Chemical functionalization of Boron Doped Graphene for novel composite materials: application to catalytic nitric oxide reduction.

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Abstract

Realization of the full potential of graphene - a single layer of carbon atoms with lateral extension that is readily tailored - requires the merging of its essential physical and chemical properties. An obvious strategy is to enhance these properties by doping the pristine graphene with foreign atoms (for example nitrogen, boron, sulfur and phosphorous). This type of modification produces changes in the electronic structure of graphene (hole or electron doping) as well as offers specific interactions with adsorbed molecules or surfaces, to which it can be linked. The new properties emerging from doping can be exploited in different areas of interest ranging from the development of new and more efficient molecular sensors[1], to the heterogeneous catalysis[2] or coatings to functionalize a substrate and prevent the corrosion of metallic materials[3].

A "socket-plug" strategy was proposed by our group recently[4]. It utilizes boron doping to provide the socket functionality in a standard coupling to connect molecular moieties to graphene whereby the electronic characteristics in the vicinity of the Fermi energy become virtually independent of the choice of the molecular "antenna". The objective is understood to be reached by making use of the properties of a Lewis acid - base coupling. While the socket property is obtained by boron atoms introduced in the graphene matrix (boron doped graphene, BG), the plug property is offered by a lone-pair of a nitrogen atom in the molecular adsorbate. In as much as boron doping introduces holes in the valence band, the dative bonding between electrophilic boron sites and nitrogen nuleophilic lone-pairs effectively achieves electronic undoping of the boron doped graphene. The Lewis acid - base connection is understood to render graphene stable towards adsorption-desorption of any "antenna" molecule. It should be underlined that the boron-nitrogen couple displaying socket-plug functionality is unique owing to the atoms' similarities to carbon.

Our study demonstrates also that in the vicinity of the Fermi level (E_F) the characteristic residual densities of states related are similar for BG with different "antenna molecules" adsorbed on it. These qualitative features validate generic properties at E_F resulting from the effective deletion of single carbon p_z orbitals by local sp^2-sp^3 rehybridization owing to substituting carbon by boron followed by adsorption of a Lewis base. A universal functionality is arrived at.

A first pilot application concerns the catalytic nitric oxide (NO) reduction from emission of ordinary combustion engines validating the potential of boron-doped graphene in this field. The NOx problem is of great interest nowadays in relation to the car manufacturing and great effort is put in researching new possible technologies that could help to reduce the emission of this pollutant. We employed our "socket-plug" strategy to explore the possible utilization of functionalized boron doped graphene for metal free NOx reduction thus circumventing the present common catalytic approach that employs a NOx storage/reduction (NSR) catalyst[5] based on platinum, barium oxide and rhodium. We propose, instead, a boron-doped graphene based photocatalysis which exploits the ability of BG to trap NO, as adsorbed $(NO)_2^-$ and $(NO)_3^-$.

References

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