Detection of Water and Its Derivatives on Individual Nanoparticles using Vibrational Electron Energy-Loss Spectroscopy

Peter A. Crozier^{1*}, Toshihiro Aoki² and Qianlang Liu¹

¹School for the Engineering of Matter, Transport and Energy, Arizona State University, 501 E. Tyler Mall, Tempe, Arizona 85287-6106, USA.

²LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe, Arizona 85287-1704, USA.

*Correspondence to: P.A. Crozier, crozier@asu.edu.

ABSTRACT

Understanding the role of water, hydrate and hydroxyl species on nanoparticle surfaces and interfaces is very important in both physical and life sciences. Detecting the presence of oxygen-hydrogen species with nanometer resolution is extremely challenging at present. Here we show that the recently developed vibrational electron energy-loss spectroscopy using subnanometer focused electron beams can be employed to spectroscopically identify the local presence and variation of OH species on nanoscale surfaces. The hydrogen-oxygen fingerprint can be correlated with highly localized structural and morphological information obtained from electron imaging. Moreover, the current approach exploits the aloof beam mode of spectral acquisition which does not require direct electron irradiation of the sample thus greatly reducing beam damage to the OH bond. These findings open the door for using electron microscopy to probe local hydroxyl and hydrate species on nanoscale organic and inorganic structures.

1. INTRODUCTION

Water and its derivatives are among the most abundant chemicals on earth and its interaction with surfaces impacts diverse fields including biology, materials, catalysis, atmospheric aerosols, electrochemistry, and geochemistry [1]. Moreover, the accumulation of hydrogen species at surfaces and interfaces may play a critical role in functionalities related to chemical activity as well as charge and mass transport [2-5]. OH bond fingerprints can be detected with vibrational spectroscopies using infrared light [6, 7], Raman scattering [8], neutrons [9], low-energy electrons [10, 11], and inelastic electron tunneling [12]. There has been significant progress on improving the spatial resolution of a variety of optical techniques for detecting vibrational modes. For IR and Raman spectroscopy, near-field techniques have been developed that can approach resolutions of tens of nanometers on relatively flat surfaces in favorable cases [13-17]. However, in spite of the high spectral resolution of this approach, local detection of oxygen-hydrogen bonds and direct correlation with nanometer and atomic structure remains extremely challenging.

Transmission electron microscopy (TEM) is ideal for exploring nanometer and subnanometer structures with atomic resolution. For imaging, a resolution of 0.5 Å has been demonstrated and 1 Å is now routinely available in both aberration corrected TEM and scanning transmission electron microscopes (STEM) [18-20]. In a STEM, a highly focused electron probe is scanned across the specimen while recording the spatial variation in a signal of interest. Electron energy-loss spectra (EELS) acquired with such a small probe may be highly localized and the associated electronic excitation allows elemental composition to be determined with atomic resolution [21, 22]. Moreover, the near-edge fine structure in EELS edges can provide a wealth of information on local bonding and electronic structure. In spite of this outstanding

spatial resolution, unambiguous, spectroscopic, local detection of water and OH species remains challenging with electronic excitation spectroscopy. The presence of hydrogen in solids must be inferred by careful analysis of near-edge fine structure or the valence-loss part of the spectrum without destroying the OH bond [23].

Recent developments in electron source monochromation have dramatically improved the energy resolution of EELS and now makes it possible to detect localized vibrational modes within the electron microscope [24]. The information available in this new form of EELS is similar to that from other vibrational spectroscopies and provides a completely new approach for high spatial resolution characterization of samples. This approach has great potential for unambiguous detection of **hydroxyl** species because a strong vibrational peak should be present in the energy-loss spectrum at around 450 meV (3600 cm^{-1}), among the highest energies for vibrational excitations. Hydrogen is particularly sensitive to radiation damage in the electron microscope because the low mass of the proton facilitates high energy transfers from the electron beam which can result in mass loss. For example, even at the relatively low accelerating voltage of 60 kV, **139** eV of energy can be transferred to a hydrogen atom from the electron beam. The delocalized component of the electron-solid interaction allows the OH vibrational signal to be excited even when the beam is outside the sample, so-called aloof beam EELS, thus greatly reducing radiation damage. Here we demonstrate that this OH stretch signal can be detected with ultra-high energy resolution EELS in hydroxides and hydrates and correlated with high spatial resolution structural information from nanoparticles. We also show that water species can be detected on the surfaces of individual 60 nm particles of MgO.

