ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Graphene oxide for cellulose hydrolysis: how it works as a highly active catalyst?†

Xiaochen Zhao,[a] Jia Wang,[ab] Chengmeng Chen,[c] Yanqiang Huang,[a] Aiqin Wang*[a] and Tao Zhang*[a]

Cite this: *Chem. Commun.*, 2014, **50**, 3439

Received 19th December 2013,
Accepted 8th February 2014

DOI: 10.1039/c3cc49634a

www.rsc.org/chemcomm

Graphene oxide (GO-ene), the two-dimensional carbon lattice decorated by abundant oxygen functionalities, is demonstrated as an efficient green catalyst towards selective hydrolysis of cellulose to glucose. The synergy of its carboxylic/phenolic groups and its layered, soft structure rendered GO-ene superior hydrolytic activity.

Hydrolysis, composed of the affixes "hydro-" and "-lysis", is defined as the cleavage of chemical bonds in the presence of water. The hydrolysis of cellulose, abundantly available in agriculture and wood waste, has raised increasing concerns due to its essential role in the degradation of cellulose and opens possibilities for subsequent transformations.[1] *Via* the hydrolysis of β-1,4 glycosidic bonds, the insoluble cellulose can be hydrolyzed to saccharides, alcohols, and subsequent hydrated platform chemicals, during which Brønsted acids (mineral acids or solid acids) are crucial to activate the water splitting and catalyze the cleavage of glycosidic bonds. In principle, homogenous acids exhibit superior activity to solid acids due to their efficient contact with insoluble cellulose and water; however, they suffer from separation difficulties and associated environmental issues.[2] To develop a greener process, sulfonated carbon solid acid (CSA) is being widely studied as the replacement of homogenous acid currently. By sulfonation of an incompletely carbonized biomass precursor, Hara reported a highly active solid acid for the hydrolysis of cellulose.[3] Later, our group fabricated a series of carbonaceous solid acids *via* changing the sulfonation conditions and obtained a 74.3% conversion of cellulose with a 62.6% yield of glucose.[4] The studies illustrated that active acid sites, in particular $-SO_3H$ groups, and large surface area are crucial for high hydrolysis activity. Besides, the phenolic OH groups of CSA are found to be strongly adsorbed to oxygen atoms of the 1,4-glycosidic bonds, so as to benefit the catalytic performance.[3*b*,5] On the one hand, though substantial improvements were achieved in CSA designs, the high catalyst/substance ratio and harsh sulfonation conditions are still great challenges for practical usage. On the other hand, the texture effect and the chemistry of CSA have been seldom balanced in the investigation of cellulose hydrolysis due to the lack of rational preparation, which in turn limited the insight into the understanding of the mechanism.

Taking advantage of the recent bomb studies on graphene-based materials,[6] graphite oxide (GO-ite), the cost-effective precursor for scale-up graphene production, is easily obtained by liquid-phase intercalation and oxidation of natural graphite.[7] During the process, oxidative species, along with a small quantity of $-SO_3H$ groups, were inserted in the graphene layers, which endowed graphite oxide an extremely hydrophilic nature, Brønsted acid sites, and a variety of oxygen functionalities. According to the previous study,[3*b*,8] the enrichment of phenolic OH groups is particularly expected to enhance the hydrolysis activity. The layered graphitic structures are accounted to possess unconventional electronic properties[9] and exhibit promising reactivity in hydrogenation,[10] oxidation[11] and other reactions.[12] More interestingly, the GO-ite suspension can be exfoliated into one to several layers of graphene oxide (GO-ene) and can be extremely dispersed in water by sonication, resembling a homogeneous solution (Fig. S1, ESI†). The quasi-homogeneous CSA system, in turn, improves the interfacial compatibility and mass transfer. Besides, along with the exfoliation, more decorated active species are exposed and become available. This will not only facilitate the hydrolysis process, but also help us to elucidate the reaction mechanism through the design of a contrast experiment.

Herein, GO-ene was employed in the hydrolysis of cellulose and showed exceptionally high activity compared to GO-ite and other CSAs at a low catalyst loading. The enrichment of hydroxyl and carboxyl groups over GO-based materials, together with the 2D, flexible, well suspended structure of GO-ene, work synergistically to activate the β-1,4 glycosidic bonds, and promote/stimulate the hydrolytic reactivity.

