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PAPER

General acid and base bifunctional graphene oxide for cooperative catalysis

Wenfeng Zhang, Hanying Gu, Zhen Li, Yuanzhi Zhu, Yang Li, Guoliang Zhang, Fengbao Zhang and Xiaobin Fan*

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In this study, bifunctional graphene oxide material (GO–AEP–UDP) with a general acid, the ureidopropyl (UDP) group, and a general base, the 3-[2-(2-aminoethylamino)ethylamino]-propyl (AEP) group, was synthesized by silylation of graphene oxide (GO) with organoalkoxysilane precursors.

10 Characterizations of the obtained GO–AEP–UDP were carried out by Fourier transform infrared spectrum (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and zeta potential. Systematic studies demonstrated the GO–AEP–UDP had superior catalytic performance in the classic Henry reaction of 4-nitrobenzaldehyde with nitromethane. It was
15 found that the relative concentration and spatial arrangement of cooperative functional groups were very important factors in the synergistic catalysis.

1. Introduction

Organocatalysis is a powerful methodology in organic synthesis, and organocatalysts have remarkable advantages over traditional
20 transition-metals catalysts such as insensitivity to moisture and oxygen, ready availability and low toxicity¹⁻⁹. However, the application of organocatalysts in chemical industry is still limited, attributed to not only their relatively lower catalytic activities (especially compared with many metal complex), but also the
25 difficulty in separation from the reaction mixtures. Therefore, development of a recyclable organocatalyst with high catalytic performance is of great importance for its practical application on an industrial scale. Among the strategies that have been developed for recycling the organocatalysts, the preparation of
30 heterogeneous organocatalysts is the most promising one. So far, lots of organic acid/base catalysts and their bifunctional systems have been successfully immobilized on various solid supports and shown impressive catalytic performances in a variety of reactions¹⁰⁻³⁰. Recently, we and others found that graphene
35 supported phenyl-SO₃H groups, amine groups and phosphotungstic acid show excellent catalytic activities and robustness in the hydrolysis rate of ethyl acetate, nitroaldol reaction and one-pot tandem reaction³¹⁻³³. However, to our knowledge, the cooperation of general acid and base groups
40 immobilized on graphene has yet to be demonstrated in chemical reaction.

Herein, we report the first graphene supported general acid and base bifunctional catalytic system that comprises a general acid, the ureidopropyl (UDP) group, and a general base, the 3-[2-(2-aminoethylamino) ethylamino]propyl (AEP) group. We also

found that this catalytic system had excellent catalytic performances in the cooperative Henry reaction of 4-nitrobenzaldehyde with nitromethane.

2. Experimental

50 2.1. Preparation of general acid/base-graphene oxide catalyst

Graphene oxide (GO) was prepared and purified by Hummers method³⁴. The resulting GO suspension (15 mL, 19.4 mg/mL) was sonicated for 30 min. it was then added to the mixture of ethanol (150 mL), ureidopropyltrimethoxysilane (0.8877 g), and
55 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (0.2228 g) in a three-necked ground flask with a condenser and a stirrer. After 24 h refluxing at 78 °C, the black solid was filtered, and washed with ethanol and deionized water successively, followed by drying under vacuum to get the GO–AEP–UDP.

60 2.2. Catalytic ability

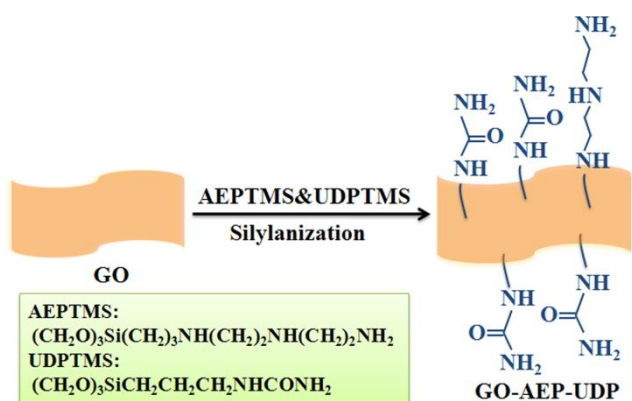
The performance of the catalysts was examined by the Henry reaction. Into a ground flask were placed catalyst (10 mg), 4-nitrobenzaldehyde (1 mmol) and nitromethane (10 mL). The resulting mixture was vigorously stirred for 24 h under 90 °C.
65 After the catalyst was separated from the mixture by filtration, the filtrate was analyzed by GC.

