Nitrogen-doped graphene for electrochemical oxygen reduction

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Fuel cells could offer an alternative to fossil fuels by using hydrogen generated from renewable sources. However, oxygen reduction in these devices is performed on a Pt catalyst which is extremely expensive. If cheap alternatives can be discovered, fuel cells may become serious contenders in the energy sector.

One candidate is nitrogen-doped carbon. Such catalysts have been extensively studied and are generally made via heat-treatment of Fe/C/N-containing materials. The performance of this class of catalysts is gradually improving.[1] The role of iron in these catalysts is debated, but recent evidence suggests that Fe-coordination to C and/or N atoms is not needed for efficient oxygen reduction.[2,3,4] However, the performance of these catalysts must improve if they are to rival platinum.

Graphene has recently taken the scientific world by storm. Among its many remarkable properties it is highly conductive, can support high current density, is chemically stable and has large surface area. Thus, graphene is an ideal material for use in fuel cells. There are relatively few reports of N-doped graphene (Figure 1a), but research in this field is growing, with various reported synthesis techniques (Figure 1b).[5,6,7,8,9,10]

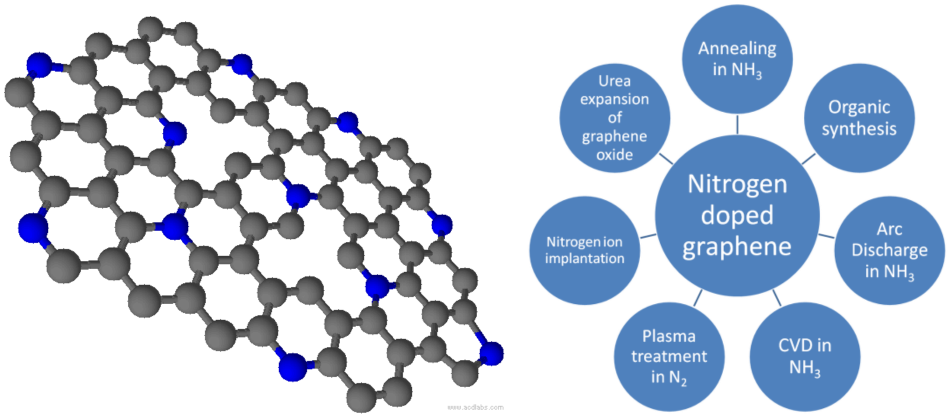

Figure 1: (a) Schematic of N-doped graphene, (b) Techniques used to produce N-doped graphene.

Using an organic synthesis protocol we have produced gram-quantities of graphene powder with extremely high N content, which can be varied by changing the chemical precursors, or by thermal treatment. This N-doped graphene is an ideal candidate for use as a catalyst for fuel cells. Figure 2(a) shows transmission electron microscopy of N-doped graphene sheets at least 10 μm in size. Various folds and crumples can be observed. Figure 1(b) shows the N1s region of the X-ray photoelectron spectum of N-doped graphene, with a large peak centered at ~400.5 eV attributed to quaternary bonded N, indicating that a significant amount of N in the basal plane. The smaller shoulder peak at ~398.5 eV is attributed to pyridinic-type N, which may indicate bonding at edges, or at vacancies in the graphene plane. Table 1 shows the N content measured by CHN analysis for N-doped graphene derived from diethanolamine, pyrolysed at various temperatures. The N content varies from 14.83 wt.% for as-produced N-doped graphene to 6.27 wt.% for N-doped graphene subjected to pyrolysis at 1000˚C. This demonstrates the ability to tune the nitrogen content as desired for a particular application. Additionally, the nitrogen content remains high even after high temperature treatment, indicating the stability of N in this material.

