In Situ Observations of the Dynamics of Pd@Pt Core-Shell Nanoparticles in Electrolyte

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Platinum (Pt) based nanoparticles are widely used as catalysts for many chemical and electrochemical reactions such as the oxygen reduction reaction. In particular, M-Pt (M=Pd, Co, Ni, etc.) core-shell nanoparticles have proven to be promising systems yielding high activity, improved stability, and efficient utilization of Pt. Controlled formation of new and desirable shapes can further provide improved activity through access to unique facets.[1] However, catalyst degradation during operation due to changes in morphology or shape, species loss caused by dissolution, and undesired migration of atoms remain an obstacle for these material. Therefore, it is important to understand the dynamics of nanoparticle evolution in the liquid environment to reveal the cause and kinetics of catalyst changes. In this talk, we present in situ TEM studies on the degradation of Pd@Pt nanoparticles.

Pd@Pt core-shell nanoparticles were drop cast onto a 50 nm thick silicon nitride membrane window, which was subsequently assembled into a liquid cell (Protochips, USA) for *in situ* studies ib a JEOL JEM2800 at 200 kV. The solution of KBr was pumped into the cell during the experiment.

We first employed cubic Pd@Pt nanoparticles to monitor the degradation dynamics due to a galvanic process in electrolyte. Regular and corner defected Pd@Pt nanocubes were compared. For Pd@Pt cubes with completed Pt shells, only the internal Pd atoms in the corners were etched at the beginning. The small voids in the corners grow along the body diagonal as the etching proceeds, eventually leaving a Pt cage, that shrank into a hollow sphere. In comparison, corner defected Pd@Pt cubes exposed the interior Pd atoms to the Br$^-$ electrolyte, the formation of $[PdBr_4]^{2-}$ leads to faster etching of the interior palladium. In contrast to regular and corner defected cubic nanoparticles, for nanoparticles with defects on the faces, the etching started from the terrace defect and proceeded with a migrating front following the oxidative etching contour similar to those observed in electrochemistry. The site-dependent etching rates were compared and summarized in Fig. 1, the fastest degradation occurring on the corner defects reveals that the most important sites to protect for the longevity of these catalysts are the corners.[2] Pd@Pt core-shell octahedral nanoparticles were then studied using in situ liquid cell with a focus on how the internal strain influences the corrosion of the interior Pd. As seen in Fig. 2, the etching started from the corner and enters areas with tensile strain in the body of the octahedron. This study shows that in locations with tensile strain and high local curvature, the etching process is much faster. Density functional theory (DFT) calculation suggests that the dissolution potential of the Pd nanocrystal decreases as the strain increases; meanwhile, Pd atoms tend to be corroded more easily on a surface under tensile strain than on one under compressive strain.[3]

In summary, we have directly observed the etching process of Pd@Pt nanoparticles with different shapes in real-time in a liquid cell TEM, which identified different etching pathways. The insights on the interaction of nanostructures with reactive liquid environments can help better engineer the surface structure to improve the stability of electrocatalysts as well as design a new porous structure that may provide more active sites for catalysis.
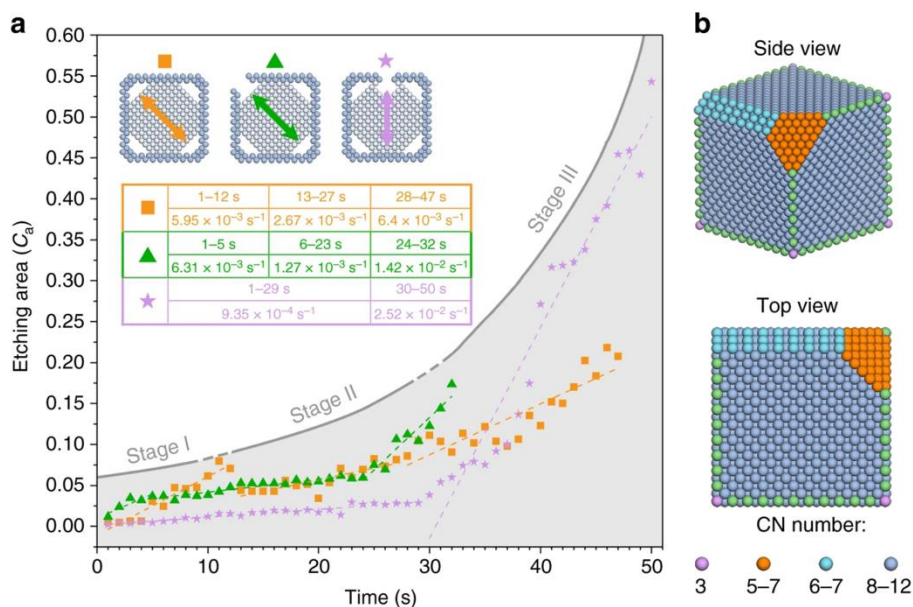
Figure 1. Figure 1. Etching rate and coordination number of Pd@Pt cubes. (a) Changes of the measured projected etching area along representative directions as a function of time in regular, corner, and terrace defected cubes. Inset table shows the values of average etching rate in the corresponding time periods. (b) Coordination number distribution of surface atoms inside a Pd cube.
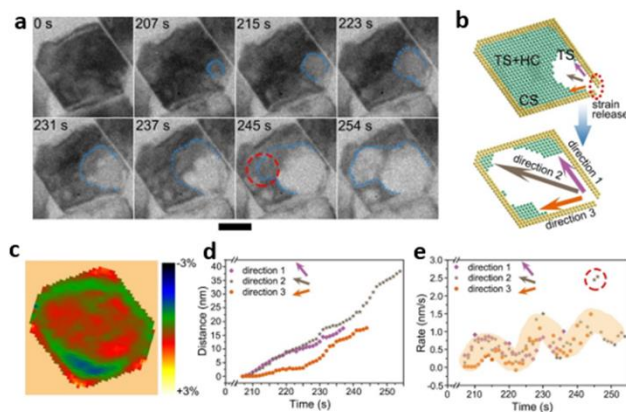

Figure 2. Figure 2. (a) Series of TEM images showing the etching process of a 37 nm octahedral Pd@Pt nanoparticle with a corner defect. Scalebar, 20 nm. (b) An illustration of the atomic structure with measured directions. (c) Strain map of the octahedron before corrosion. The color-coded bar represents a range of -3% compressive strain to +3% tensile strain. (d) Scatter diagram of the three measured distances as a function of time. (e) The corresponding etching rates of each distance.

References
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[4] This work was supported by the NSF awards under grant No. CBET-2031494 and CHE-1955786. The authors acknowledge the use of facilities and instrumentation at the UC Irvine Materials Research Institute (IMRI) supported in part by the NSF through the MRSEC program (DMR-2011967).