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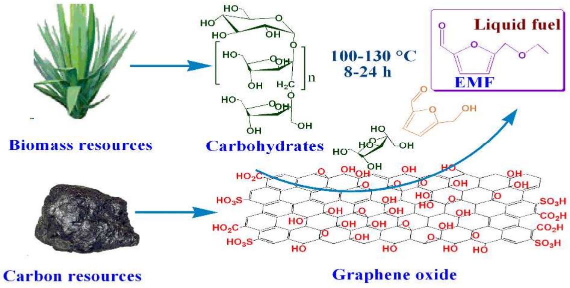

Graphene oxide was used as a facile carbon catalyst for converting renewable carbon source into a potential biofuel 5-Ethoxymethylfurfural.

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Graphene oxide as a facile acid catalyst for the one-pot conversion of carbohydrates into 5-ethoxymethylfurfural

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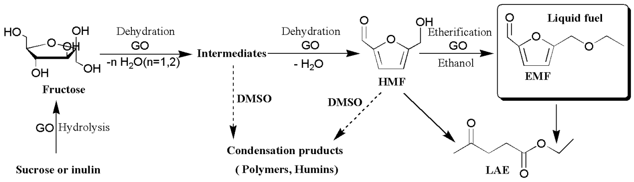
Graphene oxide obtained by Hummers method was discovered to be an efficient and recyclable acid catalyst for the conversion of fructose-based biopolymers into 5-ethoxymethylfurfural (EMF). EMF yield of 92%, 71%, 34% and 66% were achieved when HMF, fructose, sucrose and inulin were used as start materials, respectively.

The diminishing fossil reserves and environmental problems necessitate the development of processes to use sustainable, green, and environmentally benign resources for fuels and bulk chemicals production.[1-3] As a widely available and sustainable carbon source, biomass has the potential for the replacement of current non-renewable fossil resources.[4] It is predicted by the roadmap for Biomass Technologies in the U.S. that 18% of all manufactured chemicals will originate from biomass by 2020.[5] The boom in the chemical industry based on biomass demands the development of green and economical technologies for the efficient conversion of biomass into important platform molecules, as well as the ways for converting these platform molecules into various base chemicals.[6, 7]

5-Hydroxymethylfurfural (HMF), produced from carbohydrates such as fructose, glucose, sucrose, inulin and even cellulose, has been envisaged as one of the top building block chemicals in biorefinery processes.[8-11] It can be transformed into a number of important compounds with a high potential in fuel or polymer applications, including furan derivatives such as 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-bishydroxymethylfuran, 2,5-dimethylfuran, and nonfuranic compounds such as levulinic acid, 1,6-hexanediol, adipic acid, caprolactam, and caprolactone.[4, 12-14] 5-Ethoxymethylfurfural (EMF), synthesized from etherification of HMF with ethanol, has attracted much attention as a potential biofuel alternative recently.[15-18] The energy density of EMF is 30.3 MJ L^{-1}, which is 29% greater than that of ethanol (23.5 MJ L^{-1}) and very close to that of diesel (33.6 MJ L^{-1}).[19] EMF has generated positive results with a significant reduction of soot and SO_X emissions in engine tests.[19] Heteropolyacids, H-form zeolites, mesoporous silica, ion exchange resins, and a hybrid solid catalyst of $[MIMBS]_3PW_{12}O_{40}$ have been used for the synthesis of EMF from both HMF and fructose in ethanol.[15-18] Acceptable yields of EMF have been obtained when HMF was used as the start material, while it is still troublesome to achieve high yields of EMF directly from fructose or other cheaper biopolymers by a one-pot process.

