Nanoparticle Layer-by-Layer Assembly for Fuel Cell Electrodes

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A novel Pt particle synthesis technique has been developed that simultaneous bridges that atomic cluster to single crystal size transition and yields stable suspensions of mono-dispersed particles

$$(Pt - 3Sn)_{complex} \rightarrow Pt^{0}_{metal} + 2\ Sn^{4+}_{ads} + Sn^{2+}_{ads}$$

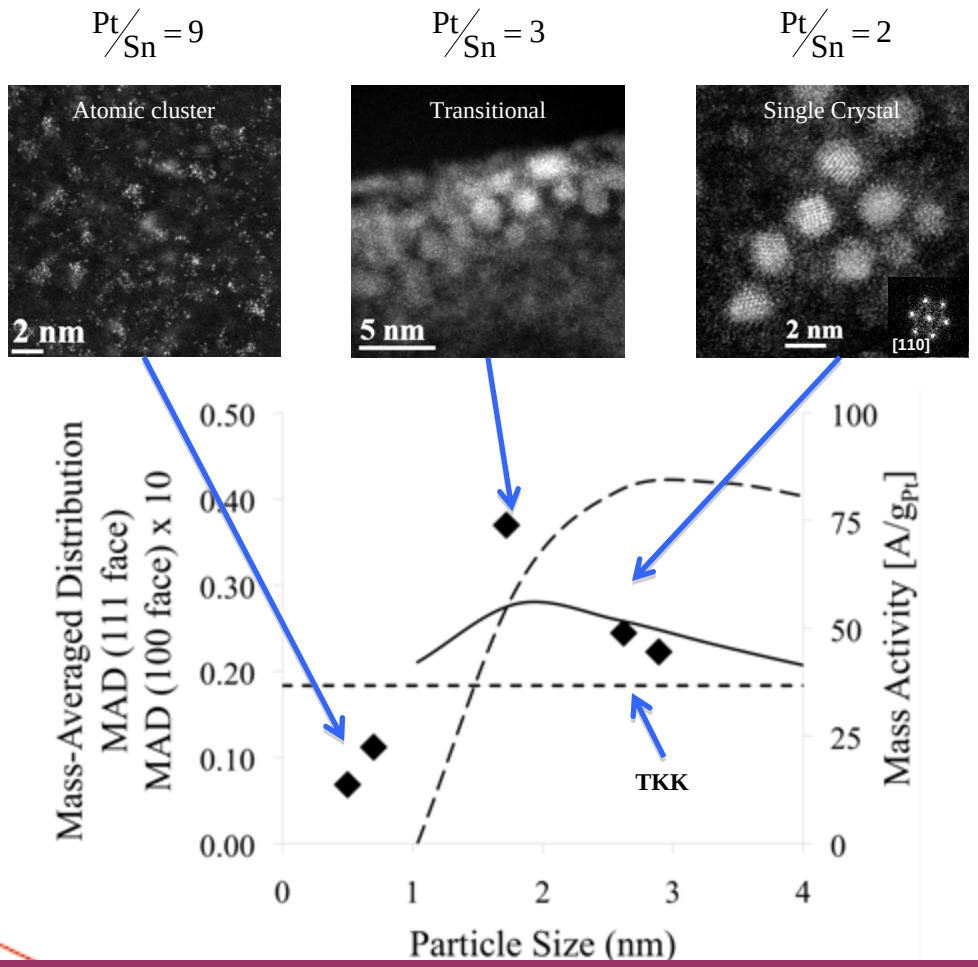

Figure 1: HAADF-STEM images of Pt nanoparticles synthesized from a reducing Sn^{2+}/Pt^{4+} ratio in solution as indicated above each image. Particle size and crystallinity increases progressively as the Sn^{2+}/Pt^{4+} falls from 9 to 2. (inset) The Fourier transforms of the Pt crystalline particles.

Figure 2: Avg. mass activity [A/g_{Pt}] plotted versus particle size (diamonds). Mass-Averaged Dist. (MAD) of face atoms in complete, truncated, cubo-octahedron Pt particles (solid line – (111) face; dotted line – (100) face x 10). Data here are based on calculations by Van Hardeveld et al.[1] Peak activity corresponds to the MAD of (111) face atoms.

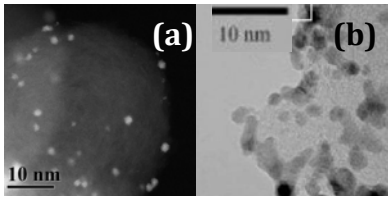

Figure 3: Vulcan LbL supported Pt electrocatalyst. (a) White spots in HAADF-STEM are transitional particles synthesized by PI's group. (b) Commercial system from Tanaka Kikinzoku Kogyo, Japan (TKK).[2] TEM image shows Pt particle agglomeration against a lighter carbon background in contrast to supported transitional Pt catalyst.

References:
1) Van Hardeveld, R.; Hartog, F. *Surf. Sci.* **1969**, *15*, 189.
2) Ferreira, P. J.; la O, G. J.; Shao-Horn, Y.; Morgan, D.; Makharia, R.; Kocha, S.; Gasteiger, H. A. *J. Electrochem. Soc.* **2005**, *152*, A2256.

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RESULTS: The data presented demonstrate that atomic clusters of Pt are electrically conductive and catalytically active. Peak ORR mass activity coincides with a transitional structure between single-crystal nanoparticles and more loosely packed atomic clusters. Mass activity is found to be about twice that measured on commercial Vulcan-supported catalyst. Such behavior is in contrast to hypotheses that have attempted to correlate peak ORR activity to the MAD of (111) atoms based on calculations for truncated, cubo-octahedral structures.