Tailoring of Graphene and Nanotubes by Nickel Cluster under Electron Beam

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Abstract An important catalytic role of transition metal clusters which lower the activation barriers of chemical transformations driven by the e-beam is revealed in two processes in carbon nanosystems: transformation of a graphene flake with attached metal cluster [1] and cutting of carbon nanotubes [2]. Extensive molecular dynamics (MD) simulations within the CompuTEM approach [3] are used to study the transformation of a graphene flake with an attached nickel cluster. New metal-carbon nanoobjects formed as a result of the transformation under the e-beam are found to range from heterofullerenes with a metal patch to particles consisting of closed fullerene and metal clusters linked by chemical bonds. The atomic-scale transformation mechanisms are revealed by local structure analysis.
The cutting of single-walled carbon nanotubes by an 80 keV electron beam catalyzed by nickel clusters is imaged in situ using aberration-corrected high-resolution transmission electron microscopy. MD simulations within the CompuTEM approach provide insight into the mechanism of this process and demonstrate that the combination of irradiation and the nickel catalyst is crucial for the cutting process to take place. The atomistic mechanism of cutting is revealed by detailed analysis of irradiation-induced reactions of bond reorganization and atom ejection in the vicinity of the nickel cluster, showing a highly complex interplay of different chemical transformations catalysed by the metal cluster. One of the most prevalent pathways includes three consecutive stages: formation of polyyne carbon chains from the carbon nanotube, dissociation of the carbon chains into single and pairs of adatoms adsorbed on the nickel cluster, and ejection of these adatoms leading to the cutting of the nanotube. Accounting for the additional knocking out of two and one-coordinate carbon atoms at all stages of this mechanism would enable a complete description of nanotube cutting processes. Significant variations in the atom ejection rate are discovered depending on the process stage and nanotube diameter. The revealed mechanisms and kinetic characteristics of the processes of transformation of a graphene flake with attached metal cluster and nanotube cutting provide fundamental knowledge for the development of new methodologies for control and manipulation of carbon structures at the nanoscale.

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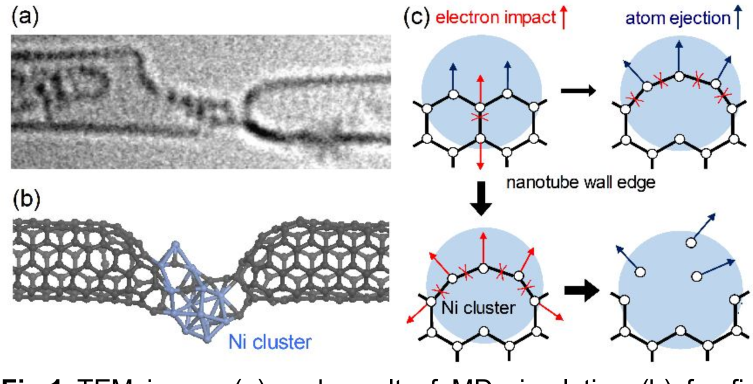

Fig.1 TEM image (a) and result of MD simulation (b) for final stage of nanotube cutting. Scheme showing the mechanism of carbon atom ejection at cutting (c). Bond breaking is shown by red crosses. Atoms that experience electron impacts and directions of momentum transfer from electrons that facilitate this bond breaking are shown by red arrows. The ejection of atoms is shown by blue arrows.