

## Nancy McGuire in Noteworthy Chemistry (ACS) Summer 2013

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August 12, 2013

**Phosphorus in flame retardants: More is not always better.** For many years, scientists assumed that aryl phosphate flame retardants require a high phosphorus content to perform effectively. These compounds tend to be volatile, and they can be contact allergens and neurotoxins. An ideal flame retardant should be used in small enough quantities to minimize its effect on the material properties of the flammable polymer matrix while being effective in reducing char formation. It would release a negligible amount of volatile material at room temperature.

K. Shin, B. J. Sung, and co-workers at Sogang University, Samsung Cheil Industries, the Korea Institute of Science and Technology (all in Seoul), and Samsung Electronics (Suwan, Korea) investigated the dynamics and mechanisms of aryl phosphates in polycarbonate matrices to assist in designing environmentally friendly flame retardants. They demonstrated that flame retardants with relatively low phosphorus contents can perform effectively if the dynamics and molecular interactions are tuned correctly.

Highly volatile flame retardants, including the widely used triphenyl phosphate (TPP), capture hydrogen and hydroxyl radicals in the vapor phase. Less-volatile oligomeric phosphates are more active in the condensed phase and provide thermally stable char layers that protect the underlying polymer. Mixtures of volatile and nonvolatile phosphates are more effective than either type alone.

The researchers conducted flammability tests that showed that 2,4-di-*tert*-butylphenyl diphenyl phosphate (DDP) should be as efficient as TPP, even though DDP contains much less phosphorus. On the other hand, 2-*tert*-butylphenyl diphenyl phosphate, with a phosphorus content intermediate between TPP and DDP, is less efficient as a flame retardant than either of those compounds.

The researchers suggest that the bulky *tert*-butyl groups play a greater role than simply decreasing the relative phosphorus content. Dynamic secondary ion MS (DSIMS) and molecular dynamics simulations (used at higher temperatures, where DSIMS is impractical) show that the diffusion of DDP through a polycarbonate matrix at low temperatures is slower by an order of magnitude than that of TPP, so more DDP is retained in the polymer over time rather than being lost to the atmosphere. Thermogravimetric analysis confirms that DDP is much less volatile than TPP at low temperatures. DDP diffusion becomes comparable to that of TPP at the ignition temperature (360 °C), enabling it to enter the vapor phase and capture free radicals.

Previous studies indicate that char formation by thermal decomposition of polycarbonates is a result of Fries rearrangement of the carbonate linkages, which produces phenolic groups that transesterify with aryl phosphate flame retardants. In the present study, potential mean force computations, supported by Fourier transform IR spectroscopy, show that DDP suppresses Fries rearrangement and char formation better than TPP. (*J. Phys. Chem. B* **2013**, *117*, [8571–8578](#); Nancy McGuire)

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August 5, 2013

**Strontium signatures authenticate the geographic origin of wines.** Certifying a wine's geographic area of origin preserves a vintner's brand reputation and satisfies legal and regulatory requirements. Analysis of stable carbon, hydrogen, and oxygen isotopes, commonly used to detect adulteration, can be used to verify provenance, but confounding factors such as yearly climate variations complicate interpretation of the results.

M. Mattei, S. Conticelli, and coauthors at the University of Florence (Florence and Sesto Fiorentino, Italy), the National Research Council (Florence), and the Third University of Rome developed an authentication approach that relies on isotopic ratios of strontium, which is commonly found in soil in which grapes are grown. Regional isotopic ratios for key trace heavy elements, including strontium, neodymium, and lead, are well mapped in the geology literature.

