Atomic surface structure of Mn$_3$O$_4$ nanoparticle and origin of its high activity in oxygen evolution reaction

Yoon, S.[1,2], Seo, H.[1], Lee, S.[1], Kwon, Y.K.[2], Nam, K.T.[1] and Kim, M.[1]

[1] Seoul National University, Republic of Korea, [2] Kyung Hee University, Republic of Korea

Catalysis, which accelerates the desired chemical reaction, is one of the most important technology to overcome energy crisis. For understanding of catalytic process, identification of active sites at the atomic scale is crucial, since catalytic reaction occurs predominately at the active sites. Such active sites may be nanostructures on the support material or a part of surface such as steps, edges, corners, or facets. Currently, aberration-corrected scanning transmission electron microscopy (ac-STEM) has become an indispensable technique to investigate active sites of catalyst, since it is an almost unique technique to provide structure information of nanomaterials in the atomic scale. Furthermore, the capability to measure electron energy loss (EEL) spectra spontaneously with images makes ac-STEM more valuable. Electron energy loss spectroscopy (EELS) enables us to investigate the chemical composition or electronic state of the active sites. Here, we have probed the atomic and electronic structure of Mn$_3$O$_4$ oxygen evolution reaction (OER) nanoparticle catalyst using ac-STEM/EELS, and investigated the origin of improvement of catalytic activity in nanoparticles

Manganese oxide draws massive interests as a promising material for the future OER catalyst. However, there are no artificial manganese-oxide based OER catalysts to date which exhibit the outstanding activity. Recently, we newly developed an efficient manganese-oxide based OER catalyst (430mV of overpotential @1mA/cm^2 under neutral condition), which is the 15nm-sized Mn$_3$O$_4$ nanoparticles. Although there have been several reports on Mn$_3$O$_4$ OER electrocatalysts, they were not much active [1]-[3]. It is interesting that our Mn$_3$O$_4$ nanoparticles exhibit high activity unlike other Mn$_3$O$_4$-based catalysts. To understand the high activity of our catalyst, we have carefully investigated the surface atomic structure of Mn$_3$O$_4$ nanoparticles using ac-STEM. Interestingly, we observed that the (001) and (011) surfaces undergo the surface reconstruction. Additionally, we revealed that Mn^{3+} ions are suppressed on the low-index reconstructed surfaces through EEL spectrum imaging, whereas Mn^{3+} ions are still exposed at the region of edges and corners. Currently, it is widely accepted that the presence of Mn^{3+} ions is essential for manganese oxide to become active in OER [4]-[7]. If accepting the current consensus, our results indicate that the edges or corners become the active sites of a Mn$_3$O$_4$ nanoparticle, whereas the reconstructed surfaces do not contribute to its catalytic activities. In other words, the high portion of edges and corners in a nanoparticle will be related to the origin of high activity of our Mn$_3$O$_4$ catalyst.

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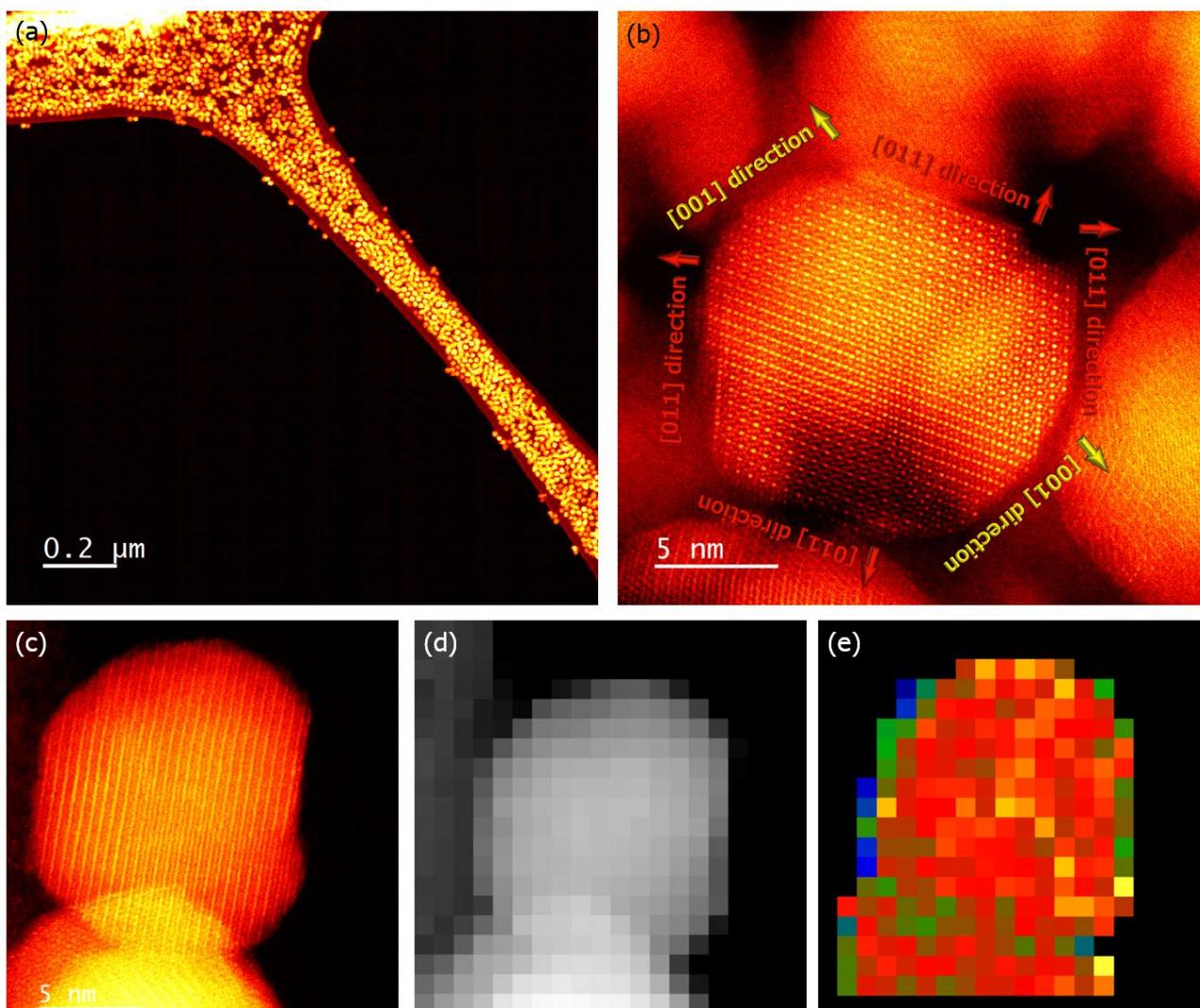[7] I. Zaharieva et al., Ener. Env. Sci. 9, 7 (2016) 2433-2443

Fig 1. Atomic surface structure and its electronic state of Mn$_3$O$_4$ nanoparticles. (a) Low-magnification HAADF STEM image of nanoparticles. (b) High-resolution HAADF STEM image of a nanoparticle viewed along [100] zone axis. (c) High-resolution HAADF STEM image, (d) EEL spectrum image, and (e) I(Mn^{3+})/I(Mn^{2+}) map image of a nanoparticle.