Carbon nanomaterials hold promise in the development of sustainable catalysts for green chemistry with low emission and high selectivity.[20, 21] Graphene-based materials in the growing field of "carbocatalysis" have become importance in recent years due to their unique chemical properties, high mechanical resistance, and propitious to the charge generation and transportation in catalysis processes.[21] Graphene oxide (GO) has functioned primarily as a precursor in the large-scale production of graphene. One of the most widely applied ways for the preparation of GO is the Hummers method, which is based on the exhaustive oxidation of graphite in strong acid conditions (in concentrated sulfuric acid) by using permanganate and hydrogen peroxide.[22] A variety of oxygen-containing functionalities (alcohols, epoxides, and carboxylates,) as well as a small quantity of sulfate groups were introduced into the graphene plane during the synthesis of GO in the harsh conditions. These extrinsic functional groups make GO an excellent catalyst for various synthetic transformations. To date, GO has been tested to be a powerful catalyst in the oxidation of benzylic alcohols, unsaturated hydrocarbons, sulfides and thiols.[23-25] In addition, GO obtained by the conventional Hummers method is reported to be a highly efficient, recyclable acid catalyst for the ring opening of epoxide.[26]



Scheme 1 The conversion of carbohydrates to EMF catalyzed by GO.

Intrigued by the previous studies, we were interested to examine if GO, a readily available and inexpensive material, can be used as an efficient carbon catalyst in the transformation of renewable carbon source into useful chemicals. GO obtained directly by the Hummers method without any further treatment was used since it not only could be conveniently prepared but

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also contains lots of recoverable Brønsted acid sites. Typically, graphite powder (8000 meshes, 5 g), suspended in sulfuric acid (115 mL, 98 wt %), was oxidized by $NaNO_3$ (2.5 g), $KMnO_4$ (15 g) and H_2O_2 (50 mL, 30wt %) in sequence. After that, it was washed by HCl (1 L, 1 mol L^{-1}) and a large amount distilled water. Then the graphite oxide suspension was ultrasonicated to form the graphene oxide. Finally the GO suspension was dried to get the GO powder. The detailed procedure of GO preparation could be seen in ESI† The performances of GO as an acid catalyst was tested for the conversion of carbohydrates into EMF, including the hydrolysis of biopolymers into fructose, dehydration of fructose into HMF and etherification of HMF into EMF (Scheme 1). It is known that all the aforementioned reactions (hydrolysis, dehydration and etherification) are readily promoted by acid catalysts.

In an optimized experiment, 0.5 mmol (63 mg) HMF was added into a 5 mL micro autoclave and dissolved with 1 mL ethanol, and then heated to 100 ℃ in the presence of 20 mg GO for 12 h. After the reaction, GO was removed by filtration. HMF was found to be transformed into EMF with a yield of 92% and a conversion of 96%, as determined by NMR and LC/MS. During the reaction, some active sites on the GO surface may dissolve into the solution, and these leached species may act as new active sites. To rule out this possibility, the reaction was first carried out with GO under the same conditions for 6 h, and then GO was filtered from the reaction mixture. An EMF yield of 74% was achieved. The solution in the absence of GO was continued to stir at 100 ℃ for another 6 h, and no further HMF conversion and product formation were observed. These results indicate that the catalysis indeed occurs on the surface of GO and GO is a truly heterogeneous catalyst. Furthermore, when GO was replaced by the natural flake graphite (used as the starting material to prepare GO) or the reduced graphene oxide (R-GO, the oxygen-containing functionalities and sulfate groups were removed by thermal treatment at 400 ℃) under the same reaction conditions, no reactions were observed. This result reveals that extrinsic functional groups existed in GO play a vital role in the catalytic etherification of HMF with ethanol.

To evaluate the catalytic performance of GO, various other common acid catalysts were used in the identical reaction conditions and the results are summarized in Table 1. Homogeneous acids such as H_2SO_4, *p*-toluenesulfonic acid (*p*-TSA) and $H_3PW_{12}O_{40}$ were tested in the reaction, and yields of EMF were 54%, 61% and 82% with complete conversion of HMF, respectively. These results are consistent with previous studies.[15, 17] The main by-product was detected to be ethyl levulinate (LAE). Moderate yields of EMF with high conversions of HMF were achieved by using H_2SO_4 and *p*-TSA probably due to the strong acidity of the two catalysts, which could give rise to ring-opening alcoholysis of HMF and thus leads to the formation of ethyl levulinate. A relatively high yield of EMF was obtained when $H_3PW_{12}O_{40}$ was used as the catalyst. However, it was dissolved in the reaction mixture, making it difficult in separation and recycle. Amberlyst-15, a widely used heterogeneous acid catalyst, was also subjected into this reaction, and it was found that the yield of EMF as well as the conversion of HMF was similar to that use of H_2SO_4. As listed in table 1, among all the screened catalysts, GO exhibited the highest yield up to 92% at a HMF conversion of 96% with a catalyst loading of 20 mg, indicating GO an excellent acid catalyst for this reaction. Furthermore, the effect of GO loading on the catalytic performances was explored. The yield of EMF was decreased to 83% at a low HMF conversion of 85% when the GO loading was reduced to 10 mg. An increase in the catalyst loading from 20 mg to 30 mg resulted in a slight improvement in HMF conversion, however caused a decrease in EMF yield. Increase of the GO loading to 40 mg resulted in a further decrease of the EMF yield. The promotion of side-reactions including the alcoholysis of HMF to LAE and the formation of insoluble products was observed during the increase of GO loading. Thus, a low catalyst loading resulted in a low HMF conversion that led to a low EMF yield; a high catalyst loading resulted in a high HMF conversion but may also induce side reactions that led to a low EMF yield. Therefore, the amount of catalyst should be properly added, and 20 mg GO was proved to be the best for the present reaction system.

