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# Biomass-derived graphene-like carbon: an efficient metal-free carbocatalysts for epoxidation reaction

Guodong Wen,*[a] Qingqing Gu,[a] Yuefeng Liu,[b] Robert Schlögl,[c] Congxin Wang,[b] Zhijian Tian,[b] and Dang Sheng Su*[a,b]

**Abstract:** N-doped graphene-like layered carbon (NG) could be synthesized via a metal-free pyrolysis route from glucose, fructose and 5-hydroxymethylfurfural (5-HMF), which are cheap and widely available biomass or biomass derivatives. Among the three kinds of NG, well-developed thin layered structure with large lateral dimension could be obtained when 5-HMF was used as the precursor. More importantly, the 5-HMF derived NG could exhibit superior performance in epoxidation reactions compared with the conventional carbon catalysts and the performance of 5-HMF derived NG was even similar to that of a Co catalyst. Co catalyst is widely studied in alkene epoxidation reactions. Characterizations by TEM and XPS accompanied by EPR analysis revealed that the origin of the enhanced catalytic properties for NG was ascribed to the activation ability both for alkene and $O_2$, which was attributed to the graphitic layered structure and graphitic N species, respectively.

It has been shown that nanocarbon could be applied as important metal-free catalysts, which is emerging as the alternative to the transition metal-based catalysts.[1] Many transition metals are rare, there being issues of sustainability. Moreover, many metals are toxic to human, thus the metal-free processes are preferred in the areas such as pharmacy manufacture. However, the use of metal is still unavoidable in many processes for these nanocarbon preparation. In order to keep low level of metal residue, harsh post treatment (e.g., inorganic acid washing and high temperature annealing) is generally involved, which is not environmentally benign and energy efficient. Therefore, the synthesis of nanocarbon catalysts via a metal-free route is urgently needed.

Biomass, which has low levels of metal content, could be converted to functional carbon materials via a metal-free route.[2] We have demonstrated that biomass glucose could be converted to functional carbon materials via a hydrothermal route and the obtained hydrothermal carbon could be used as metal-free catalysts in nitrobenzene reduction and Beckmann rearrangement.[3] García and coworkers have shown that biomass (e.g., alginic acid sodium salt and chitosan) could be converted to graphene-based metal-free catalysts.[1a,4] It should be noted that the catalytic properties of graphene-based carbon are so unique that can catalyze a wide variety of reactions including hydrogenation reactions, oxidation reactions, acid-catalyzed reactions and base-catalyzed reactions.[1a,5] In this work, we found that N-doped graphene-like carbon (NG) could be synthesized from biomass glucose, fructose and 5-HMF, which are widely available biomass or biomass derivatives. Although the preparation of NG from glucose has already been reported,[6] the synthesis of NG from fructose and 5-HMF has not been reported to the best of our knowledge. More importantly, these NG materials could be used as efficient metal-free carbocatalysts in epoxidation reaction.