2. MATERIALS AND METHODS

Samples of $\text{Ca}(\text{OH})_2$, H_3BO_3 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were prepared for TEM by crushing the powders and dispersing over holey carbon films. MgO cubes were prepared by burning Mg ribbon in air and collecting the smoke on a holey carbon film. The sample was then exposed to water vapor for 30 s by holding the TEM sample above a beaker of water. Spectra were recorded from these samples using a Nion UltraSTEM fitted with a monochromator, an aberration corrector and a Gatan Enfium spectrometer [24]. The microscope was operated at 60 kV and the typical energy resolution was between 15 – 30 meV (the larger resolution was sometimes employed to increase the signal to noise in the spectrum) with a typical dwell time of 30 – 60 s. There are two possible acquisition modes for EELS. In transmission mode (the most commonly used approach), the beam travels directly through the sample. In the so-called aloof-beam mode, the electron beam is positioned several nanometers outside the sample as illustrated schematically in Fig. 1 [25, 26]. The aloof-beam mode is employed for many of the measurements performed here because it dramatically reduces radiation damage [24, 27, 28]. Spectra were recorded in both transmission mode and in aloof beam mode with a convergence semi-angle of 12 mrad, a collection angle of 30 mrad and a probe size of about 0.5 nm. In some cases, linescans were recorded in which a series of spectra were stored as the beam was moved from the vacuum into the bulk. The zero-loss peak was usually saturated when spectra were acquired in the aloof beam mode. The spectra were calibrated by assuming the center point of the saturation plateau corresponds to zero energy loss. The systematic error in the energy calibration has not been accurately determined but based on comparison with published Raman and IR data (see Results section) appears to be better than 5 meV at around 450 meV. Sample charging was

not a significant problem in these measurement because the beam current with monochromation is low and in aloof beam mode, fewer secondary electrons are emitted by the sample.

3. RESULTS AND DISCUSSION

3.1 Detection of OH Stretch from Hydroxides

Fig. 2a is the aloof beam energy-loss spectrum obtained when the electron probe is positioned 10 nm outside the surface of an Ca(OH)_2 crystal showing a pronounced peak at 454 meV with a full-width half maximum (FWHM) of around 24 meV. The measured energy of the OH stretch mode from Raman and IR spectroscopy from the same compound lies in the rang 448 – 451 meV [29, 30] which is in agreement with the EELS value. This proves that vibrational EELS in the TEM can unambiguously detect the presence of OH bonds in samples. Other hydroxides have also been investigated with the aloof beam mode and show similar results. A typical spectrum recorded in aloof beam mode from boric acid is shown in Fig. 2b. The OH stretch was also observed in H_3BO_3 powder at an energy of about 453 ± 2 meV with a FWHM of 20 meV. The width of the peak is close to the instrumental width in this case.

Fig. 3a and b show a Z-contrast image of a Ca(OH)_2 particle and the variation in the intensity of the OH stretch peak as the probe is scanned from outside to just inside the sample. The OH signal is maximized when the probe is positioned just at the sample surface and falls to about 40% of this maximum when the probe is 40 nm away from the surface. The drop in the vibrational signal when the beam enters the sample results from both radiation damage and elastic scattering effects. The latter effect can scatter electrons through an angle larger than the spectrometer entrance aperture resulting in a reduction in the collected signal. Elastic scattering increases with increasing sample thickness. The zero-loss peak (ZLP) intensity is also affected in the same way and should be reduced by approximately the same fraction. To correct for this

