

CHEMISTRY

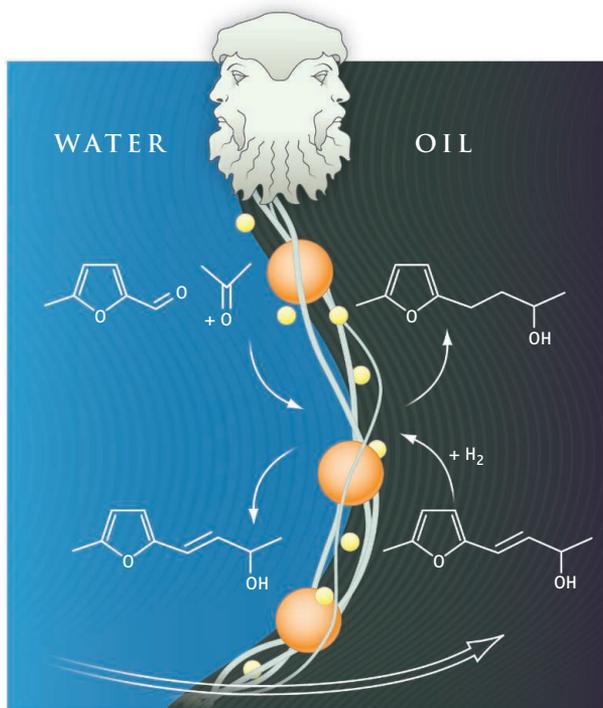
Janus Catalysts Direct Nanoparticle Reactivity

David J. Cole-Hamilton

I'm going to set you a challenge. Go and make a cup of tea. Add milk and sugar, and stir well. Now, please get just the sugar back out for me. Difficult, isn't it? The same problem faces chemists who want to make synthetic products more environmentally friendly. Soluble compounds that are used to speed up desired reactions—homogeneous catalysts—can end up in final products, where they pose a nightmare of a separation problem. Ideally, if these catalysts could be completely recovered, they could be recycled and kept out of the products, in which they could be toxic even at trace levels. One general approach to recovering such catalysts is “phase transfer,” which takes advantage of the different solubility of compounds in water versus organic solvents. On page 68 of this issue, Crossley *et al.* (1) have converted solid nanoparticles that have solubility in both water and oils into catalysts that can operate in both phases. These catalysts can be recovered even from complex mixtures, such as those that result when biomass products are upgraded into fuels.

Phase separation between organic and aqueous phases has been exploited in commercial methods for catalyst recovery (2), but the success of these approaches depends on the particular system. For example, if the reactants have some solubility in water, and the products have less solubility, then separation can be achieved by modifying the catalyst so that it dissolves in water. The catalyst can be recovered at the end of the reaction by simply decanting the oil from the water (3). However, the reaction takes place in the aqueous phase, so if the water solubility of the reactants is too low, the reaction may be unacceptably slow. Some recent approaches have tackled this problem through the use of additives (4, 5) that improve catalyst solubility.

Eastchem, School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland, UK. E-mail: djc@st-and.ac.uk



About face for catalysts. Reactions at the interface between organic and aqueous phases (blue and gray areas, respectively) can be catalyzed by different parts of the same nanoparticle. Crossley *et al.* grew carbon nanotubes (shown in white) on metal oxide nanoparticles (shown in orange) that, like the Roman god Janus, present two faces. The oxide surface prefers to be in water and the carbon nanotubes prefer to be in oil, so these particles seek out water-oil interfaces. The addition of palladium (shown in yellow) to these nanoparticles creates catalysts that can work in both phases. In the system depicted here, basic magnesium oxide catalyzes a coupling reaction of 5-methylfurfural and acetone that is useful in biofuel production. The product transfers to the oil phase, where a palladium catalyst attached to the carbon nanotubes catalyzes a subsequent hydrogenation reaction. The nanoparticle catalyst can be separated after reaction via filtration.

Crossley *et al.* have developed nanoparticles that selectively locate at the interface between the aqueous and organic phases. They deposited carbon nanotubes on metal oxide nanoparticles, such as silicon oxide (silica) or magnesium oxide, with diameters of 50 nm or less. The oxides are hydrophilic and attracted to the water, while the carbon nanotubes are hydrophobic and prefer the organic layer (hence they are described as Janus particles, like the two-faced character of mythology). Like a large surfactant molecule, the nanoparticles compromise by sitting at the interface. Unlike surfactants, the nanoparticles are solids that can be separated with methods such as filtration.

Metal oxide nanoparticles decorated with carbon nanotubes can be turned into readily recovered catalysts that function at the interface between oil and water phases.

Achieving high reaction rates depends on creating as much interfacial area between the phases as possible for the catalyst to do its job, which is accomplished by vigorous stirring to create an emulsion. The silica form of these nanoparticles can stabilize either water-in-oil or oil-in-water emulsions (6) and accumulate at high concentrations at the interfaces.

Crossley *et al.* added a catalytically active metal—palladium (Pd)—to these nanoparticles to create catalysts that achieve high reaction rates in biphasic reactions through the combination of high interface concentration and high interfacial surface area. The announcement of rate enhancements alone is an important development, but the authors further advance the field by using their catalysts in reactions to form fuels from bio-oils. Naturally derived molecules are “upgraded” for use as fuels by coupling small molecules together, removing oxygenated groups, or both.