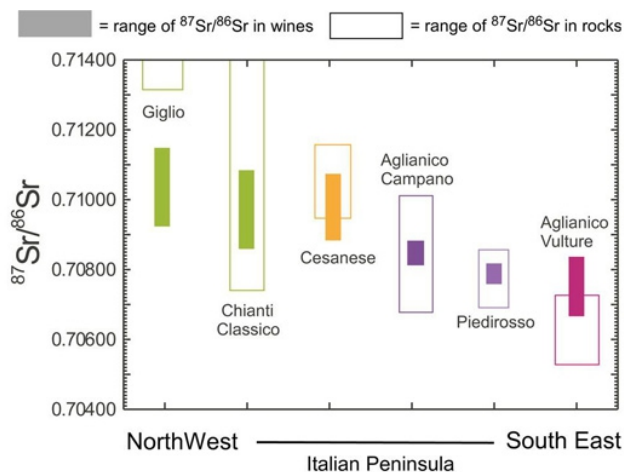
In particular the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is sensitive to the location and time of a sediment's origin because  $^{87}\text{Sr}$  is a decay product of  $^{87}\text{Rb}$ . Because a given wine district can contain a variety of lithologies, variations in isotopic compositions of the soil can be used to distinguish the grapes grown in that soil, and by extension the wines made from them, from grapes and wine from adjoining vineyards.

The researchers used thermal ionization mass spectrometry to analyze a large set of Italian commercial bottled certified wines from various regions. They also compared various vintages from the same vineyards. Their analytical procedure determines the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for wines with the same precision as generally reported for geological materials ( $\approx 20$  ppm). The results show an internal precision of  $<10$  ppm for replicate measurements and an external precision at a 95% confidence level of  $\pm 23$  ppm.

For most of the wines sampled, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio did not vary significantly with the vintage year. For one of the two wines that showed a variation, the winemaker had started using grapes from a new vineyard in 2010, but did not mix grapes from the two vineyards. Post-2010 wines made with grapes from the original vineyard had strontium isotope ratios similar to the older wines from the same vineyard. The other wine was a white wine, which probably had been treated with bentonite or limestone. Even if these additives were completely filtered out, some residual strontium could have remained in the wine. Thus, the authors believe that their method works best for red wines.

Correlation of strontium isotope ratios of the wines with those of the corresponding soils and rocks is strongest for vineyards on volcanic rocks covering limestones (see figure). The correlation is poorer for vineyards on sedimentary substrata, which are characterized by a heterogeneous mix of textures and mineralogies. (*J. Ag. Food Chem.*, 2013, 61, 6822–6831; Nancy McGuire)

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**How do inorganics in a biomass feedstock affect the environment?** Any element in the periodic table might be present in biomass feedstocks, according to P. Thy and co-workers at the University of California, Davis. [*Presumably only naturally occurring elements.*—*Ed.*] Inorganic components can make up >20% of the dry weight of some feedstocks. Sorting out the inorganic components is important for determining the composition of the flue gas, identifying soil-modifying elements in ash-based fertilizers, and identifying toxic trace elements that are concentrated in the ash. In addition, controlling inorganic inputs and removing contaminants from the synthesis gas (syngas) are critical to operating reactors effectively and avoiding catalyst deactivation. Some inorganic residues offer the prospect of an additional income stream if they can be recovered and used effectively.

The researchers conducted a broad feasibility study of syngas-generation feedstocks from California agricultural, forestry, and energy crop sources. They performed chemical analyses of each feedstock and ash residue, and they examined the effects of pretreatments and pyrolysis temperature on the ash composition. The composition of the ash was influenced in part by the minerals naturally present in the soil where the plant matter was grown and by the salinity level of the irrigation water.

The organic components of the feedstocks decomposed between 250 and 450 °C. Hydroxides, carbonates, halides, and sulfates began to decompose at >1000 °C, a typical temperature for commercial boilers. As a result, the remaining ash was enriched in less-volatile trace elements such as copper, selenium, and cadmium, which reached significant levels in some samples. Pyrolysis produces a greater ash fraction than does combustion, indicating the effect of partial oxygen pressure on the mineralogy of the resulting ash.

Pretreating the feedstock by leaching it with water reduces the ash content and the ratio of fixed carbon to volatile matter. Leaching can reduce alkali metal, chlorine, and sulfur levels significantly. Organic matter extraction during leaching can affect concentrations of inorganic elements, but it can also reduce the fuel value of the feedstock. (*Energy & Fuels*, **2013**, *27*, [3969–3987](#); Nancy McGuire)