GO-ite was prepared by a modified Hummers method (details in ESI†),[7*a*] GO-ene was exfoliated by sonicating the

---

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China. E-mail: aqwang@dicp.ac.cn, taozhang@dicp.ac.cn; Fax: +86 411 84691570; Tel: +86 411 84379015*

[b] *University of Chinese Academy of Science, Beijing 100049, PR China*

[c] *Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 Taoyuan South Road, Taiyuan 030001, PR China*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc49634a

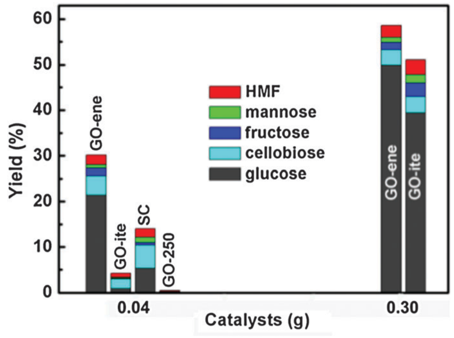

Fig. 1 Hydrolysis of cellulose over different CSAs as a function of catalyst loading.

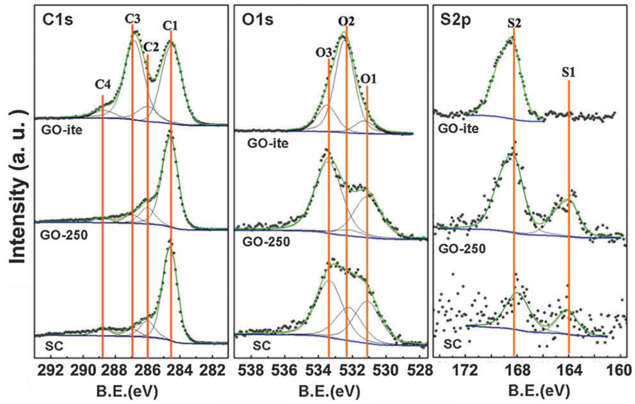

Fig. 2 XPS spectra of GO-ite, GO-250, and SC.

as-prepared GO-ite for 1 h. The hydrolysis of cellulose was conducted at a temperature of 150 °C for 24 h. According to a previous study,[4] we first used 0.30 g of catalyst to hydrolyze 0.27 g of cellulose. In this recipe, GO-ite and GO-ene both exhibited promising reactivity and glucose selectivity (Fig. 1 and Table 1). Indeed, limited by water volume, large amounts of GO-ene could not be fully exfoliated/extended, which, resulted in only a slight difference between GO-ite and GO-ene. Thus, we further reduced the catalyst loading to guarantee a sufficient dispersion of GO-ene, meanwhile testing GO-ite, sulfonated carbon (SC) and GO-250 as counterpoints (Table 1). Predictably, along with the reduction of the catalyst amount, the advantage of GO-ene (30.2% conversion of cellulose, 21.4% yield of glucose) to GO-ite becomes more obvious (Table 1 and Table S1, ESI†). In addition, it is noteworthy that the reported superior reactivity of SC[4] is subverted by GO-ene, when the catalyst amount is reduced to 0.04 g (Fig. 1 and Table 1).

Prior to further discussion, it should be noted that due to the relatively harsh hydrolysis conditions, the sulphate species will inevitably dissolve into the solution. Thus, a leaching test was carried out to exclude the contribution of homogeneous catalysis with the leached species (Table 1). The results showed no obvious reactivity, indicating that most of the effective catalysis occurred on the surface.

Clearly, a more exposed surface provided more active catalytic sites and higher reactivity. Besides, surface chemistry of different CSAs also played distinguished roles in their hydrolytic behaviour, as a higher surface area not always endowed better performance. GO-ite and its exfoliated product GO-ene were generated by liquid phase oxidation and thus shared the same surface chemistry: rich in anhydride, carboxylic, and hydroxylic groups (species designated as C3 and O2). Nevertheless, these groups are difficult to survive after a high temperature expansion (Fig. S2, ESI†). Therefore, O2 species are almost absent in GO-250 and its oxygen content is much lower than that of GO-ite (shown in Fig. 2 and Table 2). In contrast, SC, generated using a quite different strategy,[4] has a medium content of O2 species, but much less sulphur species than GO-ite. Therefore, sulphate speciation is not the only crucial element in determining the hydrolysis reactivity as commonly considered. Instead, O2 species, including anhydride, carboxylic, and hydroxylic groups, are also prefigured vital in improving the hydrolytic reactivity. However, it cannot be denied that the roles strong acid sites (*e.g.* H_2SO_4, HCl[8])

