Direct observation of hole in cuprate superconductor using STEM-EELS

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The visualization of atom, element and its electronic state with atomic resolution was one of the goals of microscopy and they had been achieved in the past decade thanks to the development of advanced electron microscopy. STEM-EELS is only way to fulfill them. And this technique has been revealed the local information for a number of materials. However, the current technique does not apply to all the materials with atomic resolution due to electron irradiation problem. Since high electron dose for one atomic column is needed to obtain high signal-to-noise ratio spectrum, electron damage prevents atomic resolution spectroscopy in many cases. Low voltage is not always the answer to this problem. In the case of conventional single scan spectrum imaging (SI) approach, the amount of electron dose necessary to obtain a high-S/N-ratio spectrum from one atomic column is higher than the critical dose for many materials. This means that the conventional approach can no longer give a high-S/N-ratio spectrum with atomic resolution for such irradiation-sensitive materials. One of those is a cuprate high-Tc superconductor. In the case of present samples of $La_{2-x}Sr_xCuO_4$ (Fig. 1(a)), the small damage leads to spectral change even if there is no change in HAADF-STEM image. Therefore, we need to follow another approach.

Recently, Jones et al. reported that non-rigid registration is very useful in correcting image drift and improving the S/N ratio [1]. In the present study, we evolved this integration technique by combining with a template-matching technique. We obtained many SI data with atomic resolution from a single-crystal region using a low current condition. Then, we automatically picked up many crystallographically equivalent regions through a template-matching technique, and applied non-rigid registration by using the SmartAlign software package (HREM Research). As a result of repeating this procedure over several thousand regions, we succeeded to obtain dramatically improved the S/N ratio, maintaining spatial resolution within a unit cell without causing irradiation damage in a realistic time.

Since the oxygen O K-edge provides the electronic structure of unoccupied 2*p* states with atomic scale, it can potentially analyze the distribution of hole doped in cuprate high-T_c superconductor [2, 3]. Here, we succeeded for the first time in atomic-resolution two-dimensional mapping of holes in $La_{2-x}Sr_xCuO_4$. Fi1 (f-h) show atomic-resolution hole maps obtained by using pre-peak signals of the O K-edge with $x = 0.15$, 0.3, and 0.4 (Fig. 1(b, c)), respectively. In the case of $x = 0.15$, the hole map exhibits an anisotropic distribution, where only the planar oxygen sites are displayed brightly. On the other hand, in the case of the over-doped samples ($x = 0.3$ and 0.4), apical oxygen sites are also displayed brightly. In addition, we have demonstrated the anisotropic chemical bond related to the difference between p_x and p_y orbitals was observed with atomic resolution. The present approach enables atomic-resolution anisotropic spectroscopy and is expected to give complementary information to the polarization-dependent X-ray absorption spectroscopy.

References

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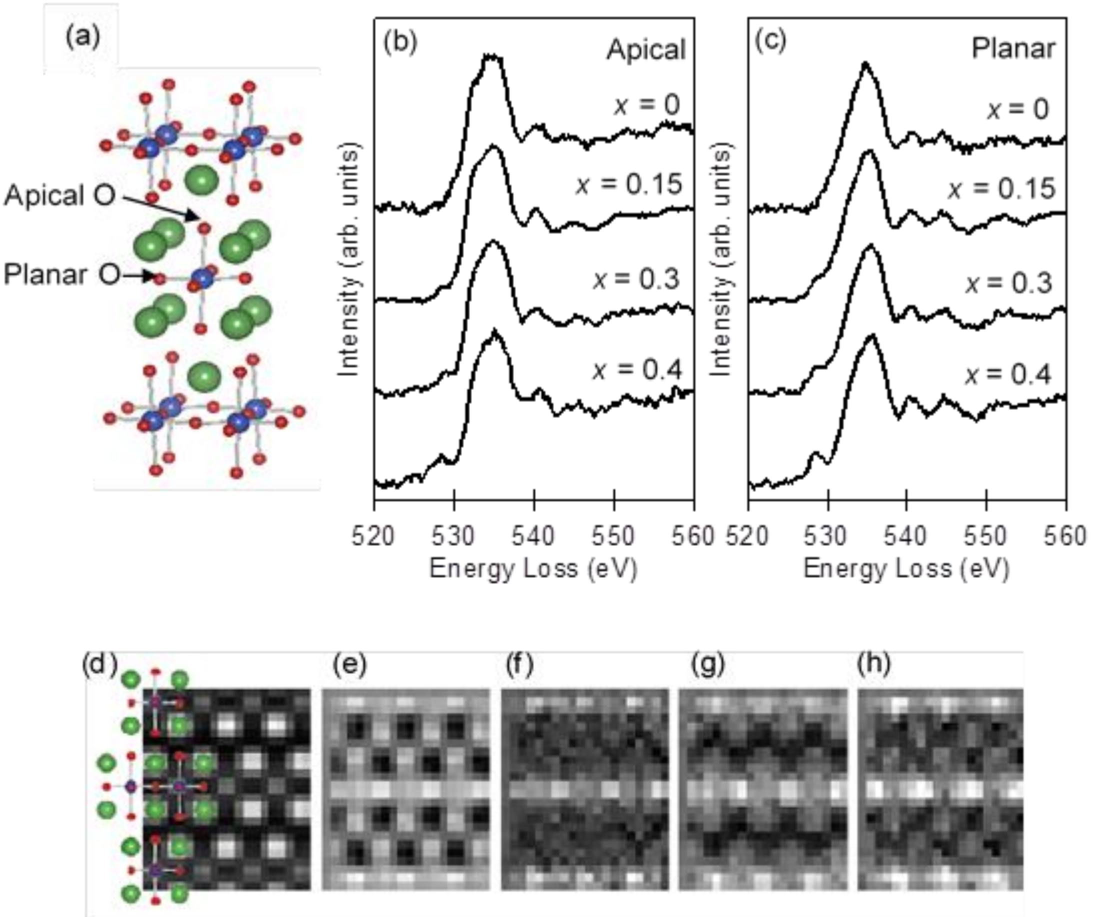

FIG. 1. (a) Crystal structure of $La_{2-x}Sr_xCuO_4$ with the different sites of oxygen (apical and planar sites) indicated. Experimental oxygen K-edge spectra from (b) apical and (c) planar oxygen. (d) Template HAADF image (e) oxygen mapping of $La_{1.85}Sr_{0.15}CuO_4$. Atomic resolution hole mapping of (f) $x = 0.15$, (g) $x = 0.3$ and (h) $x = 0.4$.