Investigation of Stability Trends in Bimetallic CuAg, CuAu, and AgAu Nanoparticles via Bond-Centric Model

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ABSTRACT

Metal nanoparticles (NPs) have attracted tremendous scientific interest over the last several decades due to their diverse technological applications, among which is catalysis. Compared to monometallic NPs, bimetallic NPs allow for a greater variation of local chemical environments and thus, control of potential catalytic sites. However, this local site variation also results in a significantly larger search space when investigating NPs of even the same bimetallic nanoparticle composition, size, and shape. Using a previously developed bond-centric (BC) model[1] as a means to calculate computationally fast a NP's cohesive energy, a code was developed to efficiently determine potential ground-state structures for any given bimetallic NP. The cohesive energy was determined for 55- and 147-atom icosahedral and cuboctahedral NPs, consisting of CuAg, CuAu, and AgAu ranging from 0-100% in metal composition. At each given composition and morphology, atomic identities within the NP are shuffled several thousand times, calculating the cohesive energy for each sampled microstate.

BACKGROUND AND AIMS

- Nanoparticles have numerous applications in electronics[2], optics[2], catalysis[3], and medicine[4]
- Bimetallic NPs (BNPs) allow for more diverse chemical properties potentially leading to enhanced catalytic activity[5]
- Cohesive Energy (CE) is a measure of NP stability
- Density Functional Theory (DFT) calculations are accurate but computationally expensive to calculate CE
- Excess Energy (EE) allows for comparison of NPs of different composition
- Previously-developed BC model[1] can efficiently calculate CE of BNPs

Aims:

- Investigate the composition and morphology of BNPs using Monte Carlo sampling in conjunction with BC model[1] to calculate CE
- Determine preferred chemical ordering in BNPs

Overall: Identify most thermodynamically stable BNPs

METHODS

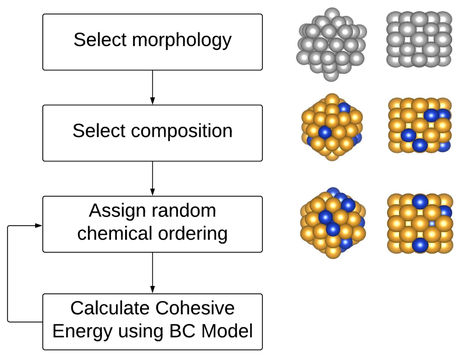
- Atomic Simulation Environment (ASE) as implemented in Python
- Wrote a code that generates NPs and calculates CE using BC Model[1]:

$$CE_{BNP} = \frac{\sum_1^m \gamma_i \frac{CE_{bulk,i}}{CN_i}\sqrt{\frac{CN_i}{CB_i}} + \gamma_j \frac{CE_{bulk,j}}{CN_j}\sqrt{\frac{CN_j}{CB_j}}}{n}$$

- EE of A_xB_y was calculated using the following formula[1]:

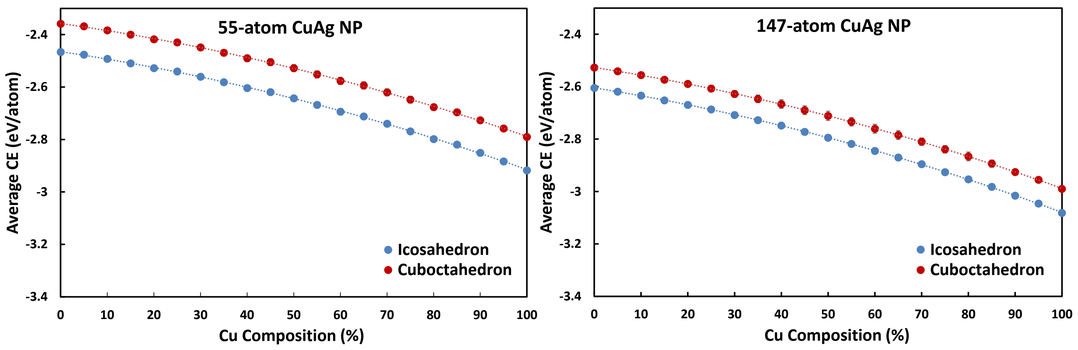
$$EE = CE_{BNP} - \frac{x}{x+y}CE_{A_{x+y}} - \frac{y}{x+y}CE_{B_{x+y}}$$

- Sampled 55- and 147-atom icosahedral and cuboctahedral BNPs consisting of CuAg, CuAu, and AgAu, from 0-100% dopant, in 5% increments
- 350,000 chemical orderings/composition were sampled on the 55-atom BNPs
- 1,000 chemical orderings/composition were sampled on the 147-atom BNPS



