JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Cite This: J. Am. Chem. Soc. XXXX, XXX, XXX−XXX
Spotlights
pubs.acs.org/JACS

Spotlights on Recent *JACS* Publications

OUT OF ONE, MANY FOR ZNSE NANOSTRUCTURES

The size and shape of nanocrystals determine their material properties. Research into how this interaction plays out in semiconductor nanocrystals has mainly focused on materials containing heavy metals, such as cadmium chalcogenide nanocrystals. These can be toxic and lead to concerns about environmental impacts, so chemists are working to synthesize heavy-metal-free "green" semiconductor nanostructures.

To that end, Uri Banin, Anatoly I. Frenkel, and co-workers have developed a protocol for producing ZnSe nanostructures with controllable shapes and sizes using well-defined molecular clusters (DOI: 10.1021/jacs.8b05941). The researchers first synthesized ZnSe clusters stabilized with oleylamine ligands. By heating the reaction solution containing these clusters, they generated ZnSe nanowires of 2.4 nm diameter and a few hundred nanometers in length. Adding small amounts of additional zinc clusters disrupted the nanowire growth, leading to significantly shorter nanowires. Increasing the amount of zinc clusters further broke up the nanowires, leading to ZnSe nanorods, and eventually nanodots. The researchers show the ability to expand this technique by replacing the zinc clusters with copper-based clusters to produce Cu-doped nanostructures. This technique opens up new paths for producing controlled semiconductor nanostructures free of heavy metals.

Christen Brownlee

A FORCE TO BE RECKONED WITH: CHEMICAL REACTIONS THROUGH MECHANICAL METHODOLOGIES

Mechanophores are materials that produce a chemical response to a mechanical stimulus, and they have applications in a wide range of settings, from sensors and catalysis. To design new polymeric mechanophores, researchers need a detailed understanding of the relationship between stress and the mechanophores' chemical response. Stephen L. Craig and co-workers demonstrate a new way to investigate these mechanisms through applying the principles of physical organic chemistry to study mechanochemical reactions (DOI: 10.1021/jacs.8b09263).

The team synthesized several spiropyran mechanophores, which included H, Br, or NO_2 in the para position relative to a C−O bond. The C−O bond breaks under mechanical tension, resulting in ring-opening of the spiropyran to afford the longer merocyanine. The authors extracted the rate constant for this ring-opening reaction as a function of force from the single molecule force curve of each spiropyran derivative. Examining these rate constants with different para substituents indicates that the reaction proceeds through a highly polar transition state. This study demonstrates the value of establishing linear free energy relationships in mechanochemical processes and lays the groundwork for future studies that can provide greater mechanistic insight into these mechanochemical reactions.

Elizabeth Meucci

SILVER NANOPARTICLES CONVERT CO_2 INTO USEFUL MOLECULES

One approach to combatting the impending environmental disaster of climate change is to remove CO_2 from the atmosphere. To make such an approach economically feasible, chemists are seeking ways to use CO_2 in reactions to make useful chemical commodities. Methyl formate is a building-block molecule, often used to synthesize industrially important chemicals such as acetic acid, ethylene glycol, methanol, and formic acid. Currently methyl formate is produced using CO and methanol. It is also possible to create methyl formate from CO_2 and H_2 using Cu or Au catalysts, but chemists are not sure of the specific roles of either metal or the metal-oxide support, and the type of reactive species that drives the reaction remains unclear as well.

Now, Atsushi Urakawa and co-workers have developed a silver nanoparticle catalyst supported on silica (DOI: 10.1021/jacs.8b08505). The researchers examine the catalytic reduction of CO_2 to methyl formate in the presence of methanol, and using both vibrational spectroscopy and theory, they uncover the important role of the silanol groups at the interface between the silica support and silver catalyst particles. This new understanding can contribute to the design of better catalysts for this important reaction.

Leigh Krietsch Boerner, Ph.D.

RADICAL STABILITY IN LARGE GRAPHENE-LIKE MOLECULE

Graphene, the wonder nanomaterial with unique mechanical and electronic properties, continues to challenge and delight chemists as they pursue synthesis of increasingly complex graphene-like molecules (GLMs). GLMs are all-benzenoid polycyclic molecules that come in a variety of geometries, including ribbons with either "armchair" or "zigzag" edges. Jishan Wu and co-workers have set a new record by successfully synthesizing the largest Z-shaped nanographene with zigzag edges to date, a super-octazethrene (SOZ) derivative that consists of 14 fused benzene units (DOI: 10.1021/jacs.8b09075).

Like other zethrene molecules, SOZ is an open-shell diradical in its ground state, and the free electrons make it unstable and difficult to synthesize. Wu and co-workers added bulky electron-withdrawing groups to the zigzag edges to kinetically block reaction sites and stabilize the structure.

GLMs serve as model graphene materials to allow scientists to better probe and understand the properties of graphene. They also serve as potential building blocks for nanoelectronic and spintronic applications. This new approach paves a way forward to synthesize even larger magnetically active GLMs.

Dalia Yablon, Ph.D.

DOI: 10.1021/jacs.8b11468
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX