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Spotlights on Recent *JACS* Publications

FLIP-FLOP NANOPARTICLES GO FROM SOLID TO HOLLOW AND BACK

Hollow nanoparticles are appealing to chemists because they can potentially be used for nanomedicine delivery, in nanoreactors, and as contrast agents in molecular imaging. These hollow structures are generally made from solid nanoparticles, which are then chemically emptied out using a variety of techniques. However, the ability to go from hollow to solid and back again is unusual, and has potential applications in performance-switchable, environment-responsive systems.

Now In Su Lee and co-workers have created manganese oxide nanoparticles that can flip between solid and hollow cores when the surrounding gas is changed from oxidizing to reducing (DOI: 10.1021/ja309142j). The solid structures are made up of MnO nanocrystals inside silica nanospheres, and become hollow when the MnO diffuses out into the silicate shell, which is more thermodynamically stable. Flooding the system with air changes the nanospheres back to solid because SiO_2-immiscible Mn_3O_4 grains grow in the cavities. In addition, the researchers found that peppering the system with platinum nanocrystals catalyzes the low-temperature reduction of Mn_3O_4, which lets the nanoparticles reversibly switch between solid and hollow through multiple cycles, under either air or hydrogen gas. This research not only introduces a new way to make nanoparticles, but also adds to the understanding of how nanoscale reactions occur. **Leigh Krietsch Boerner, Ph.D.**

DETERMINING ACIDITY OF A COMMON CLASS OF N-HETEROCYCLIC CARBENES

N-Heterocyclic carbenes (NHCs) are important organic catalysts that can be useful for building carbon−carbon bonds. An active carbene is formed during a reaction by deprotonation at a carbon−hydrogen bond sandwiched between two stabilizing atoms, like nitrogen or sulfur. Despite the range of applications for these catalysts, few studies investigate the kinetic and thermodynamic acidities of the precatalysts—properties that determine can their reactivity.

Now Andrew Smith, AnnMarie O'Donoghue, and their co-workers have measured the kinetic acidities and pK_a values of 19 different triazol-3-ylidenes by tracking deuterium exchange in water (DOI: 10.1021/ja308420c). This family of carbenes is often preferred to those derived from thiazole and imidazole precusors because a more diverse range of catalytic activities and reactivities has been observed within the family of triazol-3-ylidene-derived NHCs.

The authors believe this is the first study of the acidities of such a range of triazolium ions in any solvent. Knowing how the kinetic and thermodynamic acidities of these catalysts relate to their structure can help scientists design better NHC catalysts or new NHC-mediated reactions. **Melissae Fellet, Ph.D.**

COLLOIDAL SYNTHESIS OF INDIUM ANTIMONIDE NANOCRYSTAL SEMICONDUCTORS HITS THE TARGET

Semiconductor nanoparticles are technologically important materials with small dimensions that give them physical properties different from those of their macrocrystalline counterparts. Indium antimonide (InSb) is a particularly interesting material because it shows the highest room-temperature electron mobility among all known inorganic semiconductors and is used in both infrared detectors and ultrafast electronic circuits. However, the nanocrystalline form of InSb has not been previously synthesized. Now, Dmitri Talapin and co-workers have been able to make InSb nanocrystals using a colloidal technique, and study their size-dependent optical properties (DOI: 10.1021/ja309821j).

The researchers found that the absorption and photoluminescence spectra of the InSb nanocrystals showed the expected size-dependence, and that the photoluminescence was more efficient and stable when the surface of InSb nanocrystals was protected with a thin layer of another semiconductor, as in core−shell InSb/CdSe and InSb/CdS nanoheterostructures. In addition, these InSb nanocrystals may be useful in field effect transistors. This new method of synthesizing these valuable materials may lead to use of the nanocrystals as precursors to high-mobility InSb films in the future, as well as more tailored InSb-based core−shell nanostructures and devices. **Leigh Krietsch Boerner, Ph.D.**

BUILDING ORGANIC SOLAR CELLS WITH MOLECULES INSTEAD OF POLYMERS

Scientists look to conducting polymers as materials to convert light to electricity in solar cells, for example. While such polymers are easy to build into devices, it is difficult to consistently synthesize batches of polymers with similar purity and length distribution.

Now Guillermo C. Bazan and co-workers have built two new conducting molecules that can be synthesized easily and are more reliable than polymers (DOI: 10.1021/ja310483w). The molecules are symmetrical and linear, and are constructed from various conjugated nitrogen and sulfur heterocycles. The efficiency of a solar cell built by mixing these new molecules with fullerenes is comparable to that of the best molecular solar cells.

These molecules have a longer string of alternating electron-donating and electron-accepting groups than previous conducting molecules, so they provide a way to investigate how properties like charge mobility and thermal stability vary between polymers and molecules. Because of their reproducible synthesis, conducting molecules might help reduce organic device variability by improving the quality and purity of the material used to build the devices. **Melissae Fellet, Ph.D.**

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A NEW MECHANISM FOR DECARBOXYLATION

Decarboxylation reactions normally occur by the formation of a carbanion and release of carbon dioxide, followed by neutralization of the carbanion. Now Ronald Kluger and colleagues provide evidence for the existence of an alternative pathway that reconciles a long-standing chemical puzzle (DOI: 10.1021/ja310952a).

The research team demonstrates that mandelylthiamin, an analogue of a decarboxylase reaction intermediate, is subject to a base-catalyzed process in which water is initially added to the carboxylate group, producing an intermediate that releases bicarbonate (HCO_3^-) rather than carbon dioxide.

That reaction scheme, the authors note, can explain how some enzymes accelerate decarboxylation by avoiding recombination with carbon dioxide and "is consistent with otherwise inexplicable observations that have stood for more than a century," i.e., the fact that aniline "promotes the decarboxylation of [trichloroacetate]."

"Our results provide a basis for the development of a comprehensive view of decarboxylation that specifies a role for base catalysis," the authors conclude. **Jeffrey Perkel**