

Nanometer-scale Science and Technology Division Room A222 - Session NS+AS-FrM

Electron-Beam Promoted Nanoscience

Moderators: Omur E. Dagdeviren, Yale University, Qing Tu, Northwestern University

8:20am **NS+AS-FrM-1 Vibrational Spectroscopy in the Electron Microscope**, *Ondrej Krivanek, N Dellby, C Meyer, A Mitelberger, T Lovejoy*
INVITED

Vibrational (phonon) spectroscopy using an electron microscope's primary beam was introduced in 2014, and it has now progressed very significantly. The attainable energy resolution stands at ~ 5 meV (at 30 keV primary energy), our understanding of the electron-matter interaction has deepened, and several types of new applications have been explored.

Phonons can be excited by fast electrons in two fundamentally different ways: by dipole scattering, which is similar to exciting the sample by infrared light, and by impact scattering, which bears a closer resemblance to neutron scattering. Dipole scattering occurs only in polar materials, and it is characterized by small scattering angles (~ 0.1 mrad) and interaction distances of tens of nanometers. Impact scattering involves a direct interaction between the fast electron and an atomic nucleus, and it leads to large scattering angles. Selecting the impact scattering (with an aperture in the diffraction plane) allows the vibrational signal in h-BN to be imaged with atomic (0.2 nm) resolution [1,2]. In elemental Si, impact scattering is dominant, and it allows atomic resolution to be reached without angular selection [3].

The angular (momentum) distribution of vibrational scattering has also been explored [4-6]. Attainable spatial resolution is then inversely related to the angular resolution. Optical and acoustic branches of vibrational scattering have been mapped in hexagonal and cubic BN, and in graphene and graphite.

Dipole scattering provides another exciting possibility: probing the sample from a small distance, by "aloof spectroscopy". This approach limits the maximum energy that can be transferred to the sample with significant probability as $1/b$, where b is the distance of the confined electron beam from the sample. In this way, vibrational properties of biological and other "fragile" materials can be probed without significant radiation damage [7], and this may well revolutionize analysis in the electron microscope. The technique has recently been used to detect isotopic substitution: ^{13}C vs. ^{12}C at a specific site in an amino acid (L-alanine), and to map the distribution of the two species [8].

- [1] C. Dwyer et al., Phys. Rev. Letts **117** (2016) 256101
- [2] F.S. Hage et al., Phys. Rev. Letts **122** (2019) 016103
- [3] K. Venkatraman et al., arXiv:1812.08895 (2018)
- [4] F.S. Hage et al., Sci. Adv. 2018;4:eaar7495 1-5
- [5] R. Senga et al., arXiv:1812.08294 (2018), Nature (2019, in print)
- [6] Lovejoy et al. Proceedings 2019 M&M Conference (in print)
- [7] P. Rez et al., Nature Comms **7** (2016) 10945, doi: 10.1038/ncomms10945
- [8] J. Hachtel et al., Science **363** (2019) 525–528

9:00am **NS+AS-FrM-3 In-situ Electron Microscopy of Localized Surface Plasmon Initiated Reactions**, *Canhui Wang, W Yang, A Bruma*, UMD/NIST; *R Sharma*, National Institute of Standards and Technology (NIST) **INVITED**
Excitation of localized surface plasmon (LSP) resonance on metal nanoparticles has been shown to overcome the reduced the energy barrier for photochemical reactions, even allowing certain reactions to occur at room temperature. (1-2) Understanding the reactions promoted by LSP resonance at the nanoscale is important for designing efficient photocatalytic systems for a wide range of energy and environmental applications. However, many important questions related to this type of reaction process remain unclear due to the complexity of the reaction kinetics, and lack of spatial resolution available with optical methods. Details such as the location of gas adsorption sites, how the energy is being absorbed and released, and how those details are correlated to the structure of the catalyst nanoparticles, remain elusive and are only hinted by theoretical calculations.

Here we use *in-situ* electron microscopy and combine an ensemble of data acquisition and processing techniques to characterize LSP-initiated

chemical reactions at high spatial resolution using an aberration-corrected environmental scanning transmission electron microscope. Electron energy loss spectrum (EELS) imaging is used to acquire both elemental and LSP resonance maps from the same area that contains the plasmonic nanoparticles. The elemental maps allow us to locate the gas adsorption sites, the elemental distribution of the reactants and plasmonic nanostructures, as well as the spatial distribution of the solid reaction products, with nanometer resolution. The LSP-EELS maps provide insight into how the energy is channeled from the fast electron to the plasmonic nanostructure. Localized reactant consumption (mass loss) distribution is mapped in terms of thickness changes by subtracting the thickness map acquired after the reaction from the thickness map acquired before the reaction. This allows us to pinpoint the reaction hotspot near the nanoparticle surface. The LSP induced electric field distribution near the nanoparticle surface is simulated using the metallic nanoparticles boundary element method (MNPBEM) (3) and compared with the reactant mass loss map. These techniques allow us to explore and study previously unknown LSP initiated reactions with unprecedented details on the sub-particle level. (4) The results improved the understanding of the dynamics of LSP initiated reactions and give insights into nanoparticle engineering for optimizing reaction efficiency.