elastic scattering effect, the OH stretch signal can be normalized to the intensity of the zero-loss peak. In these experiments, the ZLP is often saturated at the center but a normalization can still be performed by using a sideband on one side of the ZLP maximum away from the peak center. In this case a region on the negative energy side of the peak was selected. The normalized OH stretch signal is plotted in Fig. 3c. The **normalized** OH signal drops more slowly than the uncorrected signal of Fig. 3b but the rate of drop is not constant or **increasing**. The reason for the significant drop in the OH signal even after normalization is not yet understood. Radiation damage does not seem to be the likely explanation due to the arguments outlined in the next few paragraphs.

The change in intensity of the aloof energy-loss signal with beam position from the sample can be calculated with dielectric theory [25]. **Assuming non-relativistic conditions and that the edge of the TEM sample can be approximated as an infinite flat slab, the spectral intensity, $S(E)$, at energy-loss, E , can be related to the complex dielectric function, ϵ , the beam position from the sample surface, b , through the relationship**

$$S(E) \propto K_o \left(\frac{2\omega b}{v} \right) \text{Im} \left[\frac{-1}{\epsilon(E)+1} \right] \quad (1)$$

with v the electron velocity, $E = \hbar\omega$, $\hbar = h/2\pi$ with h the Planck constant, and K_o is a zeroth order modified Bessel function. The Bessel function contains the spatial dependence of the signal and is also plotted scaled to the experimental data in Fig. 3b. For small probe distances, the flat slab approximation is not good for this particular irregular particle but the theory gives a good fit to the experimental observations for values of b greater than 5 nm. **The above equation ignores relativistic effects that may be observed in low-loss EELS especially when the electron beam exceeds the speed of light in the medium i.e. the Cherenkov condition is satisfied [31-36]. The**

Cherenkov condition will be satisfied if $n > c/v$ where n is the refractive index of the medium and c is the speed of light in vacuum. For 60 kV electrons, this condition will be satisfied when the refractive index exceeds 2.24. For the range of energy-loss and materials being considered here, the refractive index is always less than 1.7 so we ignore retardation effects.

The aloof beam mode is useful for minimizing radiation damage because the probability of energy transfer decreases as the electron distance from the sample increases [27]. Fig. 4a shows the valence-loss spectrum from Ca(OH)_2 recorded in aloof mode (beam 6 nm outside sample) and in transmission mode (beam 10 nm inside sample). Both spectra show a bandgap of approximately 6.5 eV but the aloof-mode spectrum shows prominent peaks at 7.3 and 8.4 eV which do not show up in the transmission spectrum. The leading tail on the conduction band edge in the transmission spectrum extends almost 3 eV into the bandgap and is consistent with a large number of defects introduced as a result of beam damage. These features are not present in the aloof-beam spectrum demonstrating that radiation damage is much smaller in the aloof-beam mode.

Interestingly, the vibrational spectra from the aloof- and transmission-modes (see Fig. 4b and c) look identical. The vibrational loss at 450 meV is much more delocalized than the valence loss at 7.5 eV. When the electron beam passes through the Ca(OH)_2 , a hole is often drilled that is a few nanometers wide. The material around the mouth of the hole is severely damaged and is likely to have been mostly depleted of hydrogen. This causes a change in the electronic structure of the material which shows up in the valence-loss spectrum. Detailed modelling of the energy-loss spectrum for cylindrical geometry has been treated in both the relativistic and non-relativistic limits [37-39]. These expressions could be employed to make an accurate estimate of the fractional contributions of different cylindrical volumes around the hole to the EELS

spectrum. However, a rough estimate can be obtained from the planar geometry of the slab model. Equation (1) gives the probability of inelastic scattering when the beam is outside the sample at distance b , the impact parameter. The relative change in the scattering probability P_{rel} with impact parameter is contained in the Bessel function term i.e.

