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Additional Information



N-doped graphene as metal-free catalyst for glucose oxidation to succinic acid

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N-containing graphenes obtained either by simultaneous amination and reduction of graphene oxide or by pyrolysis of chitosan under inert atmosphere have been found to act as catalysts for the selective wet oxidation of glucose to succinic acid. Selectivity values over 60 % at complete glucose conversion have been achieved by performing the reaction at 160 °C and 18 atm O₂ pressure for 20 h. This activity has been attributed to graphenic-type N atoms on graphene. The active N-containing graphene catalysts were used four times without observing alteration of the conversion and selectivity of the process. A mechanism having as key intermediates tartaric and fumaric acids is proposed.

Introduction

For the sake of sustainability of resources, there is much current interest in the use of biomass as feedstock for the chemical industry.¹⁻⁵ Considering that cellulose and hemicelluloses are the largest biomass components, their chemical or enzymatic hydrolysis makes available large quantities of glucose as starting material.⁶ A general type of transformation that would be highly important for the chemical industry is the conversion of glucose into monomers. In this context wet oxidation (WO) of glucose can be, in principle, a very appealing process since oxygen is the only reagent used and the reaction medium is water. However, WO of glucose is a very unselective process and a large variety of C2-C4 products are formed in unsatisfactorily low individual yields.⁷⁻¹⁰ To improve the selectivity of WO, it is possible to imagine that the use of catalysts can control this unselective process by favouring the formation of certain reactive oxygen species and promoting some pathways that would not take place in the absence of the catalyst.^{11, 12}

In this context, we have recently reported that ruthenium-amine complexes alter the product distribution of the catalytic wet oxidation (CWO) of glucose, resulting in the formation of succinic acid (SA) in selectivity values above 80 %.¹³ SA is a highly wanted compound considering its use in the preparation of polyesters and polyamides and its preparation

from glucose by other established products derived from glucose is not as straightforward as the direct CWO.

Although the use of ruthenium catalysts for the formation of SA through CWO is a breakthrough in the valorization of glucose, there is still several drawbacks associated to ruthenium deactivation by complexation with carboxylates formed in the process, requiring addition of sacrificial amines as ligands. A step forward would be the use of a metal-free catalyst to promote the CWO of glucose to SA.

The use of defective graphenes (Gs) as metal-free catalysts is currently under intense investigation,¹⁴⁻¹⁶ due to their activity to promote aerobic oxidations of a wide range of organic compounds,¹⁷⁻²¹ including benzyl alcohols and amines, benzylic and cycloaliphatic hydrocarbons and styrenes, benzene oxidation to phenol among others. More recently, it has been shown that Gs can also act as promoters in the decomposition of hydroperoxides and ozone towards reactive oxygen species.²²⁻²⁷ Considering the general activity of graphenes as oxidation catalysts and their ability to generate oxygen-centred radicals, it would be of interest to evaluate how the presence of Gs can alter the product distribution in the CWO of glucose.

Gs as catalysts allow a certain control of their catalytic properties by varying the content of heteroatoms and the density of defects. Since the presence of amines was found beneficial in the activity of ruthenium catalysts, we speculated that N-doped Gs could be suited as catalysts for CWO of glucose, particularly considering the general oxidation activity of N-doped Gs. The data obtained confirm the activity of N-doped Gs as catalysts for the selective CWO of glucose to SA.

