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Detection of water and its derivatives on individual nanoparticles using vibrational electron energy-loss spectroscopy

Peter A. Crozier^{a,*}, Toshihiro Aoki^b, Qianlang Liu^a^a School for the Engineering of Matter, Transport and Energy, Arizona State University, 501 E. Tyler Mall, Tempe, AZ 85287-6106, USA^b LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe, AZ 85287-1704, USA

ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form

19 June 2016

Accepted 23 June 2016

Available online 24 June 2016

Keywords:

Vibrational EELS

Oxides

Electron energy loss spectroscopy

Water

Hydrates

Hydroxides

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.

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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

* Corresponding author.

E-mail address: crozier@asu.edu (P.A. Crozier).

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 Enfinitum spectrometer [24]. The microscope was operated at 60 kV and the typical energy resolution was between 15 and 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

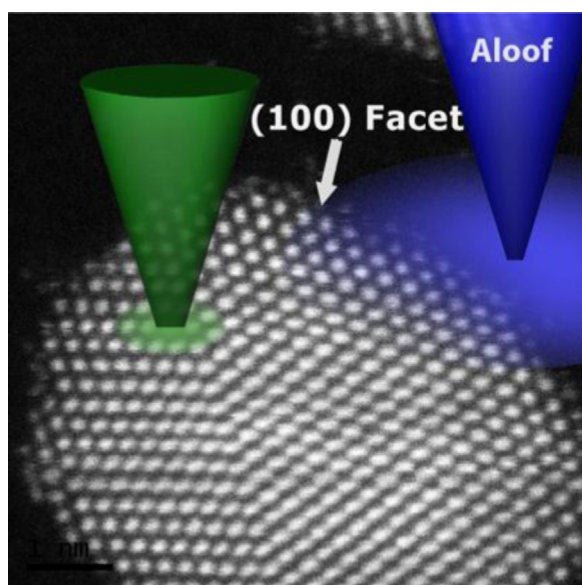


Fig. 1. Z-contrast image of Au nanoparticles and schematic positions showing electron beam for (blue) aloof and transmission (green) EELS (figure courtesy of B. K. Miller, ASU). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 Section 3) appears to be better than 5 meV at around 450 meV. Sample charging was not a significant problem in these measurements 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 $\text{Ca}(\text{OH})_2$ 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 range 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 shows a Z-contrast image of a $\text{Ca}(\text{OH})_2$ 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

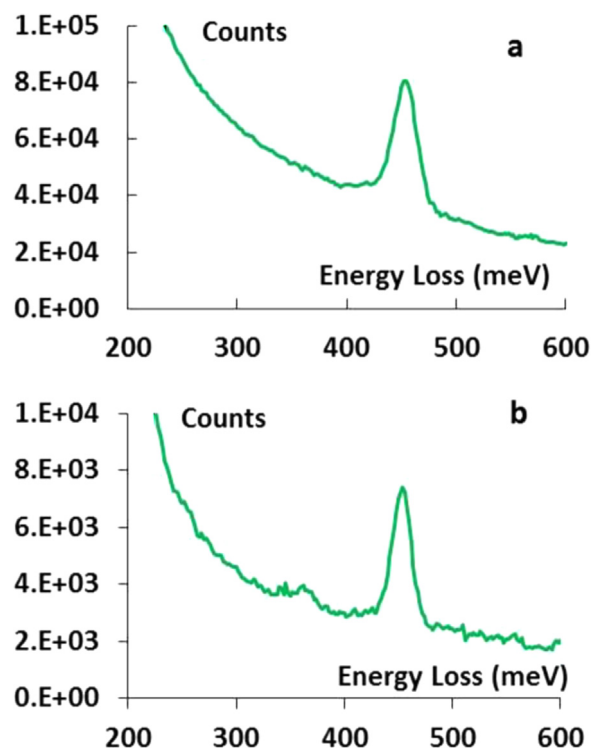


Fig. 2. (a) Aloof mode spectrum showing OH vibrational peak at 454 meV from $\text{Ca}(\text{OH})_2$. (b) Aloof mode spectrum from boric acid.

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