Organoamine-Functionalized Graphene Oxide as a Bifunctional Carbocatalyst with Remarkable Acceleration in a One-Pot Multistep Reaction

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S Supporting Information

ABSTRACT: In this work, we reported the synthesis of bifunctional carbocatalyst with acid−base dual-activation mechanism by introducing organoamines on the basal planes of graphene oxide (GO). Interestingly, GO-supported primary amine (AP-GO) exclusively promoted one-pot Henry-Michael reactions with excellent activity to give synthetically valuable multifunctionalized nitroalkanes. Notably, it also exhibited significantly higher activity than those using propylamine, activated carbon-supported primary amine, and mesoporous silica-supported primary amine as the catalysts. This superior catalytic performance originated from the unique properties of AP-GO, which provided the acid−base cooperative effect by the appropriate positioning of primary amines on their basal planes and carboxyl acids along their edges and the decreased diffusion resistance of the reactants and the intermediates during the multistep catalytic cycles because of its open two-dimensional sheet-like structure. Moreover, it could be readily recycled by simple filtration and subsequently reused without significant loss of its catalytic activity in a six times run test.

KEYWORDS: bifunctional catalyst, organoamine-functionalized graphene oxide, carbocatalyst, acid−base dual activation, one-pot multistep reaction
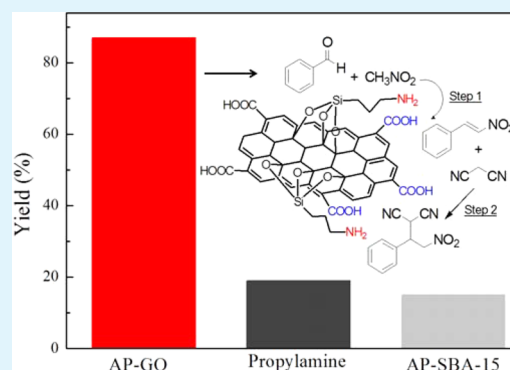
1. INTRODUCTION

Biological system can perform many complex specific transformations through highly efficient multistep enzymatic reactions.[1,2] By mimicking this extraordinary strategy, one-pot multistep reactions have emerged as an important and powerful strategy to chemical synthesis owing to the unique catalytic reactivity and the capability for rapid construction of molecular complexity.[3−5] To date, a number of homogeneous catalytic systems by one or more distinct catalysts have been successfully developed in a wide array of sequential multistep one-pot reactions.[6−10] However, the intrinsic difficulties in the separation and reuse of homogeneous catalysts inevitably add the cost and even cause the detrimental effects on the environment, especially for these reactions with expensive catalyst or high catalyst loading.[11,12] To address this dilemma, heterogeneous catalysts recently attracted much attention for their remarkable advantages of simpler operation, less toxicity, and easier recycling.[13−17] Moreover, facilitating one-pot multistep reactions with nontoxic, cost-effective metal-free solid catalysts would be particularly advantageous to gain a sustainable chemical process.[18−22] Accordingly, acid−base cooperativity that is commonly invoked in enzymatic catalysis inspired the synthesis of acid−base bifunctional heterogeneous catalysts.[23−27] Until now, the generation of both acidic and basic functions on the same solid matrix was often achieved by

the so-called isolation strategy to avoid neutralization reaction. Obviously, there are several evident barriers in the catalyst preparation such as the tedious protection−deprotection procedures or the uncontrollable and inhomogeneous positioning of catalytically active species.[28−31] Therefore, the development of a simple and efficient method for the fabrication of robust acid−base bifunctional heterogeneous catalysts to synthesize complex molecules in one pot is urgently needed.

Recently, the utility of heterogeneous carbons as metal-free carbocatalysts is increasingly attractive because of their wide availability, environmental acceptability, and low cost.[32−34] With a two-dimensional sheet-like structure, graphene oxide (GO) represents an interesting carbocatalyst since it has a large open surface area that is readily accessible to the reactants with negligible mass transfer resistance, which is distinct from conventional porous materials.[35] Notably, this unique character is considered to be able to better facilitate one-pot multistep reactions since the convenient transportation of the reactants and the intermediates in the multicatalytic cycles could undoubtedly increase reaction efficiency. Meanwhile, it possesses the hydroxyl and epoxy groups on the basal planes

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and the carboxylic acids along the sheet edges.[36,37] These rich functional groups render GO as a nice carbocatalyst in a variety of chemical transformations such as hydration, oxidation, C−H activation, polymerization, and thioacetalization.[38−43] However, most of the reported work focused on the investigation of single-step reaction, and accordingly one-pot multistep reactions were seldom explored by using GO catalysts. In addition, only a few reports were presented on GO-based hybrid catalysts with the cooperative catalytic behaviors.[44−46] Particularly, the design of appropriate positioning of different organocatalytic functionalities in GO-based composites that enables bringing the reactants in close proximity and subsequently activates them cooperatively is very rare. Herein we report a facile approach to construct graphene oxide-supported primary amine (AP-GO) as a acid−base bifunctional carbocatalyst for one-pot Henry-Michael reactions to exclusively give synthetically valuable multifunctionalized nitroalkanes. More impressively, the reactivity of AP-GO was at least 4 times higher than those of homogeneous catalyst propylamine and the physical mixture of propylamine and pristine GO. Through combined mechanistic investigation with the control catalysts by using activated carbon-supported primary amine and mesoporous silica SBA-15-supported primary amine, we revealed that the unusual catalytic properties of AP-GO came from the unique cooperative dual-activation effect between primary amines on the basal plane of GO and the adjacent carboxyl acids along the edges and the decreased diffusion resistance of the reactants and the intermediates because of the open two-dimensional sheet-like structure. Meanwhile, AP-GO catalyst could be easily recycled and reused for at least six times without loss of catalytic activity.