2.3. Characterization

The samples were characterized by Fourier transform infrared spectroscopy (FTIR) (Thermo-Nicolet 380), Raman spectroscopy
70 (NT-MDT NTEGRA Spectra), scanning electron microscopy (SEM) (Hitachi S4800), energy dispersive spectroscopy (EDS)

(Hitachi S4800), high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20), zeta potential (Malvern, nano ZS) and X-ray photoelectron spectroscopy (XPS) (PerkinElmer, PHI 1600 spectrometer). The reactions were monitored by GC (Agilent 6890N GC-FID system) and GC-MS (Agilent 6890-5973).

3. Results and discussion



Scheme 1. Illustration for the preparation of general acid/base bifunctional catalyst.

The bifunctional graphene oxide material with ureidopropyl (UDP) and 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) groups was synthesized by introducing UDP-, AEP-trimethoxysilane precursors to silylation reaction that based on the hydrolysis and dehydration condensation of the silanes with the hydroxyl and epoxy groups on GO (Scheme 1).

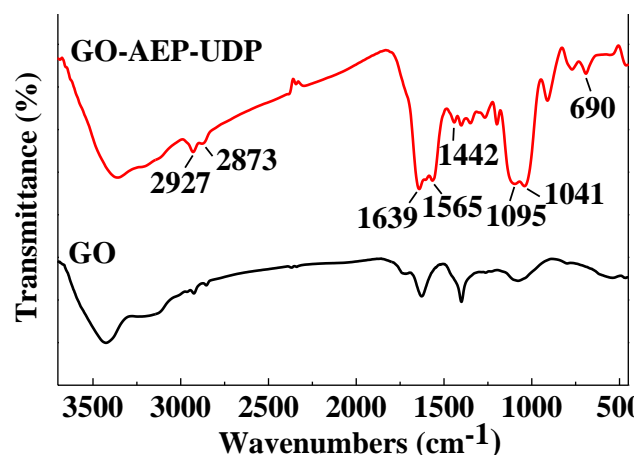


Fig. 1 FTIR spectra of GO and GO-AEP-UDP.

The catalysts were characterized after the functionalization. Fig. 1 shows Fourier transform infrared spectroscopy (FTIR) of the samples of GO and GO-AEP-UDP. Compared with GO, the peaks at 1639 cm^{-1} and 1565 cm^{-1} are associated with C=O stretching vibrations of UDP group and N-H bending vibrations of AEP group, respectively. The increased doublets at 2927 cm^{-1} and 2873 cm^{-1} , together with a new band at 1442 cm^{-1} , represent the stretching and bending vibrations of C-H from the methyl groups of UDP and AEP group. The signal of the O-H becomes

relatively smaller after forming GO-AEP-UDP. In addition, the strong stretching vibrations of Si-O at 1041 cm^{-1} , as well as the obvious stretching and bending vibrations of Si-O-C at 1095 and 690 cm^{-1} , demonstrates that the silylation reaction proceeded successfully.

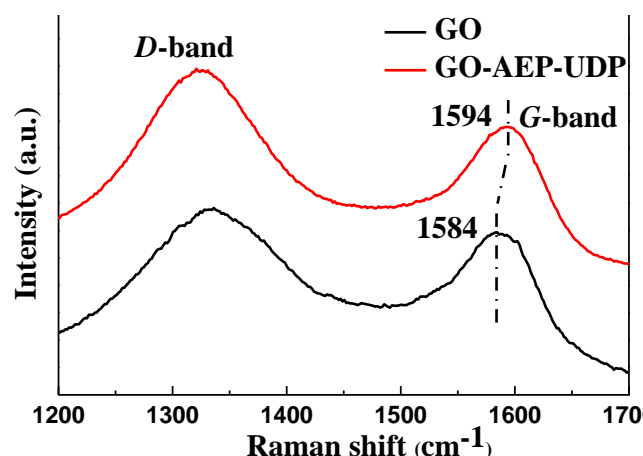


Fig. 2 Raman spectra of GO and GO-AEP-UDP.

Raman spectroscopy was used to characterize the structural change of graphene oxide in the chemical process, as can be seen in Fig. 2. GO shows absorption at 1584 cm^{-1} corresponding to the G-band. While the G band of GO-AEP-UDP shifts to 1594 cm^{-1} after the silylation reaction, implying the increased compressive local stress induced by the attached AEP and UDP groups. Moreover, the $I(D)/I(G)$ intensity ratio of GO-AEP-UDP (1.895) is slightly higher than that of the GO (1.478), this means abundant AEP and UDP groups were introduced to the sp^2 carbon network, this conclusion was further supported by our XPS analysis.