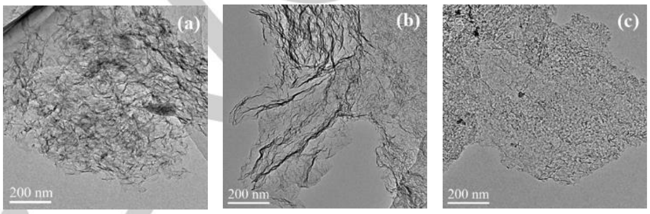

**Figure 1.** TEM images of NG from glucose (a), fructose (b) and 5-HMF (c).

The morphology of the NG from glucose, fructose and 5-HMF were shown in Fig. 1 and Fig. S1. The NG from glucose (NG(g1:5)) is small whisker-like flake carbon, larger flake with a lot of wrinkles could be found from fructose derived NG (NG(f1:5)), while the lateral dimension of the carbon from 5-HMF (NG(h1:5)) is the largest and thin layers could be observed on it. All the samples showed typical (002) and (100) graphitic diffraction peaks (Fig. S2), and the intensity of the (002) peak for the NG prepared from HMF was weaker than that of the peak for the NG prepared from glucose and fructose, indicating that the thickness of continuous orderly stacking for NG prepared from HMF was thinner. The intensity of the (002) peak decreased with the increasing of the HMF and urea ratio, indicating that the thickness of continuous orderly stacking was decreased. The XRD results are in accordance with the TEM analysis. Then, a series of 5-HMF derived NG with different urea and 5-HMF weight ratio in the precursor was prepared. Herein, the prepared NG was denoted as “NG(x1:y)” wherein x represents the precursor (“g”, “f” and “h” stands for glucose, fructose and 5-HMF, respectively) and y represents for the weight ratio between the urea and precursor. The layered structure is not obvious, and many amorphous carbons were found on 5-HMF derived NG(h1:2) and NG(h1:3). With the increasing of the urea and 5-HMF weight ratio from 5 to 10, obvious layered structure was observed (Fig. S3) and the degree of graphitization increased as indicated from the decrease of the $I_D/I_G$ ratio (Fig. S4). In the synthesis of NG process, urea was added for the temporary in situ formation of layered graphitic carbon nitride (g-$C_3N_4$), which is likely to serve as a sacrificial template.[2b,6] The synthetic process contains two steps, and the in situ formation of g-$C_3N_4$ is favorable in the first step annealing at 600 ºC. The typical layered structure of $C_3N_4$ could be observed in the carbon/$C_3N_4$ composite (Fig. S5), which was obtained by calcination of mixture of 5-HMF and urea at 600 ºC. These results indicated that the polymeric plane of $C_3N_4$ was well developed in the presence of 5-HMF or 5-HMF-derived intermediates. The

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formation of $C_3N_4$ could also be confirmed from the TG analysis shown in Fig. S6. A rapid weight loss was observed at the temperatures higher than 600 ℃, which could be attributed to the pyrolysis of $C_3N_4$. 5-HMF, which is an intermediate during the degradation of glucose or fructose, is prone to polymerize or aromatize to carbonaceous structure as compared to glucose and fructose.[7] When 5-HMF was used as the precursor for NG preparation, the carbon yield was 6.7%. In contrast, the yield was only 3.6% when fructose was used as the precursor. Therefore, the well-developed thin layered structure with large lateral dimension shown in the TEM images when 5-HMF was used as the precursor was probably ascribed to the easy polymerization of 5-HMF.

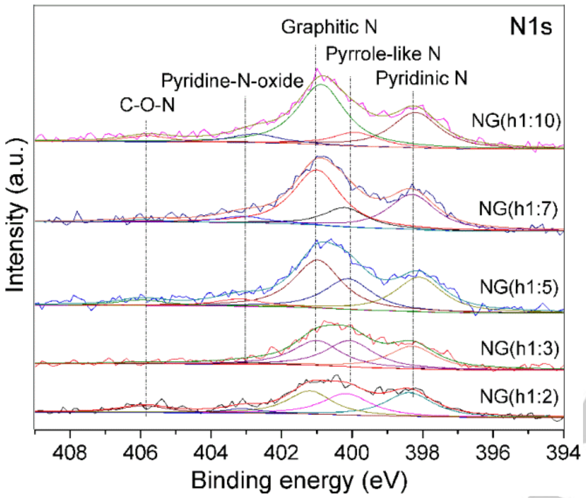

**Figure 2.** N1s XPS spectra of NG(h1:2), NG(h1:3), NG(h1:5), NG(h1:7) and NG(h1:10).

The surface N element distribution was investigated by energy-dispersive X-ray (EDX) mapping. As shown in Fig. S7, a uniform N distribution has been achieved on the NG(h1:10) catalyst. The N1s XPS spectra were shown in Fig. 2 and Fig. S8. The deconvolution of the spectra was similar to that reported by Arrigo et al., Chen et al. and our previous work.[8] It could be found that the graphitic N content gradually increased from 1.6 at% to 3.1 at%, while the pyridinic N content remained almost unchanged when the urea and 5-HMF weight ratio increased from 2 to 10 (Table S1). The pyrrole-like N content increased from 1.5 at% to 2.1 at% when the ratio increased from 2 to 3, and then slowly decreased with the further increase of the ratio. These results indicated that the content of surface N species could be well tuned by increasing the urea and precursor ratio.

The NG was tested in the aerobic epoxidation of styrene to styrene oxide. Benzaldehyde were identified as the primary byproduct from the GC-MS analysis, other minor byproducts were phenylacetadehyde, benzoic acid and 1-phenylethane-1,2-diol. It could be found from Table 1 that almost no conversion was observed on activated carbon, nanodiamond, $C_3N_4$ and flake graphite. Extremely low conversion (0.2%) was obtained on CNT. It is very interesting to note that high conversion (10.3%) was observed on reduced graphene oxide (RGO), albert no styrene oxide was detected, which demonstrated the critical roles of N doping for the epoxidation reactions.[9] Herein, a simple Co catalyst CoOx was prepared. However, no conversion was obtained. It was reported that the solvent DMF could coordinate with Co sites to form the true active sites and/or acting as a co-reductant,[9b,10] thus DMF was often selected as the optimum solvent for the Co catalysts. As expected, both the conversion (4.5%) and selectivity (87.7%) were significantly increased when the solvent was changed from cyclohexanone to DMF. Although the styrene oxide selectivity on NG(h1:10) was lower than that on CoOx, higher conversion was observed on NG(h1:10), thus similar yield was obtained.