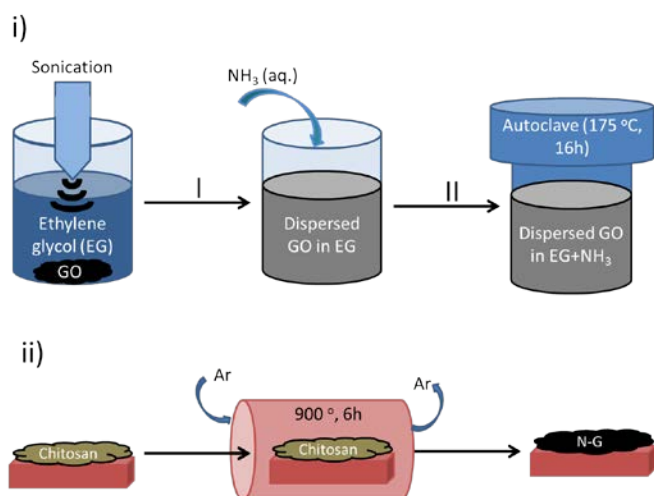
Results and discussion

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Two different types of N-doped Gs were prepared in the present study for their use as catalysts in the CWO of glucose. One of the types uses graphene oxide (GO) as starting material that is reacted with ammonia at three different concentrations,²⁸⁻³⁰ while undergoing a simultaneous reduction to form aminated reduced GO [NH₂-rGO(x), where x corresponds to the percentage of N]. For the sake of comparison a sample of rGO was prepared under the same conditions as NH₂-rGO(x), but in the absence of NH₃. The second type N-containing G was prepared by pyrolysis at 900 °C of chitosan (N-G).³¹⁻³³ Chitosan is a polysaccharide of aminoglucose that undergoes thermal graphitization and acts simultaneously as a source of C and N during the pyrolysis. Scheme 1 illustrates the preparation procedure of the set of samples used.

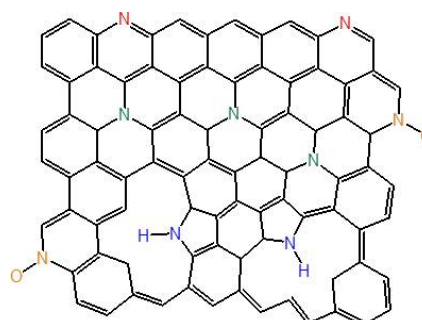


Scheme 1. Preparation procedures of the i) NH₂-rGO(x) and ii) N-G samples. The NH₂-rGO samples are prepared two steps: (I) sonication of GO in EG and subsequent addition of different amounts of aqueous NH₃, and (II) final hydrothermal treatment in teflonlined autoclave at 175 °C for 16 h. The N-G sample was obtained upon pyrolysis of chitosan at 900 °C for 6 h under Ar atmosphere.

Both types of samples NH₂-rGO(x) and N-G have been previously reported and characterized. Table 1 summarizes the G samples under study, their preparation procedure and their N content. N content was determined by combustion elemental analyses and XPS. It is known that N atoms present in G samples can be distributed among different families that can be differentiated based on their binding energy in XPS.^{29, 34-36} Scheme 2 illustrates the expected different types of N atoms and their reported binding energies. To determine the variation of the distribution of N atoms in the four samples under study, experimental high resolution XPS peaks corresponding to N atoms at binding energy about 400 eV were deconvoluted among their individual components. Figure 1 shows the experimental peaks and the best deconvolution to their individual components. A summary of the results is also listed in Table 1.

Table 1. Summary of the N content and the distribution of the N atoms based on the XPS analysis of the different samples.

Sample	N content (%)	Distribution N atoms (%)			
		Quaternary	Pyridinic	Pyrrolic	N-O
NH ₂ -GO(3.8)	3.8	75	25	-	-
NH ₂ -GO(5.3)	5.3	64	24	12	-
NH ₂ -GO(8.5)	8.5	51	35	10	-
N-G	4.8	71	28	-	1



Scheme 2. Structure of various possible types of N atoms on G. The expected binding energies in XPS of each different class of N atom are the following: quaternary N (in green, 400.4 eV), pyridinic N (in red, 398.1 eV), pyrrolic N (in blue, 399.8 eV) and N-oxide (in orange, 402.8 eV).

