

Fast XAS/SAXS Technique for *Operando* Multi-Modal Observation of Nanomaterials

We have developed a high-speed XAS/SAXS technique that enables real-time, multi-modal characterization of nanomaterials. By utilizing an energy-dispersive X-ray beam combined with a single area detector, both X-ray absorption spectrum and small-angle X-ray scattering data are simultaneously acquired within 0.1 seconds – approximately 100 times faster than conventional methods. This technique was successfully applied to Pt/Pd core-shell nanoparticles, revealing both element-specific local atomic structures and nanoscale structures including size distribution and shell thickness. This approach provides dynamical insights into the interplay between atomic-scale and nanoscale features in functional nanomaterials under working conditions, such as catalytic reactions.

Complementary use of multiple synchrotron-based techniques such as scattering and spectroscopy with different length scales and elemental sensitivities is often useful for a comprehensive understanding of hierarchical structures of materials and their physicochemical phenomena. X-ray absorption spectroscopy (XAS), which can provide element-specific chemical states and local atomic structures, and small-angle X-ray scattering (SAXS), which can provide nano-scale structures such as particle size and shape, are commonly used for the study of nanomaterials such as catalyst particles, since their reaction activity often depends on both their atomic-scale properties and nano-scale morphologies. For such a multi-modal characterization, combined XAS/SAXS techniques have been developed [1-3].

Commonly, XAS measurements require an energy scan of the incident X-rays while SAXS measurements are performed with monochromatic X-rays; therefore, the simultaneous XAS/SAXS detection is difficult. For this reason, in the previous methods XAS and SAXS were alternately measured. The resulting temporal resolution was on the order of 10 s at most, which is sometimes not enough for real-time observations of chemical reactions.

We have developed a new XAS/SAXS method that can acquire XAS and SAXS data simultaneously in a shorter time than the previous methods [4]. The new method employs an energy-dispersive X-ray beam commonly used in the energy-dispersive XAS (ED-XAS) technique [5] to eliminate the time-consuming energy scan and detects the XAS spectrum and SAXS intensities with an area X-ray detector at once (Fig. 1).

The experiments were performed at beamline AR-NW2A of the PF-AR, which is equipped with a tapered undulator that can generate white X-rays with a smooth energy spectrum suited to this type of experiment. The energy-dispersive X-ray beam was produced with a curved crystal polychromator (50 μm -thick Si wafer). The energy range of the polychromatic beam was set to 11.45–12.20 keV, targeting Pt L_3 absorption spectra. The area X-ray detector was PILATUS 300K (DECTRIS Ltd.). The sample-to-detector distance was 2,064 mm. The range of scattering vector magnitude q covered by the ED-SAXS measurements was 0.15–3.3 nm^{-1} , which can probe the structural properties on the length scales from 1 nm to several tens of nm. Details of the experimental layout are described in [4].

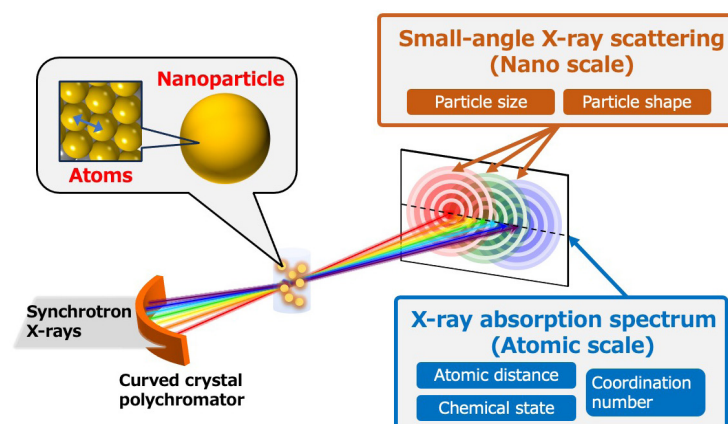


Figure 1: ED-XAS/SAXS for fast multi-modal characterization of nanoparticles [4].

