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Exploring Phononic and Photonic Excitations with Monochromated STEM EELS

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The enhanced energy resolution of recently developed monochromators now make it possible to use electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) to probe materials systems in new ways. This powerful spectroscopic capability combined with the small focused electron probe opens the door to explore photonic and phononic/vibrational excitations with high spatial resolution [1-3]. Here we describe recent advances leading to atomic resolution vibrational spectroscopy and novel approaches to probe guided photonic modes in dielectric particles.

The fast electron in the electron microscope can excite vibrational modes in materials either through dipole interactions (similar to IR absorption spectroscopy) or impact scattering (similar to inelastic neutron scattering). The spatial localization of these two scattering mechanisms is very different. Impact scattering typically involves higher momentum transfers yielding a spatially localized spectral signal. In a crystal, high momentum transfer interactions are associated with exciting the short wavelength phonon modes at the Brillouin zone boundaries (BZB). Efficient excitation of these modes requires experimental conditions that favor Bragg scattering from the associated Miller planes. This can be easily accomplished in the conventional STEM EELS geometry by tilting the crystal into a suitable zone axis orientation and using a probe convergence angle that spans the Bragg angle associated with the BZB of interest. This convergence angle also permits a small probe to be formed which enables resolution of the associated Miller plane spacing. We used this approach to demonstrate atomic resolution on a sample of Si as shown in ***Fig. 1*** [2]. The crystal is oriented along a (110) zone axis and the vibrational spectrum changes as the probe moves on and off the atomic column. The on-column spectrum shows a peak at around 59 meV predominantly from the L BZB associated with the four (111) Bragg reflections excited in this orientation. In more polar materials, the long-range dipole interaction is strong and leads to delocalized excitation of phonon modes close to the G point (small scattering angles and momentum transfer). However, when a large convergence angle is employed, additional peaks associated with the BZB phonons make a significant contribution to the spectrum [2].

EELS can also be employed to explore the characteristic photonic modes present in dielectric nanoparticles since the electron beam can provide a source of virtual photons to illuminate the object. We have explored the variation in photonic modes for high refractive index oxide particles such as TiO_2, Ta_2O_5 and CeO_2 [3]. The modes show up as peaks in the bandgap region of the spectrum. The energies of the modes are determined not only by the particle shape and size but also due to coupling between adjacent particles. An example of a complex photonic mode structure is shown in ***Fig. 2*** from an aggregate of TiO_2 anatase nanoparticles. The excitation probability is a strong function of impact parameter and the modes are most strongly excited in the aloof beam geometry. STEM EELS can be employed to investigate the variation of these cavity modes with size, shape and aggregation state.

Coupling between phonons and IR photons can give rise to phonon polaritons [4,5]. Polariton characteristics are also influenced by sample geometry, and so the polaritonic modes can be manipulated by changing the sample shape/size. Here we use STEM EELS to demonstrate variations in the polaritonic response on patterned SiO_2 thin films [6].

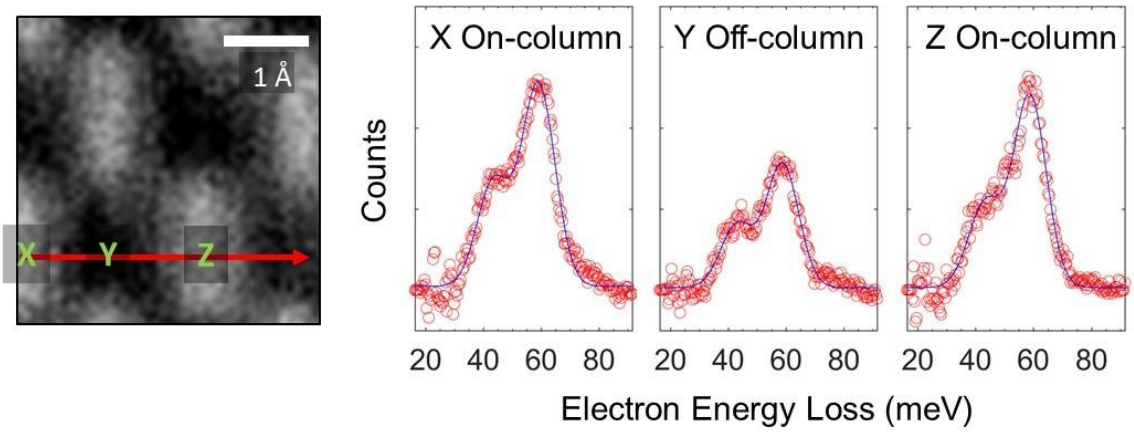

Figure 1. Z-contrast STEM image of Si (left) and three normalized spectra (right) from positions marked X, Y and Z along the linescan (red arrow in image). The STEM accelerating voltage is 60 kV.