2. EXPERIMENTAL SECTION

Catalyst Preparation. Graphene oxide (GO) was prepared by the previously reported Hummers method.[38] In a general procedure of the preparation of graphene oxide (GO), the physical mixture of 1.0 g of natural graphite powder (Sigma) and 1.0 g of anhydrous $NaNO_3$ was added slowly into 46 mL of concentrated H_2SO_4 (98%) under an ice bath. After stirring for 2.0 h, 5.0 g of $KMnO_4$ was gradually added with a 0.10 g/min adding speed. Then, the temperature of the mixture was increased to 35 °C and allowed to continuous stir for 2.0 h. After that, the temperature was adjusted to 60 °C, and subsequently 100 mL of 5% H_2SO_4 aqueous solution was added with 1.0 mL/min speed. After stirring for 1.0 h, the temperature continued to increase to 95 °C, and then 100 mL of 30% H_2O_2 aqueous solution and 1000 mL of H_2O were successively added into the mixture with 10 mL/min speed. After stirring for 0.5 h, the as-made sample was washed with 5% H_2SO_4 aqueous solution and water five times. The as-obtained graphene oxide was collected by centrifuging and vacuum drying. Then, the obtained GO sample was dried at 100 °C for 12 h in vacuum before being grafted with various organoamines including primary, secondary, and tertiary amines. After that, 0.50 g of GO was dispersed in 20 mL of anhydrous toluene and ultrasonically treated for 2.0 h. Subsequently, 0.85 mmol of organoamine silane was added and stirred under reflux condition for 12 h. The solid powder was collected by filtration, washed with dichloromethane, and vacuum-dried at 60 °C for 12 h. These final catalysts could be defined as AP-GO, MAP-GO, and DMAP-GO, corresponding to 3-aminopropyltriethoxysilane (APTS), N-methylaminopropyltriethoxysilane (MAPTS), and (N,N-dimethylaminopropyl)triethoxysilane (DPTS) that were used in the initial mixture, respectively.

For comparison, activated carbon-supported primary amine (AP-AC) was also synthesized according to the following procedure. A total of 1.0 g of activated carbon (AC) was mixed with 40 mL of concentrated nitric acid and stirred at 80 °C for 2.0 h. Then, the mixture was filtered and washed with ethanol, followed by grafting

primary amine according to the aforementioned method using 1.0 mmol of APTS for 0.50 g of AC. Also, mesoporous silica-supported primary amine (AP-SBA-15) was prepared by directly grafting primary amine onto mesoporous silica SBA-15 according to the same method with AP-AC.

Catalyst Characterization. The amounts of nitrogen, carbon, and hydrogen elements were calculated by a Vario EL III Elemental analyzer. ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectra of different solid catalysts were analyzed on a Bruker AV-400 spectrometer by using 79.5 and 100.6 MHz, respectively. The surface electronic states were recorded on an X-ray photoelectron spectroscopy analyzer (XPS, PerkinElmer PHI 5000C ESCA). The binding energy values of all the catalysts were calibrated by using C_{1S} = 284.6 eV as a reference. The catalyst morphologies were observed by transmission electron microscopy on a JEOL JEM2011 microscope. The catalyst surface acidity was determined by temperature-programmed desorption of ammonia (NH_3-TPD) technology. This experiment was carried out on a flow apparatus (Micrometrics TP-5080). The sample was saturated with a pure NH_3 gas flow, and then the physisorbed NH_3 was removed through purging with argon gas at 40 °C for 1.0 h. Finally, the solid sample was then heated up to 750 °C at a speed of 10 °C/min.

Activity Test. Henry, Michael, and one-pot Henry-Michael reactions were used as the probes to evaluate the catalytic performances of organoamine-functionalized GO catalysts. All these reactions were carried out in a 25 mL round-bottomed flask. The reaction conditions and the product analysis methods are described in the following procedures. The reproducibility was checked by repeating experiments at least three times and was found to be within acceptable limits (±5%).

General Procedure for Henry Reaction. To a mixture of 6.0 mL of nitromethane and 0.306 mL of benzaldehyde (3.0 mmol), a catalyst containing 0.075 mmol of nitrogen species was added. Then, the temperature of the mixture was heated to 100 °C and allowed to undergo magnetic stirring for 6.0 h. After that, the catalyst was separated by centrifugation, and the filtrate was extracted with ethyl acetate. The product analysis was performed on a high-performance liquid chromatograph with mass spectrometer (HPLC/MS, Agilent 6410B). The reaction conversion was calculated based on benzaldehyde since there was nitromethane excess. The reaction yield was determined by the obtained amount of the product trans-nitrostyrene.

