Configurational Thermodynamics of Alloyed Nanoparticles under Working Condition

Lin-Lin Wang

Ames Laboratory, U.S. Department of Energy, Ames, IA 50011

Transition-metal alloyed nanoparticle (NP) catalysts are key components in current and emerging energy technologies. However, the difficulty of characterizing and describing the configurational changes in alloyed NPs under working condition remains a significant challenge to understand and design NP functionality. To address this challenge, the cluster expansion (CE) method has been recently extended to predict the configurational thermodynamics of alloyed NPs on equal footing with adsorbate thermodynamics based on density functional theory (DFT) data. The ability to evaluate the energetics over a huge number of alloy configurations from the optimal CE Hamiltonian at the accuracy of the input DFT data enables the study on the configurational thermodynamics of alloyed NPs and adsorbates in detail. Ag-Au NPs have been found to prefer multi-shell configurations. The behaviors of core-shell reversal in Pd-Rh NPs as induced by oxygen adsorption have been described quantitatively well in agreement with *in situ* experimental data. Furthermore, the H-adsorption isotherms and voltammetry for hydrogen evolution reaction on Pd-Pt NPs has been simulated across the entire range of NP composition.

1.   L.-L. Wang, T. L. Tan, and D. D. Johnson "Nanoalloy composition-temperature phase diagram for catalyst design: Case study of Ag-Au", *Physical Review B., 86*, 035438 (2012).

2.   L.-L. Wang, T. L. Tan, and D. D. Johnson "Configurational thermodynamics of alloyed nanoparticles with adsorbates", *Nano Letters*, 12, 4875-4880 (2014).

3.   L.-L. Wang, T. L. Tan, and D. D. Johnson "Nanoalloy electrocatalysis: simulating cyclic voltammetry from configurational thermodynamics with adsorbates", *Phys. Chem. Chem. Phys.*, 17, 28103-28111 (2015).