1. Mukherjee S, et al. (2012) Nano letters 13(1):240-247.
2. Thomann I, et al. (2011) Nano letters 11(8):3440-3446.
3. Waxenegger, J, et al. (2015) Comp. Phys. Commun. 193, 138.
4. Yang, W.C.D, et al. (2019) Nature Mater. 1.

9:40am **NS+AS-FrM-5 Nanoscale Manipulation of Redox of Ag by Electron Beam**, *Jianguo Wen, H Sheng*, Argonne National Laboratory; *J Wang*, Wuhan University, China **INVITED**

Employing electrons for direct control of nanoscale reaction is highly desirable since it provides fabrication of nanostructures with different properties at atomic resolution and with flexibility of dimension and location. In 2016, Kalinin et al summarized past experiments of manipulating atoms with scanning transmission electron microscopy (STEM) and proposed to utilize the imaging tool to create structures atom by atom (1). Here, applying *in situ* transmission electron microscopy, we show nanoscale oxidation and reduction of Ag can be manipulated by electron beam. We demonstrated fabrication of an array of 3 nm Ag_2O nanodots in an Ag matrix.

Under high vacuum environment ($\sim 10^{-7}$ Torr pressure), oxygen in a TEM can be ionized by high-energy electron beam and causes oxidation of Ag. After enough e-beam illumination, a growth of Ag_2O on the surface is observed when electron beam flux is below $\sim 5 \times 10^5 \text{ e}/\text{\AA}^2\text{s}$. Ag_2O islands epitaxially grow on Ag surface with orientation relationship of $\langle 110 \rangle_{\text{Ag}} // \langle 110 \rangle_{\text{Ag}_2\text{O}}$ and $\{111\}_{\text{Ag}} // \{002\}_{\text{Ag}_2\text{O}}$ in most cases. In-situ high-resolution transmission electron microscopy (HRTEM) imaging shows that Ag_2O nucleates at atomic steps on Ag surfaces.

With the increase of electron-beam intensity above $\sim 5 \times 10^5 \text{ e}/\text{\AA}^2\text{s}$, the formed Ag_2O islands can be fully reduced back to Ag, such that a fully reversible oxidation and reduction of Ag is achieved by varying electron beam intensity. The growth and reduction of Ag_2O island is electron-beam dose rate dependent, a near equilibrium state has been achieved at the dose rate of $\sim 5 \times 10^5 \text{ e}/\text{\AA}^2\text{s}$. A brief explanation for this electron-beam dose rate dependence is the competition between the electron-beam ionization induced oxidation of Ag and electron stimulated desorption induced reduction of Ag_2O . Aberration-corrected HRTEM observation reveals that O atoms are preferably inserted and extracted along the $\{111\}$ close-packed planes of Ag, leading to the nucleation and decomposition of nanoscale Ag_2O islands on the Ag substrate.

Taking another step further, patterned oxidation has also been tested to verify the reliability of the electron-beam irradiation as a nanofabrication technique. By controlling probe size, electron flux, and dwell time, we demonstrated fabrication of an array of 3 nm Ag_2O nanodots in an Ag matrix. These findings do not only facilitate the basic understanding of oxidation/reduction kinetics in Ag- Ag_2O , but also open up a promising approach for precise fabrication of nanostructures with metal or semiconductor properties in devices.

- 1) Kalinin, Sergei V., Albina Borisevich, and Stephen Jesse. "Fire up the atom forge." *Nature News* 539.7630 (2016): 485.

Friday Morning, October 25, 2019

10:20am **NS+AS-FrM-7 Dynamics of Material Surfaces and Interfaces – The Good, the Bad and the Electron Beam, Jakob Birkedal Wagner**, DTU Nanolab, Technical University of Denmark, Denmark **INVITED**

A good understanding of the dynamics and formation mechanisms of surfaces and interfaces at the nanometer scale is of great importance in order to exploit the controllability of nanostructures and their applications in photovoltaics, electronics, sensors, *etc.* on an industrial scale.

In situ electron microscopy serves a unique platform for monitoring and studying structural dynamics at length scales from micrometer down to atomic scale and temporal resolution approaching millisecond range. In addition, elemental and chemical information is gained from spectroscopic techniques with spatial resolution approaching the atomic scale.