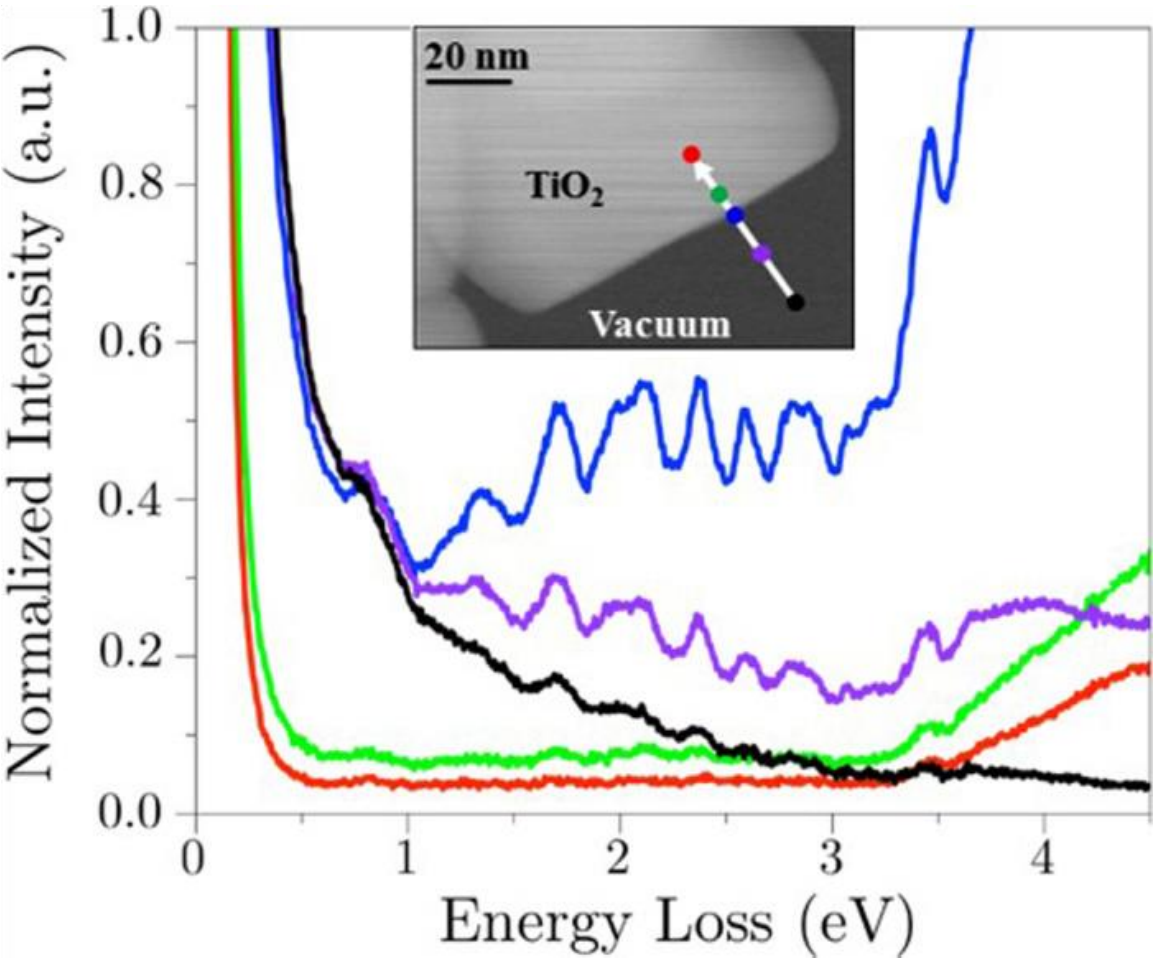

Figure 2. STEM EELS line scan of an anatase nanoparticle with electron probe moving from vacuum to penetrating configurations as shown in the inset. The STEM acceleration voltage is 60 kV. The impact parameter corresponding to each spectrum is b = 25 nm (black); b = 12 nm (purple); b = 0 (blue); b= −6 nm (green); b = −15 nm (red). The presence of resonances within the bandgap is clearly visible in the aloof beam configurations.

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