Local Chemical Environment in Cu_3N and Pd-Doped Cu_3N Nanoparticles: Insights from Spectroscopy

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Abstract. Copper nitride (Cu_3N) nanoparticles have a variety of possible applications in fields like photovoltaics, energy storage, electronics, or catalysis [1, 2]. Doping with Pd can be used to tune their electronic and optical properties [1, 2, 3] to optimize them for specific applications. When doping Cu_3N with Pd, the Pd atom can assume the position at the body center of the Cu_3N primitive cell, but can also replace Cu at the face center position, or, ultimately, form a Cu-Pd alloy. In this joint experiment-theory study, we use density functional theory (DFT) and transition potential DFT (TP-DFT) to model Pd-doped Cu_3N lattices and calculate their N K-edge [3] and Cu L-edge [4] X-ray absorption spectra. By modeling several lattice structures of perfect and defective Cu_3N and Cu_3PdN crystals with defects including Pd substitution, Pd-Cu switches, and N or Pd vacancies, we are able to reproduce the trends observed experimentally when comparing pristine Cu_3N to Pd-doped nanoparticles. In particular, both the measured N K-edge and Cu L-edge X-ray absorption spectra of the Pd-doped system can be qualitatively reproduced by a Cu_3PdN lattice with Pd and N vacancies.

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