Detection, Prediction, and Visualization of Ligand Phase Separation on Metallic Nanoparticles

Abstract

Our objective is to develop techniques that enable the detection, prediction, and visualization of ligand phase separation on small patchy nanoparticles (NPs). Silver NPs were functionalized with dodecanethiol (DDT) and one other ligand from a series alkanethiol homologues ranging from deuterated dodecanethiol (DDT[D25]) down to butanethiol. Further, monolayers were formulated from mixtures of DDT and 2-mercaptoethanol (2-ME). Ligand choice was based on the hypothesis that increased chemical and physical mismatch should lead to increased phase separation. Minimum phase separation was anticipated for DDT/DDT[D25] with only isotopic differences. At the opposite extreme, DDT/2-ME was expected to phase separate into a Janus morphology due to large chemical and physical ligand differences. Other pairings of DDT with alkanethiol ligands (4-11 carbons) have varying degrees of physical mismatch, pointing to phase separation between well-mixed and Janus morphologies.

Hence, matrix-assisted laser desorption/ionization mass spectrometry (MALDI) measurements were compared with self-consistent mean-field (SCF) calculations to detect and predict ligand phase separation on NPs. The combination of MALDI with SCF allows comparison between experimentally and theoretically-derived spectra as well as their deviation from a well-mixed state. Further, we applied energy-filtered transmission electron microscopy (EFTEM), MALDI measurements, and SCF predictions to probe and predict the phase separation of DDT and 2-ME ligands into Janus nanoparticles. The MALDI measurements point towards a very high degree of phase separation, which is further emphasized by our EFTEM results, which reveal the 2-ME ligand localized to one hemisphere of the NP. Spectra calculated from SCF for Janus formation also that match from MALDI. Hence, the measurements and predictions support Janus nanoparticle formation. Thus, we conclude that the complementary techniques of MALDI, SCF, and EFTEM therefore represent a versatile toolkit for characterizing ligand phase separation on very small NPs.

Biosketch:

David Green is an Associate Professor in Chemical Engineering at the University of Virginia. The overarching theme of his studies is to elucidate and quantify how polymers at interfaces control the actions of nanoparticles and polymer droplets in polymer solutions, melts, and blends with applications towards all facets of nanotechnology. He received his PhD at the University of Maryland at College Park (UMCP) in Chemical Engineering, his MS at UMCP in Civil and Environmental Engineering, and his BS from Boston University in Mechanical Engineering. Dr. Green has won a number of awards including a Sloan PhD Fellowship, NSF International Postdoctoral Fellowship, and an NSF CAREER Award.