**MS64.O01**

## *Dynamic structure in nanoclusters and its effect on size & shape modeling*

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As recently as 10-15 years ago, nanoparticles were described qualitatively: oblate and hemispherical, discs and rafts. Today we discriminate between different faceted nano-architectures with unprecedented accuracy using EXAFS. As an illustration (Fig. 1), we will describe a Pt particle in equilibrium with support and adsorbate. We will show how to resolve analytically metal-support, metal-adsorbate, and support-adsorbate and obtain the size and shape information. We will show new methods for circumventing the main limitation of EXAFS analysis. EXAFS works best for ordered systems while nanoparticles have strong, asymmetric bond length disorder. They also have nonbulklike dynamics: the surface bonds are soft, while the interior bonds are stiff, resulting in a bimodal distributions of bonds. This heterogeneity, if not accounted for, results in smaller coordination numbers and, hence, in smaller particle sizes compared to the actual ones [1]. Conventional EXAFS analysis, based on the solution of "inverse problem" where experimental spectra is an input, and the unknown cluster architecture is an output, is unstable for systems with strong and asymmetric disorder. We will present a new methodology for the analysis of nm-scale clusters based on solving "direct problem". The starting point is the model system investigated using DFT-MD simulations to produce theoretical EXAFS signals that could be directly compared to the experimental results. The information that is learned from theory can be compared with traditional EXAFS fitting results to identify and rationalize any errors in the experimental fit. Our study, using both supported [2] and unsupported [3] clusters, demonstrates that DFT-MD simulations accurately depict complex experimental systems, and shows the advantages of using a combined experimental/theoretical approach over standard EXAFS fitting methodologies for determining the structural and dynamic parameters of metallic nanoparticles.

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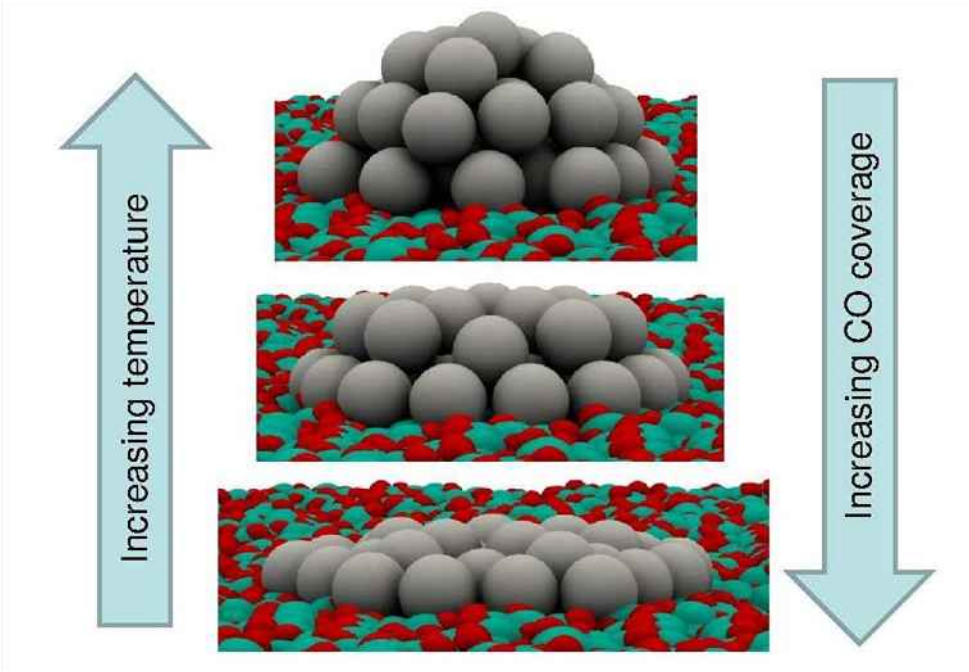


**Keywords:** structure of nanoparticles, exafs, dynamic structure