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Probing Response and Functionality in Active Materials Systems with *In Situ* Electron Microscopy

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The response of a materials system to an applied stimulus is often critical to many technological applications. While fundamental materials properties govern how a material system will respond, complex electronic, mechanical, magnetic, catalytic or optical behaviors may take place in composite systems with different geometric configurations. Static observations provide no direct information about stimuli-response behavior in a material. For example, although materials properties are governed by atomic structure, knowing the coordinates of every atom in an oxide nanoparticle does not directly reveal its electronic, optical, chemical or transport properties. While computational materials science has made great progress, *ab initio* prediction of the dynamic responses of a system is often a formidable task even with contemporary high-performance computers. Dynamic *in situ* electron microscopy is able to directly provide information on the response of materials to applied stimuli.

In an electron microscope, the stimuli-response behavior may manifest in changes to imaging, diffraction or spectroscopic signals. The speed of the system response will depend on both the thermodynamic driving force (the magnitude of the change in applied stimuli) and the underlying kinetics of the response mechanism operating in the material. The system behavior may be complex, and, unambiguously elucidating stimuli-response relationships may requires systematic variation of many experimental parameters over extended periods of time. Here we describe ways in which the *in situ* changes to such signals can be employed to describe catalytic and optical responses.

We have been developing methods to track stimuli-response of materials systems for heterogeneous catalysis. Such experiments involve simultaneous collection of many signals over extended periods of time. For example, in a recent investigation of the response of Ru nanoparticles to gases and heat, we ran a single experiment for 55 hours in order to unambiguously determine structure-reactivity relations for catalysis [1]. In addition to imaging the Ru particles, we also varied and tracked critical reactor parameters including partial pressures of O_2, CO and CO_2, temperature and the reaction rate. The extended duration of the experiment was necessary to accommodate sluggish kinetics and the requirement for the system to reach equilibrium each time a stimulus condition was changed. Changing stimuli allowed the dynamic behavior of metastable RuO_2 overlayers to be characterized and understood. Only by correlating changing stimuli and response signals, could we conclude anything about the relevance of RuO_2 surface layers to structure-reactivity relations for catalytic CO oxidation over Ru catalysts.

This work also highlighted the importance of having a deeper understanding of the ambient environment around the TEM sample. In general, a sample stimulus must be applied from an external source (electrical contact, flowing gas or liquid, external light source etc…). For gas cell reactors, the sample stimuli is created by the heat and mass transport processes taking place throughout the entire reactor system. Consequently, it is necessary to have suitable chemical engineering models to describe and fully

understand the entire system. We have employed finite element methods to model the inside of the differentially pumped reactors available on Thermo Fishers Titan environmental transmission electron microscope [2]. Such models are essential to correctly interpret dynamic processes associated with stimuli-response experiments. For example, for our recent work on the role of fluxionality on catalysis, modelling was essential to link atomic resolution structural dynamics with chemical kinetics and catalytic functionality [3, 4].

Electron microscopy approaches can also be employed to probe optical stimuli-response in materials. Since a material's response to a fast electron beam shares features in common with its response to photons, the electron beam can be used to mimic optical probes and has been successfully employ to study plasmonic, phononic and excitonic modes. The advantage of using the electron beam as a source of electromagnetic stimulation, is that it allows the stimuli/response behavior to be investigated with high spatial resolution. We have employed this approach to explore photonic modes in nanoparticles and nanoparticle aggregates [5]. These so-called guided light or cavity modes, have a strong dependence on particle shape and different modes can be excited by placing the electron beam at different locations around the nanoparticle using the so-called aloof beam geometry. The excitation strength of a particular mode also depends on the local environment such as the geometric arrangements due to long-range coupling with nearby particles. With *in situ* electron microscopy, the dynamic changes in the response can be probed during heating and gas exposures where particle shape and composition can be altered. Such an approach allows the photonic response to be engineered and explored *in situ* (see Yifan Wang work in current proceedings) [6].

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