General Procedure for Michael Reaction. A total of 0.228 mL of malononitrile (3.6 mmol), 0.448 g of trans-nitrostyrene (3.0 mmol), and a catalyst containing 0.0375 mmol of nitrogen species was mixed. The mixture was stirred at 30 °C for 6.0 h. Then, the catalyst was separated by centrifugation, and the filtrate was extracted with ethyl acetate. The product analysis was performed on a high-performance liquid chromatograph with mass spectrometer (HPLC/MS, Agilent 6410B). The reaction conversion was calculated based on trans-nitrostyrene since there was malononitrile excess. The reaction yield was determined by the obtained amount of the product 2-(2-nitro-1-phenylethyl)malononitrile.

General Procedure for One-Pot Henry-Michael Reaction. In a typical run of this one-pot reaction, a catalyst containing 0.075 mmol of nitrogen species, 0.306 mL of benzaldehyde (3.0 mmol), and 6.0 mL of nitromethane was mixed and heated to 100 °C for 6.0 h under stirring. Then, the reaction temperature was cooled to 30 °C. After that, 0.228 mL of malononitrile (3.6 mmol) was added to the mixture and allowed to stir for another 6.0 h. Then, the catalyst was separated by centrifugation, and the filtrate was extracted with ethyl acetate. The product analysis was performed on a high-performance liquid chromatograph with mass spectrometer (HPLC/MS, Agilent 6410B). The reaction conversion was calculated based on benzaldehyde since malononitrile was in excess. The reaction yield was determined by the obtained amount of the product 2-(2-nitro-1-phenylethyl)malononitrile. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36−7.50 (m, 5H), 4.88−5.04 (m, 2H), 4.46 (d, J = 8.0 Hz, 1H), 4.07−4.14 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 131.9, 130.4, 129.9, 129.6, 129.2, 127.8, 75.0, 43.6, 27.6. Meanwhile, all the other multisubstituted

Scheme 1. Schematic Illustration of the Preparation of Orgaoamine-Functionalized GO Carbocatalysts
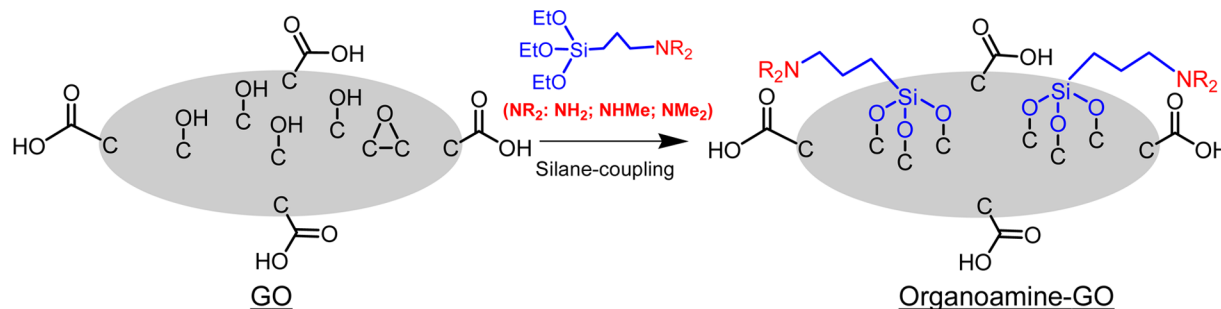
nitroalkanes product characterizations including ^{1}H and ^{13}C NMR data are provided in the Supporting Information.

Determination of Catalyst Leaching and Durability. In order to determine the recyclability of AP-GO catalyst, AP-GO was first centrifuged after each run of the reactions and the supernatant liquid was decanted. The residual catalyst powder was washed thoroughly with toluene and dichloromethane, followed by vacuum drying at 80 °C for 8.0 h. Then, the dried catalyst was reused with a fresh charge of the reactants and the solvent for the subsequent catalytic tests under the same reaction conditions.

3. RESULTS AND DISCUSSION

Synthesis and Characterization of Organoamine-Functionalized GO Carbocatalysts. The organoamimes were immobilized on the basal planes of graphene oxide (GO) through a simple and facile silane-coupling reaction to afford GO-supported organoamines, as shown in Scheme 1. Elemental analysis revealed that the nitrogen amounts were 1.076, 0.9773, and 0.8594 wt % in AP-GO, MAP-GO, and DMAP-GO, respectively, which corresponded to the use of primary, secondary, and tertiary organoamine silanes in the initial mixtures (Table 1). The presence of nitrogen species

