N-doping Graphene at Ambient Conditions with N_2-DBD-Plasma and the role of neutral species

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N-doped graphene is a promising material for the oxygen reduction reaction, battery electrodes, and more. Plasma-based methods are an excellent alternative for doping graphene with nitrogen atoms because it allows for post-production treatment, localized doping, and is possible at atmospheric pressure conditions. However, the type of reactive species generated by the plasma and resulting N-doping are not well understood. We doped nitrogen into monolayer graphene by bombarding it with reactive nitrogen species from a low-temperature plasma based on an atmospheric pressure dielectric barrier discharge. After 30 s bombardment, the graphene monolayer on copper had a moderate degree of damage I_D/I_G=1.2 and increase in N-atomand O-atom (content. N-atoms bound as pyrrolic nitrogen (N1s 400.0 eV), while it was impossible to exclude oxygen at atmospheric pressure, which formed a mixture of oxygen-containing functional groups on the graphene. At long treatment times (20 min), the treated area increased radially and the 2D-structure of graphene was destroyed. A part of the increase in N- and O-content was due to adsorbed hydrocarbons, as transfer to XPS in open-air led to an increase in the integrated C1s peak.

N-atom content increased with increasing operating voltage of the DBD source. The N-atom content and type remained unchanged when only neutral reactive nitrogen species bombarded the surface. We hypothesize, therefore, that the primary reactive species resulting in pyrrolic N-doping from the DBD are neutrals such as $N(^4S)$ and possibly $N(^2P)$.