Figure 2(c) shows linear sweep voltammograms for graphene and N-doped graphene catalysts. In these results, there is an improvement in the current density with increasing pyrolysis temperature for N-doped graphene, which is attributed to an increase in conductivity, or in the number of available active sites for oxygen reduction. There is also an increase in the onset potential (measured at 2 μA/cm^2) from 0.78 V for pristine graphene to 0.84 V for N-doped graphene pyrolysed at 1000˚C.

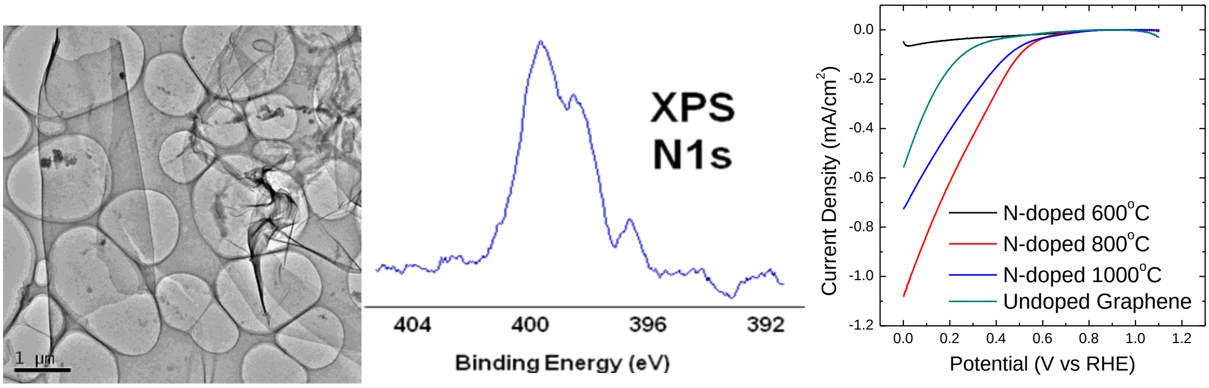

Figure 2. (a) TEM image of nitrogen-doped graphene. (b) XPS N1s signal for nitrogen-doped graphene. (c) Oxygen reduction voltammogram for N-doped graphene cathodes.

Precursor	Temperature (˚C)	Nitrogen Content (wt.%)
Ethanol	600	0
Diethanolamine	600	14.83
Diethanolamine	800	10.11
Diethanolamine	1000	6.27

Table 1. CHN analysis of graphene and N-doped graphene pyrolysed at various temperatures.

These preliminary results indicate that N-doped graphene is a suitable candidate for use as an oxygen reduction catalyst in fuel cells and give some insight into the mechanism of oxygen reduction. This material is fabricated via a cheap and scalable organic synthesis method. However, this is a work in progress and efforts are being made to increase the surface area, N content and conductivity of the material to make N-doped graphene a viable catalyst for oxygen reduction in fuel cells.

References

[1] Y. Nabae, S. Moriya, K. Matsubayashi, S. M. Lyth, M. Malon et al. Carbon **48** (2010) 2613.
[2] S. M. Lyth, Y. Nabae, S. Moriya, S. Kuroki et al J. Phys. Chem. C **113** (2009) 20148.
[3] M. Chokai, M. Taniguchi, S. Moriya, K. Matsubayashi, et al., J. Power Sources **195** (2010) 5947.
[4] S. M. Lyth, Y. Nabae, N. M. Islam, S. Kuroki, et al., J. Electrochem. Soc. **58** (2011) B194.
[5] X. Li, et al., Journal of the American Chemical Society **131** (2009) 15939.
[6] X. Wang, et al., Science **324** (2009) 768.
[7] D. Long, W. Li, L. Ling, J. Miyawaki, I. Mochida, S-H. Yoon, Langmuir **26** (2010) 16096.
[8] X. Li, et al., Journal of the American Chemical Society **131** (2009) 15939.
[9] D. Wei, et al., Nano Letters **9** (2009)1752.
[10] S. Wakeland, R. Martinez, J. K. Grey, C. C. Luhrs, Carbon **48** (2010) 3463.