Molecular Engineering of Surfaces:

Applications in Environmentally Benign Catalysis, Separations, and Medicine

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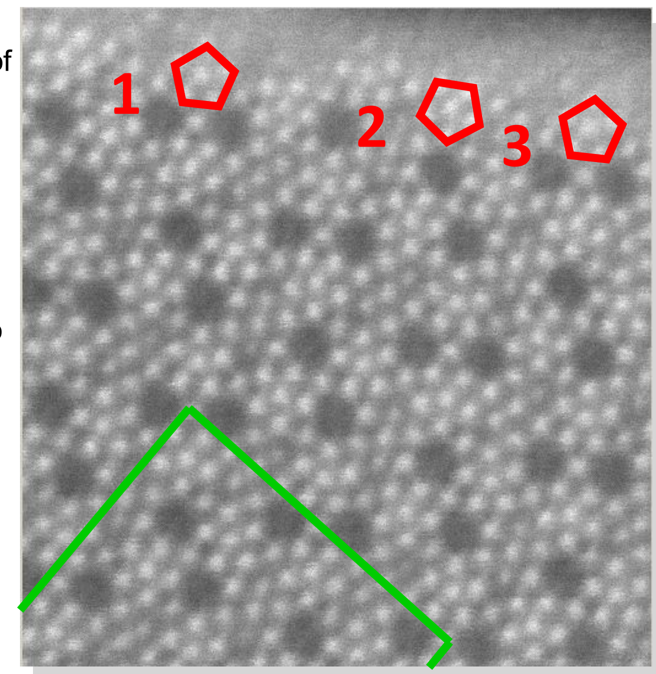
The rational design of complicated structures, from atoms and molecules to macroscale entities, remains one of the most difficult challenges of today's materials science and engineering. It is now becoming possible to design three-dimensional structures on multiple length scales from a few Å to ~100 nm by employing structure-directing agents or space-fillers.

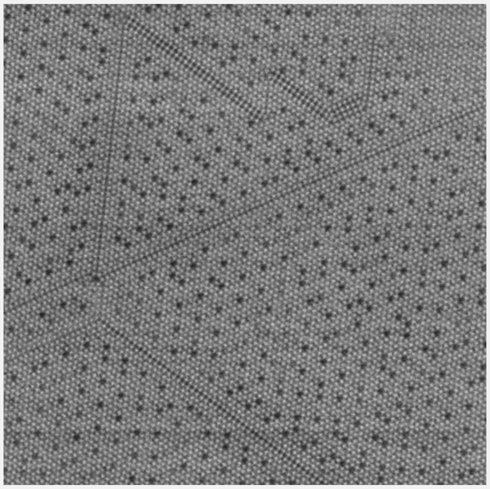
Individual organic molecules and polymers are used to control the structure, composition, particle shape and size, as well as surface sites of crystalline metal oxides, metals, and *microporous* frameworks (zeolites, metal-organic frameworks, etc.) with pores <2 nm, for applications in catalysis and separations involving small molecules.



The *ab* planes of the catalytic M1 phase containing Mo, V, Sb and Nb cations visible in this image as bright spots. The *ab* plane contains the active and selective catalytic sites responsible for the transformation of propane to acrylonitrile. The outlines of the 2x2 supercell of the M1 phase are shown in green, while so-called pentagonal sites S9 at the edge (i.e., in the surface layer) of the M1 phase are located in the middle of red pentagons. The analysis of normalized intensities of S9 and 5 other sites surrounding it in a pentagon (S5, S6, S8, S10, and S11) reveals that the surface has essentially the same chemical composition as the center of the M1 crystal.

Ordered *mesoporous* oxide structures with 2-30 nm pores obtained using surfactant arrays or block copolymers are attractive not only as catalysts, catalytic supports and adsorbents for applications involving larger molecules, such as proteins and enzymes. Even larger pores (>40 nm) are templated by emulsions and a variety of colloidal sphere arrays. Dual templating in the presence of surfactant and colloidal sphere arrays leads to hierarchical *macroporous* solids with *mesoporous* walls that exhibit several levels of structure (atomic, nano-, meso- and macroscale).

Lastly, graphene sheets, a recently discovered form of carbon, can be also organized into a broad range of *mesoporous* structures by growing them inside sacrificial porous template or by chemically bonding them to amorphous carbon nanoparticles. These novel structures offer advantages of highly tunable surface chemistry, very high surface areas (> 1,000 m^2/g) and pore volumes, as well as high thermal and electronic conductivity, that are very promising for applications in catalysis and separations.



The *ab* planes of M2 shows some very unusual structural features of a defective M2 phase: point defects corresponding to missing Te sites which are visible as dark spots, and two-dimensional (planar) defects visible as series of intersecting “zippers”.