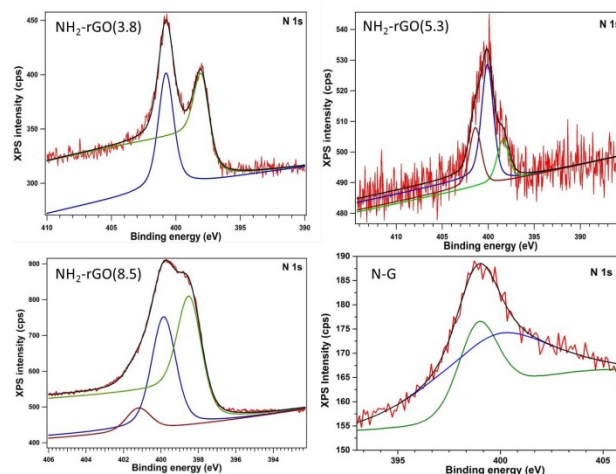


Figure 1. High resolution XPS peaks for N1s recorded for the different N-containing G samples and the best deconvolution to their individual components.

The characteristic 2D morphology of the NH₂-rGO(8.5) and N-G samples was observed by TEM. Figure 2 provides some representative images to illustrate their morphology. The single layer and few layer structure of the N containing G samples after dispersion in H₂O was established by AFM with subnanometric vertical resolution. It was observed that most of the particles present in the NH₂-rGO(x) samples present a

thickness about 0.5 nm corresponding to single layer G, while N-G has particles of a thickness of 2-4 nm corresponding to incomplete exfoliation of the sample or to the re-stacking of the sheets during the measurement. Figure 3 presents some representative images and measurements, showing the typical structure of the $\text{NH}_2\text{-rGO}(x)$ and N-G catalysts present during the CWO of glucose.

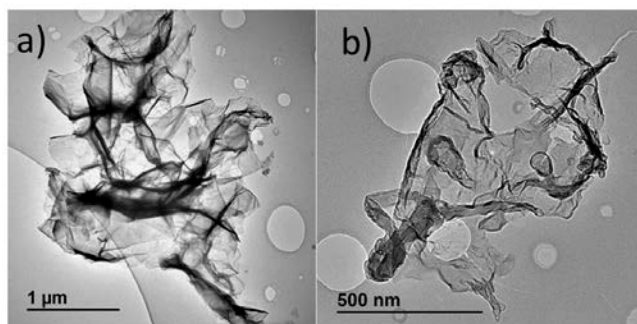


Figure 2. Representative HRTEM images of N-G (a) and $\text{NH}_2\text{-rGO}(8.5)$ (b) samples.

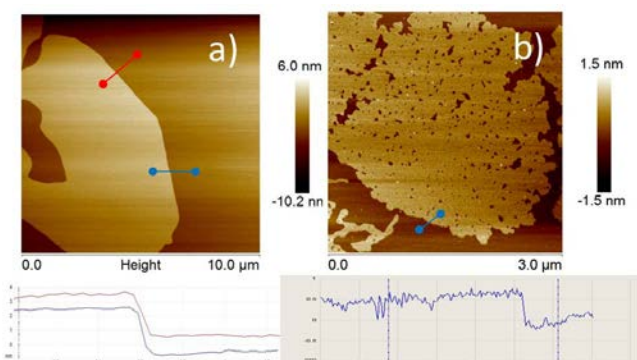


Figure 3. Frontal views of N-G (a) and $\text{NH}_2\text{-rGO}(8.5)$ (b) samples obtained by AFM. The height of two representative measurements marked on blue and red are presented in the bottom part with coincident colours.

It is expected that the presence of N atoms on the G sheet should introduce some basicity in the materials.^{37, 38} This was confirmed by thermoprogrammed desorption (TPD) measurements after CO_2 adsorption. Figure 4 presents the temperature- CO_2 desorption plots for $\text{NH}_2\text{-rGO}(x)$ and N-G sample. It was observed that the samples exhibit different behaviour depending on the preparation procedure and N content. Coarsely two broad CO_2 desorption peaks at temperatures about 95 and 270 were recorded and they were present in variable intensity and proportion depending on the sample. The assignment of the CO_2 desorption peaks was done based on the different types of nitrogen species evidenced by N1s XPS spectra (see Figure 1 and Table 1). Thus, the weak sites were attributed to the interaction of CO_2 with pyridinic N and the desorption peak at 270 °C was correlated with quaternary N. As it can be seen in Figure 4 and in agreement with XPS characterization, $\text{NH}_2\text{-rGO}(3.8)$ and N-G samples exhibit a similar TPD profile that is simpler and better defined than those of $\text{NH}_2\text{-rGO}(5.3)$ and $\text{NH}_2\text{-rGO}(8.5)$ that have a broader distribution of N atoms.

