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Probing Atom Dynamics in Excited Nanocrystals

Fu-Rong Chen[1], Dirk Van Dyck[2], Christian Kisielowski[3], Bastian Barton[3], Lars P. Hansen[4], and Stig Helveg [5,*].

[1.] Department of Materials Science and Engineering, City University of Hong Kong, Kowloon Tong, Hong Kong, SAR.
[2.] EMAT, University of Antwerp, Antwerp, Belgium.
[3.] The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, USA.
[4.] Haldor Topsoe A/S, Kgs. Lyngby, Denmark.
[5.] Center for Visualizing Catalytic Processes (VISION), Technical University of Denmark, Kgs. Lyngby, Denmark.
* Corresponding author: stig@fysik.dtu.dk

Advances in transmission electron microscopy (TEM) have opened up for astonishing visualizations of the three-dimensional (3D) atom arrangements in nanometer-sized objects. While the visualization methods often consider the objects as static structures, the atomic-resolution measurements employ intense electron illumination capable of exciting atom displacements that by far exceeds the thermal vibrations. Such beam-induced alterations are notoriously pronounced at surfaces due to the variety of exposed sites of reduced atomic coordination as compared to sites in the bulk. As a result, the dynamic response of nano-scale objects will generally be modulated in space and time and heterogenizes intensities and contrast in TEM images. Here, we present an analytical approach to extract the spatiotemporal information encoded into TEM data in order to account for induced atom dynamics, and in turn, to promote chemical meaningful observations [1].

Our approach exploits the electron exit-wave as the most informative fingerprint of atomic structures. To extract structural information, the exit-wave from a thin object in zone-axis orientation is analyzed within channeling theory. Specifically, atomic column positions in 3D are determined in the image plane from peak positions in the exit-wave and along the beam direction by propagation of intensities [1,2]. Furthermore, a new analytical model is introduced taking advantage of the full exit-wave shape of the atomic columns by a minimum number of parameters including (1) the summed pixel values of an exit-wave atom column, which is proportional to the projected electrostatic potential and thus, to the projected atomic number of the column, and (2) the atomic column radius R, which measures intensity redistribution caused by remaining aberrations as well as vibrations of the atoms [1,2].

The new approach will be showcased by analysis of exit-waves of a Co-Mo-S nanocrystal supported on graphite [1]. The exit-waves are reconstructed from focal image series acquired by bright-field TEM operated at low electron dose-rates (100-300 $e^{-}Å^{-2}s^{-1}$) to induce only weak object excitations and promote object relaxations between successively delivered electrons [3]. In the analysis, atomic column positions are determined at 1.5 Å resolution in 3D based on single-projection-images only. Surprisingly, the phase peak contrast decays, and width increases, of atomic columns located near the edges of the nanocrystal as compared its center. These changes are attributed to enhanced beam-induced atom vibrations near the edges and is sufficiently large to overwrite the chemical information in the phase signal. We demonstrate that our new model is generally applicable to account for such locally varying excitations, and thus, strengthen the stoichiometric interpretation of atomic columns even in the presence of heterogeneous vibrational column blur. Moreover, a series of successive exit-waves reveals

that the edge-confined vibrational blur correlate with substantial atom displacements, resulting in a distribution of metastable atomic motifs at the edges and irregular morphologies of the nanocrystal. A kinetic analysis of the edge restructuring provides insight into the underlying atomic mechanisms and enables an extrapolation to the expected, pristine stoichiometry at zero dose [1,4]. Thus, as a perspective, our approach uncovers a correlation between enhanced vibrations and chemical evolution of the nanocrystal edges with a crystallographic dependency and may, in turn, establish new means for studying heterogeneity in chemical reactivity in small clusters, surfaces and molecules in general.

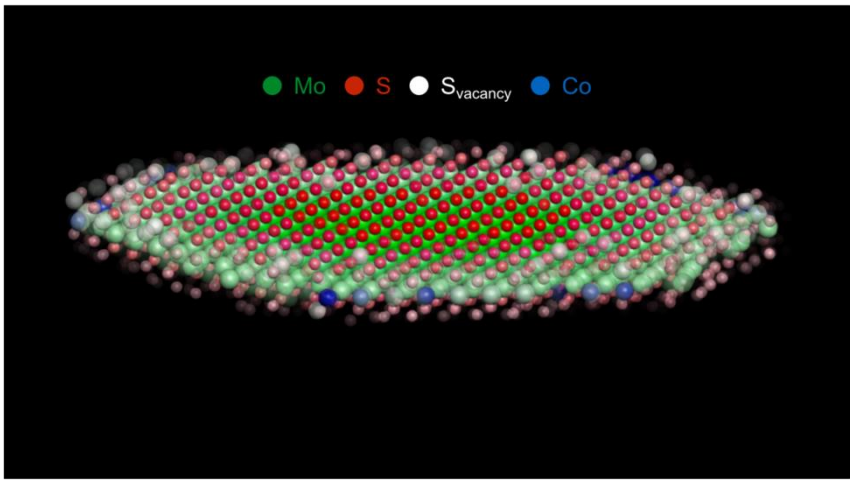

Figure 1. 3D atom dynamic image of a Co-Mo-S nanocrystal. The image is a summation of five 3D atomic-resolution images derived from five successive exit-waves of a Co-Mo-S nanocrystal supported on graphite, as detailed in [1]. The image represents the individual atomic sites in the MoS_2-structure at their 3D location with the colored balls reflecting the chemical content (green=molybdenum, blue=cobalt, red=sulfur, white=sulfur vacancy). Moreover, the color transparency reflects a partial occupancy in the five images, so the image becomes a dynamic representation of the atom displacements among successive images. Adapted from [1].

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