Table 1. Elemental Analysis of GO and Various Organoamine-Functionalized Materials

sample	C (wt %)	H (wt %)	N (wt %)
GO	51.30	1.754	0
AP-GO	46.80	1.965	1.07
MAP-GO	53.21	1.755	0.977
DMAP-GO	51.84	1.865	0.859
AP-AC	73.70	1.554	1.00
AP-SBA-15	2.739	2.091	1.06

suggested the successful immobilization of organoamine groups on the GO surface. To confirm the formation of the covalent Si−O−Si−C bonds on the GO basal planes, solid state ^{29}Si magic angle spinning NMR spectroscopy was conducted. Only one intense peak around 65 ppm indicative of a T[3] signal (T[3] = RSi(OSi)$_3$) was observed in all the GO-supported organo-amines (Supporting Information Figure S1), indicating that the Si species were covalently bonded with GO support.[47] We further determined the molecular structures of the immobilized organoamines by using ^{13}C NMR spectroscopy (Figure 1a). In comparison with pristine GO, each carbon atom of the propylene group in the different amino silanes was detected and assigned to a designated peak in AP-GO, MAP-GO, and DMAP-GO.[48] In addition, the presence of new signals at 51.8 ppm for MAP-GO and at 58.6 ppm for DMAP-GO could be attributed to their respective methyl fragments connected to the nitrogen atoms.[49] Interestingly, the remarkable decrease in

the peak intensity of two signals around 65 and 75 ppm for all the GO-supported organoamines, corresponding to the epoxy and hydroxyl groups, indicated that the triethoxy groups of three kinds of organoamine silanes had interacted chemically with the epoxy and hydroxyl groups in the basal planes of GO.[50] Furthermore, as shown in Figure 1b, the XPS analysis demonstrated that the nitrogen species in AP-GO, MAP-GO, and DMAP-GO were present in a negative trivalent state, corresponding to binding energies of 399.2, 399.6, and 399.9 eV in the N 1s level, respectively. As expected, the nitrogen binding energy values of AP-GO, MAP-GO, and DMAP-GO were much the same as those of the corresponding primary, secondary, and tertiary organoamine silanes (Supporting Information Figure S2). These results suggested the well-retained molecular structure and chemical microenvironment of active sites in all the GO-supported organoamines.[51] Meanwhile, TEM images of AP-GO, MAP-GO, and DMAP-GO clearly showed the typical two-dimensional sheet-like structure (Figure 2), confirming that the amino-sylation treatment had no significant damage on the GO structure.[52]

Catalytic Performances. Initial efforts sought to explore the cooperative catalytic properties inherent to GO-supported organoamines as a means to effect single-step carbon−carbon bond-forming reactions. We examined the Henry reaction between benzaldehyde and nitromethane to give the resulting nitroaldol addition and dehydration products in the presence of various catalysts (Table 2). The individual GO sample could not generate any products while all the GO-supported organoamines promoted this reaction with high conversion, indicating that organoamines were the real active species. Interestingly, GO-supported primary amine (AP-GO) obtained the absolute β-nitrostyrene product with excellent yield of 90%. However, for GO-supported secondary and tertiary amines (MAP-GO and DMAP-GO), the additional β-nitroalcohol products were observed, and meanwhile the yields of β-nitrostyrene decreased gradually with the increasing base strength. To explore the support effects associated with GO, we tested the catalytic performance of pure propylamine as homogeneous catalyst, which gave a significantly lower yield of 39%. Moreover, we found that the physical mixture of GO and propylamine exhibited much lower catalytic activity, which could be explained by the cross-poisoning reaction between the carboxyl acids on the edge of the GO sheet and free propylamine. We furthermore investigated the catalytic activity of the acidified AP-GO (AP-GO-A) and the basified AP-GO (AP-GO-B) catalysts, which were prepared by immersing AP-GO in 1.0 mol/L HCl and 1.0 mol/L NaOH aqueous solution for 1.0 h, respectively. The results (Table 2) showed that AP-GO-A catalyst almost lost its activity while AP-GO-B catalyst displayed the significant decreased catalytic efficiency. The
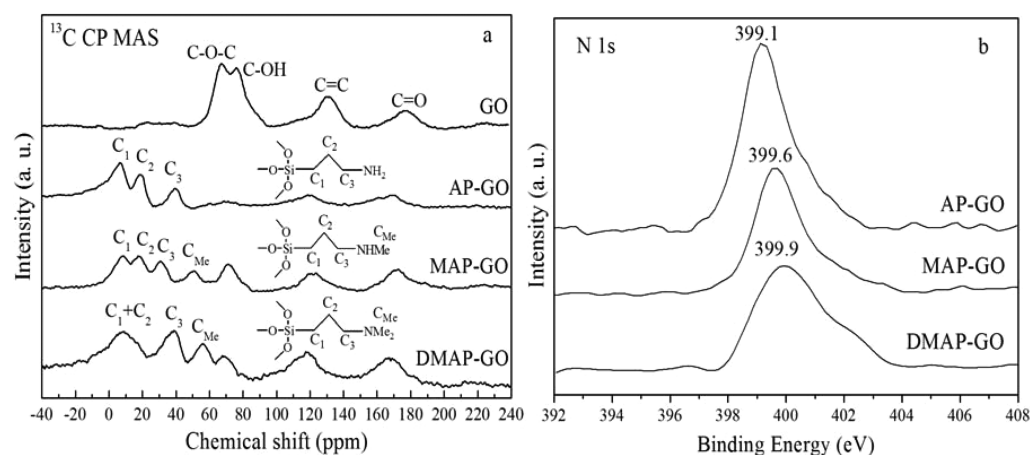
Figure 1. ^{13}C CP-MAS solid NMR spectra (a) of GO, AP-GO, MAP-GO, and DMAP-GO samples and N 1s XPS spectra (b) of AP-GO, MAP-GO, and DMAP-GO samples.
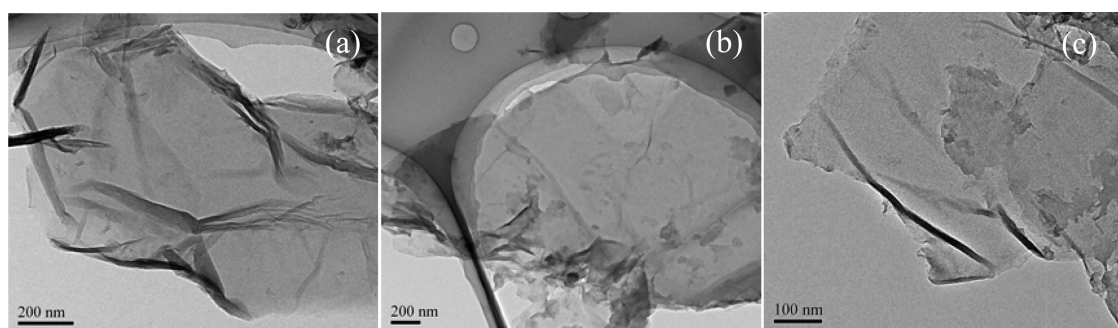