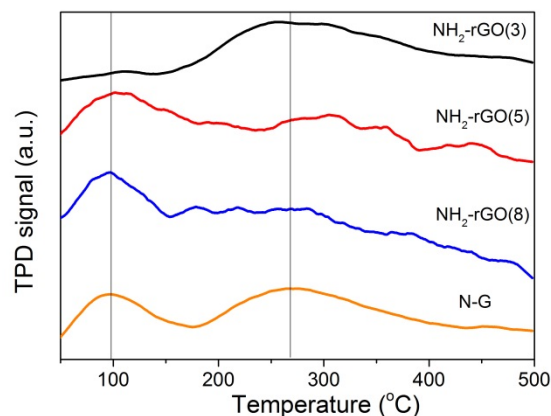


Figure 4. CO_2 -TPD profiles of the N-containing Gs.

As commented in the introduction, the purpose of the study was to evaluate the catalytic activity of $\text{NH}_2\text{-rGO}(x)$ and N-G samples for the selective CWO of glucose to SA. Initial screening experiments varying the experimental conditions were unsuccessful and SA was formed in very complex reaction mixtures with percentages generally about 3 % and always below 15%. Table 2 presents some of the unsatisfactory results obtained under non-optimal conditions.

It is known that the product distribution of WO remarkably depends on the experimental conditions and the reaction time as consequence of the instability of the primary products, their evolution over the time and the simultaneous concurrency of different reaction pathways. Fortunately, experiments carried out at 160 °C under 18 atm of O_2 pressure at 20 h using $\text{NH}_2\text{-rGO}(3.5)$ and N-G led to reaction mixtures in which SA was present in significant percentages at complete glucose conversions. Other products that were identified in significant percentages when the reaction is carried out at 160 °C under 18 atm O_2 at 20 h were C2 (lactic and glycolic acids) and C3 (glyceric acid) acids. Blank controls under these optimized conditions in the absence of any catalyst or in the presence of rGO that does not contain N atoms result in a selectivity toward SA below 3 %, showing the influence of the use of the appropriate N-containing G catalyst. Table 2 lists some of the results of glucose CWO to SA obtained using different metal-free catalysts.

Table 2. Summary of the results of the catalytic test and their conditions.

Sample	T(°C) [Time (h)]	P _{O₂} (atm)	Conv (%)	Selectivity (%)			
				SA (C4)	LA (C3)	GlyA (C3)	GA (C2)
$\text{NH}_2\text{-rGO}(3.8)$	180 [1.5]	10	10.9	2.8	0	7.0	17.1
$\text{NH}_2\text{-rGO}(3.8)$	180 [20]	10	100	13.5	71.0	0	15.5
$\text{NH}_2\text{-rGO}(3.8)$	180 [20]	18	100	0	76.7	0	23.3
$\text{NH}_2\text{-rGO}(3.8)$	160 [20]	18	100	67.9	8.1	0	3.7

NH ₂ -rGO(5.3)	180 [1.5]	10	17.3	3.7	0	8.6	5.6
NH ₂ -rGO(5.3)	160 [20]	18	100	4.8	4.5	17.8	29.3
NH ₂ -rGO(8.5)	180 [1.5]	10	8.7	4.9	0	2.3	3.7
N-G	180 [1.5]	10	11.3	3.1	0	7.0	17.1
N-G	160 [20]	18	100	60.8	6.1	-	24.0
rGO	160 [20]	18	12.0	<5	<5	<5	13
blank	160 [20]	18	10.5	<5	<5	<5	10

Reaction conditions: 0.5 mmols glucose, 0.025 g N-containing G, 10 ml H₂O. The difference until 100% in selectivity corresponds to lactones, hexoses and glucose isomers. SA: succinic acid; LA: lactic acid; GlyA: glyceric acid; GA: glycolic acid.

