

3-D Tracking and Visualization of Hundreds of Fuel Cell Nanocatalysts During Electrochemical Aging

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One of the major cost barriers for the commercialization of low-temperature fuel cells is the rapid degradation of the catalyst nanoparticles in the cathode by coarsening. Much effort has been spent on the ex-situ study of the particles after aging in a membrane-electrode-assembly (MEA, the power generating component of a fuel cell). In these experiments, the MEA needs to be sectioned for transmission electron microscopy (TEM), making repeated observations on the same particles impractical [1]. Consequently, the trajectory of the particles is missing, making it difficult to unscramble the effects of coalescence vs. Ostwald ripening on particle coarsening[2]. Further, with 2-D images alone, we cannot determine how the nanocatalyst particles are distributed on a 3-D carbon support. We approach the problem by running the electrochemical (e-chem) experiments directly on a TEM support grid [3]. A carbon-coated gold index grid was used as the working electrode in a three electrode e-chem experiment (Fig. 1a). The fuel cell materials were sprayed on the grid prior to the e-chem experiments. The grid (Fig. 1b) contained indexed windows for locating specific regions of the specimen, allowing us to perform ADF-STEM tomography on exactly the same region of the catalyst material before and after e-chem aging (Fig. 1c), from which we are able to identify hundreds of nanoparticles in 3-D with *one-to-one* correspondence. This enables us to study the coarsening evolution of the particles by tracking location changes on support surfaces, observing particle volume changes, and directly visualizing coalescence events. It allows us to answer questions such as how did the particles loose surface area, how did they move, and what was the particle-support interaction.

Fig. 2a-b shows the 3-D overlay of the reconstructed nanocatalysts before (*gold*) and after (*red*) e-chem aging. Overall, most particles did not move, yet the total number of particles dropped from 378 to 362. By comparing only the projected images in Fig. 2a-b, it would be implausible to track coarsening of nanoparticles on these 2-D images. However, the 3-D reconstruction results allow us to track the missing particles *one-by-one* and reveal the coarsening mechanisms. In general, we found that the majority of the coarsening events were caused by particle coalescence, which are illustrated in Fig. 2c-e. In Figure 2c, a small particle migrated first and then merged with the large particle. This is in contrast to Ostwald ripening, where the particles dissolve and uniformly redeposit onto larger particles nearby. The loss of the surface area took place during the dissolution-redeposition process when the connection between the coalesced particles is rounded off to minimize surface energy. This is in agreement with our previously proposed synergistic interplay between coalescence and Ostwald ripening[2]. Figures 2d-e highlight several coarsening events happened during e-chem aging, in which both migration and coalescence could be seen. Moreover, we can also visualize the likely path of particle movement on the surface of the carbon support. Fig. 2f presents such case of nanocatalyst particle “falling” from the negative curvature (summit) into the positive curvature (valley) of the carbon support.

Overall, the direct 3-D visualization of particle trajectories provides strong evidence of coalescence of metallic nanocatalysts and will be helpful in improving the electrocatalytic durability of fuel cell nanocatalysts and their supports [4].

[1] S. Chen *et al.*, Journal of Physical Chemistry C **113**, 1109 (2009).

[2] H. Xin *et al.*, Microscopy and Microanalysis **16**, 104 (2010).

[3] Z. Y. Liu *et al.*, Journal of the Electrochemical Society. **157**, B906 (2010).

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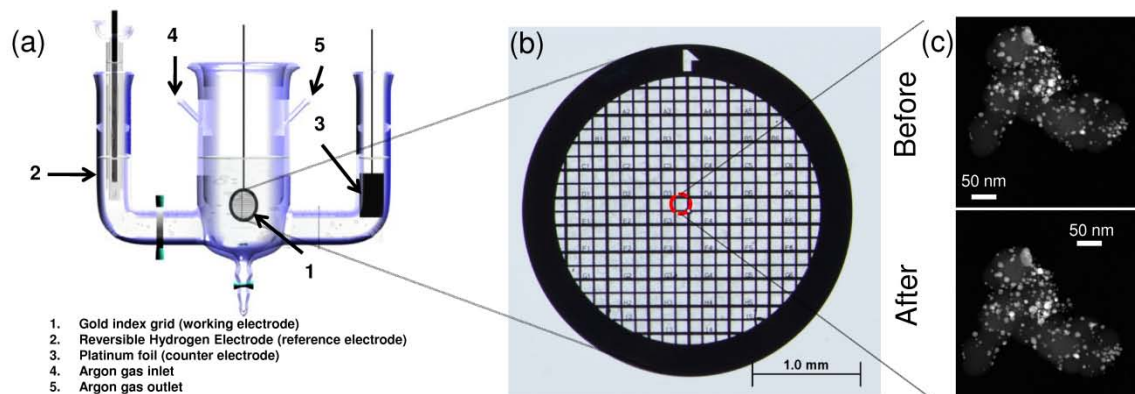


Fig. 1 (a) The schematics of the electrochemistry experiment. (b) The carbon-coated gold finder grid. (c) ADF-STEM images of the same fuel cell materials (metallic nanocatalysts loaded on 3-D carbon-black supports) before and after e-chem aging.