Figure 2. TEM images of AP-GO (a), MAP-GO (b), and DMAP-GO (c) samples.

**Table 2. Catalytic Performance of Various Catalysts in Henry Reaction**[a]

catalyst	conv. of A (%)	yield of B (%)	yield of C (%)
GO[b]	0	0	0
AP-GO	90	90	0
MAP-GO	91	76	15
DMAP-GO	84	53	31
propylamine	39	39	0
GO + propylamine[c]	22	22	0
AP-GO-A[d]	13	13	0
AP-GO-B[e]	36	36	0

[a]Reaction conditions: 0.306 mL of benzaldehyde (3.0 mmol), 6.0 mL of nitromethane, a catalyst containing 0.075 mmol nitrogen species, 100 °C, 6.0 h. [b]100 mg. [c]100 mg GO + 6.2 μL propylamine. [d]Acidified primary amine-functionalized GO. [e]Basified primary amine-functionalized GO.

former was attributed to the protonation of primary amine groups while the latter was ascribed to the formation of sodium carboxylate salt. These control tests revealed that the negative cross-poisoning effect is negligible for AP-GO catalyst. The similar phenomenon was also observed in the other important Michael reaction. Under the optimized reaction conditions (Supporting Information Table S2), AP-GO achieved almost a quantitative coupling product while both propylamine and the GO/propylamines physical mixture displayed the obvious
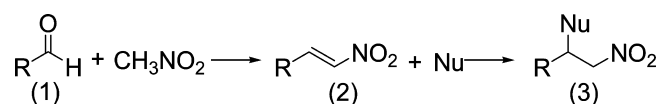
decrease in the yields. On the basis of these results, we supposed that there existed the cooperative interaction between the primary amine and carboxyl groups in AP-GO catalyst, which accelerated base-catalyzed carbon–carbon bond-forming reactions.

Encouraged by these promising results, we next investigated the capability of AP-GO catalyst to promote the one-pot Henry-Michael reaction (Table 3). Much to our delight, a good yield of 2-(2-nitro-1-phenylethyl)malononitrile (87%) was obtained after 12 h when only using a 2.5 mmol % AP-GO, which exhibited a 4.6-fold higher yield than that of homogeneous catalyst propylamine. Particularly noteworthy is that the enhancement of catalytic reactivity in the two-step Henry-Michael reaction was more significant than those of single-step Henry and Michael reactions. It is probably due to the fact that the unique two-dimensional structure of GO is more beneficial to the multistep reactions owing to the effective transportation of the reactants and the intermediates in the multicatalytic cycle. To further confirm the advantage of the present system, two control catalysts including activated carbon-supported primary amine (AP-AC) and mesoporous silica SBA-15-supported primary amine (AP-SBA-15) with almost the same primary amine loadings were tested. As shown in Table 3, AP-AC received 31% yield of D while AP-SBA-15 only got the yield of 15%, and these values were remarkably inferior to that of AP-GO. To demonstrate the general applicability of this acid–base heterogeneous bifunctional carbocatalyst, a wide range of simple and readily available aldehydes were examined without further optimization (Table 4). We were pleased to find that various functionalized

Table 3. Catalytic Performance of Various Catalysts in the One-Pot Henry–Michael Reaction[a]
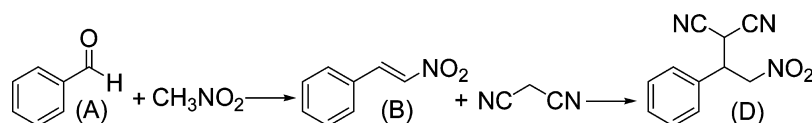
catalyst	conv. of A (%)	conv. of B (%)	yield of D (%)
AP-GO	90	97	87
propylamine	39	49	19
AP-AC	53	58	31
AP-SBA-15	38	40	15
AP-GO-M[b]	34	39	13

[a]Reaction conditions: 0.306 mL of benzaldehyde (3.0 mmol), 6.0 mL of nitromethane, 0.228 mL of malononitrile (3.6 mmol), a catalyst containing 0.075 mmol nitrogen species, 12 h. [b]Added 3.0 mL of methanol.