Table 1 Etherification of HMF with ethanol into EMF over GO and other catalysts.[a]

Entry	Catalyst	Loading	HMF conversion (%)	EMF yield (%)
1	GO	20 mg	96	92
2 [b]	graphite	20 mg	—	—
3 [c]	R-GO	20 mg	—	—
4	H_2SO_4	3 mol%	100	54
5	*p*-TSA	3 mol%	100	61
6	$H_3PW_{12}O_{40}$	5 mol%	100	82
7	Amberlyst-15	10 mg	99	59
8	GO	10 mg	85	83
9	GO	30 mg	99	89
10	GO	40 mg	99	85

[a] Reaction conditions: 0.5 mmol HMF with specific catalyst was mixed in 1 mL ethanol and reacted at 100 ℃ for 12 h. [b] Natural flake graphite was purchased from Sinopharm Chemical Reagent Co. Ltd. China and used without further purification. [c] Reduced graphene oxide was prepared by thermal treatment at 400 ℃.

The effects of reaction temperature and reaction time on the etherification of HMF were also studied (Fig. 1). At a low temperature of 80 ℃, the yield of EMF was only 68% for 12 h. Even if the reaction time was prolonged to 20 h, the EMF yield slightly increased to 80%. While, it was significantly improved to 92% within 12 h by just increasing the reaction temperature to 100 ℃, indicating the high temperature enhanced the rate of HMF conversion. When the reaction was further carried out at 120 ℃, EMF yields were obviously higher than those at 100 ℃

in the initial 8 h, and the maximum yield of 85% was obtained within 7 h. In order to better understand the effect of temperature on the etherification of HMF to EMF, we have constructed the kinetics profiles at different temperatures and calculated the activation energy. The detailed calculation method could been seen in ESI† The value of *k* (rate constant for HMF conversion) increased from 1.07 h^{-1} to 0.219 h^{-1} and 0.418 h^{-1} when the temperature increased from 80 ℃ to 100 ℃ and 120 ℃, respectively. Based on the rate constants we obtained, the activation energy (*Ea*) was calculated by the Arrhenius equation, and the apparent activation energy of the catalytic system was to be about 39.93 kJ mol^{-1}.Thus, it could be confirmed that temperature has a positive effect on promoting this reaction, the higher the reaction temperature, the higher the etherification rate. However, HMF is unstable at high temperatures since it can be readily transformed into LAE and humins by alcoholysis and polymerization. This leads to a low yield of the EMF as shown in Fig. 1.

