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Observation of Pt-atom complexes in $CaTi_{1-x}Pt_xO_{3-\delta}$

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The 'intelligent catalyst' concept, involving cyclical movement of precious metal atoms in and out of a perovskite oxide lattice, was proposed by Nishihata et al. in 2002, and the precious metal atom (Pd) was then believed to occupy the B site in the perovskite ($LaFeO_3$) lattice, based on X-ray anomalous diffraction measurements [1]. Since then, B site occupancy has generally been assumed for all other cases in most theoretical and experimental studies [2-4]. In the present work, Pt-atom complexes, involving both B and A site occupancy, were observed in aberration-corrected (Cs-corrected) High-Angle Annular Dark-Field (HAADF) images of $CaTi_{1-x}Pt_xO_{3-\delta}$, providing an unexpected example of precious metal bonding in this case.

In our study, 50-60 nm $Ca_{0.96}Ti_{0.91}Pt_{0.09}O_{1.97}$ thin films were grown by pulsed laser deposition on (001) $SrTiO_3$ substrates. An image of the as-grown film, with abnormally bright spots, most likely corresponding to Pt atoms distributed in some fashion throughout the film, is shown in Figure 1a. Although these bright spots cannot account for nearly all the Pt atoms in the film, most of the columns containing these spots correspond to B sites. The as-grown film was then subjected to reduction at 800 °C (in 10% H_2 balanced with N_2) for 1 h, after which Pt atoms tend to precipitate out of the lattice and form 1-2 nm nanoclusters embedded within the perovskite lattice. Some of the Pt atoms apparently remain on both A and B sites, however, as indicated in Figure 1b. The reduced film was then subjected to an oxidation treatment in dry air at 800 °C for 1 h. As shown in Figure 1c, some of the nanoclusters dissolve into the perovskite lattice, resulting in the reappearance of bright spots, some of which exhibit short-range order, and most of which are on columns that correspond to A sites.

More details about the overall process can be obtained from off-zone-axis (with 5-10 degrees of tilt) images. Such an image of the as-grown film is shown in Figure 2a. The brighter streaks correspond to Ti (B site) columns, while the darker streaks correspond to Ca (A site) columns. Again, most of the unusually bright spots are found on B site columns, though some are on A site columns. Those spots marked with yellow arrows appear to be single Pt atoms, while the elongated features, marked with orange arrows, are quite likely short rows of Pt atoms. On the contrary, most of the unusually bright spots in the oxidized film are found on A site columns, have even higher brightness enhancement, and are mostly elongated features. Since the material is isotropic and there appears to be short-range order in the plane of the film (as indicated in Figure 1c), we suspect that the dissolved Pt nanoclusters may form small three-dimensional ordered Pt-atom complexes. A series of image simulations, aimed at providing a semi-quantitative estimation of the number and spatial distribution of Pt atoms producing the abnormally bright spots, is currently underway.

In summary, we have shown that the distribution of Pt atoms in our films is not as previously assumed, and that a redistribution of Pt bonding site, B➔A, occurs to some extent during the initial redox-induced Pt atom-to-nanocluster-to-atom exchange process.

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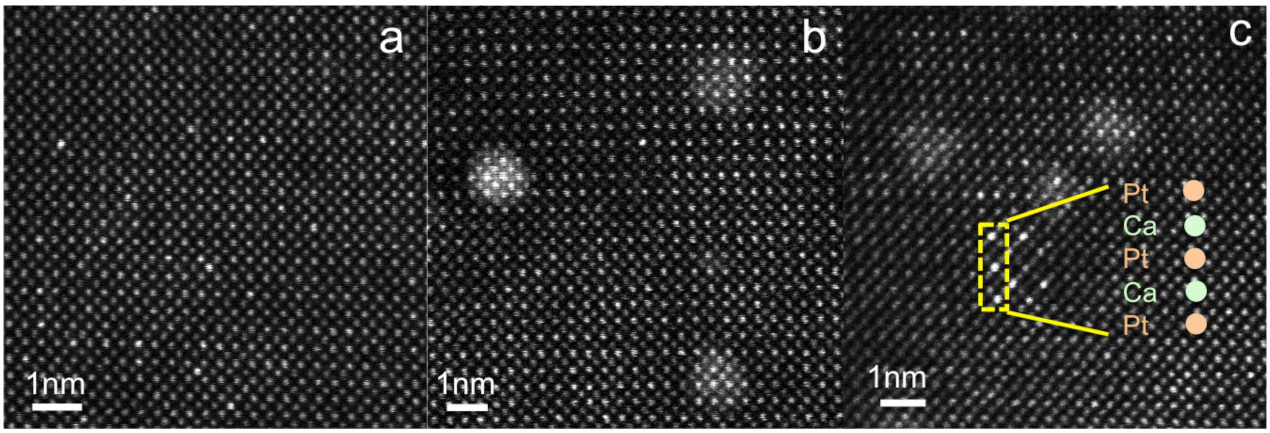

Figure 1. HAADF images of $Ca_{0.96}Ti_{0.91}Pt_{0.09}O_{1.97}$ thin films: (a) as-grown (b) as-grown, then reduced (c) as-grown, then reduced, and finally oxidized.

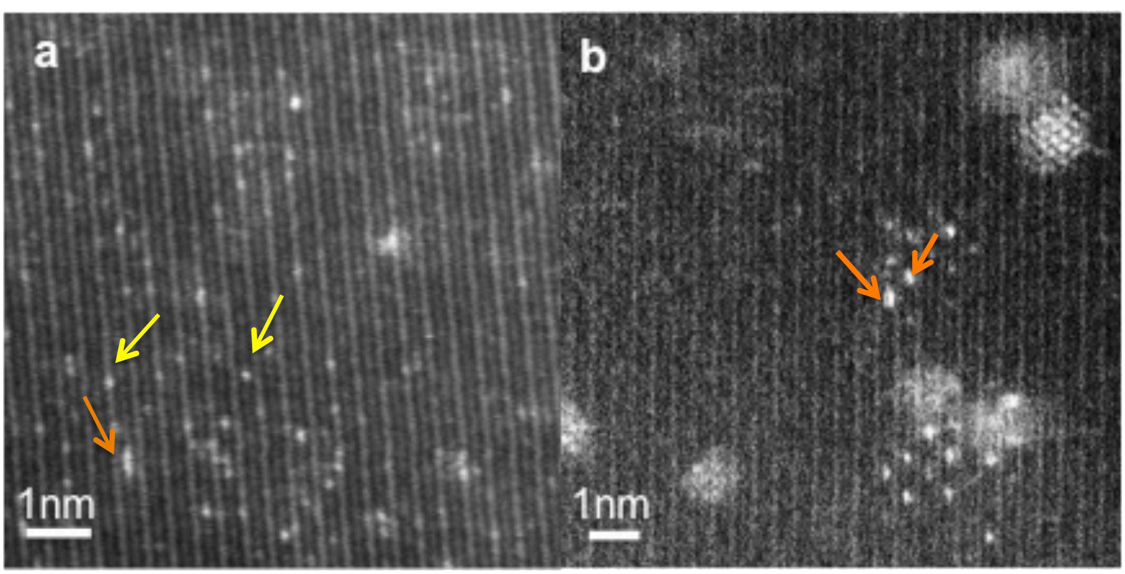

Figure 2. HAADF off-zone axis images: (a) as-grown, (b) reduced, and oxidized. Yellow arrows may indicate single Pt atoms, while orange arrows likely indicate short rows of Pt atoms.

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