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 imaging 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
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, while undergoing a simultaneous reduction to form aminated reduced GO \([\text{NH}_2\text{-rGO}(x)]\), where \(x\) corresponds to the percentage of N. For the sake of comparison a sample of rGO was prepared under the same conditions as \(\text{NH}_2\text{-rGO}(x)\), but in the absence of \(\text{NH}_3\). The second type N-containing G was prepared by pyrolysis at 900 °C of chitosan (N-G). 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.

Both types of samples \(\text{NH}_2\text{-rGO}(x)\) 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. 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N content (%)</th>
<th>Distribution N atoms (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quaternary</td>
</tr>
<tr>
<td>(\text{NH}_2\text{-rGO}(3.8))</td>
<td>3.8</td>
<td>75</td>
</tr>
<tr>
<td>(\text{NH}_2\text{-rGO}(5.3))</td>
<td>5.3</td>
<td>64</td>
</tr>
<tr>
<td>(\text{NH}_2\text{-rGO}(8.5))</td>
<td>8.5</td>
<td>51</td>
</tr>
<tr>
<td>N-G</td>
<td>4.8</td>
<td>71</td>
</tr>
</tbody>
</table>

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).

The characteristic 2D morphology of the \(\text{NH}_2\text{-rGO}(8.5)\) 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 \(\text{H}_2\text{O}\) was established by AFM with subnanometric vertical resolution. It was observed that most of the particles present in the \(\text{NH}_2\text{-rGO}(x)\) 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 NH$_2$-rGO(x) and N-G catalysts present during the CWO of glucose.

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

Figure 3. Frontal views of N-G (a) and NH$_2$-rGO(8) (8.5) 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 NH$_2$-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 XP 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, NH$_2$-rGO(3.8) 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 of O$_2$ pressure at 20 h using NH$_2$-rGO(3.5) and N-G are C$_2$ (lactic and glycolic acids) and C$_3$ (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.

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 NH$_2$-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 NH$_2$-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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(°C) [Time (h)]</th>
<th>P$_{O_2}$ (atm)</th>
<th>Conv (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$-rGO(3.8)</td>
<td>180 [1.5]</td>
<td>10</td>
<td>10.9</td>
<td>SA (C4) 7.0 17.1</td>
</tr>
<tr>
<td>NH$_2$-rGO(3.8)</td>
<td>180 [20]</td>
<td>10</td>
<td>100</td>
<td>LA (C3) 71.0 15.5</td>
</tr>
<tr>
<td>NH$_2$-rGO(3.8)</td>
<td>180 [20]</td>
<td>18</td>
<td>100</td>
<td>GlyA (C3) 76.7 23.3</td>
</tr>
<tr>
<td>NH$_2$-rGO(3.8)</td>
<td>160 [20]</td>
<td>18</td>
<td>100</td>
<td>SA (C4) 67.9 3.7</td>
</tr>
</tbody>
</table>
The difference until 100% in the distribution of N atoms (case of NH$_2$-rGO(5.3) and NH$_2$-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 NH$_2$-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.

<table>
<thead>
<tr>
<th>N-containing Gs</th>
<th>Glucose conversion (%)</th>
<th>SA (%)</th>
<th>Lactic acid (%)</th>
<th>GC (%)</th>
<th>GA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$-rGO(5.3)</td>
<td>180 [15]</td>
<td>10</td>
<td>17.3</td>
<td>3.7</td>
<td>0</td>
</tr>
<tr>
<td>NH$_2$-rGO(5.3)</td>
<td>160 [20]</td>
<td>18</td>
<td>100</td>
<td>4.8</td>
<td>4.5</td>
</tr>
<tr>
<td>NH$_2$-rGO(8.5)</td>
<td>180 [15]</td>
<td>10</td>
<td>8.7</td>
<td>4.9</td>
<td>0</td>
</tr>
<tr>
<td>N-G</td>
<td>180 [15]</td>
<td>10</td>
<td>11.3</td>
<td>3.1</td>
<td>0</td>
</tr>
<tr>
<td>N-G</td>
<td>160 [20]</td>
<td>18</td>
<td>100</td>
<td>60.8</td>
<td>6.1</td>
</tr>
<tr>
<td>rGO</td>
<td>160 [20]</td>
<td>18</td>
<td>12.0</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>blank</td>
<td>160 [20]</td>
<td>18</td>
<td>10.5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 mmols glucose, 0.025 g N-containing G, 10 ml H$_2$O. 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. 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 %.

The catalytic stability of NH$_2$-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 NH$_2$-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 NH$_2$-rGO(5.3) and NH$_2$-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 NH$_2$-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.
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.

**XPS measurements characterization.**

XPS measurements were performed at normal angle emission in a Specs setup, by using Al Kα monochromated radiation (hν = 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 backgrounds. The Gaussian width of all lines and thresholds do not differ considerably from one spectrum to another, being backgrounds. The Gaussian width of all lines and thresholds do not differ considerably from one spectrum to another, being backgrounds.

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**Notes and References**