Strongly Size-Dependent Oxidation and Reduction of Cu Clusters

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At the nanoscale, the processes of oxidation and reduction are known to be strongly size-dependent, which has important implications for issues such as catalytic activity and cytotoxicity. Copper clusters are used as catalysts for several industrially significant reactions; for some of these it is preferable that the clusters are in their elemental state, while for others a certain degree of oxidation is desirable. One would therefore like to know whether or not Cu clusters would be oxidized for a given size and specified set of environmental conditions. We have used a combination of ab initio density functional theory and ab initio atomistic thermodynamics to generate size-dependent phase diagrams of copper clusters in oxidizing and reducing environments. We find that these phase diagrams differ both qualitatively and quantitatively from the corresponding phase diagrams of the bulk materials. From these phase diagrams, we can extract transition temperatures at which the clusters change their oxidation state. We obtain remarkably good agreement between these theoretically predicted values and the experimental values extracted from XANES measurements. We also suggest a new way of correlating the theoretical predictions with the experimental measurements.