Ultrafast Core-Loss Spectroscopy

Probing Structural Dynamics in Nanomaterials on Ultrafast Time Scales

Electron microscopy (EM) has evolved into a tool of tremendous value to determine the structure of materials down to the atomic level. The time resolution in EM is typically too slow to resolve fast catalytic reactions or phase transformations. Here, we demonstrate core-level spectroscopy in ultrafast (4D) electron microscopy as a new method to follow element-specific structural dynamics with femtosecond-to-nanosecond time resolution in nanoscale materials.

Introduction

Electron energy-loss spectroscopy (EELS) in electron microscopy has become an invaluable tool for unraveling the chemical composition and structure of materials, enabling the imaging of individual atoms and their bonding states with unprecedented resolutions [1]. The energy loss event involves the excitation of valence or tightly bound core electrons into higher lying electronic states and into the continuum. The binding energy of core electrons depends on the atomic weight of the atom, which renders core-loss EELS an element-specific “local” probe of chemical bonding and structure. In this sense, core-loss EELS is very similar and complementary to core-level X-ray spectroscopy, with the difference that EELS is more sensitive to tiny amounts of samples (e.g. nanoparticles) and it can be easily combined with atomic-scale imaging and diffraction inside the same table-top transmission electron microscope.

So far, time-resolved EELS studies were limited to the millisecond regime, with applications to, e.g., the in situ study of catalytic oxidation and reduction reactions at surfaces [2]. Here [3], we demonstrate core-loss EELS with ultrafast (femtosecond-nanosecond) time resolution that allows, for the first time, the study of photo-induced changes in structure, orbital occupancy, local spin states, and angular momenta of specific atoms in the material. This development represents a significant addition to the palette of ultrafast probing techniques already available in 4D electron microscopy [4, 5].

Nanosecond-Resolved EELS
We apply ultrafast core-loss EELS to the investigation of the structural dynamics in graphite thin films by recording changes in the carbon K-edge spectrum around 280 eV, which originates from the excitation of a core 1s electron into empty conduction bands of π- and σ-symmetry [6].

The static EELS spectrum of a 50-nm thin graphite film is shown in figure 1A, together with the corresponding transient spectrum at Δt = 20±10 ns after nanosecond laser excitation at 532 nm. The transient spectra result from subtracting the EELS spectrum before excitation from the spectrum after laser excitation at various delay times between the excitation laser pulse and the short electron probing pulse.

The laser excitation causes pronounced changes in the EELS spectrum. In particular, the σ* resonance around 293 eV shifts to lower energies, giving rise to a derivative-like feature around the ionization edge, which decays on the time scale of ~1 μs as shown in figure 1C. In principle, such a red-shift is unexpected, because the thermal expansion coefficient for graphite in the basal plane is negative, i.e. a laser-induced increase in temperature gives rise to a contraction of the lattice [7]. Based on a simple orbital picture of sp\(^2\) orbitals forming the σ/σ* bands, the latter should therefore cause a blue-shift of the σ* resonance, contrary to what is observed. The explanation for this contradiction lies in the fact that we hitherto neglected the influence of thermal disorder and the extraordinary thermal properties of graphite.

**Molecular Dynamics Simulations**

In order to take into account the effect of thermal disorder, we performed ab initio molecular dynamics (MD) simulations and used the snapshots from these simulations to calculate the (transient) EELS spectrum and compare it to the experimental spectrum. The results for a simulation performed at 900 K (the temperature of the film after laser excitation) are shown in figure 1B and 2. First, we note in figure 2B that the in-plane carbon-carbon bonds elongate, as evidenced from the slightly asymmetric radial distribution function. This elongation is crucial to explain the observed red-shift of the σ* resonance, as described above. Since core-level spectroscopy is sensitive to the local structure surrounding the absorbing atom, we were able to observe this small bond elongation, despite the overall thermal contraction of the in-plane lattice that is caused by the population of specific phonon modes with negative Grüneisen parameters [8]. Second, we see in figure 2A and C that the radial distribution for distances between the graphite planes significantly broadens and shifts to longer distances. This is directly related to the pronounced dynamic disorder and the large, positive thermal expansion.
Using the results from the MD simulations, we calculated the EELS spectra at room temperature (298 K) to represent the spectrum before laser excitation, and at an elevated temperature of 900 K, corresponding to the temperature at ~20 ns after laser excitation as derived from heat diffusion simulations (fig. 1C). The calculated static and transient EELS spectra, depicted in figure 1B, show good agreement with the experiment. All transient features, in particular, the red-shift of the $\sigma^*$ band, are reproduced by theory. These results emphasize the importance of accurately incorporating dynamic disorder in the interpretation of transient core-loss spectra, particularly in the case of highly anisotropic materials such as graphite.

**Femtosecond-Resolved EELS**

On the nanosecond time scale we assume that the observed dynamics are purely thermal in nature, i.e. the graphite film is electronically relaxed. On faster time scales, however, the laser pulse excites the electron system into a non-equilibrium state, which relaxes by means of electron-phonon and phonon-phonon coupling on the femtosecond/picosecond time scale. Despite the extensive amount of research on graphite and its rather simple electronic band structure, there are still open questions regarding the relaxation mechanism of electron-hole pairs after photo-excitation and its impact on the out-of-equilibrium structural properties of the material [9].

By means of femtosecond-resolved core-loss EELS we demonstrated that the shifts of the electronic bands on the picosecond time scale, responsible for the debated transient optical signals reported in the literature, have a structural origin. Figure 3 shows the static and transient EELS spectrum at a time delay of $20\pm10$ ps after femtosecond laser excitation at 519 nm. A clear transient feature is seen at 290 eV, which corresponds to a red-shift of the $\sigma^*$ resonance caused by a prompt band-gap renormalization. The latter originates from a temperature-dependent electron-phonon coupling, as well as in-plane bond length elongation, as described above. From the time trace in figure 3C it is seen that the band-gap shrinkage remains almost constant up to the longest time scale of the experiment (~37 ps).

**Conclusions**

We demonstrated for the first time the feasibility of ultrafast core-level spectroscopy in 4D-electron microscopy with femtosecond and nanosecond time resolutions, and at deep core-level ionization edges >100 eV. Besides the technological advances that these results represent, they deliver new insights into the photo-excited dynamics of graphite. By adding core-loss spectroscopy to the
palette of probing techniques in 4D-EM, we expect numerous future applications in the field of nanoscale chemical dynamics, including optical switching, charge-transfer, and photo-induced phase transitions.

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References


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