Comparison of the catalytic activity of N-containing Gs at 20 h with those previously reported by us using Ru catalysts at 1.5 h show that, in general terms, longer reaction times are required in the present case to achieve complete glucose conversion for the same reaction temperatures.¹³ This comparison also shows that the N-containing G samples tested in the present study exhibit somewhat lower selectivity to SA than those reached for Ru catalysts under optimal conditions that were above 80 %.¹³

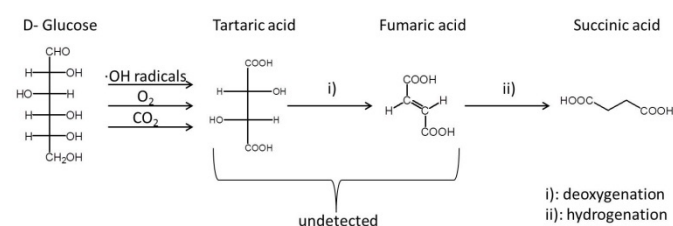
The catalytic stability of NH₂-rGO(3.5) and N-G was established by performing four consecutive uses of these samples, recovering the catalyst at the end of the reaction by filtration, washing with distilled water and dispersing in a fresh glucose solution, observing consistently complete glucose conversions and the same SA selectivity. Note that recycling of reported Ru catalyst required the addition of amines as co-catalyst in each new run and that the Ru catalyst exhibit some decrease in the catalytic activity upon reuse. In the present case, reuse of NH₂-rGO(3.5) and N-G does not require any sacrificial amine and the catalytic activity is notably maintained.

Concerning the catalytic activity of the different N-containing samples, Table 2 data clearly shows that there is a remarkable influence of the N content and its distribution on the performance of the N-doped Gs. It seems that the absence of N (case of rGO as catalyst) or high loadings with broad distribution of N atoms (case of NH₂-rGO(5.3) and NH₂-rGO(8.5)) is detrimental for the catalytic activity. In fact the two active samples have as main characteristic the presence of a high population of graphenic N atoms, suggesting that these atoms are the active sites of the process. It is worth noting that in the case of NH₂-rGO(3.8) the reaction mixture is remarkably simple and that the combined selectivity of SA and lactic acid accounted for over 75 % selectivity, this making the process very attractive.

The proposal of graphenic N atoms as active sites is in agreement with earlier reports on electrochemical oxygen reduction reaction that have shown that graphenic N atoms are the most efficient to reduce O₂ by two or four electrons.²⁸

Although the mechanism of WO is very complex with simultaneous pathways, oxygen reduction with the generation of oxygen-centred radicals is one of the necessary elementary processes taking place and for this process and graphenic N atoms appear among the most general active sites on G to activate O₂.^{15, 28}

However, formation of SA also requires other steps, particularly those related to deoxygenation and hydrogenation. In the case of Ru-catalyzed CWO of glucose, formation of SA was proposed to occur through a mechanistic pathway involving tartaric and fumaric acids as precursors of SA.¹³ This proposal was supported by control experiments showing the feasibility of fumaric acid hydrogenation by polyols acting as hydrogen source and also deoxygenation of tartaric acid, presumably taking place by transferring oxygen atoms to Ru. A similar reaction mechanism is proposed in the present case. Scheme 3 illustrate this proposal. This mechanism would be in agreement with prior reports in the literature that have shown the ability to rGO to gain oxygen from organic substrates and also to act as hydrogenation catalysts.³⁹



Scheme 3. Proposed mechanism for the CWO of glucose to SA using N-containing Gs as catalysts.

