

## X-Ray Nanospectroscopic Characterization of Single Molecular Ferromagnetic $Ti_{1-x}Co_xO_2$ Nanosheet

Recent developments in nanotechnology require the investigation of local electronic structures of individual nanostructures, which is essential in understanding their interesting physical properties. Currently, scanning probe microscopy and electron probe microanalysis occupy a central position in the characterization of these nanostructures. In these techniques, however, it is almost always difficult to monitor how the local electronic structure changes in an individual nanostructure.

Photoelectron emission microscopy (PEEM) provides some clues to answer this issue, as it provides a simple probe of local electronic structures of nanomaterials directly in real space with a high spatial resolution (<100 nm). In particular, PEEM combined with synchrotron radiation is ideally suited for studying nanomaterials since it allows the element-specific imaging of local electronic and domain structures owing to the tunability of photon energy and polarization in synchrotron radiation.

We present here, for the first time, nanoscale PEEM measurements of a single molecular ferromagnetic  $Ti_{0.8}Co_{0.2}O_2$  nanosheet [2,3], which allow not only the determination of the local electronic structure of a 1-nm-thick ferromagnetic material but also the characterization of the chemical states of stacking structures.

A  $Ti_{0.8}Co_{0.2}O_2$  nanosheet (Fig. 1) is a new room-temperature (RT) ferromagnetic nanomaterial derived from a layered titanate by exfoliation. In many ways, the  $Ti_{0.8}Co_{0.2}O_2$  nanosheet represents an ideal system for addressing the feasibility of PEEM in nanomaterial researches.  $Ti_{0.8}Co_{0.2}O_2$  nanosheets exhibit the ultimate two-dimensional nature with a thickness of ~1 nm, which is a model system for investigating the lower detection limit of PEEM. Our focus in this study is on the unexplored electronic properties of an individual  $Ti_{0.8}Co_{0.2}O_2$  nanosheet.

Samples used here are monolayer films composed of well-dispersed  $Ti_{0.8}Co_{0.2}O_2$  nanosheets. A colloidal suspension of  $Ti_{0.8}Co_{0.2}O_2$  nanosheets (with a lateral dimension of 2~10  $\mu m$ ) was synthesized from layered titanate by exfoliation. Monolayer films of  $Ti_{0.8}Co_{0.2}O_2$  nanosheets were fabricated by Langmuir-Blodgett deposition.

X-ray nanospectroscopic measurements were performed at beamline **BL17SU**. We have conducted nanoscale X-ray absorption spectroscopy (nano-XAS) with a high spatial resolution using PEEM.

Since the number of emitted secondary electrons is proportional to the X-ray absorption intensity, the PEEM contrast directly reflects the XAS intensity. For nano-XAS measurement, we scanned the photon energy and obtained a secondary electron emission

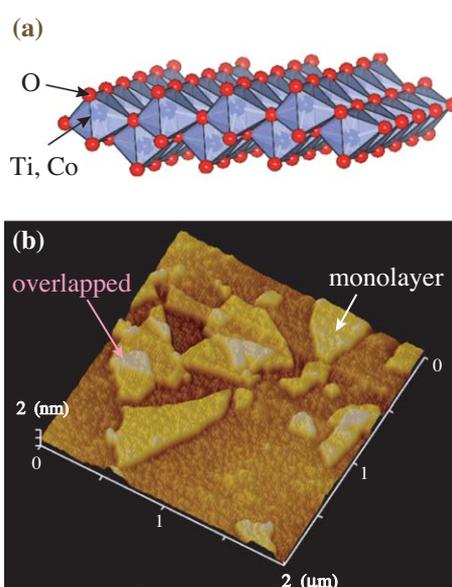


Fig. 1. (a) Structure of two-dimensional  $Ti_{0.8}Co_{0.2}O_2$  nanosheet. Ti and Co atoms are coordinated with six oxygen atoms and the resulting  $Ti(Co)O_6$  octahedra are joined via edge sharing to produce the two-dimensional lattice. The thickness of the nanosheet is about 0.75 nm, and the nanosheet consists of two edge-shared octahedra. (b) AFM image of  $Ti_{0.8}Co_{0.2}O_2$  nanosheets. The monolayer and overlapped nanosheets are observed.

