Synthesis of Nitrogen-doped graphene with enhanced oxygen reduction activity by pyrolysis of graphene functionalized with imidazole derivatives

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Abstract

Replacing noble metal catalysts with cheaper and durable catalytic materials for the oxygen reduction reaction (ORR) is a key issue in the development of fuel cell technology. In this regard, nitrogen-doped carbon nanomaterials and in particular nitrogen-doped graphene have received increasing attention as effective metal-free electrocatalysts [1-5]. Nitrogen doping suppresses the density of states near the Fermi level of graphene thus opening a band gap between the conduction and valence bands. Nitrogen dopants modify spin density and charge distribution of carbon atoms, inducing "activated regions" in graphene that participate in catalytic reactions such as the ORR. Nitrogen doping of graphene can be carried either "in situ" during graphene growth or post-synthesis. Post-synthesis doping methods typically consist of plasma treatment or thermal annealing of graphene or graphene oxide with different nitrogen precursors such as NH_3, melamine, urea or dicyandiamide or some ionic liquids (IL).

Here, we have used an imidazolium-based poly(ionic liquid) (PIL), poly(3-butyl-1-vinylimidazolium bromide) (PBVIBr) as precursor (Figure 1) for nitrogen doping of graphene nanoplatelets (GNP) by thermal annealing of the corresponding PIL-functionalized GNP. To the best of our knowledge, pyrolysis of PIL-functionalized graphene to produce N-doped graphene has not been reported so far. In addition, two other imidazole derivatives of different nature and charge, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) and the neutral polymer poly(vinylimidazole) (PVI), Figure 1, have been investigated as precursors for nitrogen doping of GNP using the same strategy. Total nitrogen content and the chemical bonding configuration of nitrogen atoms in the N-GNP samples produced with the different precursors were examined by XPS, which confirms the incorporation of nitrogen atoms in the surface of N-GNP (Figure 2).

All N-GNP showed enhanced electrocatalytic activity for oxygen reduction reaction in alkaline media compared to pristine GNP. The ORR electrocatalytic activity of N-doped GNP obtained from the three precursors ($BMIBF_4$, PVI and PBVIBr) was examined and rationalized in terms of total nitrogen content, relative distribution of nitrogen bonding configurations, surface area and porosity of the resulting N-doped GNP. We will show how these parameters are influenced by the nature of the precursor. Interestingly, ORR catalytic activity in N-GNP did not correlate with total nitrogen content but was more affected by the BET surface area. Thus, the most active N-GNP materials were produced by pyrolysis of GNP functionalized with the ionic imidazolium-based nitrogen precursors, the IL and the PIL, which led to more porous and high surface area N-GNP. We believe that these results can be inspiring in the choice of suitable nitrogen precursors for doping carbon materials and hence achieve metal-free ORR electrocatalysts with enhanced activity.

References

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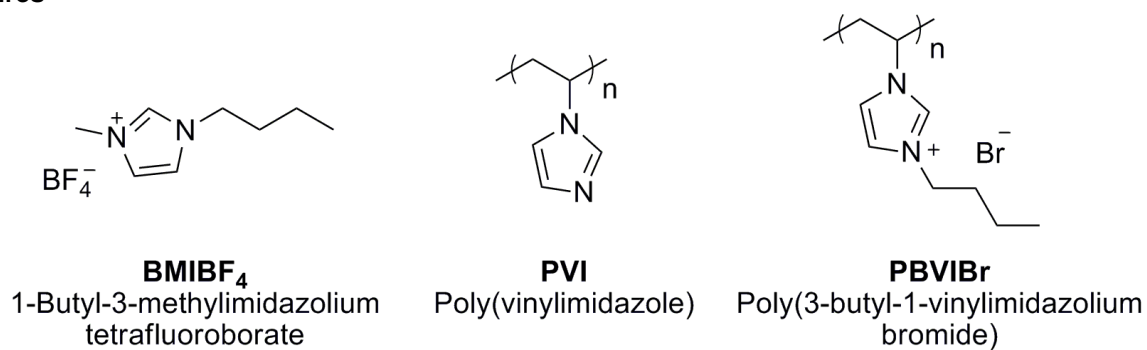
Figures

BMIBF$_4$
1-Butyl-3-methylimidazolium
tetrafluoroborate

PVI
Poly(vinylimidazole)

PBVIBr
Poly(3-butyl-1-vinylimidazolium
bromide)

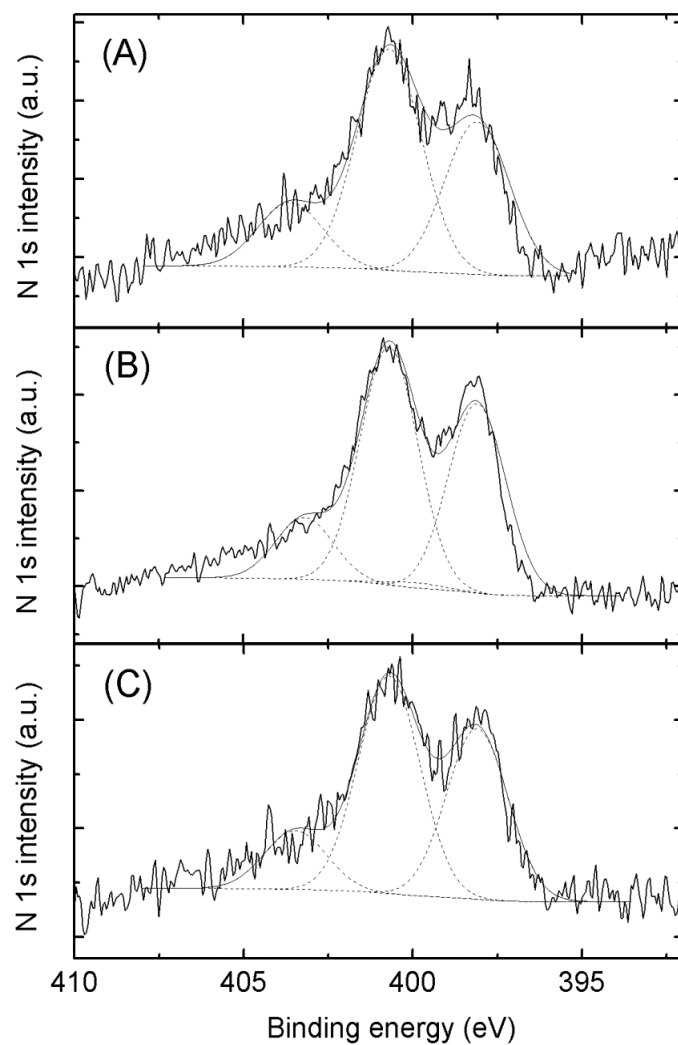**Figure 1**. Nitrogen precursors used for GNP functionalization and subsequent N-doping.

Figure 2. Core level high resolution N1s XPS spectra of N-GNP obtained from pyrolysis of GNP functionalized with the different nitrogen precursors: (A) BMIBF$_4$, (B) PVI and (C) PBVIBr.