To provide some support to our mechanistic proposal, several reactions with some proposed intermediates were carried out. Thus, it was observed that tartaric acid under the conditions of the CWO in the presence of NH₂-rGO(3.8) undergoes complete disappearance to a mixture containing fumaric acid (73 %) as the major product, accompanied by glycolic acid (26 %). This result lends support to step I in Scheme 3 of the mechanism and shows that G can act as deoxygenating catalysts. When tartaric acid was reacted in the presence of glucose as hydrogen donor in a 1-to-1 mixture under CWO conditions in the presence of N-G, then, complete disappearance of tartaric acid accompanied with the formation of SA (17 %) and glycolic acid (38 %) as major products was observed. A reaction in which N-G was able to promote hydrogenation in isopropanol as hydrogen source of fumaric acid to SA was performed. On the other hand, fumaric acid in water does not react in the presence of N-containing G catalysts, showing that in the absence of hydrogen donors, no hydrogenation occurs. Table 3 summarizes the results of these controls.

In conclusion, in the present article it has been shown that N-doped graphenes can promote the CWO of glucose with a notable selectivity to SA. The available data suggest that this catalytic activity is related to the presence of graphenic N atoms. N-doped Gs can be used four times without observing a decay in the catalytic activity.

Experimental

Catalyst preparation.

Synthesis of doped G. Low molecular weight chitosan (Sigma Aldrich) was the precursor of N-G. This polysaccharide was pyrolyzed as powder under argon atmosphere using the following program for the oven temperature: annealing at 200 °C for 2 h and, then, heating at 10 °C/min up to 900 °C, maintaining this temperature for 6 h. The system was then cooled at room temperature under argon.

The NH₂-rGO(x) samples were prepared by dispersing 100 mg of GO obtained by Hummers method in 40 ml of ethylene glycol upon sonication at 700 W for 3 h and subsequent addition of increasing aqueous ammonia concentrations (5, 10, 25 %) as amine precursor. The dark brown solutions were transferred to teflon-lined autoclave and the dispersion heated at 175 °C under autogeneous pressure for 16 h. The resulting precipitate was filtered and washed with distilled water until a neutral pH value was measured for the washing. Finally, the dark solid was dried at 60 °C for 24 h.

Suspensions of the corresponding G were obtained by sonicating at 700 W for 1 h in the aqueous solution the black solid graphitic powders.

Catalysts characterization.

XPS measurements were performed at normal angle emission in a Specs setup, by using Al K_α monochromated radiation ($h\nu = 1486.7$ eV) of an X-ray gun, operating at 300 W (12 kV/25 mA) power. A flood gun with electron acceleration at 1 eV and electron current of 100 μA was used to avoid charge effects. Photoelectron energy was recorded in normal emission by using a Phoibos 150 analyzer, operating with pass energy of 30 eV. The XP spectra were fitted by using Voigt profiles combined with their primitive functions, for inelastic backgrounds. The Gaussian width of all lines and thresholds do not differ considerably from one spectrum to another, being always in the expected range of 2 eV.

CO₂-TPD measurements were carried out using the AutoChem II 2920 station. The samples (30-50 mg) were placed in a U-shaped quartz reactor of an inner diameter of 0.5 cm and, then, they were pre-treated at 100 °C for 1 h with high purity He (Purity 5.0, from Linde), and then exposed to a flow of CO₂ (from SIAD) for 1 h. After that, the samples were flushed with a flow of He (50 mL min⁻¹) for 20 min at 25 °C in order to remove the weakly adsorbed CO₂ species. TPD measurements were then carried out heating at a rate of 10 °C min⁻¹ till 700 °C. The CO₂ desorbed, was quantified with a TC detector using

a calibration curve. The results are expressed as mmoles of CO₂ per gram of catalyst.

Atomic force microscopy (AFM) measurements were conducted in the tap mode in air at ambient temperature using a Veeco AFM apparatus. AFM images were taken for samples exposed to ambient dust.

