Plasma based N-graphene synthesis – *in-situ* and post treatment approaches

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Free-standing N-graphene sheets were synthesized by graphene post treatment in a low-pressure microwave N_2-Ar large-scale plasma reactor. The graphene sheets were placed in the remote plasma region, where they were treated for various durations and gas mixture compositions. Optical emission spectroscopy was used to diagnose the plasma source. The N-doped graphene sheets were analyzed by applying scanning and transmission electron microscopy, Raman, X-ray photoelectron, and Fourier-transform IR spectroscopy techniques. *In situ* synthesis of N-graphene was also achieved in a single step method by introducing N-containing precursor together with carbon precursor in the reactive microwave plasma environment at atmospheric pressure.

1. Introduction

N-graphene demonstrates outstanding electrochemical properties and shows better performance as catalyst than commercially available Pt-based electrodes [1-3]. Numerous methods for synthesis of N-graphene, such as chemical vapour deposition, bottom-up synthesis, wet chemical methods, plasma methods etc., which can be categorized into *in situ* and post-treatment approaches, were developed. In situ methods allow simultaneous graphene synthesis and N-doping, whilst in post-treatment previously fabricated graphene is further doped with nitrogen. In this study, plasma-based methods of N-graphene synthesis both in situ and post-treatment are presented.

2. Synthesis methods

In the frame of post-treatment N-graphene fabrication, free-standing graphene sheets were first synthesized using microwave argon plasma working at atmospheric pressure conditions. The method is based on injecting a carbon-containing precursor (ethanol) into the active plasma zone, where decomposition of ethanol into carbon atoms and molecules take place. Gas-phase carbon atoms/molecules diffuse into the colder zones and aggregate into solid carbon nuclei. The main stream of carbon nuclei is withdrawn into the outlet plasma zone, where the processes of assembly and growth take place. Selective synthesis of free-standing sheets is achieved via tailoring of the microwave plasma environment only. Afterwards, the produced graphene sheets are immersed into the remote plasma region of a low pressure N_2-Ar discharge. Raman and XPS analysis of the produced structures demonstrate that the doping level and type of functional groups attached to the graphene lattice can be controlled by changing the exposure time, while keeping the nitrogen percentage constant. The nitrogen atoms were incorporated into the hexagonal carbon lattice in pyridinic, pyrrolic and quaternary functional groups, mainly.

Microwave argon plasma working at atmospheric pressure was used to directly create N-graphene by passing through the active plasma environment ammonia solution in ethanol. This way the N-graphene sheets are synthesized in a single step by actively controlling the gas temperature and nitrogen/carbon atom fluxes.

3. References

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