***Table 1.*** Epoxidation of styrene over different carbon catalysts.[a]

| Catalyst | Conv. % | Styrene oxide selectivity (%) | Benzaldehyde selectivity (%) | Styrene oxide yield (%) |
|---|---|---|---|---|
| NG(h1:10) | 7.9 | 44.7 | 54.2 | 3.5 |
| RGO | 10.3 | 0.0 | 100.0 | 0.0 |
| Activated carbon | 0.0 | 0.0 | 0.0 | 0.0 |
| Nanodiamond | 0.0 | 0.0 | 0.0 | 0.0 |
| $C_3N_4$ | 0.0 | 0.0 | 0.0 | 0.0 |
| CNT | 0.2 | 0.0 | 100.0 | 0.0 |
| Flake graphite | 0.0 | 0.0 | 0.0 | 0.0 |
| CoOx | 0.0 | 0.0 | 0.0 | 0.0 |
| CoOx[b] | 4.5 | 87.7 | 12.3 | 4.0 |

[a] Reaction conditions: 1 mmol styrene, 10 mL solvent cyclohexanone, 50 mg catalyst, 60 °C, 8 h, 0.1 MPa, $O_2$ flow rate 10 mL/min. [b] The solvent is DMF.

Then the effect of solvents was studied (Fig. S9), the results indicated that high conversion and selectivity could be obtained in cyclohexanone, and almost no conversion was observed when DMF, toluene and acetonitrile were used as the solvents. The effect of pyrolysis precursor was also studied (Fig. S10). Low conversion and no styrene oxide formation were observed when glucose and fructose were used as the precursor. In contrast, higher conversion was obtained, and selectivity as high as 49.8% could be observed on NG derived from 5-HMF. It was shown in Fig. S8 and Table S1 that similar surface N contents were observed on NG derived from these precursors. It seems that the improved performance on 5-HMF derived NG was ascribed to its unique structure, namely well-developed thin graphitic layered structure. In order to exclude the catalytic roles of underlying metal residues, the metal content in these three NG was qualified by ICP-MS and quantified by ICP-AES. The results showed that Fe was the possible impurity, and the Fe contents in NG derived from glucose, fructose and 5-HMF were 127 ppm, 79 ppm and 101 ppm, respectively. The Fe content is not correlated with the performance, which further confirmed that the metal impurities have a minor effect on the performance of the NG catalysts.

In order to study the roles of different N species, the catalytic performance of the five NG catalysts prepared from 5-HMF with different N species contents was investigated. The conversion increased with the increase of the urea and 5-HMF ratio from 2 to 10 (Table 2), which is in accordance with the increase of the

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graphitic N content. These results suggested that the graphitic N was closely related to the activities, which was likely to be ascribed to the activation ability for $O_2$ as reported from DFT calculations and in situ high-resolution synchrotron techniques.[1c,11]

***Table 2.*** Epoxidation of styrene over 5-HMF derived NG.[a]

| Catalyst | Conv.% | Styrene oxide selectivity (%) | Benzaldehyde selectivity (%) | Styrene oxide yield (%) |
|---|---|---|---|---|
| NG(h1:2) | 0.1 | 0.0 | 100.0 | 0.0 |
| NG(h1:3) | 0.3 | 0.0 | 100.0 | 0.0 |
| NG(h1:5) | 5.9 | 49.8 | 49.7 | 3.0 |
| NG(h1:7) | 7.2 | 45.2 | 53.1 | 3.3 |
| NG(h1:10) | 7.9 | 44.7 | 54.2 | 3.5 |

[a] Reaction conditions: 1 mmol styrene, 10 mL solvent cyclohexanone, 50 mg catalyst, 60 °C, 8 h, 0.1 MPa, $O_2$ flow rate 10 mL/min.