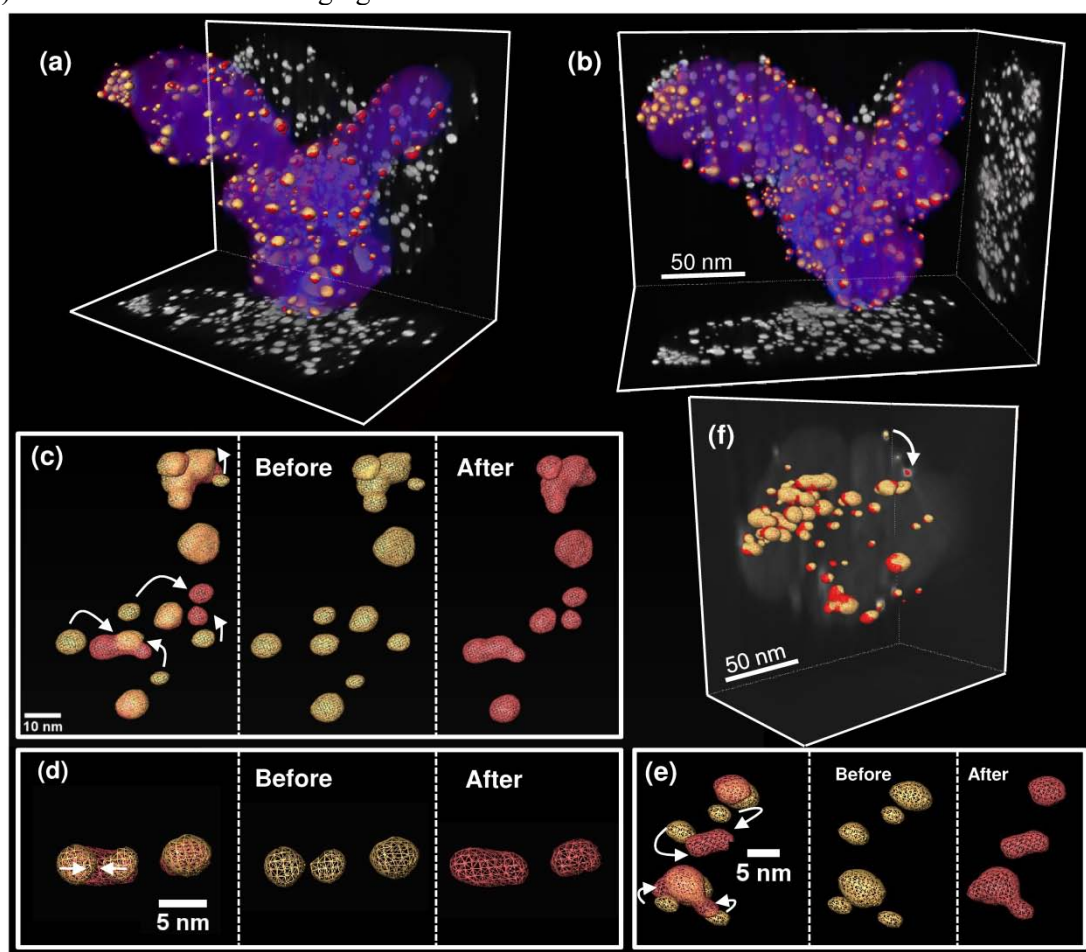


Fig. 2 One-to-one correspondence of nanocatalyst particles before (*gold*) and after (*red*) e-chem aging—same color scheme used in all figures. (a) 3-D reconstruction of nanocatalyst particles, on the carbon support (*violet*) with projected 2-D images shown at each side. (b) Alternate viewing angle. (c,d,e) Several incidents of nanocatalyst particles coalescence and migration, with particle positions indicated by arrows. (f) One example of nanocatalyst particle moving into the positive curvature (valley) from the negative curvature (summit). The arrow points out the trajectory of particle movement. Grey shading is the carbon support.