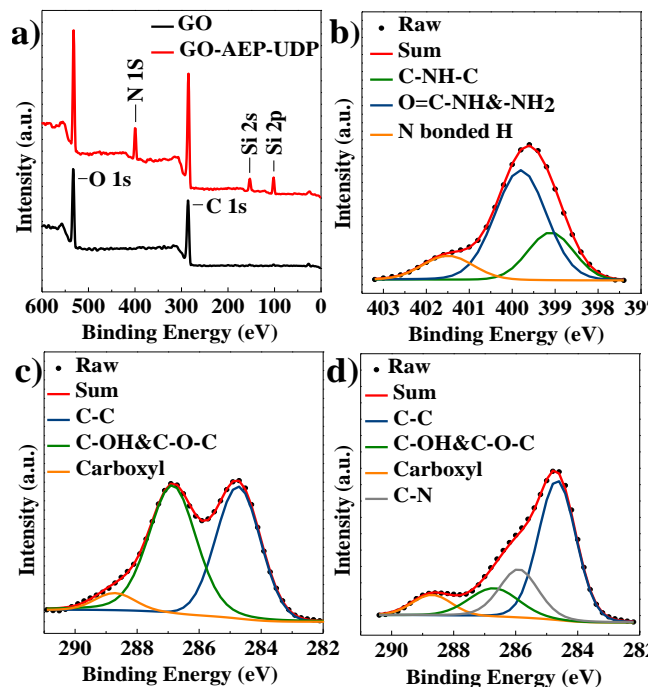


Fig. 3 XPS spectra of GO and GO-AEP-UDP (a), N 1s XPS spectra of GO-AEP-UDP (b), C 1s XPS spectra of (c) GO and (d) GO-AEP-UDP

The X-ray photoelectron spectroscopy (XPS) spectra of the samples of GO and GO–AEP–UDP were shown in Fig. 3. In comparison to GO, the increased signals of C, O, the N, Si signals were observed in GO–AEP–UDP (Fig. 3a). Furthermore, a significant decrease of the C–O–C & C–OH bonds and slight increase of the carboxyl groups in C 1s peak (Fig. 3c, d), together with the formation of Si–O–C observed at 102.4 eV in the Si 2p XPS spectrum (Fig. S1 of Supporting Information), indicate the successful hydrolysis and dehydration condensation of the hydroxyl and epoxy groups on the GO with the AEP–, UDP–trimethoxysilane precursors. Moreover, the peak at 399.1 eV corresponds to C–NH–C of AEP groups, another one at 399.8 eV represents –NH₂ and O=C–NH of UDP groups in N 1s spectrum (Fig. 3b). Calculated by the two integral areas, the molecule ratio of AEP and UDP group is about 1:4. Note that the element atomic ratios of N in the GO–AEP–UDP are 9.62%, That is, the density of the introduced AEP and UDP groups is about 0.62 and 2.48 mmol g⁻¹, respectively.

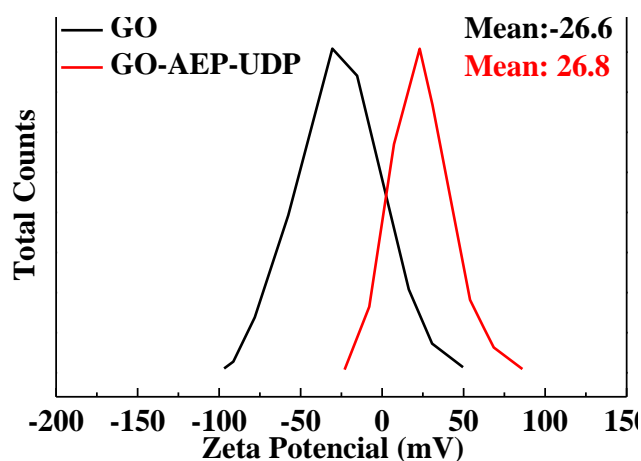


Fig. 4 The zeta potential of GO and GO–AEP–UDP

Fig. 4 shows the zeta potential of GO and GO–AEP–UDP. GO displays a zeta potential of –26.6 mV under neutral conditions because of the negatively charged carboxylate groups. However, GO–AEP–UDP shows positive charged surfaces with a zeta potential of 26.8 mV, which is assigned to the abundant grafted amine groups. The successful silylation reaction was verified again.

