α,β -unsaturated aldehyde through hydrogen bonding to the carbonyl group, while the neighbouring imidazole groups of ZIF-8 on the sheets of GO attacked the dione. Then, both the Lewis acids and base moieties stabilized the intermediate and generated the condensation product after eliminating one molecule of water. After the electrocyclic ring closure process, the ZIF-8@SO₃H-GO composite gave the final pyranyl heterocycle product.³¹

Furthermore, we examined the durability of ZIF-8($3SO_3H-GO-2$ in the [3 + 3] formal cycloaddition reaction with 1,3-cyclohexanedione and 3-methyl-2-butenal as the reactants. No significant decrease could be found in the yield of 7,8-dihydro-2,2-dimethyl-2*H*-chromen-5(*6H*)-one after being used repetitively ten times (Fig. 4). Elemental analysis (Table S1[†]) revealed that after being used ten times, the nitrogen content in the



Fig. 4 The recycling test of $ZIF-8@SO_3H-GO-2$ in the [3 + 3] formal cycloaddition reaction between 1,3-cyclohexanedione and 3-methyl-2-butenal. Reaction conditions are given in Table 2.

recycled ZIF-8 $@SO_3H$ -GO-2 remained almost the same (13.2 wt%). Meanwhile, the TEM image of the recycled ZIF-8 $@SO_3H$ -GO-2 confirmed almost no remarkable change in the structure before and after reuse (Fig. S4†). These results were in good agreement with an excellent retention of the activity of the ZIF-8 $@SO_3H$ -GO-2 catalyst.

Conclusions

In summary, we have synthesized a functionalized graphene oxide and nano-ZIF-8 composite *via* a facile coordinationinduced approach. With highly dispersed basic ZIF-8 nanoparticles and rich Lewis acids in this composite, it showed a cooperative catalytic behavior in [3 + 3] formal cycloaddition reactions and obtained high catalytic reactivity and selectivity for a wide range of reactants. It is worth mentioning that it was advantageous for the large size molecules due to the diminished diffusion limitation derived from the added mesopores in the junctions between GO sheets and ZIF-8 nanoparticles. Meanwhile, it can be recycled and reused at least 10 times without loss of activity. The presented strategy could be further extended to the development of more robust MOF@GO nanocomposites for multistep synthesis of synthetically valuable and complex molecules.

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