Localized Vibrational Spectroscopy on Catalytic Nanoparticles with Focused Electron Beams

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Introduction
Probing and understanding the interactions between molecules and nanoparticle surfaces remain a major challenge which significantly impacts the field of surface chemistry and catalysis. Vibrational spectroscopies such as infrared and Raman scattering are powerful techniques that can analyze bonding arrangements, identify chemical compounds and probe many other important properties. They provide fingerprints of functional groups and play a critical role in elucidating the surface intermediates that may be formed during a catalytic reaction. There has been remarkable progress on improving the spatial resolution of a variety of optical techniques for detecting vibrational modes. The ultimate goal for high spatial resolution vibrational spectroscopy would be the ability to perform the analysis with molecular resolution. This would provide a completely new tool for probing local structure and chemistry by, for example, allowing individual molecules to be detected and correlated with local atomic structure. Recent work has pushed the energy resolution of electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) to be better than 10 meV. This makes it possible to probe vibrational excitations with a resolution which may ultimately be limited by the electron probe size of 1 Å [1]. Here we employ this new ability to perform high resolution EELS to locally detect the vibrational modes of adsorbate molecules on nanoparticle surface and correlate this with atomic structure. This provides a new tool for probing catalytically relevant adsorbates on nanoparticle surfaces.

Materials and Methods
Ta2O5 nanoparticles were synthesized using a solvothermal process followed by calcination to give better crystallinity and relatively well-defined morphology. The material was subject to typical water splitting conditions by submerging in liquid water and exposing to UV light (xenon lamp) for several hours. The powders were prepared for TEM by dispersing over a holey carbon film. They were loaded into a Nion UltraSTEM electron microscope equipped with a C3 aberration corrector capable of forming a focused electron probe of 1 Å. The microscope is equipped with an electron source with monochromator and yields electron energy-loss spectra with a resolution of better than 15 meV. Energy-loss spectra were recorded from the Ta2O5 surface region using the so-called aloof beam mode. In this mode, the electron beam is positioned outside the nanoparticle and scanned from the vacuum onto the particle. The delocalized character of the electrostatic interaction allows vibrational spectra to be detected in this mode while minimizing electron beam damage to the particle surface.

Results and Discussion
Figure 1 shows atomic resolution Z-contrast images from a facet of Ta2O5 nanoparticles that were used in water splitting experiments. The atomic fringes terminate below the surface and the surface appears to be covered with a disordered layer. The insert is the aloof beam energy-loss spectrum which clearly shows a peak at about 460 meV associated with the O-H stretch on the disordered surface. Other nanoparticles that do not show the disorder layer give a much weaker O-H stretch. This demonstrates that it is now possible to correlate the vibrational fingerprint from a nanoparticle surface with its atomic structure.

We will apply this approach to a series of TiO2 and Ta2O5 based model water splitting photocatalysts. They will be functionalized with metallic and oxide co-catalysts for water reduction and oxidation. We have already employed Ni-NiO core-shell architectures and demonstrated both high initial activity and deactivation due to photocorrosion of the Ni core component. Aloof beam vibrational spectroscopy will be employed to map the hydroxide concentration on different surfaces of used and partially deactivated catalysts. The local concentration of hydroxide will be correlated with the degree of photocorrosion observed in the particles.

Figure 1: Z-contrast image from a Ta2O5 nanoparticle. The lattice fringes terminate 0.5 nm below the particles surface. The inset shows the aloof beam EELS with a peak at 466 meV corresponding to the O-H stretch.

Significance
This work shows a completely new form of high resolution vibrational spectroscopy. The approach is based on exciting the vibrational modes with subnanometer focused electron beams. It has great potential for catalyst research because it allows adsorbate layers to be locally probed on the surfaces of nanoparticles.

References
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