Table 1 Catalytic activity for the hydrolysis of cellulose

Catalyst	Amount[a] (g)	Yield$_{\text{glucose}}$[b] (%)	Conv.[c] (%)
GO-ite	0.31	39.4	51.1
GO-ene	0.30	49.9	58.6
GO-ite	0.04	0.9	4.2
GO-ene	0.04	21.4	30.2
SC[d]	0.04	5.2	14.1
GO-250[e]	0.04	0.3	0.5
Leaching test[f]	0.04	1.4	3.1
H_2SO_4[g]	13 ppm (S)	9.1	14.0
S-free GO-ene[h]	Without S	1.1	2.8

The reaction was conducted in a 50 mL autoclave in the presence of 0.27 g cellulose and 27 mL water, at the temperature of 150 °C for 24 h. [a] The catalyst amount employed in the reaction. [b] The carbon-based glucose yield. [c] The carbon-based cellulose conversion. [d] Activated carbon (Norit) was treated in concentrated sulphuric acid at 250 °C for 24 h and washed with hot water. The recovered materials were heated at 200 °C for 2 h in N_2.[4] [e] GO-ite is carbonized at 250 °C in a vacuum. [f] 0.06 g GO-ene was dispersed in 40 mL of water and heated in an autoclave at 150 °C for 12 h. 27 mL of the filtrate was then used to hydrolyze 0.27 g of cellulose at 150 °C for 24 h. [g] 12.7 ppm S is detected in 0.04 g of GO-ene by ICP, thus H_2SO_4 containing 13 ppm S was employed in a contrast experiment. [h] S-free GO-ene was obtained by pretreating GO-ene under hydrothermal conditions for 12 h at 150 °C (Fig. S3, ESI).

Table 2 Surface species distribution of CSAs determined by XPS

	GO-ite (wt%)	GO-250 (wt%)	SC (wt%)
C	62.1	82.4	80.1
C1 (284.6 eV)	25.5	61.9	59.0
C2 (286.0 eV)	5.4	11.1	10.7
C3 (287.0 eV)	28.4	5.7	4.9
C4 (288.8 eV)	2.8	3.7	5.5
O	36.6	15.7	19.4
O1 (531.1 eV)	3.6	5.5	6.2
O2 (532.2 eV)	25.7	0.7	4.8
O3 (533.4 eV)	7.3	9.5	8.4
S	1.3	1.9	0.5
S1 (163.9 eV)	1.3	0.6	0.2
S2 (168.2 eV)	—	1.3	0.3

C1: sp^2 and sp^3 carbon, C2: carbon in phenolic, alcohol, and ether, C3: carbon in carbonyl groups, C4: carbon in carboxyl or ester groups;[13] O1: carbonyl oxygen in quinines, O2: carbonyl oxygen atoms in anhydrides/esters and oxygen atoms in hydroxyl groups, O3: non-carbonyl oxygen atoms;[13] S1: sulphide, S2: sulphate.[14]

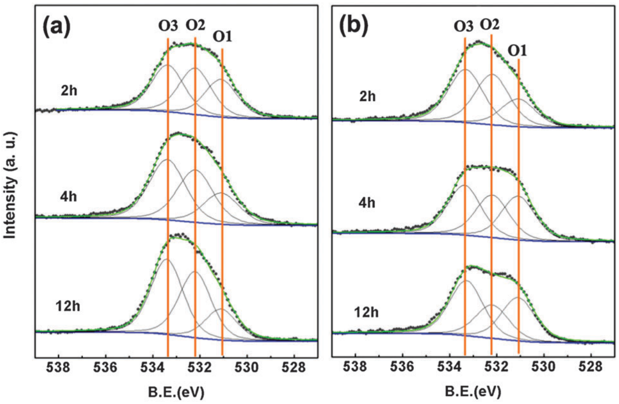

Fig. 3 XPS spectra of GO-ene as a function of time in the processes of cellobiose hydrolysis (a) and hydrothermal treatment (b).

Table 3 Surface species distribution determined by XPS during the hydrolysis and the hydrothermal process

Sample		Reaction conditions			Hydrothermal conditions		
Time (h)		2	4	12	2	4	12
Element (wt%)	C	79.3	74.9	73.5	76.4	78.2	79.2
	O	20.7	25.1	26.5	23.6	21.8	20.8
Speciation (wt%)	O1	6.0	5.5	4.7	5.0	7.0	6.8
	O2	7.3	9.1	10.2	9.1	6.8	5.3
	O3	7.4	10.5	11.6	9.5	8.0	8.7

The designations of O1–O3 are the same as in Table 2.

playing, even with trace amount, are also very important, as the hydrolyzation of glycosidic bonds is almost negligible over the S-free GO-ene.

