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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Spotlights on Recent *JACS* Publications

HETERONANOSTRUCTURE POLYMORPHS WITH ENHANCED PHOTOELECTROCHEMICAL PROPERTIES

Heteronanostructures—materials known for their ability to exist in several different forms—gain tremendous attention because they can be tailored to have desirable photoelectrochemical properties, making them good candidates for applications in optoelectronic devices and photocatalysis. Copper sulfides ($Cu_{2-x}S$) are a well-known example of heteronanostructures that exhibit varying band gaps and crystal structures based on the stoichiometry of the structure. Scientists explore the possibility of combining different copper sulfide polymorphs to create heterojunctions for more robust functions.

Shu-Hong Yu, Zhenyu Li, and co-workers report a simple route for the formation of self-coupled copper sulfide polymorphs mediated by metal ion precursors (DOI: 10.1021/jacs.6b06609). The team combines 1D $Cu_{194}S$ nanocrystals and 2D CuS nanoplates to form a dumbbell-like architecture that exhibits significantly enhanced photoelectrochemical properties originating from the interfacial charge separation. The manganous precursor plays a crucial role in inducing and directing the chemical transformation and shape evolution process. This method is a powerful supplement to controllable fabrication of heteronanostructures using foreign ions as regulators and may offer new insights into rational tuning of nanostructures with unique properties.

Christine Herman, Ph.D.

NEW CHIP-BASED METHOD DETECTS CIRCULATING TUMOR DNA

Tumors are known to release DNA from their cells into the bloodstream. The so-called circulating tumor DNA (ctDNA)—if it can be detected with a robust, sensitive, and specific method—may lead to the development of new diagnostic tools for cancer. One of the biggest challenges is finding a way to distinguish between DNA from healthy cells and diseased cells.

Researchers led by Shana Kelley describe a new method for the electrochemical detection of mutated ctDNA in samples collected from lung cancer and melanoma patients (DOI: 10.1021/jacs.6b05679). The team designs DNA clutch probes (DCPs) that ensure only mutated DNA sequences associate with chip-based sensors. Using the assay, researchers can detect 1 fg/μL of a mutated DNA strand in the presence of 100 pg/μL of the nonmutated strand, which gives it a specificity approaching 0.01%. The method does not require the use of enzymatic amplification and yields results comparable to what is obtainable with standard PCR-based methods, yet can be completed in only 30 min as opposed to a few hours.

Christine Herman, Ph.D.

SHINING A LIGHT ON QUANTUM DOT REDOX CHEMISTRY

The redox activity of surface species on quantum dots (QDs) can significantly affect their performance in applications such as electronic and optical devices and photocatalysts. However, finding ways to probe this redox chemistry has been challenging. Research suggests that photodoping can provide insight on redox states in QDs, but the mechanism behind these reactions is unclear.

In a new study, Daniel Gamelin and co-workers use a broad array of photochemical reducing agents to study this phenomenon in CdSe QDs (DOI: 10.1021/jacs.6b06548). The researchers find that before photoexcitation, a "dark" prereduction reaction takes place on the QD surfaces. This step appears to occur at oxidized selenium sites. Different reducing agents, including borohydrides, organometallic reagents, organotin compounds, and hydrazine compounds, are then used to probe the chemistry of these selenium surface moieties in more detail. The authors suggest that the new understanding of colloidal semiconductor QD redox properties resulting from this study offers new means to customize them potentially for future fundamental studies and applications.

Christen Brownlee

SHATTERING THE GLASS CEILING FOR POROUS MOF-BASED GLASS

Beyond the classic silicate glasses, virtually every class of liquid, including metallic, molecular, covalent, and ionic liquids, can be used to form glassy materials. However, there are few examples thus far of nanoporous glass, a structure that could be useful for numerous applications. In a new study, Omar Yaghi, C. Austen Angell, and colleagues report a novel glass based on a metal–organic framework (MOF), the compound type composed of metal cluster "nodes" connected by a network of organic ligand "struts" (DOI: 10.1021/jacs.6b07078).

Starting with a MOF made of titanium-oxo nodes and bisphenol struts, the researchers dissolve this material in the solvent modulator *m*-cresol, which competitively coordinates to the metal nodes. After the solvent modulator is gradually removed with evaporation through low heat, the monolithic glassy solid left behind has the porosity of a MOF, but more robust mechanical properties. Further investigation shows that the solid has pores separated by about 2 nm, with a total internal surface area of approximately 300 m^2/g. The results demonstrate that the porosity of MOFs can be translated to glassy materials that have great potential for industrial applications.

Christen Brownlee

Published: October 5, 2016

DOI: 10.1021/jacs.6b09932
J. Am. Chem. Soc. 2016, 138, 12691–12691