

Electrostatic forces drive the formation of nanostructured hydroxide films on mica

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When predicting the properties of nanoparticles and nanostructured materials, scientists often resort to macroscopic conceptual models, envisioning the particles as microscopic fragments of an idealized bulk material. This is exemplified in the classical nucleation theory, in which the energetic properties of nanoscale nuclei are typically modeled using the ‘capillarity approximation’ as a sum of volume-scaling, surface-scaling, and/or edge-scaling energy terms, which may be estimated from bulk-scale properties. However, nanoparticles exist in a size-regime where such idealized scaling laws may not hold.

State-of-the-art imaging tools like *in situ* atomic force microscopy (AFM) now make it possible to directly observe nanoparticles and determine their true energetic properties. In recent work, we used AFM to track the growth metal-hydroxide films (gibbsite, brucite, etc...) at the mica-water interface. In the case of gibbsite, we observed populations of dynamically fluctuating nanoscale metal-hydroxide clusters prior to film formation. By measuring these populations, we were able to calculate size-dependent energy landscapes, and we observed stark discrepancies with classical expectations.

We explain these deviations through new ‘charge-frustrated’ simulations that consider the electrostatic interactions between the metal-hydroxide clusters (which are positively charged), and the mica substrate (which is negatively charged). Our simulations predict new energetic scaling laws and strong electrostatic couplings between neighboring clusters. When clusters are sufficiently charged, they spontaneously form a pattern of interdigitated nanoscale islands and gaps, which forms via a barrierless process of ‘microphase separation’ rather than classical nucleation and growth. The resulting film is not a two-phase system of particles and bare surface, but rather a single phase that is intrinsically nanostructured. These models are further tested in AFM by using nanoscale charge-mapping techniques. We have observed this microphase separation for several trivalent metals (i.e. Fe³⁺, Cr³⁺, Al³⁺) that create highly charged hydroxide films, but divalent metals (i.e. Mg²⁺, Co²⁺, and Ni²⁺) create less highly charged films, and display classical nucleation and growth.

Our results highlight the ability of advanced experimental methods to provide new insights into the behavior of nanoparticles, and demonstrate how charged nanomaterials display unique phenomena that are intrinsically linked to their size.