To further understand the hydrolytic process, we employed cellobiose, the structural unit of cellulose, as a model substance to avoid the separation problem and tested the hydrolysis reactivity as a function of time. Meanwhile, XPS spectra were recorded on GO-ene, with and without the presence of cellobiose (details in ESI†), to monitor the variance of surface chemistry during this process (Fig. 3 and Table 3). At the beginning stage (*e.g.* 2 h), the O2 species reduced drastically compared with original GO-ite either under the hydrothermal or the reaction conditions, indicating a dramatic loss of hydroxyl groups over GO-ene (Fig. 3). This tendency was maintained upon extending the reaction time in the absence of cellobiose (Fig. 3(b)), which actually acted as a hydrothermal reduction treatment for GO-ene[15] to remove oxygen functionalities and obtain low oxygen-containing carbons with a large number of defects and imperfections (Fig. S4, ESI†). In contrast, in the case of hydrolysis, the sharp loss of O2 species was suppressed, implying that the hydroxyl groups were protected by the introduction of cellobiose. This protection can be explained by its effective adsorption for cellobiose during the hydrolytic process, since Brønsted acid OH groups, in particular phenolic hydroxyls bound to graphene sheets, were convinced to form hydrogen bonds with the glycosidic oxygen of β-1,4 glucan.[3b,16] In fact, instead of decreasing, the content of O2 species accreted with O3 species as the reaction proceeded (Fig. 3(a) and Table 3). These increased O-containing groups can be designated as esters and/or anhydrides,[13] generated from the esterification of cellobiose hydroxyls and the inherent/hydrolyzed carboxyls of GO-ene.

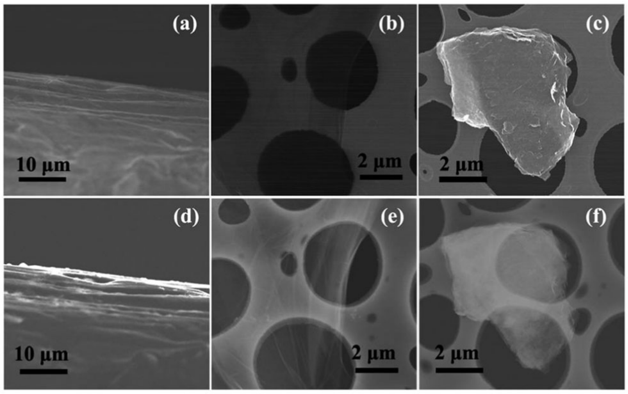

Fig. 4 SEM and TEM of GO-ite (a) and (d); GO-ene (b) and (e); and GO-ene after reaction (c) and (f), respectively.

Therefore, it is proposed that while cellobiose adsorbed on GO-ene *via* β-1,4 glycosidic oxygen by forming hydrogen-bonds, its hydroxyl groups esterified with the carboxyls of GO-ene concurrently. The ester formation may further activate the hydrogen-bonds and in turn the glycosidic bonds. On this occasion, the strong Brønsted acid sites (sulphate groups on GO-ene), even in trace amounts, can easily hydrolyze cellobiose/cellulose into glucose. In this mechanism, vicinal carboxylic and phenolic groups are supposed to display a synergistic effect in the activation of β-1,4 glycosidic bonds, consistent with Fukuoka's previous conclusion.[8] Coincidentally, GO-ene is thought to be a typical soft matter and able to crease and bend freely when suspended in an aqueous solution. Its flexible, layered, quasi-homogenous structure may facilitate the neighboring carboxylic and phenolic groups, and hence their synergistic work in the hydrolysis reaction. The kinetic study, which showed that the apparent activation energy of GO-ene is lower than GO-ite (Fig. S5, ESI†), confirmed the positive function of this specific feature for GO-ene.

As aforementioned, large amounts of hydroxyl groups, serving as surfactants to stabilize the GO-ene suspension,[17] tended to be eliminated under hydrolytic conditions, and resulted in aggregation of GO-ene sheets (Fig. 4) with a more ordered, oriented structure (Fig. S6, ESI†). This certainly facilitates the separation of products, however, at the cost of a less hydrophilic catalyst for cycling. Fortunately, despite the leaching of loosely grafted S species and the decomposition of labile O functionalities, most of the active sites were well preserved during the reaction (Fig. 3 and Table 3), and thus the fourth cycled catalysts surprisingly maintained their fresh run reactivity in the hydrolysis of cellobiose (Table S2, ESI†). Even though, sufficient effort still should be devoted to improve the hydrothermal stability of GO-ene, and employ these types of catalysts in non-aqueous systems in future.

