

In situ electron microscopy for electron radiolysis effect and dose dependence of functional metal oxides

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Advancements of aberration-corrected electron optics system and data acquisition schemes have enabled TEM to acquire images with sub-Ångström resolution and single-atom sensitivity. However, bottleneck of radiation damage is still challenging TEM imaging of soft materials and Knotek-Feibelman effect materials at the atomic level. For the radiation damage, it has been shown that the electron beam may not only alter the shape and surface structure at atomic level, but also induce radiolytic artifacts in chemical reactions at nanoscale, e.g., photocatalysis, metal-insulator transformation (MIT), super-dissolution of oxides [1, 2, 3]. The electron beam effects at nanometer resolution are discussed in this work. One example shows a dose-rate dependence of hydrogen bubble generation accompanying with water dissociation of Pt loaded TiO₂ nanoparticles in a liquid cell during in situ TEM observations. As the dose rate of electron beam is setup to be order of $1 \text{ e}^{-}\text{Å}^{-2}\cdot\text{sec}^{-1}$, the hydrogen bubble appears at around 240 seconds, while as the dose rate is increased to the order of $10^3 \text{ e}^{-}\text{Å}^{-2}\cdot\text{sec}^{-1}$, the appearance of hydrogen bubble is faster by 4 times (at around 60 seconds). It clearly shows that the in-situ observations of photocatalysis can really mix up with radiolysis from the electron beam. Another example, an insulator phase of VO₂ is known to transform to metal phase at 68°C. A nano probe at high electron dose-rate can stimulate phase transformation from insulator phase to metal phase in a VO₂ nanowire even at room temperature.

The electron beam effect must be taken into account for interpretation of in-situ EM observation. The dose-rate of incident electrons becomes a very critical and inevitable degree of freedom that must be controlled to suppress radiolysis artifacts and to reveal pristine structure at atomic resolution. In the present paper, we present a systematical analysis of electron microscopy methodology towards probing in-situ dynamics at high temporal resolution and emphasize in particularly the role of controlling the electron delivery.

References:

[1] Y. Lu, .etc, F.-R. Chen and M. L. Sui, ACS Nano, 2017, 11, 8018–8025, DOI: 10.1021/acsnano.7b02656

[2] Y. Lu, .etc, F.-R. Chen and M. L. Sui, NATURE COMMUNICATIONS, 2018, 9, 2752, DOI: 10.1038/s41467-018-05144-1

[3] Z. Zhang, etc., F.-R. Chen and M. L. Sui, Nano Lett. 2017, 17, 851–855, DOI: 10.1021/acs.nanolett.6b04118