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July 22, 2013

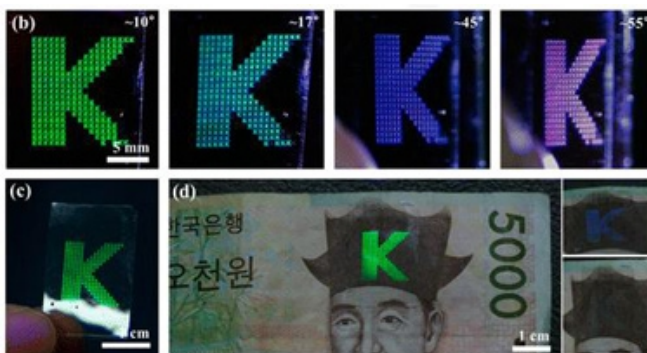
**Colorful colloid crystals combat counterfeiters.** Anticounterfeiting efforts often rely on materials whose colors arise from physical rather than chemical properties. Iridescence, dichroism, diffraction, and other color properties are difficult to imitate convincingly. Colloidal crystal films, thin films formed from monodisperse colloidal particles self-assembled into periodic lattices, would seem to be ideal candidates for this type of application. Difficulties in production and the fragility of the resulting films, however, present obstacles to practical applications. Freestanding films and micropatterns often require complicated preparation processes. Strong light scattering makes the films milky or opaque, limiting the ability to mix colors using multiple layers.

S.-M. Yang, S.-H. Kim, and co-workers at the Korea Advanced Institute of Science and Technology (Daejeon) developed a practical method for creating highly transparent colloidal photonic crystal films in a variety of colors. They dispersed colloidal silica particles with the desired size in a photocurable ethoxylated trimethylolpropane triacrylate resin. To reduce light scattering and increase the transparency of the resulting film, the authors chose a resin with a similar refractive index to the particles.

The suspension was drawn between two glass plates by capillary forces and then photopolymerized under UV light. The resulting crystalline films can be micropatterned by using conventional photolithography.

Because the films are transparent, multicolored patterns can be made by superimposing two or more colored layers. Combining red, green, and blue structural colors produces the secondary colors cyan, magenta, yellow, and white. The colors produced lie within a narrow spectral range to provide a high degree of specificity, and they vary with the viewing angle and the size of the colloidal particles. The films are highly transparent under ambient light, but when the incident angle of the light is the same as the angle of observation, the films appear to be brightly reflective.

In the figure, the optical images (b) of the colloidal crystal pattern composed of letter Ks show a reflection color that strongly depends on the angle of incidence of the light, which is given in each image. Optical image (c) is a freestanding film that contains a pattern of Ks. Image (d) is a patterned photonic crystal film on a Korean bank note. The pattern exhibits a bright green color under normal reflection (main image), whereas it displays a blue color for high incident and reflection angles (top right). The film is highly transparent and difficult to



distinguish when the viewing angle is different from the angle of incidence of the light (bottom right).

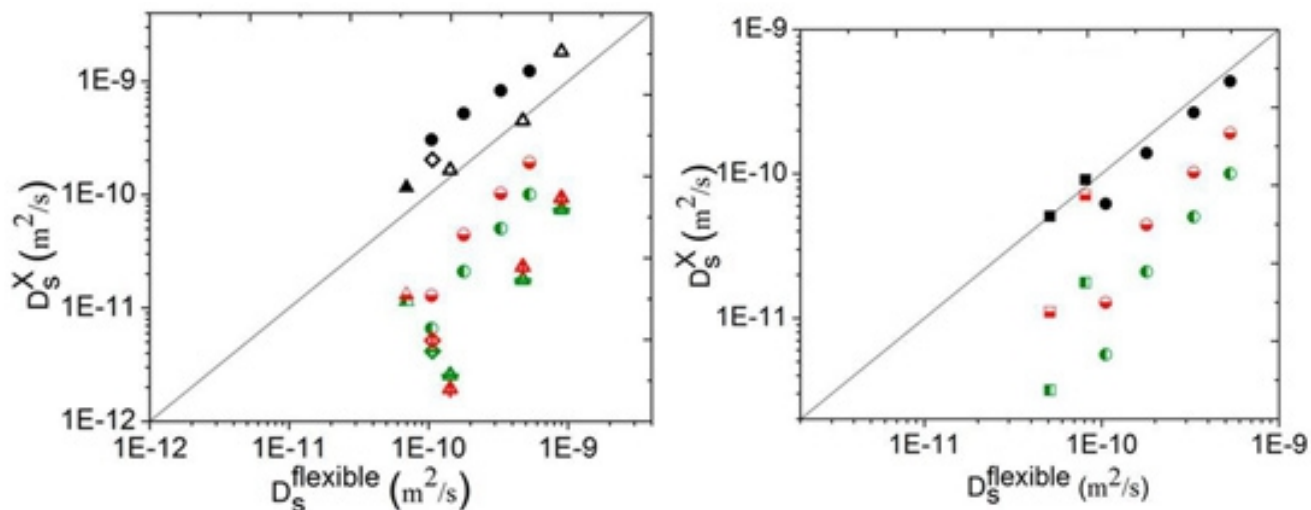
The authors note that their colored films can also be used in decorative coatings, paints, or cosmetics. (*Chem. Mater.* **2013**, *25*, [2684–2690](#); Nancy McGuire)