Here, I will present a few cases of the surface and interface dynamics studied at the microscopy facility at Technical University of Denmark. This includes surface dynamics of supported nanoparticles (catalyst) [1] under harsh environment (elevated temperature, gas and electron beam), as well as interface dynamics of grain boundaries in metal thin films [2], growth of nanostructures from bottom-up processes [3-6] and volatility of soot oxidation catalysts. [7]

The influence of the high-energetic electron beam will also be discussed in terms of sample damage and controlled reaction enhancement.

References

- [1] P. Liu, PhD thesis (2018), Technical Unity of Denmark
- [2] A. Bastos Fanta *et al.* Materials Characterization 139, 452 (2018)
- [3] J. Kling *et al.* Carbon 99, 261 (2016)
- [4] L.. Zhang *et al.* ACS Nano 11, 4483 (2017)
- [5] S. Rackauskas *et al.*, Scientific Reports 7, 12310 (2017)
- [6] W. F. van Dorp *et al.*, Nanotechnology 24, 345301 (2013)
- [7] D. Gardini *et al.*, Appl. Catal. B, 183, 28 (2016)

11:00am **NS+AS-FrM-9 Atomic-Scale Mechanism of Unidirectional Oxide Growth, Xianhu Sun, W Zhu, D Wu**, SUNY Binghamton University; Z Liu, University of Pittsburgh; X Chen, L Yuan, SUNY Binghamton University; G Wang, University of Pittsburgh; R Sharma, National Institute of Standards and Technology (NIST); G Zhou, SUNY Binghamton University

A fundamental knowledge of the unidirectional growth mechanisms is required for precise control on size, shape, and thereby functionalities of nanostructures. Using transmission electron microscopy that spatially and temporally resolves CuO nanowire growth during the oxidation of copper, here we provide direct evidence of the correlation between unidirectional crystal growth and bicrystal boundary diffusion. Based on atomic scale observations of the upward growth at the nanowire tip and oscillatory downward growth of atomic layers on the nanowire sidewall, we clearly show that bicrystal boundary diffusion is the mechanism by which Cu atoms are delivered from the nanowire root to the tip. Together with density-functional theory calculations, we further show that the asymmetry in the corner-crossing barriers promotes the unidirectional oxide growth by hindering the transport of Cu atoms from the nanowire tip to the sidewall facets. We expect broader applicability of our results in manipulating the growth of nanostructured oxides by controlling the bicrystal boundary structure that favors anisotropic diffusion for unidirectional, one-dimensional crystal growth for nanowires or isotropic diffusion for two-dimensional platelet growth.

11:20am **NS+AS-FrM-10 Application of Electron-beam-excited Localized Surface Plasmon Resonance to Provide Guidelines for Plasmonic Catalysts, Wei-Chang Yang¹, C Wang, L Fredin, H Lezec, R Sharma**, National Institute of Standards and Technology (NIST)

Optically-excited localized surface plasmon (LSP) resonances have been used to induce chemical reactions, such as hydrogen dissociation and ethylene epoxidation. Energy harnessed by plasmonic nanostructures and transferred to adsorbed reactants is theorized to initiate these chemical processes by compensating for the heat required otherwise. As we know, there are three important steps for designing a plasmonic catalyst system: (1) adsorption of reactants; (2) adequate resonance energy to overcome the reaction barrier; and (3) desorption of products. However, they have not been resolved at a sub-nanoparticle scale using optical methods. Herein, we demonstrate that the sub-particle information, gained from electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL), can be used to measure these steps for selected reactions.

LSP resonances, excited by electrons, on shape-controlled Au nanoparticles, were exploited to drive CO disproportionation: $2\text{CO}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{C}_{(s)}$, at room temperature (commonly initiated by heat above 400 °C) in an environmental scanning transmission electron microscope equipped with a monochromated electron gun. Triangular Au nanoprisms were synthesized and loaded on TiO₂ support in a cantilevered configuration. *In situ* core-loss EELS was used to detect CO adsorption on the Au surfaces, for the first time, revealing the preferential adsorption sites at selective edges but not on the entire surfaces. Low-loss EELS maps of the Au nanoprisms showed that the electron beam was most efficiently coupled with the LSP dipole mode, indicated by the maximum EELS intensity, when placed at the cantilevered corner, suggesting a strong electric field caused by this specific mode at the same corner. *In situ* EELS showed that energy shifts occurred to the LSP resonance in CO environment and disappeared after CO evacuation, indicating a change in electron density of the Au particle as CO was adsorbed and desorbed, respectively. Energy transferred to the adsorbed CO was identified based on the spectral difference between EELS and CL. Carbon deposits, resulting from room-temperature CO disproportionation mediated by the LSP resonance, were detected by core-loss EELS at the cantilevered corner edge after evacuating CO. This shows that the active sites on the nanoprisms are where the preferable CO adsorption sites and the locations of maximum field amplitude superimpose.

Our findings provide unprecedented information on an LSP-induced chemical reaction with nanometer precision, shedding light on the design principles for new plasmonic catalysts that enable low-temperature reactions.

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