Probing Chemical Kinetics in Two Dimensional Materials Using Atomic Resolution Imaging

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The imaging electron beam can be usefully harnessed as a controlled source of energy to promote reactions, increasing their rates and activating additional reaction channels that can be further explored. This enables accurate control of chemical reactions using the key parameters of temperature, electron beam energy, and electron dose rate (flux); variation of these parameters enables the decoupling of contributing mechanisms. The result is a quantitative understanding of thermal pathways in addition to the beam induced mechanisms, maintaining the general relevance of our method rather than it being constrained to only studying the effects of the electron beam.

Focussing on specific examples of atomic-scale defect dynamics in graphene, our first study [1], involving the Stone-Wales defects, exemplifies this principle. Two surprising results emerged concerning the healing of these defects: the thermal route was accessible at room temperature, with comparisons to barrier calculations suggesting that a previously hypothesized catalytic route is active. In addition, our measured rates of the beam induced process invalidated the widely held assumption that the SW healing process must be dominated by kinetic energy transfer from the beam to the atomic nucleus, implying that the electronic nature of defects in graphene is relatively poorly understood.

Although this study successfully determined the kinetics of a specific system, it also highlighted fundamental limitations of the used experimental methodology. Firstly, the sensitivity and frame rate of traditional indirect electron detectors impose a minimum electron dose and temporal resolution per image, resulting in an imaging rate comparable to the average lifetime of the species being studied. In turn this leads to significant difficulties in defect detection. Secondly, manual identification of each defect severely limits the extent of the available statistical data.

In our second study, we overcome the above limitations by using fast counting electron detectors (direct detection) and machine learning to probe graphene defect kinetics at millisecond time resolution. Using a deep neural network data processing protocol, we collect and classify a very large number of divacancy defects $V_2(585)$, $V_2(555\text{-}777)$ and $V_2(5555\text{-}6\text{-}7777)$ and identify specific defect transition processes.

The proposed approach greatly expands the scope of kinetics studies and introduces a "bottom-up" statistical method to the previously "top-down" macroscopic field. It uses direct imaging of materials at atomic resolution as an analytical tool for the quantitative analysis of kinetics of dynamic processes. This provides a new route to the experimental determination of reaction mechanisms and key chemical kinetic parameters such as rate constants, activation energies, and reaction cross-sections.

References

[1] Skowron, S. T., Koroteev, V. O., Baldoni, M., Lopatin, S., Zurutuza, A., Chuvilin, A., & Besley, E. (2016). Reaction kinetics of bond rotations in graphene. *Carbon*, *105*, 176-182.