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July 15, 2013

**Model zeolite framework flexibility effects on molecular diffusion** rapidly and accurately. For calculating molecular diffusion through nanoporous materials, stipulating a rigid host framework saves considerable computation time and compensates for a lack of force field information. This technique, however, can limit the accuracy of the results. R. V. Awati, P. I. Ravikovitch, and D. S. Sholl\* at Georgia Tech (Atlanta) and ExxonMobil Research and Engineering (Annandale, NJ) introduce two new methods for approximating framework flexibility that are based on a set of discrete rigid snapshots obtained from simulating the dynamics of an empty small-pore eight-member-ring silica zeolite framework.

In the first method, the authors introduced random snapshots into a molecular dynamics calculation at a frequency corresponding to the breathing motion of the nanopore windows. The positions of the methane adsorbate molecules are kept constant. The left-hand plot in the figure shows the accuracy of predicting self-diffusivity ( $D_s$ ) of methane in the flexible structures of three zeolites using this method (black), time averaging (red), and energy minimization (green), compared with theoretical calculations that use a flexible structure.



In the second method, the researchers performed transition-state theory calculations of cage-to-cage hopping rates in each snapshot and then averaged them over a distribution of snapshots. The right-hand plot shows a comparison for this method.

Both methods produce excellent agreement with direct molecular dynamics simulations that use fully flexible structures. These methods can predict infinite dilution and finite loading diffusivities of simple molecules through nanoporous frameworks even in the absence of accurate flexible force field information. (*J. Phys. Chem. C* **2013**, *117*, [13462–13473](#); Nancy McGuire)

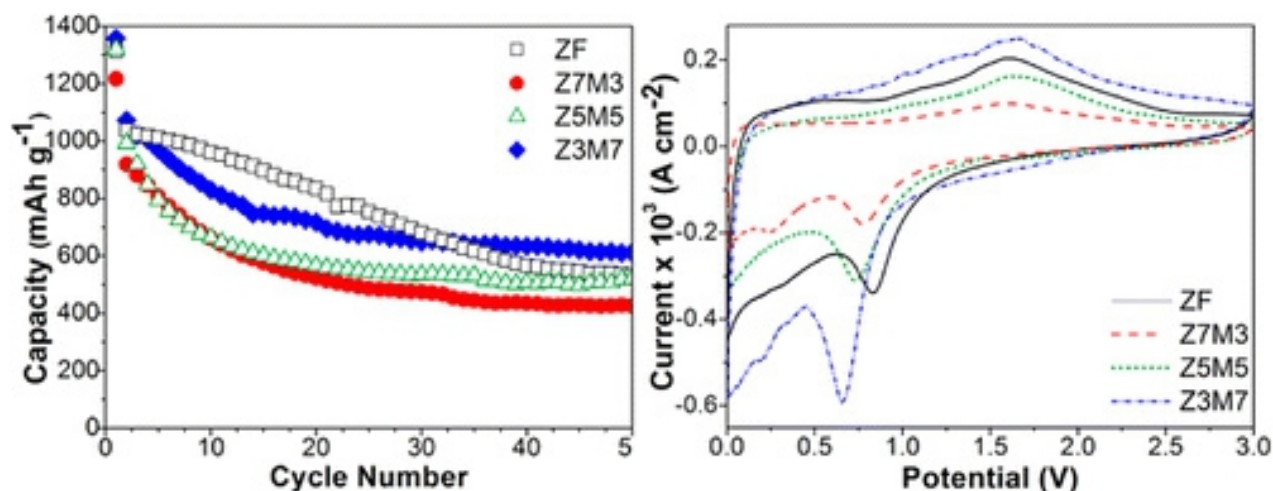
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July 8, 2013