TEM images were recorded in a JEOL JEM 2100F operated at an accelerating voltage of 200 kV. Samples were prepared by applying one drop of the suspended material in ethanol onto a carbon-coated copper TEM grid, and allowing them to dry at room temperature.

Catalytic wet oxidation of glucose.

Reactions were carried out in batch mode according to the following procedure: 25 mg of the corresponding G catalyst were added to a solution of 90 mg (0.5 mmols) glucose in 10 mL water. After closing, the Teflon-lined stainless steel reactor was pressured at 10-18 bars with molecular oxygen and heated up to 160-180 °C, under stirring (1200 rpm), for 1-20 h. After reaction, the pressure was released, the catalyst was recovered by centrifugation and liquid phase was concentrated by removing water under reduced vacuum. The reaction mixture was silylated, diluted with 1 mL of toluene and analyzed by GC-FID chromatography (GC-Shimadzu apparatus). Product identification was made by comparison with authentic samples and by using a GC-MS Carlo Erba Instruments QMD 1000 equipped with a Factor Four VF-5HT column.

The recovered catalyst was dispersed in distilled water and centrifuged three times, then, dried at ambient temperature and used in a consecutive reaction of glucose.

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Notes and References

1. D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chemical Society Reviews*, 2012, **41**, 8075-8098.
2. F. Cherubini, *Energy Conversion and Management*, 2010, **51**, 1412-1421.
3. C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning and K. Egeblad, *ChemSuschem*, 2008, **1**, 283-289.
4. J. P. Lange, *Biofuels Bioproducts & Biorefining-Biofpr*, 2007, **1**, 39-48.
5. A. Corma, S. Iborra and A. Velty, *Chemical Reviews*, 2007, **107**, 2411-2502.
6. M. J. Climent, A. Corma and S. Iborra, *Green Chemistry*, 2011, **13**, 520-540.
7. A. B. Bjerre, A. B. Olesen, T. Fernqvist, A. Ploger and A. S. Schmidt, *Biotechnology and Bioengineering*, 1996, **49**, 568-577.