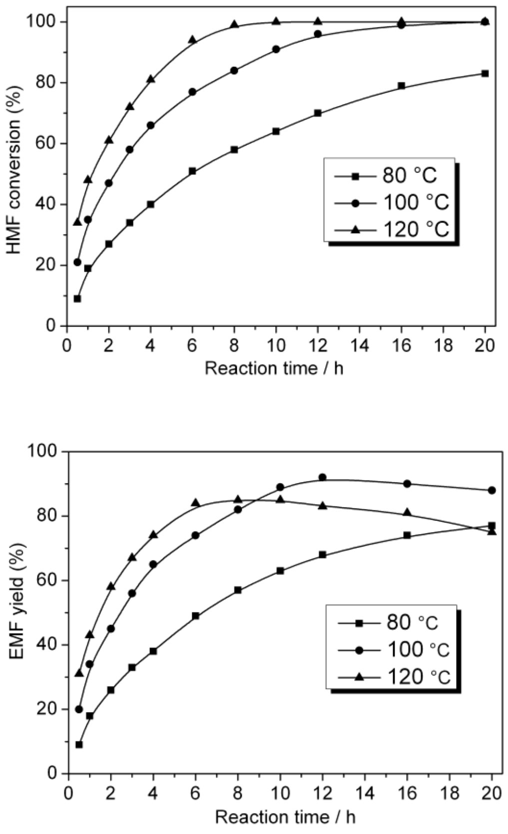

Fig. 1 Effects of reaction temperature and reaction time on the conversion of HMF to EMF. Reaction conditions: 0.5 mmol HMF, 20 mg GO, 1 mL ethanol.

HMF can be obtained from dehydration of carbohydrates, especially readily from fructose, by using acid catalysts which are similar to those used in the aforementioned etherification reaction. Thus one-pot synthesis of EMF from low-cost carbohydrates was investigated in this work and the results are listed in Table 2. Initially, fructose was used as the substrate in the reaction. The main products detected were HMF and EMF with yields of 9% and 18%, respectively, when fructose instead of HMF was used as the start material in the reaction under conditions similar to those used in the etherification reaction (Table 2, Entry 1). The total yield of furan products was much low (27%) as compare with the high conversion of fructose (95%). LAE was detected, but its yield was low, too. Moreover, a small amount of brownish black humins was observed. The low selectivity towards furans in the reaction at 100 ℃ may root in two aspects. The one is that there may be existence of abundant of partially dehydrated intermediates produced from the process of fructose dehydration to HMF at a low reaction temperatures (<130 ℃), and the other is that side reactions such as polymerization of these intermediates and alcoholysis of HMF have occurred in ethanol.[27] In our previous studies, [16] it was found that adding a certain volume of DMSO (dimethylsulfoxide) into ethanol could efficiently improve the yields of furan products without causing much trouble in the product separation. Thus, 0.3 mL DMSO mixed with 0.7 mL ethanol was used as the reaction solution. The yield of HMF was significantly enhanced when DMSO was introduced (Table 2, Entry 2), indicating that DMSO plays a positive role in the promotion of dehydrated intermediates into HMF.

Table 2 Production of EMF from various carbohydrates over GO under different conditions.[a]

Entry	Substrate	Tempe. (℃)	Cat. Loading (mg)	Substrate conversion (%)	HMF yield (%)	EMF yield (%)
1[b]	Fructose	100	20	95	9	18
2	Fructose	100	20	98	31	23
3	Fructose	130	20	100	14	64
4	Fructose	130	30	100	9	71
5	Fructose	150	30	100	3	62
6	Fructose	130	40	100	6	67
7	Sucrose	130	30	100	4	34
8	Inulin	130	30	100	7	66
9	Glucose	130	30	99	1	3

[a] Reaction conditions: 0.5 mmol carbohydrate based on monosaccharide with specific amount of GO mixed in 0.7 mL ethanol and 0.3 mL DMSO reacted for 24 h. [b] 0.5 mmol fructose with GO mixed in 1 mL ethanol and reacted at 100 ℃ for 24 h.

Subsequently, effects of reaction temperature and catalyst loading on the performance of GO were investigated in DMSO-ethanol solution. The total yield of furan products was increased from 54% to 78%, when the temperature increased from 100 ℃ to 130 ℃. These results reveal that the dehydration of fructose requires higher temperature than that for etherification of HMF. The yield of EMF was further improved when the GO

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loading was increased to 30 mg. However, further increasing the reaction temperature or GO loading resulted in a drop in the furan products yield, since side reactions could be promoted by high temperature or overmuch active acid sites. Moreover, the conversion of fructose and the formation of products as a function of reaction time were carefully studied. As depicted in Fig. 2, complete fructose conversion is achieved within 2 h. In the initial stage of the reaction HMF is observed with a maximum yield of 54% at about 6 h, and then it decreases gradually. Meanwhile, the yield towards EMF gradually increases to a maximum of 71% at about 24 h. This behaviour supports that the conversion of fructose in ethanol–DMSO system is a typical consecutive reaction, and HMF is an intermediate in EMF production from fructose.