$$P_{rel} \propto K_0\left(\frac{2\omega b}{v}\right) \quad (2)$$

with v the electron velocity, $E = \hbar\omega$ and K_0 is a zeroth order modified Bessel function. This relative probability is plotted as a function of the b for the OH stretch at 450 meV and the valence band edge of Ca(OH)_2 at 7.5 eV in Fig. 4d. This shows that, for a given value of impact parameter, it is much easier to excite low-energy modes than high-energy modes. This demonstrates why aloof beam vibrational EELS is ideal for probing beam sensitive materials. The vibrational modes are easily excited at impact parameters greater than 20 nm but the ionization probability (the conduction band edge in this case) is only very weakly excited. The absence of knock-on damage, which requires direct collisions with the material [40], and the large reduction in ionization events greatly reduces beam damage in hydroxides and hydrates.

As Fig. 4 shows, the vibrational spectra from the aloof and transmission modes look identical whereas the valence loss signals at 7.5 eV is quite different. This is because the valence loss excitations are more localized and more sensitive to the damaged materials around the mouth of the hole. Fig. 4d shows that the valence-loss signal drops by 80% within 7 nm whereas the vibrational signal does not fall by the same percentage until 60 nm. The vibrational EELS probes a much larger volume than the damaged zone and this explains the relative insensitivity of the vibrational EELS to localized damage.

3.2 Detection of OH Stretch from Hydrates

Hydrates also have vibrational peaks at similar positions in the spectrum. The number and location of the peaks will be influenced by the chemical environments of the water and dissociated water in the structure. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is a prototype example of a typical hydrate. It is extremely sensitive to electron irradiation and easily loses both water and nitrogen groups [41]. Fig. 5a shows the OH vibrational fingerprint for $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ obtained when the probe was positioned about 10 nm outside the sample. The peak is centered at around 430 meV which is almost 25 meV below the corresponding stretch for the hydroxides. It is also asymmetric and much broader than the corresponding hydroxides with a FWHM of around 80 meV. The energy-loss spectrum is compared to the infrared spectrum from published data in Fig. 5b and c [42]. The EELS signal was integrated over several positions outside the sample, corrected for background, inverted and plotted against wavevector (in units of cm^{-1}). Even taking the poor spectral resolution into account, there is good agreement between the aloof-beam EELS and the IR spectrum showing that hydrate species can be readily fingerprinted and differentiated from hydroxyl species with EELS.

3.3 Analysis of Nanoparticle Surface Layers with STEM EELS

At the present time, the spatial resolution of the aloof beam vibrational EELS is tens of nanometers. However, having this nanometer resolution vibrational signal in a high resolution electron microscope allows it to be directly correlated with subnanometer or atomic level structural information obtained from imaging. Fig. 6a shows an annular dark-field image of a 60 nm MgO particle which was exposed to water vapor. The nanoparticle is bounded by {100} facets and the valence-loss spectra in transmission and aloof beam modes are displayed in Fig. 6b. The transmission spectrum shows the usual bulk bandgap of 7.3 eV whereas the spectrum recorded in the aloof beam mode shows intensity within the bandgap starting at around 5.6 eV.

This bandgap feature is discussed in considerable detail in another manuscript published from the FEMMS meeting [43]. In this case this feature is associated with the presence of hydroxyl species on the surface of the MgO crystal. However, in general it is not always easy to identify the origin of a feature in the valence-loss spectroscopy and this is where vibrational EELS can be helpful.

The vibrational spectrum recorded in aloof beam mode is also shown in Fig. 6c and shows a broad peak at 430 meV which unambiguously demonstrates the presence of water species on the surface [44]. EDX nanoanalysis (not shown) indicates only the presence of Mg and O at the surface suggesting that the surface species is some form of $\text{Mg}(\text{O}_x\text{H}_y)$. Thus the vibrational spectroscopy allows us to conclude that the (100) surface of this particular MgO cube is terminated with water species. This is the first time that vibrational spectroscopy has been employed to probe the surface composition of a single 60 nm oxide particle. The sensitivity of the approach is not well known at the moment although preliminary calculations suggest that subnanometer sensitivity on oxides should be achievable. A detailed exploration of this will be provided in future work.