8. H. B. Klinke, B. K. Ahring, A. S. Schmidt and A. B. Thomsen, *Bioresource Technology*, 2002, **82**, 15-26.
9. A. S. Schmidt and A. B. Thomsen, *Bioresource Technology*, 1998, **64**, 139-151.
10. P. R. Gogate and A. B. Pandit, *Advances in Environmental Research*, 2004, **8**, 501-551.
11. V. S. Mishra, V. V. Mahajani and J. B. Joshi, *Industrial & Engineering Chemistry Research*, 1995, **34**, 2-48.
12. J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chemical Reviews*, 2010, **110**, 3552-3599.
13. I. Podolean, C. Rizescu, C. Bala, L. Rotariu, V. I. Parvulescu, S. M. Coman and H. Garcia, *Chemsuschem*, 2016, **9**, 2307-2311.
14. C. C. Huang, C. Li and G. Q. Shi, *Energy & Environmental Science*, 2012, **5**, 8848-8868.
15. S. Navalon, A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chemical Reviews*, 2014, **114**, 6179-6212.
16. D. S. Su, S. Perathoner and G. Centi, *Chemical Reviews*, 2013, **113**, 5782-5816.
17. A. Dhakshinamoorthy, A. Primo, P. Concepcion, M. Alvaro and H. Garcia, *Chemistry-a European Journal*, 2013, **19**, 7547-7554.
18. H. Huang, J. Huang, Y. M. Liu, H. Y. He, Y. Cao and K. N. Fan, *Green Chemistry*, 2012, **14**, 930-934.
19. X. H. Li, J. S. Chen, X. C. Wang, J. H. Sun and M. Antonietti, *Journal of the American Chemical Society*, 2011, **133**, 8074-8077.
20. H. Q. Sun, Y. X. Wang, S. Z. Liu, L. Ge, L. Wang, Z. H. Zhu and S. B. Wang, *Chemical Communications*, 2013, **49**, 9914-9916.
21. J. H. Yang, G. Sun, Y. J. Gao, H. B. Zhao, P. Tang, J. Tan, A. H. Lu and D. Ma, *Energy & Environmental Science*, 2013, **6**, 793-798.
22. R. P. Rocha, A. G. Goncalves, L. M. Pastrana-Martinez, B. C. Bordoni, O. Soares, J. J. M. Orfao, J. L. Faria, J. L. Figueiredo, A. M. T. Silva and M. F. R. Pereira, *Catalysis Today*, 2015, **249**, 192-198.
23. Y. X. Wang, Y. B. Xie, H. Q. Sun, J. D. Xiao, H. B. Cao and S. B. Wang, *Acs Applied Materials & Interfaces*, 2016, **8**, 9710-9720.
24. X. G. Duan, C. Su, L. Zhou, H. Q. Sun, A. Suvorova, T. Odedairo, Z. H. Zhu, Z. P. Shao and S. B. Wang, *Applied Catalysis B-Environmental*, 2016, **194**, 7-15.
25. J. Kang, X. G. Duan, L. Zhou, H. Q. Sun, M. O. Tade and S. B. Wang, *Chemical Engineering Journal*, 2016, **288**, 399-405.
26. H. Q. Sun, C. Kwan, A. Suvorova, H. M. Ang, M. O. Tade and S. B. Wang, *Applied Catalysis B-Environmental*, 2014, **154**, 134-141.
27. X. B. Wang, Y. L. Qin, L. H. Zhu and H. Q. Tang, *Environmental Science & Technology*, 2015, **49**, 6855-6864.
28. L. F. Lai, J. R. Potts, D. Zhan, L. Wang, C. K. Poh, C. H. Tang, H. Gong, Z. X. Shen, L. Y. Jianyi and R. S. Ruoff, *Energy & Environmental Science*, 2012, **5**, 7936-7942.
29. X. L. Li, H. L. Wang, J. T. Robinson, H. Sanchez, G. Diankov and H. J. Dai, *Journal of the American Chemical Society*, 2009, **131**, 15939-15944.
30. D. H. Long, W. Li, L. C. Ling, J. Miyawaki, I. Mochida and S. H. Yoon, *Langmuir*, 2010, **26**, 16096-16102.
31. C. Lavorato, A. Primo, R. Molinari and H. Garcia, *Chemistry-a European Journal*, 2014, **20**, 187-194.
32. A. Primo, P. Atienzar, E. Sanchez, J. M. Delgado and H. Garcia, *Chemical Communications*, 2012, **48**, 9254-9256.
33. A. Primo, E. Sanchez, J. M. Delgado and H. Garcia, *Carbon*, 2014, **68**, 777-783.
34. L. H. Chan, K. H. Hong, D. Q. Xiao, T. C. Lin, S. H. Lai, W. J. Hsieh and H. C. Shih, *Physical Review B*, 2004, **70**.
35. B. D. Guo, Q. A. Liu, E. D. Chen, H. W. Zhu, L. A. Fang and J. R. Gong, *Nano Letters*, 2010, **10**, 4975-4980.
36. L. Sun, L. Wang, C. G. Tian, T. X. Tan, Y. Xie, K. Y. Shi, M. T. Li and H. G. Fu, *Rsc Advances*, 2012, **2**, 4498-4506.
37. E. Asedegbega-Nieto, M. Perez-Cadenas, M. V. Morales, B. Bachiller-Baeza, E. Gallegos-Suarez, I. Rodriguez-Ramos and A. Guerrero-Ruiz, *Diamond and Related Materials*, 2014, **44**, 26-32.
38. H. Z. Jiang, X. L. Yu, R. F. Nie, X. H. Lu, D. Zhou and Q. H. Xia, *Applied Catalysis a-General*, 2016, **520**, 73-81.
39. A. Primo, V. Parvulescu and H. Garcia, *The Journal of Physical Chemistry Letters*, 2017, **8**, 264-278.

Graphical abstract.

