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Spotlights on Recent *JACS* Publications

VISCOSITY STUDY OFFERS TELLING TALE OF TELOMERE STRUCTURE

The ends of each of our chromosomes are composed of short, repetitive stretches of DNA called telomeres that protect chromosomes from degradation and other damaging events. Telomere regulation, or misregulation as the case may be, has been linked to complex processes such as aging and cancer. Detailed exploration of telomere behavior at a molecular level offers insight into how these remarkable structures have such profound effects on cell growth and survival. However, the DNA sequences of telomeres can adopt many different structures, complicating their investigation.

Toward gaining a better understanding of the factors that influence telomere DNA structure, Nicholas Hud and co-workers examine how solvent viscosity affects the folding of DNA with a telomere-derived sequence (DOI: 10.1021/ja303499m). They find that in a highly viscous solution, the telomere DNA adopts a distinct structure and folds much more slowly than it does in water, which is important because the solvents of their study have viscosities that are closer to that of the cellular environment in which telomeres normally exist. This study highlights the importance of considering solvent viscosity in structural studies of telomeres, a finding that can be extended to the study of other DNA and RNA structures as well. **Eva J. Gordon, Ph.D.**

GLUCOSE FUEL CELL BASED ON MOLECULAR CATALYST

Complete oxidation of glucose, the most abundant monosaccharide, produces a large amount of chemical energy. Researchers are interested in harvesting this energy as an alternative fuel cell approach to energy conversion. For the first time, researchers led by Serge Cosnier have fabricated and characterized a nonenzymatic glucose fuel cell based on a molecular catalyst (DOI: 10.1021/ja304589m).

Prior to this study, researchers looked to either enzymes or metals to perform glucose oxidation. Although naturally occurring redox enzymes have excellent substrate specificity, they suffer from instability and can be difficult to attach to electrode surfaces without compromising enzymatic activity. Metals, such as platinum and its alloys, can achieve high catalytic efficiency but are not substrate selective and are easily poisoned in complex biological media.

As an alternative to both these approaches, the team sought out a molecular catalyst capable of selective and efficient glucose oxidation. They immobilized a rhodium porphyrin catalyst to a multi-walled carbon nanontube-based electrode, which has greater surface area and can boost electrocatalytic performance. They found the molecular catalyst-based fuel cell performed as well as existing glucose fuel cells. The results from this in-depth study will help lay the groundwork for future applications of rhodium complexes in energy conversion. **Christine Herman, Ph.D.**

ECONOMICAL SYNTHESIS OF AN EFFECTIVE ANTIMALARIAL DRUG

Despite malaria being a preventable and curable disease, there were 216 million cases and 655,000 malaria-related deaths in 2010. Artemisinin-based combination therapy (ACT) is the standard and most effective treatment for uncomplicated *Plasmodium falciparum* malaria. Unfortunately, current isolation methods for obtaining artemisinin, a natural product, are too expensive to meet demand, especially in areas where malaria is most prevalent. To overcome this challenge, Chunyin Zhu and Silas Cook sought to economically synthesize artemisinin (DOI: 10.1021/ja3061479).

Zhu and Cook's synthesis begins with commercially available and inexpensive cyclohexenone. The brief synthesis produces (+)-artemisinin on the gram scale, more than all previous syntheses combined. The authors' strategy is shorter than previously published total syntheses and uses predominantly commodity chemical feedstocks. Such a process could potentially be optimized to compete favorably against both isolation and microbial production methods in terms of cost.

The researchers demonstrate that laboratory synthesis of artemisinin could be part of the solution to the distribution problem of ACT, as it could be more economical than what is currently used—natural product extraction. The next step is to determine if it is possible to scale up their synthesis from the gram to the kilogram scale. In addition, the authors may be able to adapt their synthesis to make derivatives of artemisinin that are also effective antimalarials. **Yun Xie, Ph.D.**

COMPUTER MODELING SHOWS WHY PHOTOVOLTAIC CELLS WORK

By simulating what happens when electrons are liberated in photovoltaic cells, researchers led by Oleg V. Prezhdo have found that processes that create free electrons are much faster than the relaxation processes that prevent these electrons from being harvested (DOI: 10.1021/ja3063953).

The efficiency of photovoltaic cells depends on the rate at which electron–hole pairs are formed at the interface of a hole conductor and the electron carrier into which the electrons are injected. However, the power conversion rate is decreased by the recombination of electrons with holes in the donor material. A series of experiments using composites of TiO_2 with graphene have shown that the power conversion rate in these systems is quite high, indicating that electron–hole recombination does not play a dominant role.

To verify this observation, the researchers modeled the electron transfer process as well as energy relaxation processes that allow the electron–hole combination. They used real-time non-adiabatic molecular dynamics within the time-dependent density functional theory framework. In a model consisting of six atomic layers of TiO_2 and a graphene sheet of 42 carbon atoms, replicated periodically along the two interface dimensions, they allowed photo-exited electrons to evolve

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and found that electron injection in the acceptor material is consistently faster than the electron losses caused by recombination in the donor material. **Alexander Hellemans**

■ ELECTRODE SHOWS POTENTIAL FOR CARBON DIOXIDE RECYCLING

For a society that cannot seem to reduce its ballooning carbon dioxide production, converting CO_2 into usable fuels is an appealing alternative. Yet in experiments, scientists have needed to apply too much external voltage and obtained too little usable fuel to make CO_2 reduction a practical process. One promising electrode seems to require less input energy and produces more predictable fuel products: p-doped gallium phosphide (p-GaP).

Ana B. Muñoz-García and Emily A. Carter apply density functional theory in order to analyze how a p-GaP(110) electrode would behave in the kind of aqueous environments used to perform CO_2 reduction (DOI: 10.1021/ja3063106). Density functional theory is a quantum mechanical method that evaluates the spatially varying electron density, rather than an electronic wave function.

The researchers predict that proton transfer from water to phosphorus atoms on the surface of p-GaP(110) produces negatively charged hydrogen atoms attached to the surface. This change suggests that surface hydride (negatively charged hydrogen atoms) species may be involved in the CO_2 reduction. Accounting for that activity should help the future development of efficient CO_2-reducing electrodes. **Lucas Laursen**

■ THE MULTIPLE FORMS OF VANADATE

Vanadate, an inorganic compound made up of the transition metal vanadium and oxygen atoms, has intriguing biological activities, including potential for the treatment of diabetes. Its ability to inhibit phosphatases, enzymes with instrumental roles in cell signaling events, has also made it a key molecular tool for exploring biological processes. However, this seemingly simple molecule can exist in multiple forms with varying numbers of vanadium and oxygen atoms bonded in distinct geometries, and little is known about the roles of these different forms in vanadate's activity.

Vyacheslav Kuznetsov, Anastassia Alexandrova, and Alvan Hengge use computational methods and crystallography to examine the structure of vanadate bound to a phosphatase (DOI: 10.1021/ja305579h). While current models suggest that a single vanadate structure is the dominant form that interacts with various proteins, the authors propose that the phosphatase may also initially interact with a dimeric form of vanadate and then trigger a reaction in which another form called metavanadate is generated. Their findings provide compelling evidence for how enzymes might interact with different forms of vanadate, and could help in the design of more effective vanadate-based enzyme inhibitors and drug candidates. **Eva J. Gordon, Ph.D.**

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