Large scale production of edge-functionalized graphene nanoplatelets

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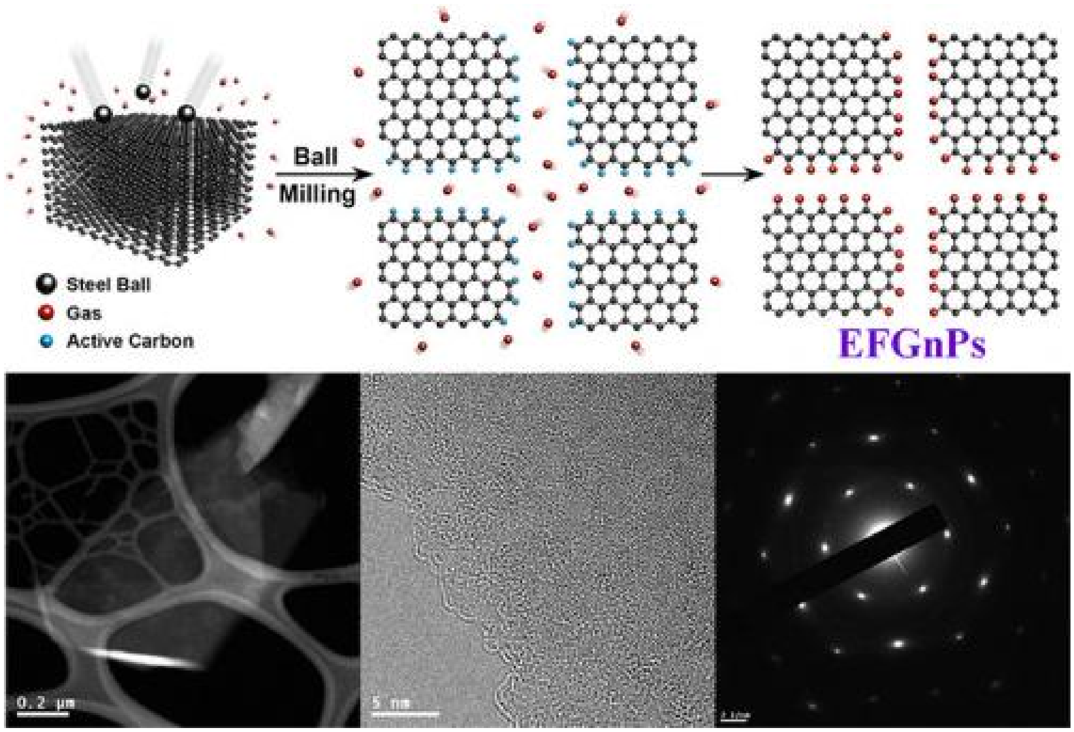

Schematic representation of the mechanochemical reaction between in situ generated active carbon species and reactant gases in a sealed ball-mill crusher. Credit: JACS

Researchers from the Ulsan National Institute of Science and Technology (UNIST), South Korea have pioneered a simple, but efficient and eco-friendly way to produce Edge-selectively functionalized graphene nanoplatelets (EFGnPs) by dry ball milling graphite in the presence of various gases.

The electrocatalytic activity of heteroatom-doped carbon-based nanomaterials has become a growing interest in the past few years due to their potential applications for fuel cells and metal-air batteries.

Several approaches currently exist for the doping of heteroatoms into graphitic structure, but these suffer from high manufacturing costs and technical difficulties.

Researchers at Ulsan National Institute of Science and Technology (UNIST) have come up with a simple, but efficient and eco-friendly alternative which sees the production of edge-selectively functionalized graphene nanoplatelets (EFGnPs) via a dry ball milling graphite in the presence of various gases. The dry ball mill is effectively a type of grinder, traditionally use to grind ores, chemicals and other raw materials into fine powder. It can also be used on a atomic level, as is the case when producing EFGnPs.

Due to the versatility of mechanochemical reactions driven by ball milling, various functional groups could be introduced to the broken edges of graphene nanoplatelets (GnPs) in the presence of appropriate chemical vapors, liquids, or solids in the ball-mill crusher.

The mechanism of edge-selective functionalization in the ball-milling process involves the reaction between reactive carbon species generated by a mechanochemical cleavage of graphitic C-C bonds and gases in a sealed ball-mill crusher. The dormant active carbon species, which remain unreactive in the crusher, could be terminated by subsequent exposure to air moisture. As a result, some oxygenated groups, such as hydroxyl (-OH) and carboxylic acid (-COOH), can be introduced at the broken edges of the preformed EFGnPs with minimal basal plane distortion.

A scanning electron microscope (SEM) is used to demonstrate the mechanochemical cracking of a large grain sized piece of graphite into a small grain size of EFGnPs. Due to the reaction between the newly formed active carbon species at the broken edges of the GnPs and corresponding gases, the ball milling and subsequent workup procedures were found to increase the weight of all the resultant EFGnPs with respect to the graphite starting material. These results indicated that the mechanochemical functionalization of graphite was efficient. The resultant EFGnPs are active enough for the oxygen reduction reaction (ORR) in fuel cells, and hence they will make expensive platinum (Pt)-based electrocatalysts to take a back seat.

Jong-Beom Baek, professor and director of the Interdisciplinary School of Green Energy/Low-Dimensional Carbon Materials Center at UNIST commented:

"We have developed a simple, but versatile ball-milling process to efficiently exfoliate the pristine graphite directly into EFGnPs. Various microscopic and spectroscopic measurements were performed to confirm the reaction mechanisms for the edge functionalization of graphite by ball milling in the presence of corresponding gases and their superior slectrocatalytic activities of the ORR," said Prof. Baek.

More information: Jeon, I. et al. Large-scale production of edge-selectively functionalized graphene nanoplatelets via ball-milling and their use as metal-free electrocatalysts for oxygen reduction reaction, *Journal of the American Chemical Society*, 135(4): 1386–1393. pubs.acs.org/doi/full/10.1021/ja3091643

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