

Spotlights on Recent JACS Publications

■ FILLING A NICHE WITH SELECTIVE POLYMER REMOVAL

Mesoporous materials are full of holes, usually between 2 and 50 nm, and for this reason they are useful for the purposes of separations, drug delivery, catalysis, chemical detection, bone tissue engineering, and more. One way to create a mesoporous structure is to begin with a two-component blend and then dissolve one of the materials, leaving a porous scaffold. Geoffrey Coates, Ulrich Wiesner, and their colleagues extend this technique to a material with three components—specifically a triblock polymer (DOI: 10.1021/jacs.5b01915).

The researchers are able to selectively degrade two of the three polymer types to create highly intricate mesoporous materials. Further, the researchers have used a stepwise process to deposit different metals into the vacant spaces left by these two polymers, creating complex polymer–inorganic hybrids. The technique affords precise control: two of the three blocks of the ABC tripolymer can be degraded and refilled independently, without interference from the other. Researchers have previously reported such dual loading in copolymer thin films, but not in bulk materials as detailed here.

The authors anticipate that the deposition of multiple materials could expand to include several combinations of metals, metal oxides, and ceramic materials for various applications, including tandem and size-selective catalysis.

Jason Morber, Ph.D.

■ BRIGHT FUTURE FOR HOT ELECTRONS IN PHOTOCATALYSIS FOR ALTERNATIVE ENERGY

Hot electrons—those with very high kinetic energy from incident voltage or light—have become a hot research topic because they can promote energetically expensive chemical reactions by lowering barriers for electron transfer. In a new study, Dong Hee Son and co-workers demonstrate a significantly improved method to produce hot electrons from semiconductor quantum dots (QDs) by exciting them with UV and visible light; the energy from these hot electrons can enhance a hydrogen production reaction (DOI: 10.1021/jacs.5b02026).

By using CdSSe/ZnS core/shell QDs doped with manganese, the researchers show that the “upconversion” of the energy of two excitons can produce hot electrons. The manganese-based intermediate’s long-lived excited state permits this process to work efficiently even with a relatively slow excitation rate, which, crucially, makes this system particularly suitable for harvesting solar radiation.

The manganese-doped QDs generate a lot more hydrogen than undoped QDs, with production increasing quadratically with light intensity in the doped QDs compared to a linear increase in the undoped QDs. Taken together, these findings suggest that manganese-doped QDs show promise for harnessing renewable energy that could be used to generate hydrogen as an alternative fuel source.

Christen Brownlee

■ CARBON QUANTUM DOTS HAVE THEIR DAY IN THE SUN

A major focus in solar energy conversion research is applying technology to split water and generate renewable hydrogen. However, solar hydrogen production systems typically use precious-metal-containing dyes, cadmium-based quantum dots, or organic dyes as photosensitizers, which are expensive, toxic, or unstable. In a new study, Erwin Reisner and co-workers show that carbon quantum dots (CQDs) can be effective photosensitizers without this slew of drawbacks (DOI: 10.1021/jacs.5b01650).

After synthesizing CQDs from citric acid, the researchers show that this material absorbs light from a broad spectrum encompassing wavelengths in the UV and near-visible regions. The material also displays strong electron-transfer capabilities and reducing power. These qualities, when combined with a molecular nickel catalyst and electron donor, make CQDs effective in generating hydrogen from water using simulated sunlight.

The authors find that the efficiency of this system is comparable to those of systems previously developed using unstable or costly photosensitizers. Though this newly reported solar hydrogen production system loses efficiency after a few hours, the researchers determine that this slow-down is caused by degradation of the hydrogen evolution catalyst rather than the light-absorbing CQDs, which show remarkable photostability over at least 24 h. Future research, the scientists say, will focus on finding catalysts that can match CQDs’ longevity.

Christen Brownlee

■ PALETTE OF FLUORESCENT TAGS FOR TARGETED BIOMOLECULE LABELING

Researchers continually seek to identify the perfect fluorescent label—one that specifically tags selected molecules within cells and tissues without disrupting the natural biological functions of these molecules. Now, Carolyn Bertozzi and colleagues describe an assortment of fluorescent labels that come in variety of colors and allow detection, with great sensitivity, of specific classes of molecules in several biological sample types (DOI: 10.1021/jacs.5b02383).

The CalFluors labels—whose name is derived from “Click activated luminescent Fluorophores”—act as universal azide–triazole fluorogenic switches. In the azide form, internal photoinduced electron transfer quenches fluorescence. But when the azide converts into a triazole group through reaction with an alkyne, quenching is disrupted and the label fluoresces brightly. The researchers have incorporated the azide–triazole switch into differentially functionalized xanthene molecules to produce a collection of dyes that emit visible light with wavelengths spanning from green to the near-infrared spectrum.

The investigators selectively react CalFluors with alkyne-modified biomolecules, including glycans and DNA. The dyes work across a range of samples, including fixed tissue sections

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and whole zebrafish embryos. Furthermore, the labeling is specific enough to eliminate the need for a rinse step to wash away remaining dye that could cross-contaminate other biomolecules.

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