Surface chemistry of these novel materials could be further tuned by grafting various organic functional groups, such as hydrophobic alkyl, aryl and thiol; and hydrophilic, charged or uncharged, such as alcohol, carboxylate, amine, and quaternary ammonium cations.

The technological potential of these materials is to be realized through our ability to tailor their exceptional size-dependent properties for novel (bio)catalytic, biomaterials, adsorbent, and other applications. By tying together chemical engineering principles, surface science and materials chemistry, my group seeks to understand the process chemistry and structural physics of nanocrystalline and nanoporous systems. As a result, most projects involve three stages:

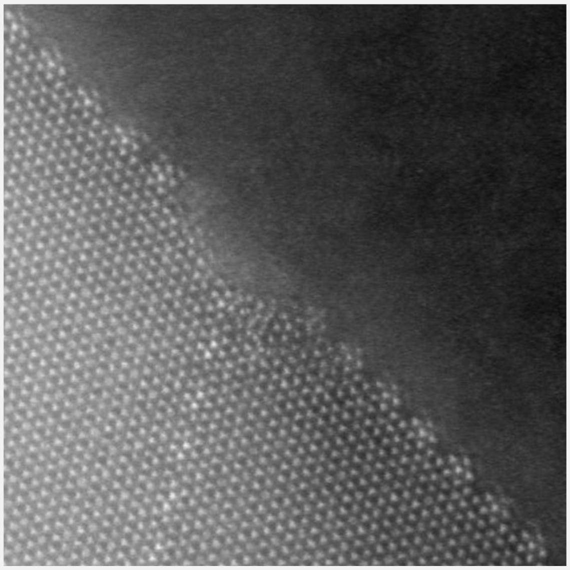
1. **The design stage** with the development of self-assembly approaches and the study of mechanisms
2. **The synthetic stage** with the preparation of novel materials
3. **The characterization stage** with characterization of structure, properties, and function

Current Research In Heterogeneous Catalysis

- The development of nanostructured mixed metal oxide catalysts for the conversion of propane, a major component of shale gas, into acrylonitrile, a top 50 chemical in the world, that is primarily used in manufacturing plastics
- The development of novel metal nanoparticle catalysts for the conversion of C5 and C6 furans obtained from biomass into alternative fuels, chemical intermediates, solvents, and food additives
- The development of environmentally benign, Cr-free, and sulfur-resistant water-gas-shift catalysts to produce hydrogen from coal for electricity generation

Current Research In Gas and Medical Separations

- carbon dioxide separation from flue gas and natural gas employing zeolite-type imidazolate frameworks;
- separation of toxic heavy metal cations from wastewater employing surface-functionalized, high surface area oxides;
- the removal of excess phosphate from blood of chronic kidney disease (CKD) patients using La-containing graphene adsorbents to prevent cardiovascular disease that leads to high mortality and morbidity in the CKD population



The *ab* planes of another catalytic phase, so-called M2 phase, that works together with the main catalytic M1 phase to transform propane to acrylonitrile. This phase has a simpler structure than the M1 phase and also lacks characteristic pentagonal sites S9 that contain either Nb or Ta in its bulk. However, this image shows that the M2 phase synthesized in the presence of Ta has no Ta in its bulk, but exhibits regular arrays of Ta-containing pentagonal sites that terminate the surface of the M2 phase.

Educational Outreach

A diverse cohort of postdoctoral associates, graduate and undergraduate students is conducting surface engineering research that presents them with numerous unique opportunities to interact with industrial partners, publish peer-reviewed papers, and present at prime scientific conferences in the US and internationally. Over the last ~10 years, these students appeared more than 150 times as co-authors in scientific publications and conference presentations on novel materials with engineered surfaces for applications in catalysis, separations, and medicine.

More about Dr. Guliants

Dr. Guliants, Professor of Chemical Engineering, has been teaching and conducting research at UC since 1999. He has served as Chair of the Energy and Materials Engineering program and earned a number of prestigious awards, including the Outstanding Research Award for Young Faculty (from UC's College of Engineering), UC's Teaching Diversity Award, and the National Science Foundation's CAREER and NIRT Awards.

Recent Publications

- J.-H. Lin, **V. V. Guliants**, "Alumina-Supported Cu@Ni and Ni@Cu Core-Shell Nanoparticles: Synthesis, Characterization, and Catalytic Activity in Water-Gas-Shift Reaction", *Applied Catalysis* 445-446 (2012) 187-194.
- J. Yu, J. Woo, A. Borisevich, Y. Xu and **V. V. Guliants**, "A Combined HAADF STEM and Density Functional Theory Study of Tantalum and Niobium Locations in the Mo-V-Te-Ta(Nb)-O M1 Phases", *Catalysis Communications* 29 (2012) 68-72.