



Thomas E. Mallouk

Pennsylvania State University

Tuesday, October 24, 2017; 2:15 PM

Tom Mallouk is Evan Pugh University Professor of Chemistry, Biochemistry and Molecular Biology, and Physics and Head of the Department of Chemistry at Penn State University. He was an undergraduate at Brown University, where he worked with Aaron Wold, was a graduate student with Neil Bartlett at the University of California, Berkeley, and did postdoctoral research with Mark Wrighton at MIT. He began his independent career at the University of Texas at Austin before moving to Penn State in 1993. His research is focused on problems in materials chemistry, including photoelectrochemistry, electrochemical energy conversion, low-dimensional physical phenomena, and motion on the nanoscale. He

is a member of the National Academy of Sciences and of the American Academy of Arts and Sciences, a Fellow of the American Chemical Society and of AAAS, and has received numerous awards for teaching and research.

Abstract: Assembly and Disassembly of Layered Solids

Layered solids – which have strong bonds in two dimensions and weaker links in the third - are interesting building blocks for composite materials and devices because they potentially offer control over structure at the molecular level. Our research in this area began with the question of whether such compounds could be built up one layer at a time in controlled sequences on surfaces. This was possible by using either molecular precursors, in the case of metal phosphonates, or exfoliated sheets derived from lamellar microcrystals. Many layered oxides consist of negatively charged sheets interleaved by exchangeable cations. These oxides are particularly amenable to exfoliation (and to other topochemical reactions) by simple ion-exchange and acid-base reactions. Recently we have found that van der Waals solids such as graphite, hexagonal BN, and MoS₂ can also be intercalated and exfoliated without incurring damage to the sheets by means of acid-base and redox reactions.

An interesting consequence of the layer-by-layer assembly processes is the overcompensation of the surface charge of nanosheets. This effect can be exploited to invert the layer charge of nanosheets (which is typically negative for sheets derived from early transition metal oxides) and enable the intercalation of negatively charged molecules and nanoparticles. While studying these reactions, we observed surprisingly strong bonding between late transition metal oxide nanoparticles and early transition metal oxide nanosheets. Calorimetric measurements and electronic structure calculations suggest that d-acid/base interactions – originally proposed by Leo Brewer to explain the anomalous stability of early-late transition metal alloys – contribute to the strength of nanoparticle/nanosheet covalent bonding. This finding helps us understand the strong metal support interaction (SMSI) in catalysis and provides a prescription for stabilizing catalytically active late transition metal nanoparticles.