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Spotlights on Recent *JACS* Publications

REDOX TRANSFER IN BACTERIAL MICROCOMPARTMENTS

The design of bionanoreactors may have far-reaching applications in cell biology and bioengineering, as well as medical diagnostics and therapeutics. Bacterial microcompartments (BMCs) are organelles consisting of a protein shell that encloses enzymes and other proteins, and they have attracted interest recently as they can be used for the templated design of new functional bionanoreactors.

The enclosed enzymes dictate the customized function of the bionanoreactor; in particular, conferring an electron-transfer functionality to the shell could be very useful to sustain encapsulated oxidoreductive reactions. Now, Cheryl Kerfeld and colleagues report the first successful incorporation of a redox active [4Fe-4S] cluster into a BMC shell protein (DOI: 10.1021/jacs.5b11734).

[Fe-S] clusters are ubiquitous in nature and are found in a variety of metalloproteins, such as ferredoxins, hydrogenases, nitrogenases, and more. They are best known for their role in oxidation−reduction reactions. BMC shell proteins engineered with [4Fe-4S] clusters enable redox transfer between the lumen of the BMC and the outside medium. This work represents a major development toward constructing synthetic BMCs that can transfer electrons for biotechnological applications, and it advances the broader goal of engineering new catalytic activities into shell proteins, which naturally function only as passive barriers.

Lingling Chen, Ph.D.

STRAINED OXACYCLIC ALKYNES AS HANDY SYNTHETIC BUILDING BLOCKS

Cycloalkynes in small ring sizes have profound geometric constraints and can therefore be highly reactive. Such strained species may be trapped by various reaction partners to construct valuable structural motifs, and this tactic has been widely applied with nitrogen heterocyclic alkynes under strain. On the other hand, examples of strained oxacyclic alkynes are scarce, as are synthetic applications using these molecules.

Now, Neil Garg and co-workers have developed a new method to trap two strained oxygenated cycloalkynes with nucleophiles and cycloaddition partners under mild conditions and with high regioselectivity (DOI: 10.1021/jacs.6b01986). The regioselectivity increases as the degree of distortion between the C≡C bond termini increases, an outcome that is qualitatively predictable by the distortion/interaction theoretical model developed earlier by Houk.

Using this method, the researchers have prepared an array of oxacyclic frameworks present in many bioactive natural products and pharmaceuticals, making it a useful tool for designing and optimizing routes to structurally complex oxygen-containing heterocycles. The current work, while providing further evidence for the distortion/interaction model, has significantly enriched the scope of strained alkyne chemistry in organic synthesis.

Xin Su, Ph.D.

HYDROGEN EVOLUTION REACTION KINETICS OVER TWO-DIMENSIONAL MoS_2 CATALYST

Inexpensive and efficient hydrogen evolution reaction (HER) catalysts are vitally important for sustainable hydrogen production associated with renewable energy applications. The layered molybdenum disulfide (MoS_2)—with the advantages of low cost and favorable properties when compared with commonly used platinum catalysts—has been extensively studied as a promising candidate for large-scale, commercial HER catalysis. In addition to its well-characterized active edge sites, the basal plane of MoS_2 was recently successfully activated by introducing sulfur vacancy and strain. However, little is known about the effect of those S vacancies on HER kinetics or about the structural effects from tensile strain.

Xiaolin Zheng, Allen Bard, and colleagues combine scanning electrochemical microscopy and multiphysics modeling to quantify the HER kinetics of both strained and unstrained S vacancies on the basal plane of MoS_2 monolayers (DOI: 10.1021/jacs.6b01377). They find that 2% uniaxial tensile strain accelerates HER by a factor of 4 compared to unstrained S vacancy in this system. "The methodology presented here provides a general way to study the electrochemical kinetics of MoS_2-like two-dimensional catalytic systems", the authors conclude.

Hui Jin, Ph.D.

GIVING NITROGEN-FIXING CATALYSTS A CLOSER LOOK

Nitrogen fixation, or the conversion of molecular nitrogen (N_2) into ammonia (NH_3), is an important process for both biology and industry. Because the only industrial process that efficiently fixes nitrogen requires high temperatures and pressures, significant research has centered on finding alternate ways to generate ammonia. In a recent study, Jonas Peters and co-workers take steps toward this goal, demonstrating the advantages of a new iron-based catalyst for nitrogen fixation at unusually low temperature and pressure (DOI: 10.1021/jacs.6b01706).

The researchers characterize these nitrogen-fixing catalysts using various methods including cyclic voltametry, kinetic studies, and freeze-quench Mossbauer spectroscopy, a powerful technique that can provide snapshots of reaction intermediates. Together, these methods show that the iron catalysts—species with three phosphine donors bonded to a central iron atom through various *ortho*-phenylene linkers—are robust, maintaining activity after several cycles, and show features consistent with a single-site catalyst model.

They determine that a hydride complex is a likely resting state of this catalytic system and suggest that hydrogen evolution may prevent this intermediate from inhibiting catalysis. The authors conclude that these insights could eventually lead to better industrial catalysts for ammonia production and to a greater understanding of iron-based biological enzymes for nitrogen fixation.

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