

Enabling atomic resolution electron microscopy at elevated temperature and beyond pressures of a few bar

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Background

Transmission electron microscopy (TEM) is an invaluable tool in knowledge-driven optimization of catalysts. Over the years, important mechanistic insights in chemical processes have been gained by combining the atomic resolution of TEM with miniaturized reactors. This type of reactors confines gas or liquid phase reaction environments to the vicinity of the catalyst between pairs of thin electron-transparent windows and has opened up for in situ and operando studies of catalysts during reactions conditions mimicking industrial catalysis. However, the electron beam has to traverse the reaction environment as well as the windows which, in turn, have to remain impermeable and mechanical stable to sustain pressure differences of up to several bars and therefore typically consist of 15-30 nm thick Si-based membranes. In practical terms, such membranes reduce signal contrast, and eventually resolution. Thus, thinner windows of similar strength and impermeability are needed to further improve imaging conditions.

The class of two-dimensional (2D) materials, and especially graphene, are interesting in this regard. It has been observed that graphene membranes sealing small volumes in a substrate can sustain pressure differences beyond 15 bars before delaminating from the substrate, and in addition, even a single layer of graphene is highly impermeable. 2D materials adhere to substrates via the Van der Waals force, and so graphene's ability to seal off a substrate, is of utmost importance, if graphene is to be employed as window material. At this stage, the performance of graphene-based seals at room temperature, i.e. leakage circumventing the graphene-based seal, exhibits large variation and allows gasses to leave sealed volumes through the interface between seal and substrate, making graphene-based windows impractical. Furthermore, the temperature dependence of the leakage have until now been unknown.

Methods

To investigate the leak from graphene-sealed volumes, we prepared electron transparent cavities and sealed them by mechanically exfoliating few-layer-graphene sheets on top. After exfoliation, the samples were cut to fit a GATAN heating holder. Prior to inserting the sample into the holder and subsequently the electron microscope, the cavities were filled with argon in a pressure chamber. Inside the vacuum of the TEM, the gradual decrease in argon content of the cavities was monitored as a function of time and temperature with Electron Energy Loss spectroscopy using a bottom-mounted Gatan Image Filter.

Results

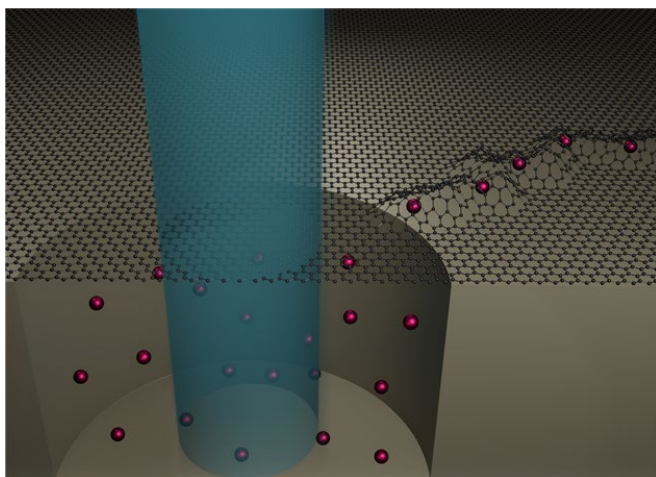
At elevated temperature, the argon content of the cavities was found to decrease exponentially with time in accordance with what has been found at room temperature in previous studies. Furthermore, the exponential rate constant of the decay was itself exponentially dependent on the temperature, i.e. exhibiting an Arrhenius dependency. This indicates that the diffusion from the graphene-sealed cavities is a thermally activated process in which the argon atoms are surpassing an energy barrier. This behavior was found across

different samples and cavities sealed by the same flake, showing the generality of the phenomenon. Surprisingly, repeated emptying and filling of the cavities at elevated temperature drastically improved the leak tightness of the seals, and in one case, the leak rate at room temperature improved 6 orders of magnitude from an already decent origin, as compared to previously reported leak rates. Consequently, some graphene-sealed cavities could after repeated experiments sustain pressures up to approximately 10 bars at 500 °C, while exhibiting a remarkably low leakage.

Conclusion

Our investigations reveal that graphene-based windows can be used for in situ and operando high resolution electron microscopy at elevated temperature and beyond pressures of a few bar. However, thermal engineering of the graphene seal is needed to tune the graphene-based seals' performance properly.

Graphic:



Keywords:

Graphene, Thermal, Seal, TEM, Heating

Reference:

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