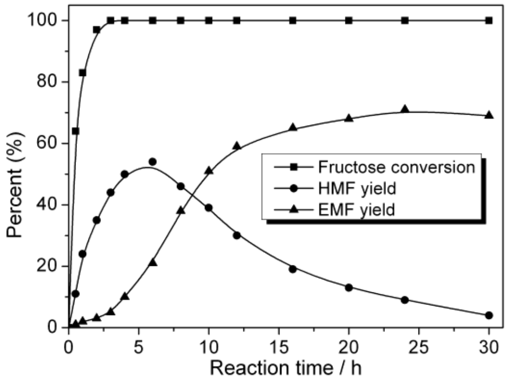

Fig. 2 Fructose conversion and products distribution as a function of time over GO catalysis. Reaction conditions: 0.5 mmol fructose, 30 mg GO, 0.3 mL DMSO, 0.7 mL ethanol, T= 130 ℃.

Next, fructose based disaccharide (sucrose) and polysaccharide (inulin) were tested as the start materials over GO catalysis. Sucrose is the most abundant and cheapest disaccharide, and one molecule of sucrose contains one molecule of glucose and one molecule of fructose. No sucrose was detected after the reaction; a 4% yield of HMF and a 34 % yield of EMF were obtained. When glucose was subjected to this reaction, the conversion was high (99%) however the total furan products yield was low (4%). The major product was found to be ethyl glucoside. These results suggest that only fructose in sucrose can be converted into HMF and EMF, and GO cannot be used as the catalyst for the isomerization of glucose to fructose. Much higher EMF yield (66%) was obtained, when inulin was used as the substrate for the reaction. This result may be due to the fact that one molecule of inulin contains one molecule of glucose and 1–59 molecules of fructose.[28] All the results indicate GO can not only catalyze reactions of etherification and dehydration, but also can catalyze the reaction of hydrolysis. Thus, GO can be used as a facile and efficient acid catalyst for the one step conversion of abundant and cheaper fructose based carbohydrates into a promising biofuel of EMF.

Finally, the reusability and stability of GO was investigated for the one-step conversion of fructose into EMF in DMSO-ethanol solvent system under identical conditions as described in Fig. 2. After reactions, the solid GO was separated from the reaction mixture by filtration, and washed by 95% ethanol and acetone for three times, respectively. Then the washed GO was dried in an oven at 60 ℃ for 12 h. It was found the activity of the catalyst for the conversion of fructose to EMF had a little drop but not obviously after four consecutive reuses (Fig. S1, ESI†), and this might be due to the fact that GO may undergo partial thermal reduction (some oxygen-containing functionalities were lost under thermal treatment) with long time exposure of high temperature.[29] The partial thermal reduction could lead to a minor decrease in the acid strength of GO, and this was supported by results of the Infrared Fourier Transform spectroscopy (FT-IR) (Fig. S3, ESI†) and the ammonia adsorption Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) (Fig. S4, ESI†). While, it is not troublesome to hand that partial thermal reduced GO in the Hummers method conditions to recover the fully catalytic activity of the catalyst. Therefore, GO can be reused as a green and efficient acid catalyst in practical usage.

Conclusions

In conclusion, we discovered that GO synthesized from Hummers oxidation of graphite can be used as a facile acid catalyst for the one-step conversion of fructose-based carbohydrates into a high-heating value liquid biofuels. GO showed an excellent catalytic activity for the etherification of HMF in ethanol with a high EMF yield of 92%. GO also performed well in the one-pot conversion of fructose, sucrose and inulin in DMSO-ethanol solvent system into EMF with yields of 71%, 34% and 66%, respectively. The reaction temperature and catalyst loading had a notable effect on EMF yield. Compare with the etherification reaction, the hydrolysis and dehydration reactions need higher reaction temperature and catalyst loading. Finally, GO can be reused for several times without much loss in catalytic activity. Given the fact that the production of GO is now being scaled up industrially, it may open up a new way to apply GO in the catalytic conversion of biomass-based compounds into value-added chemicals and open a new route in green and sustainable industry.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