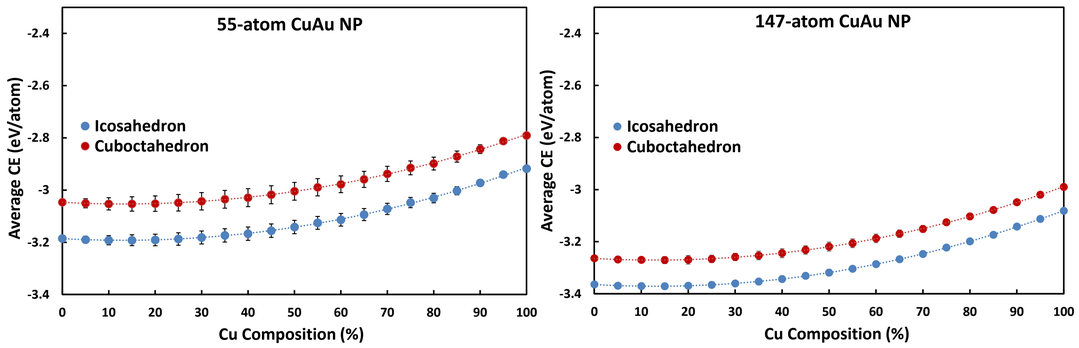
RESULTS

Cohesive Energy (Metal Binding)



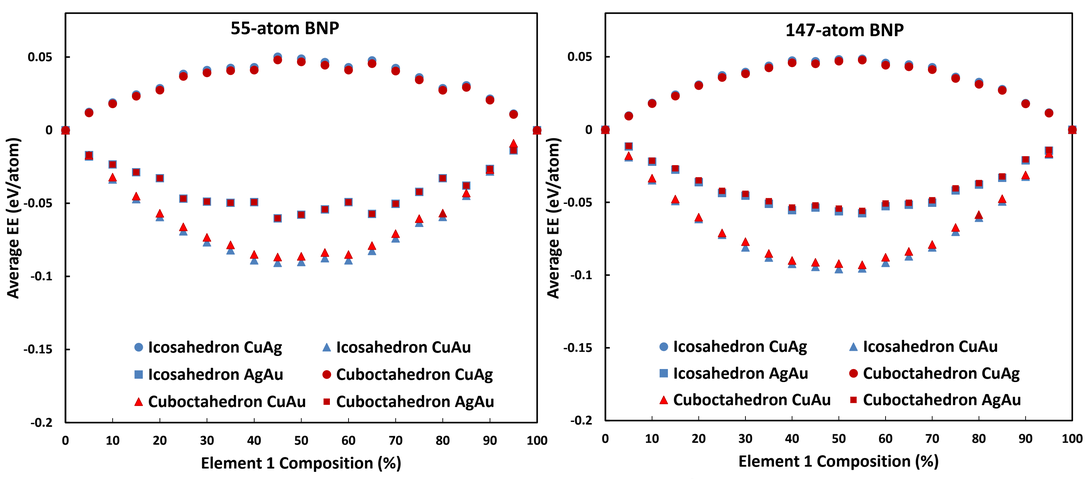
- Average CE decreases (more exothermic) as the Cu composition increases in CuAg BNPs

- Average CE increases (less exothermic) as the Ag composition increases in AgAu BNPs



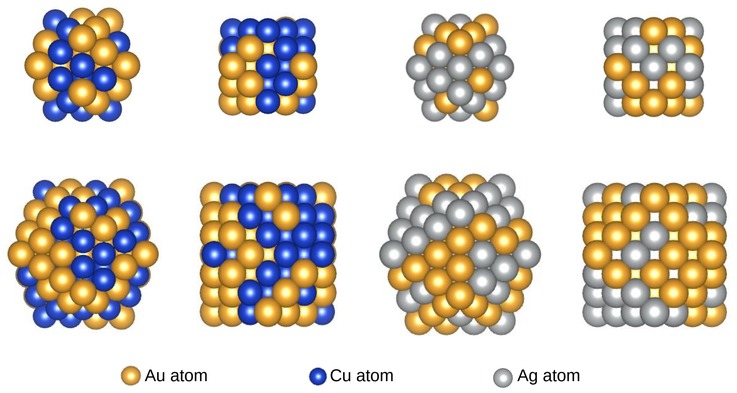
- Average CE increases (less exothermic) as the Cu composition increases in CuAu BNPs

Excess Energy (Metal Mixing)



- Suggests that Cu and Ag do not form 55- or 147-atom icosahedral/cuboctahedral BNPs
- Suggests the favorable formation of 55- and 147-atom CuAu and AgAu icosahedral/cuboctahedral BNPs tending towards 50% elemental composition

RESULTS



- Minimum-energy structures of the 55- and 147-atom cuboctahedral and icosahedral 50/50 CuAu and 50/50 AgAu BNPs

SUMMARY

- Investigated BNP stability by calculating CE and EE using a previously developed BC model[1]
- Compared different chemical orderings within the same composition
- Identified the favorable formation of 55- and 147-atom icosahedral and cuboctahedral CuAu and AgAu BNPs

Future Work: Incorporate symmetry operations to simulate BNPs of larger size

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