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Atomic Resolution Studies of Self-Stabilizing Metal-Perovskite Catalysts

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The three-way automotive exhaust catalyst is an indispensable tool for reducing the levels of undesired gases generated by the internal combustion engine. Currently, a substantial fraction of the world's supply of Pt, Pd, and Rh are used in the production of these catalysts. However, if the metal nanoparticles in the fresh catalyst could be stabilized against coarsening during operation and maintain a higher specific catalytic activity, this fraction could be substantially reduced. A Pd-perovskite catalyst had been found to maintain an unusually high resistance to aging, then explained as a self-regenerating mechanism [1], was corroborated by indirect bulk characterization techniques. Using atomic-resolution STEM as our characterization technique, we propose an alternative mechanism – self stabilization – as the rationale for this maintenance of activity [2].

We utilize model single crystal thin films of $LaFeO_3$ as our Pd support, as they are well suited for STEM study. Fig. 1(a) shows a Pd/$LaFeO_3$ PLD film after oxidation for 1 h at 800 °C. The Pd, formerly about a monolayer, has coarsened into small, nanometer-sized particles. Most strikingly, however, they have heavily reacted with the $LaFeO_3$ support and have partially embedded within the formerly nearly atomically flat $LaFeO_3$ surface. This would have the effect of stabilizing the particles against further, extended coarsening. The embedded particles show a clear reaction zone in their immediate vicinity, shown in Fig. 1(b), which is shown by EELS to have a slight increase in the Fe/La ratio. EDS mapping also reveals some regions with a high Pd content at the expense of Fe, consistent with the self-regeneration mechanism, however these were not numerous. We also performed a parallel experiment using an MBE $LaFeO_3$ film in order to eliminate the effects of defects on the metal-support interaction. Though the resultant metal particles were slightly smaller in size, as shown in Fig. 2, the effect was largely similar. We performed cyclical redox aging on an additional Pd/$LaFeO_3$ MBE film to much the same result (Fig. 3(a, b)), with very little particle growth relative to the previous film, which was oxidized only once. The particles on the redox-aged film showed varying degrees of epitaxiality.

In order to study the extrusion of metal from the support, we also fabricated by PLD and reduced a thin film of $LaFe_{0.95}Pd_{0.05}O_3$, after the formulation in Ref. [1]. Only after a relatively aggressive reduction could we extrude even a small amount of the Pd from the support, in the form of 2-3 nm epitaxial Pd particles, shown in Fig. 4. The extruded metal represents the equivalent content of only the top 2-3 nm of the support.

We propose that it is the self-stabilization mechanism discussed above, rather than the self-regeneration mechanism, that is predominantly responsible for the apparent extended life of these metal-perovskite catalysts.

References

[1] Y. Nishihata *et al.*, *Nature* 418 (2002) 164
[2] M.B. Katz *et al.*, *in preparation*
[3] This work was supported through NSF grant DMR-0820404, CBET 0933239, and DMR 0723032.

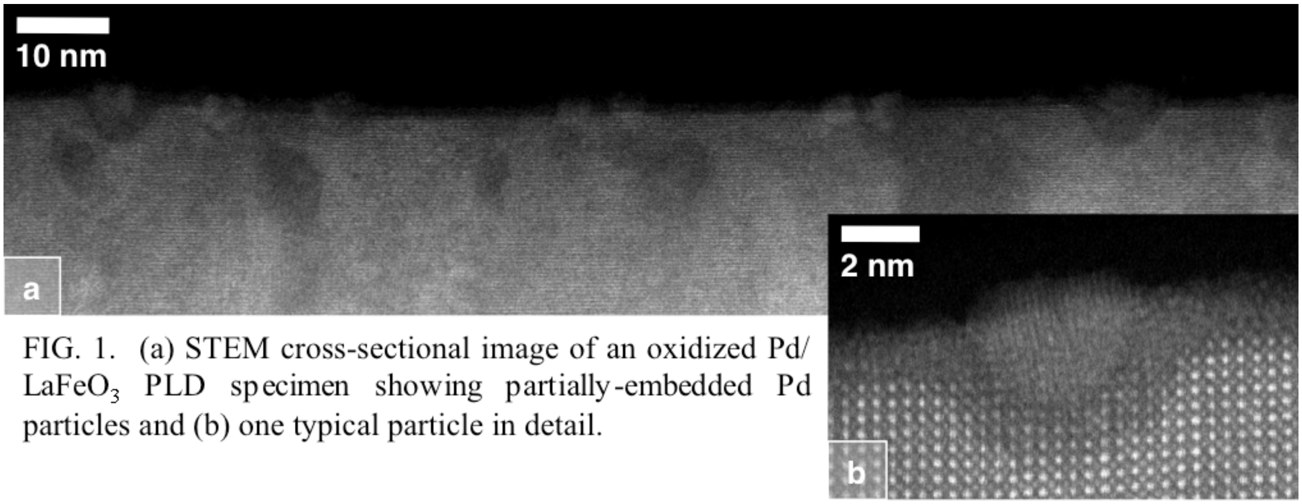


FIG. 1. (a) STEM cross-sectional image of an oxidized Pd/LaFeO$_3$ PLD specimen showing partially-embedded Pd particles and (b) one typical particle in detail.