Table 4. Synthesis of Multisubstituted Nitroalkanes from Aldehydes[a]

Entry	Aldehyde	Nucleophile	t (h)	Conv. of 1 (%)	Yield of 3 (%)
1	H₃CO—	NC͡CN	12	92	89
2	H₃CO— (OH)	NC͡CN	48	73	70
3	(cyclohexyl)	NC͡CN	12	91	87
4	(pyridyl)	NC͡CN	12	93	90
5	(thiophene)	NC͡CN	12	91	87
6	(phenyl)	(indole)	12	67	64
7	(phenyl)	(coumarin)	12	73	69

[a]Reaction conditions are shown in Table 3.

benzaldehydes were converted smoothly and selectively into the multifunctionalized nitroalkane products with good to excellent yields. Even for sterically hindered benzaldehyde with reactive hydroxyl groups in the ortho-position (Entry 2), 2-hydroxy-4-methoxybenzaldehyde was also efficiently converted and obtained the corresponding product with 70% yield after 48 h. To the best of our knowledge, we believe that this is the first sample of using solid catalyst to activate this challenging substrate in the heterogeneous basic catalytic system. Moreover, AP-GO could catalyze these aldehydes with saturated ring or heterocycles into the desired product with the satisfactory yield (Entries 3–5). We also used the other nucleophiles to investigate the effectiveness of our AP-GO catalytic system. Two heterocyclic reactants with indole or coumarin structure were tested (Entries 6–7). As expected, both of them could be transformed to multisubstituted nitroalkanes with good yields.

Catalytic Mechanism Investigation. On the basis of these results, we suggested that the rate enhancement of AP-GO was attributed to the cooperative interactions between the carboxylic acid in the edges of GO and the organoamines on the GO basal planes. The appropriate positioning of the acidic

and basic functionalities in the AP-GO catalyst enables us to bring two substrates in close proximity and activate them cooperatively. Also, we supposed that this one-pot reaction catalyzed by AP-GO might follow the imine mechanism rather than a simple base-catalyzed process.[53−56] To prove the above hypothesis, we first used XPS analysis of the carbon element to confirm the existence of carboxylic acids in AP-GO. As expected, it displayed a well-resolved peak at binding energy around 289.1 eV indicative of the O—C=O bond (Supporting Information Figure S3), confirming the presence of carboxylic acid groups.[42] Moreover, the NH₃-TPD curves (Supporting Information Figure S4) revealed that, besides the desorption peak at 550 °C owing to the decomposition of organoamine groups on the supports, AP-GO exhibited a much stronger desorption peak than that of AP-AC in the temperature range from 150 to 400 °C, implying more carboxylic acid sites in the AP-GO sample. In addition, AP-SBA-15 showed the worst peak intensity in this range since it has plenty of silicon-hydroxyl groups (Si—OH) instead of carboxylic acid groups (−COOH). Furthermore, we designed one control experiment by using the excess benzaldehyde in the initial reaction system to prove the

existence of the imine intermediate during one-pot Henry-Michael reaction catalyzed by AP-GO. Surprisingly, no products could be observed in this reaction condition. Then, we analyzed the washed and dried AP-GO by XPS spectrum for nitrogen element. The result indicated the peak at 399.2 eV corresponds to primary amine completey shifted to 398.1 eV, indicative of a C=N bond, demonstrating the formation of the imine intermediate (Figure 3). On the contrary, for the reaction
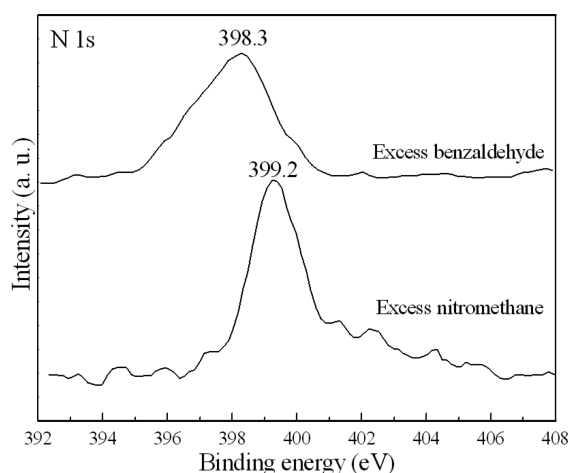

Figure 3. N 1s XPS spectra of AP-GO after the reaction with different excess reactants.