Graphene oxide was demonstrated as a highly active catalyst for the hydrolysis of cellulose. Especially when employing a modicum of catalysts, the conversion of cellulose and the selectivity of glucose over GO-ene far surpassed that of GO-ite and other conventional carbon solid acids. The high catalytic activity of GO-ene can be attributed to the synergy of its layered, soft structure and the abundance of its hydroxyl/carboxyl functionalities.

The authors appreciate financial support by the National Natural Science Foundation of China (21303187, 21176235 and 51302281). The authors gratefully acknowledge Junying Zhang and Jifeng Pang for fruitful discussion and Hua Wang, Guangyi Li and Lin Li for experimental assistance.

Notes and references

1 Y.-B. Huang and Y. Fu, *Green Chem.*, 2013, **15**, 1095.
2 (*a*) F. Bergius, *Ind. Eng. Chem.*, 1937, **29**, 247; (*b*) W. L. Faith, *Ind. Eng. Chem.*, 1945, **37**, 9; (*c*) R. A. Antonoplis, H. W. Blanch, R. P. Freitas, A. F. Sciamanna and C. R. Wilke, *Biotechnol. Bioeng.*, 1983, **25**, 2757.
3 (*a*) M. Toda, A. Takagaki, M. Okamura, J. N. Kondo, S. Hayashi, K. Domen and M. Hara, *Nature*, 2005, **438**, 178; (*b*) S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787.
4 J. F. Pang, A. Q. Wang, M. Y. Zheng and T. Zhang, *Chem. Commun.*, 2010, **46**, 6935.
5 Y. Wu, Z. Fu, D. Yin, Q. Xu, F. Liu, C. Lu and L. Mao, *Green Chem.*, 2010, **12**, 696.
6 (*a*) D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228; (*b*) C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem., Int. Ed.*, 2009, **48**, 7752.
7 (*a*) C.-M. Chen, Q. Zhang, M.-G. Yang, C.-H. Huang, Y.-G. Yang and M.-Z. Wang, *Carbon*, 2012, **50**, 3572; (*b*) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
8 H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita and A. Fukuoka, *Acs Catal.*, 2013, **3**, 581.
9 Y. Kobayashi, K.-i. Fukui, T. Enoki, K. Kusakabe and Y. Kaburagi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 193406.
10 Y. Gao, D. Ma, C. Wang, J. Guan and X. Bao, *Chem. Commun.*, 2011, **47**, 2432.
11 (*a*) Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D. S. Su, J. Wang, X. Bao and D. Ma, *Angew. Chem., Int. Ed.*, 2013, **52**, 2109; (*b*) H.-P. Jia, D. R. Dreyer and C. W. Bielawski, *Tetrahedron*, 2011, **67**, 4431.
12 (*a*) D. R. Dreyer, K. A. Jarvis, P. J. Ferreira and C. W. Bielawski, *Polym. Chem.*, 2012, **3**, 757; (*b*) H. Wang, T. Deng, Y. Wang, X. Cui, Y. Qi, X. Mu, X. Hou and Y. Zhu, *Green Chem.*, 2013, **15**, 2379; (*c*) V. Deepak, T. Rashmi and S. Anil Kumar, *RSC Adv.*, 2013, **3**, 13265.
13 (*a*) J. H. Zhou, Z. J. Sui, J. Zhu, P. Li, C. De, Y. C. Dai and W. K. Yuan, *Carbon*, 2007, **45**, 785; (*b*) X. Zhao, Q. Zhang, B. Zhang, C.-M. Chen, J. Xu, A. Wang, D. S. Su and T. Zhang, *RSC Adv.*, 2013, **3**, 3578.
14 X. Zhao, Q. Zhang, C.-M. Chen, B. Zhang, S. Reiche, A. Wang, T. Zhang, R. Schlögl and D. S. Su, *Nano Energy*, 2012, **1**, 624.
15 (*a*) Y. Zhou, Q. Bao, L. A. L. Tang, Y. Zhong and K. P. Loh, *Chem. Mater.*, 2009, **21**, 2950; (*b*) S. Pei and H.-M. Cheng, *Carbon*, 2012, **50**, 3210.
16 O. M. Gazit and A. Katz, *J. Am. Chem. Soc.*, 2013, **135**, 4398.
17 J. P. Rourke, P. A. Pandey, J. J. Moore, M. Bates, I. A. Kinloch, R. J. Young and N. R. Wilson, *Angew. Chem., Int. Ed.*, 2011, **50**, 3173.