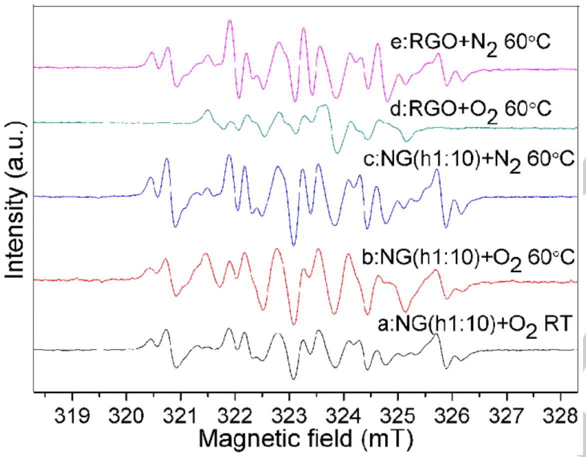

**Figure 3.** EPR spectra of styrene epoxidation on NG(h1:10) and RGO at room temperature (RT) or 60 °C in $O_2$ or $N_2$.

Radicals were generally involved in the aerobic oxidation reactions over carbon catalysts.[1c,1d] The electron paramagnetic resonance (EPR) technology was adopted to detect the radical intermediates. When no catalyst was added in the reaction, the signal was so weak that could be neglected (Fig. S11). Similar spectra were shown in Fig. 3c and 3e, indicating that both the NG and RGO catalysts have the ability to activate styrene to radicals, thus the activation of styrene is correlated with the graphitic layered structure, which is similar to that reported by Peng and coworkers.[1d] When $O_2$ was introduced in the reaction, the radical signal over the RGO catalyst was severely attenuated (Fig. 3d), indicating that many radicals were quickly reacted with $O_2$ molecules to form side product, namely benzaldehyde. In contrast, the intensity of the signal was not obviously attenuated and some part of the signal was even intensified over the NG(h1:10) catalyst when $O_2$ was introduced (Fig. 3b). These results suggested that $O_2$ could be activated on NG(h1:10) catalyst at 60 °C, but could not be activated on RGO catalyst. It is very difficult for us to clearly identify the different radicals, because the signals of several radicals overlapped with each other. It seems that Ph-CH(CH$_2$)$^{\bullet}$ DMPO-trapped species and hydrogen radical trapped DMPO-H species were formed, because the radical signals were very similar to that reported by Shimakoshi and coworkers.[12]

A possible mechanism was proposed (Fig. 4), styrene was activated on graphitic layer surface to form Ph-CH(CH$_2$)$^{\bullet}$ radical, $O_2$ was activated on the carbon adjacent to the graphitic N. The graphitic N has an unpaired electron that delocalized over the basal plane of graphene, which provided the possibility for electron transfer from the adjacent carbon atoms to the $O_2$ to form $O_2^{\bullet}$ radical.[1c,13] Then the two radicals interacted with each other to form Ph-CH(CH$_2$)OO$^{\bullet}$ radical, followed by the dissociation of O-O bond to form styrene oxide. In this process, both the graphitic layered structure and graphitic N species are critical.

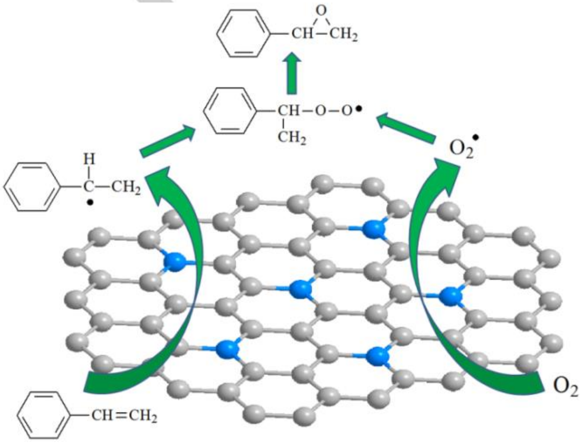

**Figure 4.** Possible mechanism for the epoxidation of styrene over NG catalysts.

The ATR-IR spectra showed that there was an interaction between the styrene and solvent cyclohexanone, because the characteristic peaks at 697 and 776 cm$^{-1}$, which is the indicative of mono substituted benzene ring, were shifted to lower wavenumbers when cyclohexanone was added into styrene (Fig. S12a). The peak at 1630 cm$^{-1}$ could be attributed to C=C vibration of styrene, and its intensity gradually decreased with the increasing of the reaction time from 30 min to 6 h (Fig. S12b and Fig. S13a), indicating the gradual conversion of styrene. A shoulder peak appeared at 758 cm$^{-1}$ (Fig. S12c), which is the indicative of mono substituted benzene ring of styrene oxide, indicating the formation of styrene oxide during the reaction over NG(h1:10) catalyst. In contrast, no shoulder peak at 758 cm$^{-1}$ was appeared when RGO was used as catalyst (Fig. S13b). A small peak at 1140 cm$^{-1}$ was formed when NG(h1:10) was used as catalyst, its intensity increased from 30 min to 2 h, and then decreased with the further increase of the reaction time. This signal is probably indicative of a stretching vibration of C-O-O bonds in alkyl peroxides,[14] which strongly support the formation of Ph-CH(CH$_2$)OO$^{\bullet}$ radical intermediate.

