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Prediction and Design of Materials from Crystal Structures to Nanocrystal Morphology and Assembly[1]

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Predictions of structure formation by computational methods have the potential to accelerate materials discovery and design. Here we present two computational approaches for the prediction of crystal structures and the morphology of nanoparticles. Many materials properties are controlled by composition and crystal structure. We show that evolutionary algorithms coupled to ab-initio relaxations can accurately predict the crystal structure and composition of compounds without any prior information about the system. We will discuss results for various systems including the prediction of unexpected quasi-1D and 2D electronic structures in Li-Be compounds under pressure [1] and of the crystal structure of the superconducting high-pressure phase of Eu [2]. The self-assembly of nanocrystals into mesoscale superlattices provides a path to the design of materials with tunable electronic, physical and chemical properties for various applications. The self-assembly is controlled by the nanocrystal shape and by ligand-mediated interactions between them. To understand this, it is necessary to know the effect of the ligands on the surface energies (which tune the nanocrystal shape), as well as the relative coverage of the different facets (which control the interactions). Density functional calculations for the binding energy of oleic acid-based ligands on PbSe nanocrystals determine the surface energies as a function of ligand coverage. The Wulff construction predicts the thermodynamic equilibrium shape of the PbSe nanocrystals as a function of the ligand coverage. We show that the different ligand binding energies on the 100 and 111 facets results in different ligand coverages on the facets and predict a transition in the equilibrium shape from octahedral to cubic when increasing the ligand concentration during synthesis. Our results furthermore suggest that the experimentally observed transformation of the nanocrystal superlattice structure from fcc to bcc is caused by the preferential detachment of ligands from particular facets, leading to anisotropic ligand coverage [3].

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