**Electrospun nanofibers make tunable anodes for lithium-ion batteries.** Rechargeable lithium-ion batteries provide lightweight, energy-dense power supplies for small consumer electronic devices, but they cannot satisfy the power, energy density, and safety requirements for larger applications. S. Madhavi and coauthors at Nanyang Technological University (Singapore) and the Indian Institute of Technology (Saharanpur) noted that cathode development is limited by low theoretical capacity, so they focused on transition-metal oxides to improve anode performance.

The authors chose electrospinning as a simple, economical, scalable method for producing anode nanofibers. Spinel-structured  $\text{ZnFe}_2\text{O}_4$  outperforms binary iron oxides and is less toxic than the corresponding cobalt spinel. Substituting manganese for some of the zinc lowers the working voltage of the anode and increases its capacity, while retaining its high cyclability. In the figure, the symbols ZF, Z7M3, Z5M5, and Z3M7 stand for pure  $\text{ZnFe}_2\text{O}_4$ , 70:30 Zn/Mn, 50:50 Zn/Mn, and 30:70 Zn/Mn, respectively.



The spinel takes in  $\text{Li}^+$  on the first discharge to form an oxide nanocomposite, with a corresponding irreversible loss in crystallinity. After the first cycle,  $\text{Li}^+$  insertion and extraction are reversible. The  $\text{Li}^+$  uptake varies with the Zn/Mn ratio, making it possible to tune the performance of the anode. (*ACS Appl. Mater. Interfaces* **2013**, *5*, [5461–5467](#); Nancy McGuire)

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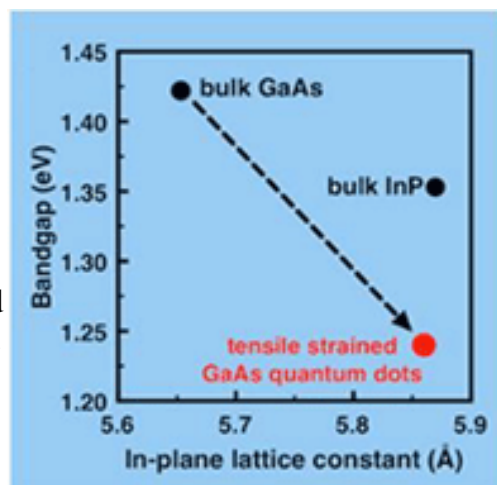
June 24, 2013

**Tensile-strained quantum dots luminesce below the bulk band gap.** Many III–V semiconductors have band gap energies in the 0.6–1.0 eV range, slightly above the mid-IR region. Lowering the band gap energies by  $\approx 0.5$  eV would make these materials usable in mid-IR optoelectronic devices for detecting trace gases, in vivo diagnostics, environmental monitoring, and other applications. Growing self-assembled quantum dots (SAQDs) under 4% tensile strain could reduce the band gap energy by the desired amount, but difficulties in producing defect-free tensile dots hamper efforts to use this phenomenon.

P. J. Simmonds, M. L. Lee, and coauthors at Yale University (New Haven, CT), the University of California, Los Angeles, and the University of Arkansas (Fayetteville) propose a model for dislocation-free self-assembly of zinc blende-structured SAQDs under tensile strain that uses (110) and (111) crystal surfaces as substrates. They previously used this model to grow optically inactive tensile GaP nano-islands on GaAs(110). They now report the growth of optically active tensile GaAs SAQDs on  $\text{In}_{0.52}\text{Al}_{0.48}\text{As}/\text{InP}(110)$  with a band gap energy  $\approx 0.2$  eV less than the bulk value (see figure).

The authors used molecular beam epitaxy to grow the GaAs quantum dots, which have a 3.7% tensile lattice mismatch with the substrate. The authors believe that this is the first reported instance of photoluminescent emission from type I quantum dots in which the peak energy is lower than the bulk band gap. This energy decreases with increasing temperature and dot size.