The effect of reaction time (Fig. S14) and temperature (Fig. S15) were also studied, and a styrene oxide yield of 24.2% could be obtained at 80 °C for 8 h, which was similar to that reported by Dhakshinamoorthy and coworkers from the chitosan-derived NG (the yield given at 100 °C for 8 h was

17.8%).[4b] Various alkenes including trans-stilbene, cyclohexene and 1-hexene were tested as substrate. Extremely high conversion (80.4%) and selectivity (84.5%) could be observed when trans-stilbene was used as the substrate, however the yield was low when cyclohexene and 1-hexene were used as the substrates, which were only 8.0% and 0.7%, respectively. These results indicated that the epoxidation reaction could be well conducted on C=C bond that connected with benzene ring, which might be ascribed to the conjugated π systems. Moreover, it was found that the NG(h1:10) catalyst is relatively stable during the recycle test (Fig. S16).

In conclusion, we have shown that NG could be prepared from glucose, fructose and 5-HMF, which are widely available biomass or biomass derivatives. Among the three kinds of NG, well-developed thin layered structure with large lateral dimension could be obtained when 5-HMF was used as the precursor. More importantly, the 5-HMF derived NG could exhibit superior performance in epoxidation reactions compared with the conventional carbon catalysts and the performance of 5-HMF derived NG was even similar to that of a Co catalyst (CoOx). Co catalyst is widely studied in the epoxidation reactions. Characterizations by TEM and XPS accompanied by EPR analysis suggested that the origin of the enhanced catalytic properties for NG was ascribed to the activation ability both for alkene and $O_2$, which were probably resulted from the graphitic layered structure and graphitic N species, respectively. The mechanism understanding for the carbon catalysts is different from that for the conventional metal-based catalysts, which is helpful to shed some light on the mechanism research of metal-free catalysis.

## Experimental Section

Nitrogen-doped graphene-like layered carbon (NG) was synthesized as follows: first, the biomass precursor (glucose, fructose or 5-HMF) was dissolved into saturated urea aqueous solution, follow by drying at 60 °C. The obtained solid was transferred into a tubular furnace for pyrolysis under Ar flow (100mL/min). The sample was heated to 600 °C at a heating rate of 1 °C/min and maintained at this temperature for 1 h, then calcined at 900 °C for 1 h at a heating rate of 1 °C/min. The solid was dispersed in deionized water, sonicated at 237.5 W for 1 h, and finally dried at 60 °C.

The epoxidation reaction was conducted in the presence of 1 mmol substrate, 10 mL solvent and 50 mg catalyst with $O_2$ flow (10 mL/min) at atmosphere pressure at the temperatures ranging from 50 °C to 100 °C under vigorous stirring. Full experimental details can be found in the Supplementary information.

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**Keywords:** biomass • graphene • metal-free • carbocatalysts • epoxidation reaction

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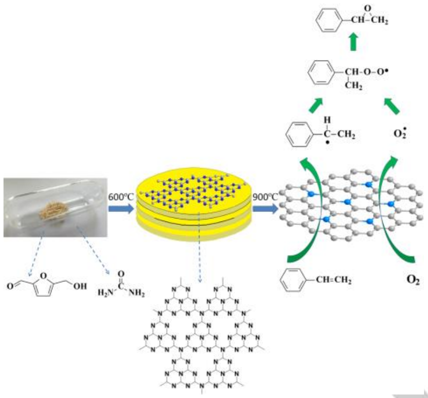
# COMMUNICATION

N-doped graphene-like layered carbon (NG) could be synthesized via a metal-free pyrolysis route from glucose, fructose and 5-HMF, which are widely available biomass or biomass derivatives. Well-developed thin layered structure with large lateral dimension could be observed on 5-HMF derived NG, which could be used as metal-free catalysts in alkene epoxidation. The origin of the activities was resulted from the graphene layer and graphitic N species.



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