The high degree of delocalization in the aloof beam mode raises the question about the spatial resolution of the technique. The early work on low-energy EELS discusses long-range dipole scattering and short-range impact scattering [11]. Moreover, high-angle annular dark-field imaging arising from phonon scattering suggests that there is a high spatial resolution contribution to vibrational EELS. It is still too early to form any general conclusions about the ultimate practical resolution available with vibrational EELS using the current generation of monochromated instruments. For the forward scattering, aloof beam spectroscopy shown here, the more delocalized dipole scattering seems to dominate. Although the dipole scattering is

delocalized, the ability to perform spatially resolved spectroscopy will often allow the vibrational signature to be correlated with nanometer resolution features determined with atomic resolution STEM signals. Thus even with the current practical resolution constraints, these findings open the door for probing local hydroxyl and hydrate species on the surfaces of oxide nanoparticles.

4. CONCLUSIONS

We have shown that vibrational EELS in a STEM can be employed to unambiguously detect the presence of hydroxide and hydrates species in and on nanomaterials. The delocalized nature of the vibrational signal allows spectra to be recorded with the aloof beam geometry thus greatly reducing electron beam induced damage. Hydroxides give a sharp peak in the spectrum at around 450 meV whereas hydrates and water species give broader peaks centered close to 430 meV. We have demonstrated the application of this approach to analyze the composition of the (100) surface of individual 60 nm MgO cubes. A peak was present at 430 meV in the aloof beam vibrational spectrum demonstrating that hydrate species were on the MgO surface facet. The delocalization limits the spatial resolution of the current implementation of the technique to some tens of nanometers. However, the unambiguous vibrational fingerprint of the hydrogen-oxygen bond can be directly correlated with highly localized structural and morphological features obtained from electron images. These findings open the door for probing local hydroxyl and hydrate species on nanoscale organic and inorganic structures.

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Fig. 1. Z-contrast image of Au nanoparticles and schematic positions showing electron beam for (blue) aloof and transmission (green) EELS. (figure courtesy of B.K. Miller, ASU)

Fig. 2. (a) Aloorf mode spectrum showing OH vibrational peak at 454 meV from Ca(OH)_2 . (b) Aloorf mode spectrum from boric acid.

Fig. 3. (a) Z-contrast image and (b) OH peak intensity as a function of position from Ca(OH)_2 surface. The open diamonds are experimental points, the solid square show the prediction of the infinite slab model. (c) Variation in OH stretch signal normalized to the zero-loss peak intensity (ZL) as function of position. Negative position correspond to probe in vacuum, positive position to the probe in sample. Position of zero is sample surface.

Fig. 4. (a) Valence loss EELS from Ca(OH)_2 showing spectrum in aloof beam (green) and transmission mode (red). (b) Vibrational spectrum recorded in aloof mode and (c) in transmission mode. (d) Variation in the relative probability of exciting the OH stretch signal (450 meV) and the conduction band edge in Ca(OH)_2 as a function of impact parameter b . In both cases the signal has been normalized to the value at $b = 1$ nm.

Fig. 5. OH vibrational peak from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. (a) Raw EELS spectrum, (b) background subtracted and inverted EELS plotted against wavenumber (c) IR spectrum showing same wavenumber range as (b) (data from reference 36).

Fig. 6. Surface analysis of (100) facets of MgO nanocubes. (a) Annular dark-field image of MgO cubes. (b) The transmission (red) and aloof (green) valence-loss spectra showing bandgap at 7.5 eV and interband intensity at 5.6 eV. (c) aloof-mode vibrational spectrum showing OH stretch at 430 meV associated with surface OH layer (the insert shows the vibrational peak after background subtraction).