

Morphology, Properties and Reactivity of Nanostructures

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Metal nanoparticles have long been of paramount importance in many areas such as: emission reduction in cars, hydrogen production via the water-gas shift reaction, and lithium-ion storage in batteries. For these purposes, the size and shape of the nanoparticles have been shown to play a crucial role in improving nanoparticle performance.

In catalytic applications, reduced nanoparticle sizes generally lead to higher activity per unit mass of the catalyst, but also the tendency to sinter due to concomitant increases in the surface free energy, leading to catalyst deactivation especially at elevated temperatures. To investigate this phenomena, (Pt,Au)-iron oxide heterodimer (HD) nanoparticles were irradiated with a 532 nm pulsed laser, with laser powers of 4-25 mW within a TEM microscope to investigate particle sintering in an *in-situ* condition. The Au and Pt phases were both found to wet over the Fe₃O₄ phase, a behavior opposite of Strong Metal Support Interactions (SMSI) which was expected from previous work by others. This new behavior demonstrates that not only nanoparticle size, but also the support size can affect catalytic properties. This is shown by the fact that the size of the support oxide in these HD nanoparticles are only 3 times the diameter as large as the active metal nanoparticles, compared to at least 20 times size difference for a standard supported metal oxide system.

Nanoparticle metal catalysts can also undergo significant catalytic improvement by the addition of promoting metals. Kinetics were measured on a Pt/Co on carbon nanotube support, and addition of Co was seen to improve the turnover frequency by 10 times. Leaching of the bulk Co phases, while preserving PtCo alloy structures, reduced activity by more than 18 times demonstrating the need for a Pt/CoO_x interface for catalytic promotion, and that PtCo alloying did not produce the promotion effect.

Yet another important field in which nanoparticle morphology research is essential is that of development of lithium-ion batteries. The current commercial graphite anode for lithium batteries is unfortunately prone to formation of lithium plating during use, from which well-documented safety issues arise. We demonstrated the use of an alternative anode, antimony, to have a measured specific capacity that is 1.6x higher than the theoretical capacity of graphite. Antimony, however, suffers from low cyclability due to large volumetric changes (~150%) upon expansion. To combat this problem, several different synthesis methods to produce nanoparticles of differing structures were tested and it was found that amine boranes produce a unique 3D nanochain structure with stable particle sizes of ~30 nm. These “3D nanochains” were found to have a stable charge capacity retention (98%) after 100 cycles due to their unique morphology which allows for the expansion that occurs during the lithiation process.