PEEM image at each photon energy. In nano-XAS measurements, we chose the appropriate regions of interest (ROIs) in the PEEM image and integrated the intensities in ROIs to obtain nano-XAS intensity. It should be noted that, due to a sample drift during the measurements, it is rather difficult to obtain a reliable nano-XAS spectrum with a high spatial resolution, and therefore, drift correction was applied to all images using image analysis to reduce the drift within 20 nm.

Figure 2(a) shows the PEEM image of a single molecular  $\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_2$  nanosheet. The image was taken at the area where the coverage of the nanosheet is comparatively low to observe the local electronic structure within an individual nanosheet. Figure 2(b) shows the Co 2*p* nano-XAS spectra for five different areas in the nanosheet shown in Fig. 2(a). The ROI of each spectrum is about 400 nm by 400 nm. The Co 2*p* X-ray absorption peak is observed only in the nanosheet region. The nano-XAS spectra of the different areas in the nanosheet show a clear resemblance, which indicates that the electronic structure and chemical state of doped Co is uniform in a single nanosheet. It is suggested that there is no Co concentration distribution or Co segregation in the single nanosheet.

The Co 2*p* X-ray absorption spectra in Fig. 2(b)

show complex multiplet structures due to Coulomb interaction between the Co 2*p* core hole and 3*d* electrons. From the comparison of the spectral line shape and peak position with atomic-multiplet simulations, the valence of doped Co ions in the  $\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_2$  nanosheet was estimated to be  $\text{Co}^{2+}$ .

In summary, we have investigated the local electronic structures of ferromagnetic  $\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_2$  nanosheets by state-of-the-art X-ray nanospectroscopy techniques. Our results clearly indicate the feasibility of PEEM in addressing some fundamental issues on the determination of the local electronic structure of an individual  $\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_2$  nanosheet. We should also note the characteristics and sensitivity of PEEM. Compared with other microscopy techniques, PEEM offers a convenient means of direct material characterization in real space with a high spatial resolution. PEEM is also a nondestructive method without any contact to samples, and therefore, it is ideal for the study of nanomaterials already incorporated into devices. With these characteristics, our method is therefore expected to provide a powerful and versatile technique for the nanoscale characterization of different nanomaterials and other nanosheets including graphene sheets.

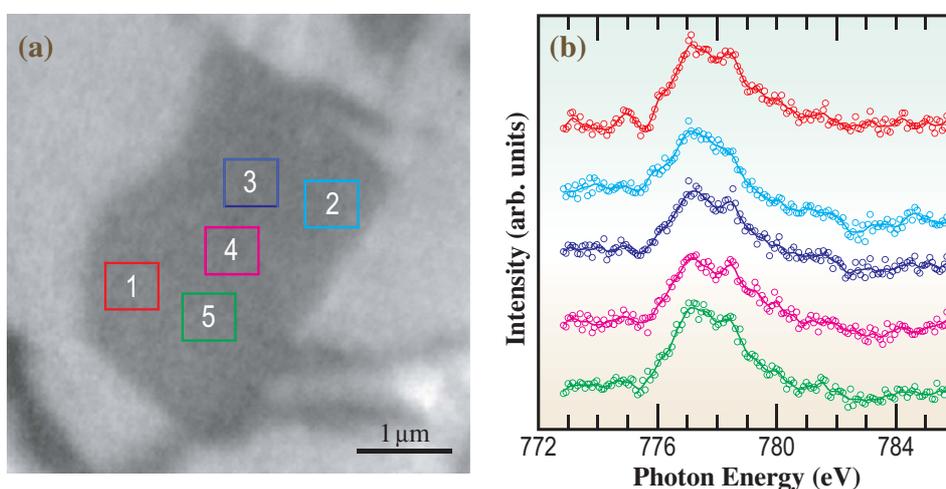


Fig. 2. (a) PEEM image of single molecular  $\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_2$  nanosheet on Au substrate taken at photon energy of 773 eV. Five different areas (1–5) with sizes of about  $400 \times 400 \text{ nm}^2$  are shown in the figure. (b) Co 2*p* nano-XAS spectra for five different areas in  $\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_2$  nanosheet. The numbers and colors of each spectrum correspond to the area shown in (a).

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## References

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