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

REVEALING THE MAGIC BEHIND NANOSCALE CRYSTALLIZATION

That scientists have been studying crystallization and mixing for over 100 years and continue to make new discoveries speaks to the complexity of these processes. Even today, our ability to control nanoparticle properties is limited because we do not understand exactly how they form. Metallic and bimetallic nanoparticles are used in protein tagging, drug delivery, magnetic recording, and catalysis, and greater control over their composition should allow more effective property engineering.

To provide some clues, Jerome Delhommelle and Caroline Desgranges use computational simulations to study the complex and incredibly fast crystallization and separation processes of a two-metal mixture (DOI: 10.1021/ja500621m). The researchers choose palladium and silver because they can mix completely into each other, are of similar size, and form solid solutions as large crystals. Despite the material similarities, the researchers find that strong cohesion between palladium atoms promotes crystal nuclei rich in palladium and deficient in silver.

Competition between mixing and separation continues as the crystal grows and produces particles with a core composition quite different from that at the surface. Understanding the interactions that create these local changes is especially important at the nanoscale, where for some applications control over local composition is crucial.

Jenny Morber, Ph.D.

PUTTING A LABEL ON LONG RNAS

Claudia Höbartner and colleagues report a new, efficient approach for labeling long strands of RNA at specific sites with the help of deoxyribozymes (DOI: 10.1021/ja503864v). The work could enhance the study of RNA structure and interactions.

Attaching probes or labels to specific RNA sites allows researchers to investigate how the molecules fold and interact with proteins and ligands. Although this modification can be done using solid-phase synthesis, it is limited in application to relatively short RNAs. Ligation and enzymatic manipulation are often required to label longer molecules. To get around these constraints, biochemists have recently pioneered DNA-catalyzed approaches to post-transcriptionally label RNA, but even these approaches have faced technical hurdles.

Now Höbartner and co-workers introduce a new post-transcriptional strategy that can introduce labels to RNA strands up to about 160 nucleotides long. The approach uses deoxyribozymes, or DNA enzymes, to catalyze the attachment of a labeled guanosine triphosphate to an adenosine at specific sites in *in vitro*-transcribed RNA. The process is accelerated by a terbium cofactor. The team uses the method to label the RNA with a variety of fluorescent, biotinylated, paramagnetic, and photoreactive probes. The work could be applied to study RNA splicing on single molecules or the interaction of non-coding RNAs with proteins, the researchers say.

Deirdre Lockwood, Ph.D.

ENZYME CRAFTS DNA BUILDING BLOCKS WITH NOVEL RADICAL

Every time a cell replicates, ribonucleotide reductase needs to churn out a genome-long supply of nucleotides for the new DNA. The enzyme converts ribonucleotides to deoxynucleotides, providing the essential precursors for DNA replication and repair in all living organisms. Scientists suspect that sulfur-based radicals are involved in the catalytic mechanism for all three classes of ribonucleotide reductase, but these radicals have proven difficult to observe experimentally. Now Yifeng Wei, JoAnne Stubbe, and colleagues have spied a never-before-seen radical in a class III ribonucleotide reductase from *Escherichia coli*, supplying evidence that this novel intermediate is part of the catalytic mechanism for all ribonucleotide reductases (DOI: 10.1021/ja5030194).

To find the elusive radical, Stubbe's team denies the ribonucleotide reductase formate, a co-substrate that supplies electrons for the reaction. The enzyme becomes trapped in an intermediate state, revealing the new radical species. Using electron paramagnetic resonance spectroscopy, the researchers tease out the structure of the radical species and find a three-electron bond between a cysteine and methionine residue. This observation suggests the enzyme applies a coordinated attack on substrates, using multiple residues that protect the radical from participating in unwanted reactions.

Erika Gebel Berg, Ph.D.

GRAPHENE RIBBONS GET SOME QUALITY CONTROL

Graphene is a sheet of carbon atoms spread out like chicken wire in a single layer. It is an amazingly fast conductor, an efficient sensor, and even works well as an anti-ice coating component. Until recently, graphene nanoribbons were created largely by cutting open a carbon nanotube or cutting apart a large graphene sheet. The problem with such techniques is that the edges become jagged and unpredictable, and the nanoribbons' electrical properties depend on these edge patterns.

Though recent research has reported a chemical method to synthesize very long, uniform, graphene nanoribbons, challenges including how to place the ribbons exactly where they are needed and how they fare in devices remain. Now Chongwu Zhou and colleagues outline how to deposit these atomically perfect nanoribbons onto surfaces suitable for field effect transistor fabrication (DOI: 10.1021/ja502764d). Their method coaxes the graphene ribbons to stick to a target surface instead of to each other, which allows easier property evaluation and device building.

The researchers use their technique to create a simple nitrogen dioxide sensing device, and find that it can detect gas molecules down to a few parts per billion. The results lay a

Published: June 3, 2014

   dx.doi.org/10.1021/ja505351b | *J. Am. Chem. Soc.* 2014, 136, 8143–8144

foundation for these researchers and others to improve the performance of devices and sensors based on graphene nanoribbons.

Jenny Morber, Ph.D.

A WELCOME ADDITION TO NATIVE CHEMICAL LIGATION

Richard J. Payne and co-workers present an efficient method for the chemical synthesis of proteins (DOI: 10.1021/ja502806r). Such de novo synthesis offers the opportunity to investigate protein structure and activity in ways not possible with proteins obtained using other methods, such as isolation from cell extracts or other biological materials.

The authors use the alkanethiol trifluoroethanethiol (TFET) as an additive in native chemical ligation−desulfurization, a powerful process for constructing the backbone structure of peptides or proteins in aqueous solution without protecting groups. TFET facilitates the peptide ligation step and enables a subsequent desulfurization reaction in one pot, thus eliminating the need for intermediate purification steps. The investigators demonstrate the utility of their method by synthesizing two proteins, chimadanin and madanin-1, anti-thrombotic agents that are produced naturally in the salivary glands of ticks.

The method presented in this study offers a significant improvement over the current process for the chemical synthesis of proteins. The simplicity and enhanced efficiency that comes with the addition of TFET to native chemical ligation will facilitate the generation and investigation of diverse proteins with a variety of biological activities.

Eva J. Gordon, Ph.D.

dx.doi.org/10.1021/ja505351b | *J. Am. Chem. Soc.* 2014, 136, 8143−8144