The authors predict that dislocation-free, tensile self-assembly is possible on the (110) and (111) surfaces of all zinc blende and related materials, including III–V and group IV semiconductors. Because GaAs and germanium have almost the same lattice constant, the InAlAs buffers used here may also provide an important template for growing germanium SAQDs under  $\approx 3.7\%$  tensile strain. (*ACS Nano* **2013**, *7*, [Article ASAP](#); Nancy McGuire)



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<http://www.acs.org/content/acs/en/noteworthy-chemistry/archive/june-24.html#link5>

June 24, 2013

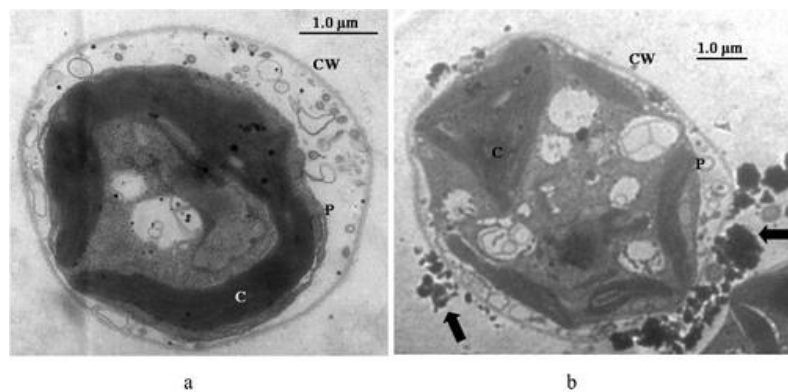
**Do engineered nanoparticles poison algae?** Engineered nanoparticles (ENPs)—those that are designed and produced intentionally rather than unintentionally or naturally—are used in numerous consumer products, for example, as antibacterial coatings. However, their fate and behavior in the environment, especially in aquatic ecosystems, is largely unknown.

Their small size gives ENPs unique physicochemical characteristics and versatile applications; but these characteristics can also affect living organisms by inhibiting photosynthesis, changing behavior and reproduction, and affecting the oxidation of lipids, proteins, and DNA. The hydrophilicity or hydrophobicity of ENPs affects their bioavailability and biological uptake and is a key factor in their ability to reach coastal waters.

A. Quigg and coauthors at Texas A&M University (Galveston and College Station), the University of California at Merced, and Nanjing University (China) reviewed the current information about the effects of ENPs on freshwater and marine algae. Surface algae account for about half of all photosynthetic activity, making them a driving force in sequestering CO<sub>2</sub> from the atmosphere. About half of their photosynthetic production is released into the ocean as exopolymeric substances (EPS) to contribute to the dissolved organic carbon pool.

The researchers found that although the surface properties of ENPs control their aggregation behavior, and ionic strength controls their dissolution, their toxicity is determined by EPS produced by the algae. EPS production reduces the bioavailability and toxicity of ENPs and their ions, not by affecting aggregation or solubility, but by changing the stability of the ENPs. When algae are exposed to ENPs, EPS production increases, possibly as a protective mechanism.

Capping agents and surface coatings are applied to ENPs during manufacture to stabilize them in suspension and prevent aggregation or dissolution. Surface treatments also provide catalytic or pharmacological activity or specific binding sites. Stable ENP suspensions interact more efficiently with algae, but some surface coatings reduce or eliminate toxicity by preventing dissolution or direct contact between the organism and the interior of the ENP (see figure).



The figure contains transmission electron microscope images of the green alga *Chlamydomonas reinhardtii* in the presence of (a) 100 mg/L well-dispersed polyacrylate-coated TiO<sub>2</sub> nanoparticles and (b) their aggregated bare counterparts. Arrows indicate the attachment of bare particles to the cell wall (CW). No coated particles were found on the cell wall or in the interior.

High molecular-weight natural organic matter (NOM) can promote ENP aggregation and sedimentation and reduce the bioavailability of the ENPs. Conversely, lower molecular-weight NOM can act as a surfactant and produce the opposite effect. (*ACS Sustainable Chem. Eng.* **2013**, *1*, [Article ASAP](#); Nancy McGuire) [Copyright © 2013 American Chemical Society](#)