system with the excess nitromethane, no obvious difference of binding energy of N 1s could be found in the used AP-GO, suggesting this catalytic cycle proceeded through the generation of the imine intermediate.[57]

Moreover, in a previous report, the Davis group supposed that the primary amine could remain free in the nonpolar aprotic solvent for acid−base bifunctionalized solid catalyst.[55] In our one-pot Henry-Michael reaction, we speculated that the use of nitromethane as both the reactant and the solvent did not easily shuttle the protons from the carboxylic acids to primary amines in AP-GO, resulting in the free primary amines

that can react independently with the reactants. To demonstrate this hypothesis, we added 3.0 mL of ethanol as the protic solvent to investigate the catalytic performance of AP-GO catalyst in the one-pot Henry-Michael reaction (Table 3). Interestingly, the AP-GO catalyst exhibited the remarkable decreased yield of 13%, which was probably due to the formation of the NH_3^+ group that resulted from the H^+ proton in the carboxylic acids. Meanwhile, we tested the pH values of GO and AP-GO with the concentration of 2.0 mg/mL in water or NaCl aqueous solution. The pH value of GO in water was 3.36 while the pH value of AP-GO was 4.51 due to the existence of basic groups. When water was replaced with NaCl aqueous solution, the pH value of AP-GO decreased to 4.40, indicating the faster proton shuttle from the carboxylic acids to primary amines in the presence of NaCl electrolyte. Therefore, we supposed that the primary amines in the AP-GO catalyst could remain free in our catalytic system.

Accordingly, a plausible mechanism for AP-GO catalyzed one-pot Henry-Michael reaction was proposed in Scheme 2. The carboxylic acids in the edges of GO activated benzaldehyde through hydrogen bonding to the carbonyl group, while the neighboring primary amines on the basal planes of GO attacked the activated benzaldehyde, forming the imine intermediates after eliminating one molecule water. Then, nitromethane attacked this imine with the assistance of carboxylic acids, and the following elimination of amine species generated trans-β-nitrostyrene. After that, carboxylic acid activated trans-β-nitrostyrene once again, and meanwhile primary amines served to deprotonate and activate malononitrile, resulting in the formation of the final Michael adducts. On the basis of this mechanism, the poor catalytic activity of AP-SBA-15 was explained as the worse acid strength of Si−OH groups, which was hard to efficiently activate the reactants. Meanwhile, the inferior catalytic performance of AP-AC was mainly attributed to the unfavorable substrate transportation due to the remarkable diffusion resistance the came from the irregular micropores.[58]

Catalyst Recycling. To ensure the reactivity originated from the immobilized organoamines rather than from the leaching organoamines, the following procedure was carried

Scheme 2. Plausible Catalytic Mechanism of AP-GO Catalyzed One-Pot Henry-Michael Reaction
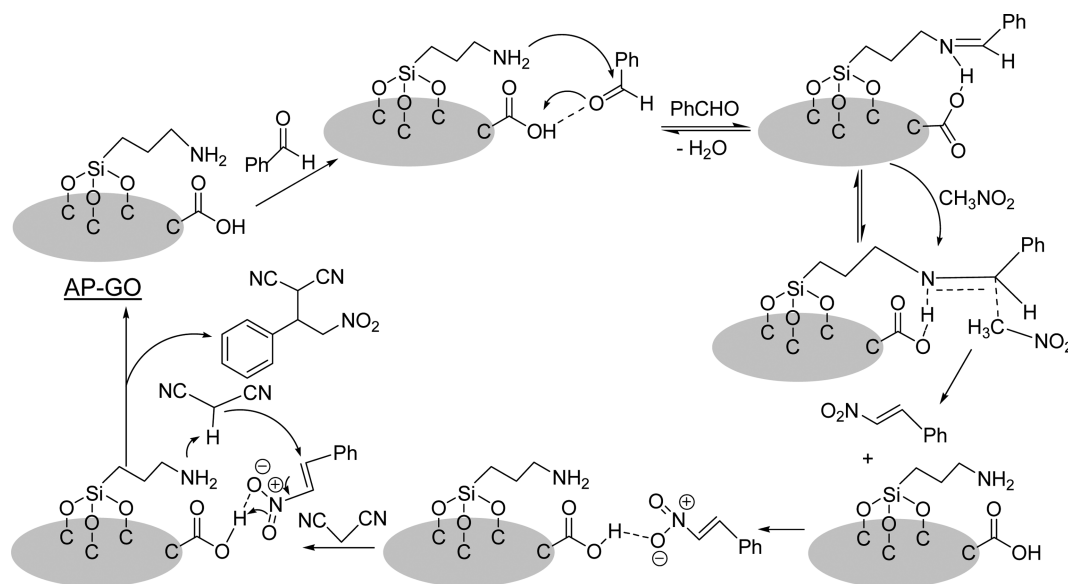
out.[59] After reaction for 1.0 h so that the conversion exceeded 50% in Henry reaction between benzaldehyde and nitromethane, the mixture was filtered to remove the solid catalyst, and then the mother liquor was allowed to react for another 3.0 h under the same reaction condition. No significant activity in either the conversion of benzaldehyde or the yield of target product was observed, demonstrating that the active species were not the dissolved amines leached from AP-GO catalyst. Also, elemental analysis confirmed the presence of extremely low amounts of nitrogen (less than 0.25%) in the reaction mixture. Therefore, it was reasonable to suggest that the present carbocatalysis was heterogeneous in nature. Furthermore, we examined the durability of AP-GO in the one-pot Henry-Michael reaction. No significant decrease could be found in the yield of 2-(2-nitro-1-phenylethyl)malononitrile after being used repetitively for six times (Figure 4). Elemental
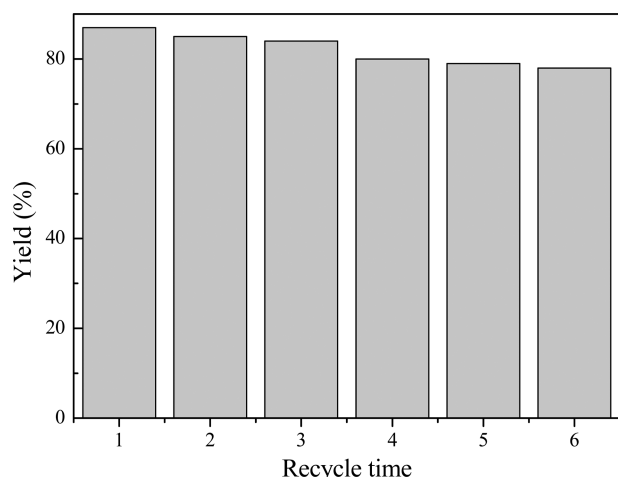

