

Ligand-Mediated Interactions between Nanoparticles

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Many inorganic nanoparticles are covered in ligand monolayers, which can undergo a temperature-dependent order-disorder transition in solution that switches the particle-particle interaction from repulsive to attractive.[1] In this work [2] we examine how changes in the ligand surface coverage and facet dimensions, going from the macroscale to the nanoscale, affect the ordering of the ligand and solvent molecules and the interaction between the ligand monolayers. In particular, we consider the case of strongly bound octadecyl ligands on the (100) facet of CdS in the presence of an explicit *n*-hexane solvent (Fig. 1a).

Depending on the facet dimensions and surface cover, we observe three distinct ordered states that differ in how the ligands are packed together (Fig. 1b) and which affect the thickness of the ligand shell and the structure of the ligand-solvent interface. The temperature-dependence of the order-disorder transition also changes substantially, broadening and shifting to lower temperature in a non-linear manner as the nanoscale is approached. Significantly, we find that ligands on nanoscale facets can behave very similar to those on macroscopic surfaces, and that some facet dimensions affect the ligand alignment more strongly than others.

As the ligands order, the interaction between the monolayers becomes attractive, even well below full cover (Fig. 1c). The strength of attraction per unit area is strongly affected by the ligand cover but only weakly by the facet width.

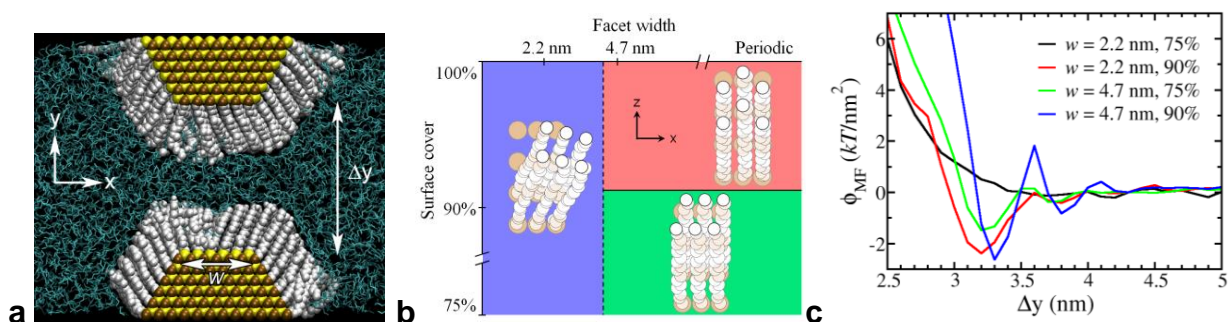


Fig. 1 (a) Octadecyl ligands order on two CdS(100) surfaces in *n*-hexane at 290 K. The facet width w and surface cover strongly affect (b) the structure of the ordered state and (c) how the surfaces interact with one another (ϕ_{MF} is the potential of mean force per unit facet area).

Our results add to a growing body of evidence that ligand-mediated interactions can exert a particularly strong influence on the assembly of faceted nanoparticles.[3] The strongly temperature-dependent mode of interaction we have examined suggests new ways to control assembly by modulating ligand structure, for example by reversibly activating strong face-to-face attraction between ordered ligand layers through modest changes in temperature. Such control levers can be used to determine whether ligand-covered particles remain suspended in solution, randomly aggregate, or undergo controlled assembly into large-scale ordered structures.

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2) A. Widmer-Cooper and P.L. Geissler, *ACS Nano* **2016**, *10*, 1877-1887.

3) (a) P. Born and T. Kraus, *Phys. Rev. E* **2013**, *87*, 062313. (b) M.R. Jones, R.J. Macfarlane, A.E. Prigodich, P.C. Patel and C.A. Mirkin, *Nature* **2011**, *133*, 18865-18869. (c) X. Ye, J. Chen, M. Engel, J.A. Millan, W. Li, L. Qi, G. Xing, et al. *Nat. Chem.* **2013**, *5*, 466-473.