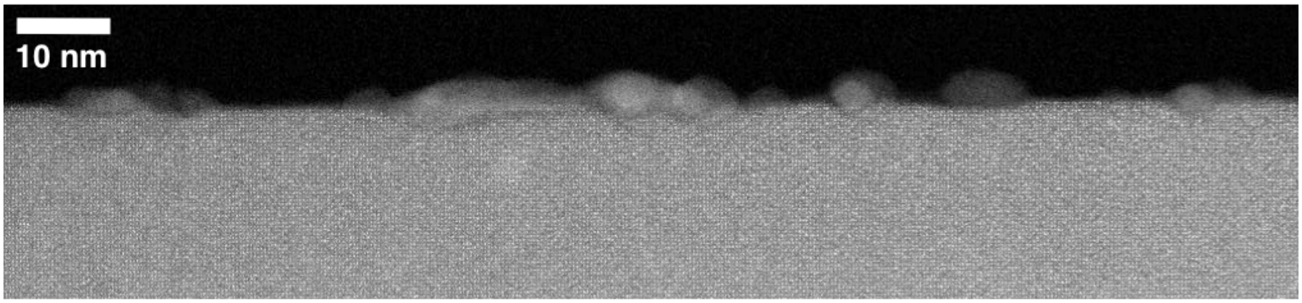
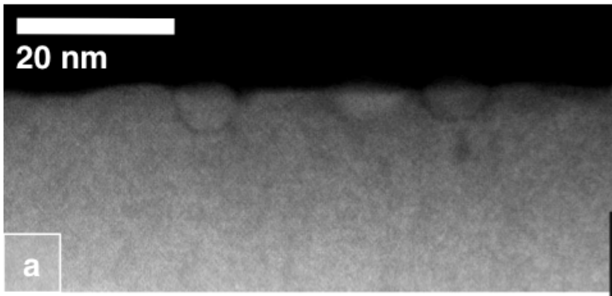


FIG. 2. STEM image of an Pd/LaFeO$_2$ MBE specimen showing similar embedding behavior.



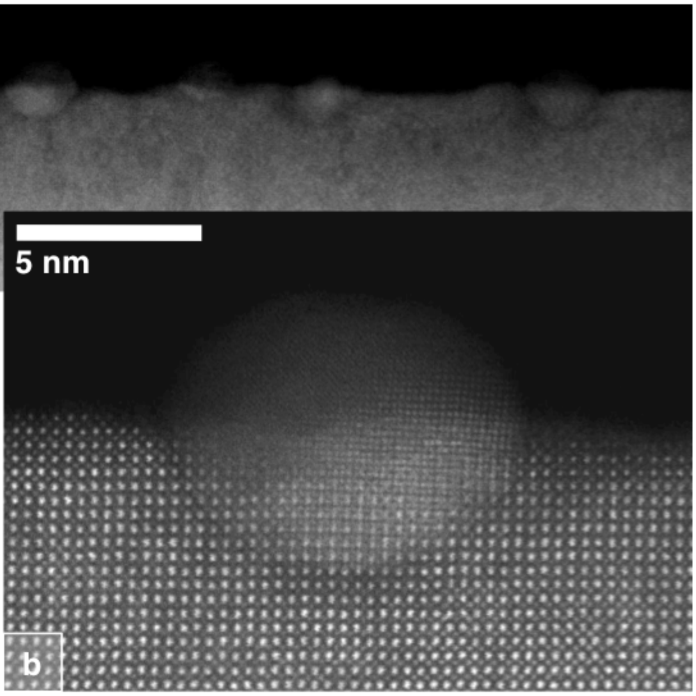


FIG. 3. (a) STEM image of an Pd/LaFeO$_2$ MBE specimen after extended redox cycling and (b) one typical particle in detail.

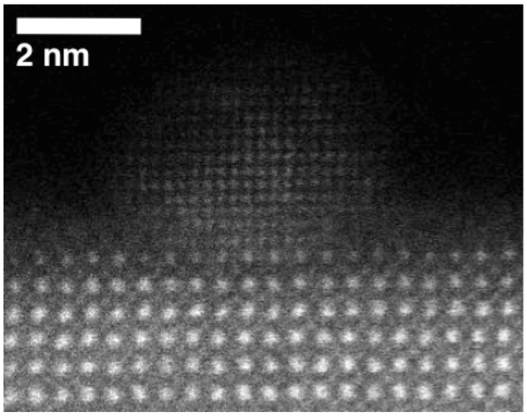


FIG. 4. STEM image of a small epitaxial Pd particle extruded from a LaFe$_{0.95}$Pd$_{0.05}$O$_3$ film after aggressive reduction.