Figure 4. Recycling tests of AP-GO catalyst during one-pot Henry-Michael reaction. Reaction conditions are shown in Table 3.

analysis revealed that, after being used for six times, the nitrogen content in the recycled AP-GO remained almost the same (1.01 wt %). Meanwhile, the XPS spectrum and TEM image of the recycled AP-GO confirmed almost no change in the chemical microenvironment of the primary amine or the two-dimensional sheet-like structure of the GO support before and after reuse (Figure 5). These results were in good
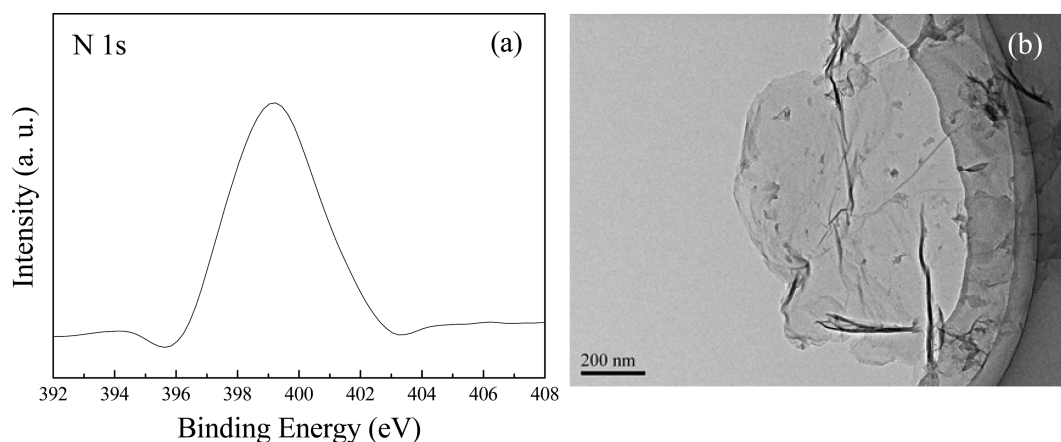
agreement with an excellent retention of the activity of AP-GO catalyst.

4. CONCLUSIONS

In summary, we have successfully developed a facile and efficient strategy for the development of metal-free bifunctional carbocatalyst, featuring organoamines on the basal planes of graphene oxide (GO) via the silane coupling reaction. The primary amine-functionalized GO exhibited excellent catalytic reactivity and selectivity in one-pot Henry-Michael reactions. Also, it exhibited significantly improved catalytic efficiencies compared with homogeneous catalyst propylamine and primary amine-functionalized solid catalysts prepared by using activated carbon and mesoporous silica as the supports. This unusually high catalytic efficiency could be attributed to the combination effects of acid−base cooperative catalytic behavior and the unique two-dimensional open structure offered by GO support. In addition, this catalyst was stable and reusable without significant loss of activity after six cycles. This achieved success in the GO-based acid−base bifunctional carbocatalysis is envisaged to pave the way to new opportunities in the development of highly active and reusable metal-free heterogeneous multifunctional catalysts for more one-pot multistep chemical transformations.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Catalytic performances of the different solid catalysts in the Michael reaction, solid ^{29}Si MAS spectra of different organoamine-functionalized GO, N 1s XPS spectra of various organoamines, C 1s XPS spectrum of AP-GO, NH_3-TPD profiles of different solid catalysts, and ^{1}H and ^{13}C NMR spectra of the multifunctionalized nitroalkanes products. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

Figure 5. N 1s XPS spectrum (a) and TEM image (b) of the recycled AP-GO sample.

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