Fig. 5 shows the scanning electron microscopes (SEM) image and corresponding quantitative energy dispersive X-ray spectroscopy (EDS) mapping of GO–AEP–UDP. Fig. 5a reveals the GO–AEP–UDP shows crumpling structures that can also be observed in HRTEM image (Fig. S2 of Supporting Information). Element distribution analysis demonstrates that elements O, Si, N (Fig. 5b, c, d,) are homogeneously distributed on the whole surfaces of GO–AEP–UDP, which indicates AEP and UDP groups are anchored on GO uniformly. These features of the GO–AEP–UDP make active sites utilized efficiently, because all the active sites located on the surface of the layer are accessible, which will render the GO–AEP–UDP efficient for the catalytic reaction.

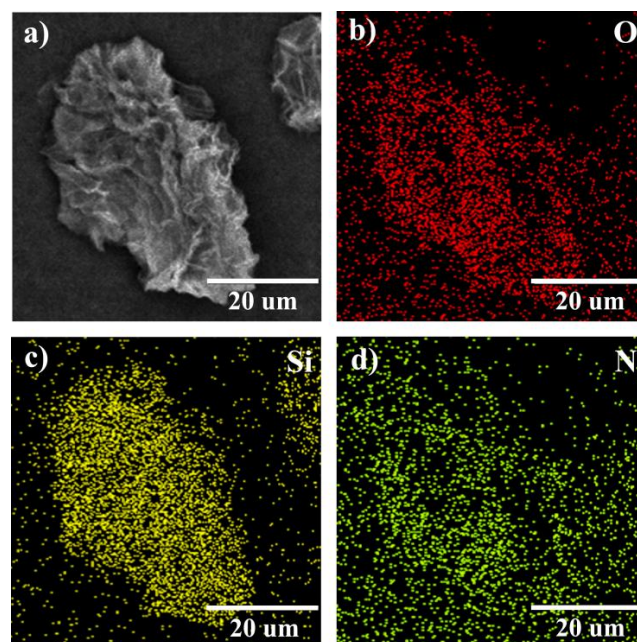
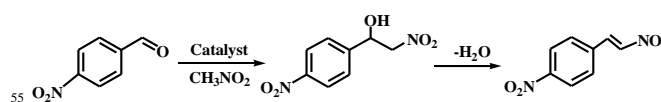


Fig. 5 SEM image of (a) GO–AEP–UDP and corresponding quantitative EDS element mapping of (b) O, (c) Si and (d) N.

The catalytic efficiency of the resultant GO–AEP–UDP catalyst was investigated by using the Henry reaction of 4-nitrobenzaldehyde and nitromethane to *p*,*β*-Dinitrostyrene (Scheme 2). The first step of this reaction is the classic nucleophilic addition of aldehyde and nitromethane to nitroalcohol^{35–37}, followed by an intramolecular dehydration of the –OH with the ortho–H of nitroalcohol at high temperature (GC-MS results of the final products can be seen in Fig. S3 of supporting information). Note that equivalent amounts of GO, GO–UDP and GO–AEP were also examined for comparison purposes, and the results are presented in Table 1.



Scheme 2. The catalytic preparation of *p*,*β*-Dinitrostyrene from 4-nitrobenzaldehyde and nitromethane.

Yield of product catalyzed by GO, GO–UDP, GO–AEP and GO–AEP–UDP is 3.2%, 12.2%, 6.7% and 88.4%, respectively (entry 1, 2, 3, 5 in Table 1), which is in accordance with the product color (Fig. S4 of Supporting Information), a synergistic effect between the AEP and UDP groups was clearly observed. This result can be explained by the fact that the secondary amines of the AEP group were responsible for the deprotonation of CH₃NO₂³⁸, and the UDP group could activate the carbonyl group of 4-nitrobenzaldehyde to nucleophilic attack through double hydrogen bonding³⁹ (the mechanism can be seen in Fig. S5 of Supporting Information). The yield of product by using the heterogeneous mixture with GO–AEP and GO–UDP (1.8%, entry