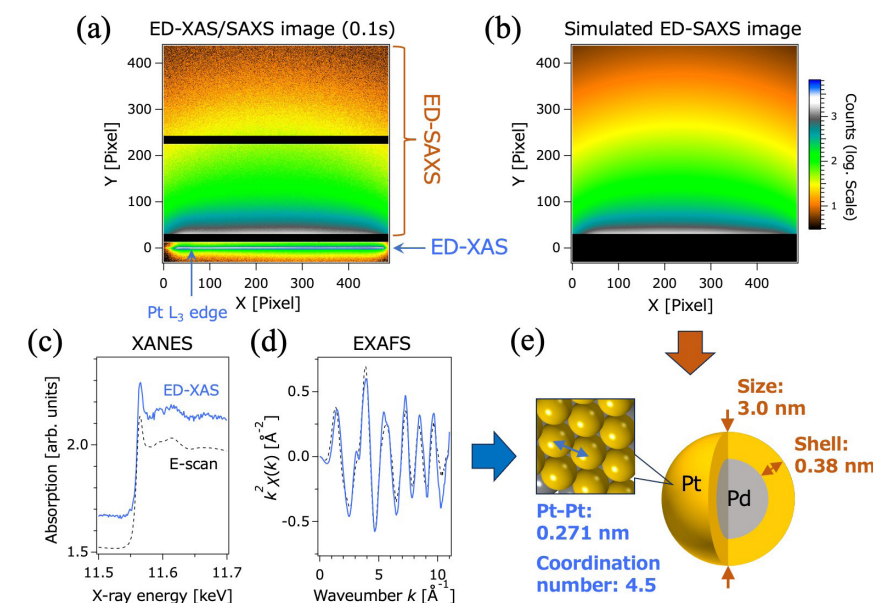


Figure 2: ED-XAS/SAXS analysis of Pt@Pd core-shell nanoparticles. (a) ED-XAS/SAXS image acquired with an exposure time of 0.1 s. (b) Simulated ED-SAXS image. (c) Pt L_3 edge XANES and (d) Fourier-transformed EXAFS spectra obtained from (a). Dashed lines are the reference spectra obtained by conventional energy scan measurements. (e) The atomic and nano-scale structures obtained from the ED-XAS/SAXS data [4].

Figure 2 (a) shows an ED-XAS/SAXS image of Pt-covered Pd (Pt@Pd) core-shell catalyst nanoparticles (4 wt% Pt/Pd, loaded on a carbon support). The data acquisition time was 0.1 s. The ED-XAS data was obtained from the lower part of the image and the ED-SAXS was detected at the upper part. Figures 2(c) and (d) show XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) spectra obtained from the ED-XAS data, which can provide chemical states of Pt and atomic-scale structures around Pt, respectively. These spectra agree well with those obtained by a conventional energy scan XAS measurement (dashed lines). Quantitative analysis of the ED-EXAFS spectrum provided the bond length and coordination number of Pt-Pt in the shell region (Fig. 2(e)).

Analysis of the ED-SAXS data is more complicated than the conventional monochromatic SAXS. This is because the detected ED-SAXS intensity is a superposition of SAXS intensities of the X-ray components, each of which has a different energy and incident vector (i.e., scattering vector). However, we overcame this problem successfully by taking into account the energy-dependent scattering strength (anomalous scattering) and incident vector, both of which can be obtained from the ED-XAS data [4]. The particle size and shell thickness were obtained by model fitting (Fig. 2(e)), and the optimized values agree with those obtained by a conventional

monochromatic SAXS measurement. The simulated ED-SAXS image for the structure model nicely reproduces the experimental image (Fig. 2(b)).

These results demonstrate that the ED-XAS/SAXS method can provide atomic and nano-scale structures of nanoparticles with a measurement time as short as 0.1 s, which is about 100 times faster than the conventional energy-scan XAS/SAXS methods, suggesting its capability of real-time multi-modal observations of nanomaterials.

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