References

1. E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gartner and J. A. Dumesic, *Science*, 2008, **322**, 417-421.
2. D. R. Dodds and R. A. Gross, *Science*, 2007, **318**, 1250-1251.
3. P. Gallezot, *Chemical Society Reviews*, 2012, **41**, 1538-1558.
4. R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chemical Reviews*, 2013, **113**, 1499-1597.
5. Biomass Research and Development Technical Advisory Committee, Roadmap for Biomass Technologies in the U.S. , U.S. Government, 2002. http://www.usbiomassboard.gov/pdfs/final_biomass_roadmap_2002kw.pdf
6. E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen and C. H. Christensen, *Chemsuschem*, 2008, **1**, 75-78.
7. M. Balakrishnan, E. R. Sacia and A. T. Bell, *Green Chemistry*, 2012, **14**, 1626-1634.
8. H. Xie, Z. K. Zhao and Q. Wang, *Chemsuschem*, 2012, **5**, 901-905.
9. M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Chemical Reviews*, 2011, **111**, 397-417.
10. A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chemistry*, 2011, **13**, 754-793.
11. T. Deng, X. Cui, Y. Qi, Y. Wang, X. Hou and Y. Zhu, *Chem Commun*, 2012, **48**, 5494-5496.
12. S. Dutta, S. De and B. Saha, *Chempluschem*, 2012, **77**, 259-272.
13. D. J. Braden, C. A. Henao, J. Heltzel, C. T. Maravelias and J. A. Dumesic, *Green Chem*, 2011, **13**, 1755-1765.
14. R. Alamillo, M. Tucker, M. Chia, Y. Pagan-Torres and J. Dumesic, *Green Chem*, 2012, **14**, 1413-1419.
15. P. Che, F. Lu, J. Zhang, Y. Huang, X. Nie, J. Gao and J. Xu, *Bioresource Technol*, 2012, **119**, 433-436.
16. H. Wang, T. Deng, Y. Wang, Y. Qi, X. Hou and Y. Zhu, *Bioresource Technol*, 2013, **136,** 394-400
17. L. Bing, Z. Zhang and K. Deng, *Ind Eng Chem Res*, 2012, **51**, 15331-15336.
18. C. M. Lew, N. Rajabbeigi and M. Tsapatsis, *Ind Eng Chem Res*, 2012, **51**, 5364-5366.
19. G. J. M. Gruter and F. Dautzenberg, U.S. Patent Appl. 2011/ 0082304 A1, 2011.
20. D. S. Su, J. Zhang, B. Frank, A. Thomas, X. C. Wang, J. Paraknowitsch and R. Schlogl, *Chemsuschem*, 2010, **3**, 169-180.
21. C. Huang, C. Li and G. Shi, *Energy & Environmental Science*, 2012, **5**, 8848-8868.
22. W. S. Hummers and R. E. Offeman, *J Am Chem Soc*, 1958, **80**, 1339-1339.
23. D. R. Dreyer, H.-P. Jia and C. W. Bielawski, *Angew Chem Int Edit*, 2010, **49**, 6813-6816.
24. D. R. D. D. R. Dreyer, H. P. Jia, A. D. Todd, J. Geng and C. W. Bielawski, *Organic & biomolecular chemistry*, 2011, **9**, 7292-7295.
25. H. P. Jia, D. R. Dreyer and C. W. Bielawski, *Tetrahedron*, 2011, **67**, 4431-4434.
26. A. Dhakshinamoorthy, M. Alvaro, P. Concepcion, V. Fornes and H. Garcia, *Chem Commun*, 2012, **48**, 5443-5445.
27. J. Wang, W. Xu, J. Ren, X. Liu, G. Lu and Y. Wang, *Green Chemistry*, 2011, **13**, 2678-2681.
28. S. Sirisansaneeyakul, N. Worawuthiyanan, W. Vanichsriratana, P. Srinophakun and Y. Chisti, *World Journal of Microbiology & Biotechnology*, 2007, **23**, 543-552.
29. Y. W. Zhu, M. D. Stoller, W. W. Cai, A. Velamakanni, R. D. Piner, D. Chen and R. S. Ruoff, *Acs Nano*, 2010, **4**, 1227-1233.