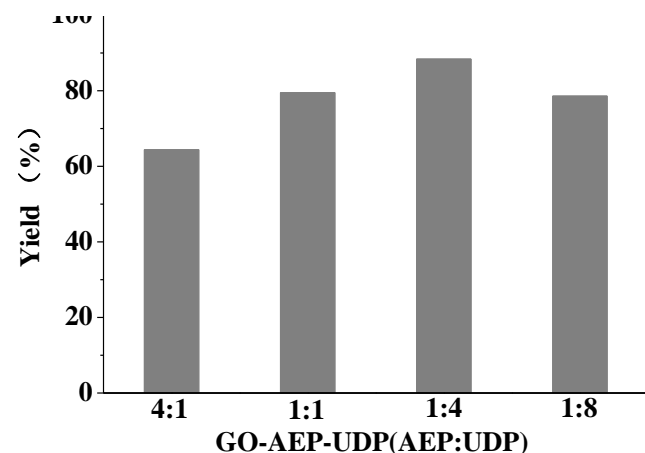
Table 1 Performances of different catalysts in Henry reaction^a

Rank	Catalyst	Yield (%)	TON ^b
1	GO	3.2	–
2	GO–UDP	12.2	16.9
3	GO–AEP	6.7	9.0
4	Heterogeneous mixture ^c	1.8	2.5
5	GO–AEP–UDP ^d	88.4	124.5
6	Homogeneous mixture	11.5	6.78

^a Reaction conditions: 4-nitrobenzaldehyde (1 mmol), CH₃NO₂ (10 mL), catalyst (10 mg), 90 °C, 24 h. ^b TON (turnover number) = mmol product per mmol catalyst during 24 h reaction time with 10 mg of catalysts. ^c

GO–AEP (2 mg) + GO–UDP (8 mg). ^d The initial molar ratio of AEP/UDP = 1/4

4 in Table 1) was clearly lower than that by using GO–AEP–UDP (88.4%), this result suggests that spatial arrangements between these active molecules are crucial for this reaction. Note that homogeneous mixture of AEP and UDP give poor yield of 11.5% (entry 6 in Table 1) due to a great deal of byproducts. The turnover numbers (TON) of these catalysts give similar results, the GO–AEP–UDP give the best performance with the TON of 124.5. Compared with the existing studies on silica-based catalysts^{40–43}, the TON of our catalyst GO–AEP–UDP is comparable to (if not better than) most of the existing catalysts. This promising result should be attributed to the two-dimensional GO that not only provides a huge surface to support the catalytic active sites but also facilitates the mass transport process.

**Fig. 6** Yield of product catalyzed by the catalyst with different ratios of AEP and UDP groups.

To further evaluate the synergistic effect of GO–AEP–UDP, catalysts with different relative concentrations, initial molar ratio of the organoalkoxysilane precursors as AEP/UDP=4/1, 1/1, 1/4 and 1/8, were synthesized and systematically studied for their catalytic performances. As summarized in Fig. 6, catalyst with AEP/UDP of 1:4 shows the highest catalytic activity with a yield of 88.4% towards the product.

4. Conclusions

In conclusion, we have successfully prepared a bifunctional graphene oxide material that comprises a general acid group, UDP, and a general base group, AEP, by silylation. Systematic studies demonstrated these active groups could be readily loaded on the both sides of graphene oxide sheets with homogeneous distributions. Notably, the obtained bifunctional graphene oxide materials (GO–AEP–UDP) show excellent catalytic performances and synergistic catalytic effect in the Henry reaction. By adjusting the relative concentrations and spatial arrangement of the cooperative functional groups, our bifunctionalized graphene-based catalyst could have a better application prospect in other organic reactions.

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Notes

State Key Laboratory of Chemical Engineering, School of Chemical Engineering & Technology, Tianjin University, Tianjin, China. Fax: (+86) 22-27408778; Tel: (+86) 22-27408778; E-mail: xiaobinfan@tju.edu.cn
 † Electronic Supplementary Information (ESI) available: Si 2p XPS spectrum and HRTEM spectrum of GO–AEP–UDP, photographs and GC-MS result of product, mechanism of the catalytic reaction. See DOI: 10.1039/b000000x/

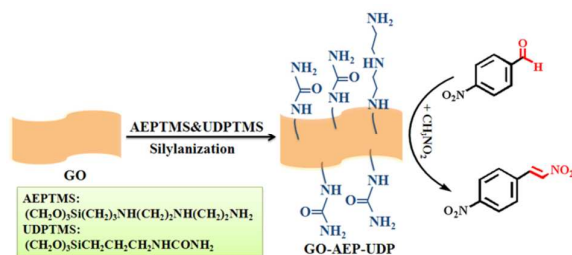
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Table of contents entry

Colour graphic:



Text:

General acid and base bifunctional graphene oxide was prepared by silylation for cooperative catalysis.