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Real-time Analysis of Oxygen Vacancy of Indium Oxide via Environmental Transmission Electron Microscopy

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This paper reports an *in situ* electron microscopy analysis of oxygen vacancies of indium oxide, which is an emerging photothermal catalyst. Such real-time observation has the advantages over the *ex situ* characterizations [1-3] by directly studying the structure, morphology and stoichiometric ratio during the catalytic reactions. Owing to the wide bandgap and limited number of oxygen vacancies of stoichiometric indium oxide, the utilization of solar energy is significantly hindered and limits its further development in the field of photothermal catalysis [4]. Recently, it is found that the non-stoichiometric black indium oxide (In_2O_{3-x}) exhibited three orders of magnitude higher photothermal catalytic performance towards reverse water gas shift (RWGS) reaction than the stoichiometric indium oxide with 100% CO selectivity [5]. The oxygen vacancies act as active sites and responsible for the remarkable photothermal activity. Furthermore, it is well known that higher temperature could induce a general thermal expansion of bulk materials, it would be of great scientific interest and technological important if a nanosized catalyst could be thermally expanded at high temperatures and induce the formation of oxygen vacancies.

To understand the relationship between microstructure and catalytic performance, we performed *in situ* environmental scanning/transmission electron microscopy (S/TEM). Hitachi HF-3300 ETEM equipped with a cold field-emission gun at an accelerating voltage of 300 kV was used to conduct both static and dynamic experiments. The Blaze *in situ* heating-gas holder (Hitachi High-Tech Canada) uses MEMS heating chips designed and fabricated by Norcada Inc., Canada (Figure 1 a–c) [6]. The operation temperature ranges from room temperature to 450 ℃ with a rate of 0.5 ℃/s. The surface and center of the same nanoparticle were analyzed (Figure 2 a and c). At room temperature, the In_2O_3 NPs have a standard d-spacing of (222) plane which is 2.91 Å at both surface and center regions (Figure 2b insets). Intriguingly, as the temperature increases to 450 ℃, the d-spacing of the surface region expands to 3.03 Å whereas that of the center region remains 2.91 Å (Figure 2d insets). The electron energy loss spectroscopy (EELS) was performed to further detect the cause of d-spacing expansion from an oxygen concentration perspective. The energy scale for the EEL spectra was calibrated by setting the maximum point of In-*M* edge at 515 eV. Figure 2b demonstrates O-*K* edges for surface and center regions are located at the same energy loss positions (537.5 eV) at room temperature. In sharp contrast, as shown in Figure 2d, at the temperature of 450 ℃, the surface O-*K* edge shifts to a lower energy loss position of

532.25 eV whereas the center O-*K* edge also shifts left side to 535 eV. Both absolute energy shifts to lower energy loss positions, indicates the formation of oxygen vacancy and the larger shift of O-*K* edge indicates a higher concentration of oxygen vacancy [7]. Therefore, it is believed that oxygen vacancies in In_2O_3 NPs, which are more favorably generated at particle surface, are the primary factor to d-spacing expansion and the higher CO production rate at 450 ℃. Our findings provide valuable insights into the nanoscale thermally local expansion attributed to oxygen vacancies that is responsible for the improved thermal catalytic activity [8].

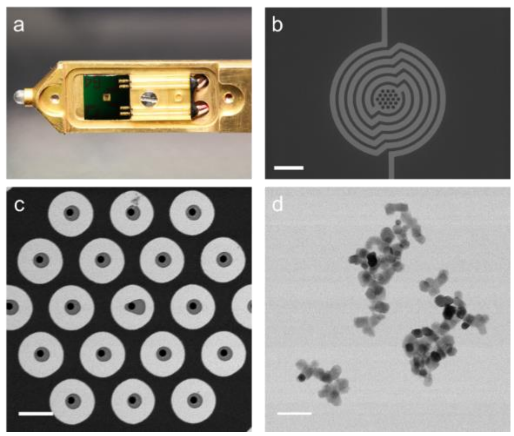

Figure 1. (a) Hitachi Blaze heating-gas holder with Norcada MEMS heating chip. (b) SEM image of heating area configuration. Scale bar: 100 µm. (c) STEM-Z-contrast image of sample loading area. Scale bar: 10 µm. (d) STEM-bright field image of In_2O_3 NPs at room temperature. Scale bar: 100 nm.

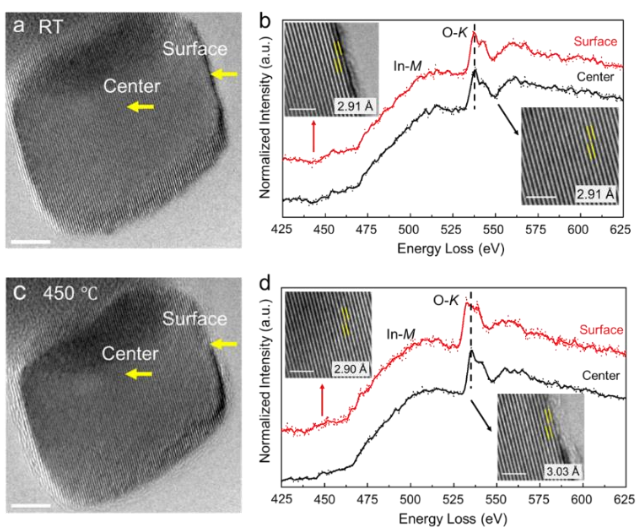

Figure 2. *In situ* heating results of In_2O_3 NPs. (a,c) High-resolution TEM (HRTEM) images of the target particle at room temperature and 450 ℃, respectively. Scale bars: 5 nm. (b,d) EEL spectra of O-*K* edge and In-*M* edge obtained at surface and center areas indicated by the yellow arrows in (a) at room temperature and in (c) at 450 ℃, respectively. Insets are HRTEM images of the surface and center area showing the (222) plane lattice fringes at room temperature and 450 ℃, respectively. The d-spacing presented in each lower right corners is measured as an average value. Scale bars: 2 nm.

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References:

[1] Zhang, X. *et al.*, Nat. Catal. **3**, (2020), p. 411. doi.org/10.1038/s41929-020-0440-2
[2] Yoshita, H. *et al.*, Science **321**, (2008), p. 317. doi.org/10.1126/science.1213194
[3] Nolte, P. *et al.*, Science **321**, (2008), p. 1654. doi.org/10.1126/science.1160845
[4] Sato, S. & Kadowaki, T., J. Catal. **106**, (1987), p. 295.
[5] Wang, L. *et al.*, Nat. Commun. **11**, (2020), p. 2432. doi.org/10.1038/s41467-020-16336-z
[6] Howe, J. Y. *et al.*, Microsc. Microanal. **23**, (2017), p. 66.
[7] Torruella, P. *et al.*, J. Phys. Chem. C. **121**, (2017), p. 24809. doi.org/10.1021/acs.jpcc.7b06310
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