The removal of oxygenated groups illustrates the power of this method. Acid and alcohol groups increase the water solubility of molecules, but if the molecules are coupled together in a way that removes these groups, then the desired product will be more soluble in the organic phase. The catalysts not only accelerate the coupling

reactions, but the biphasic system also allows the desired product to move into the organic phase and leave everything else, including the recoverable catalyst, in the aqueous phase. In systems with a single liquid phase—even ones that use insoluble heterogeneous catalysts on solid supports—all of the products would remain together in solution. Separation would require complex distillation steps that might decompose or rearrange the thermally sensitive products.

Crossley *et al.* also exploit another asymmetry of these Janus particles: The carbon nanotubes grown on silica are more perfect than those grown on magnesium oxide. When they deposit the Pd catalyst in the silica sys-

tem, almost all of it binds on the silica side. Because the catalyst orients itself at the interface with the silica in contact with the water, and the carbon nanotubes in the organic phase, the catalyst is predominantly in contact with the water. Reactants that are water-soluble react more readily in the emulsion than those in the organic phase. Thus, the catalyst will select among reactants in a complex mixture only on the basis of water solubility.

When the Pd catalyst is deposited in the magnesium oxide system, some of it now binds to the carbon nanotubes at defect sites. Hydrogenation reactions can occur in the organic phase, and the magnesium oxide, which is basic, catalyzes coupling reactions in

the aqueous phase. The result is that different reactions can be run in the oil and in the water phases at the same time (see the figure).

One intriguing extension would be to rethink conventional organic synthesis of drug molecules, which depends on several cycles of reaction and separation. A complex molecule could undergo reaction on just one of its functional groups in water. The product could rearrange and become organic-soluble, and then transfer to the other phase, where a different reaction could occur. In this way, a series of reactions could create a desired molecule in one pot, without needing to protect vulnerable functional groups in the reactants. Simple filtration followed by phase separa-

tion and solvent removal would then give the desired product in high yield and containing no catalyst residues—a pharmaceutical chemist's dream come true.

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BIOCHEMISTRY

Some Enzymes Just Need a Space of Their Own

Sebyung Kang and Trevor Douglas

In many ways biology is defined by the idea (and reality) of containers and well-defined barriers. These enable the distinction of self from the rest of the universe, separation of cells from each other, and the definition of organelles within a cell. Although many biological barriers and compartmental boundaries are lipid-based membranes, there is a growing awareness, brought about by some spectacular structural biology, of protein-based compartments that act as isolated environments within the cell. On page 81 of this issue, Tanaka *et al.* (1) add to the growing number of examples of protein-based microcompartments, reporting the structure of a microcompartment that sequesters ethanolamine metabolism in the bacterium *Escherichia coli*. These protein-based containers challenge a long-standing assumption that bacteria and archaea, which lack membrane-enclosed organelles, are devoid of internal compartmentalization.

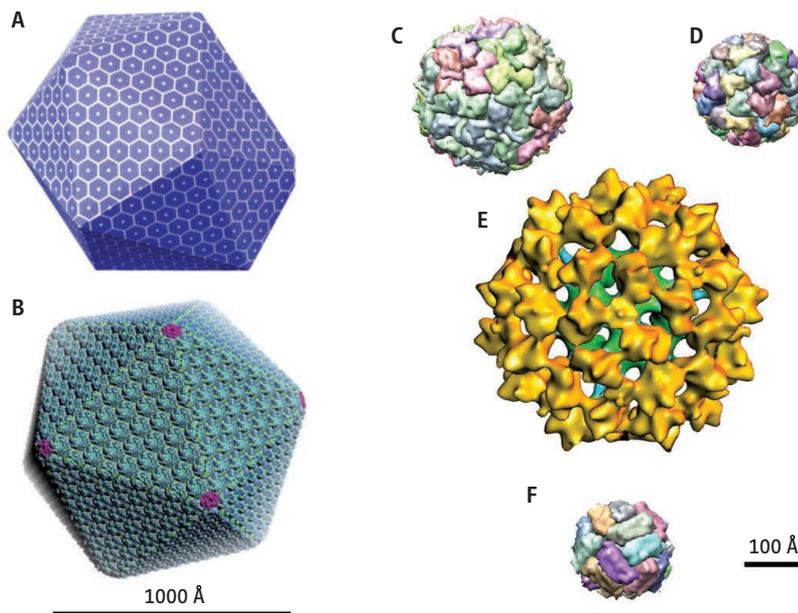
Protein-based compartments often exhibit highly symmetric structures assembled from a limited number of subunit building blocks. These structures are reminiscent of viruses and share properties (2) that make them more than just curiosities—they incorporate catalytic activities and sequester reactions from the cellular environment, and control small-

molecule access across the protein barrier through structural dynamics.

Tanaka *et al.* report the three-dimensional crystal structures of the major shell constituents (EutS, EutL, EutK, EutM) of an ethanolamine utilization (Eut) microcompartment

Protein shells that sequester enzymatic reactions are found in diverse organisms and may provide blueprints for nanoparticle design.

ment, where ethanolamine metabolism is isolated in *E. coli* (see the figure). The Eut microcompartment prevents the release of acetaldehyde into the cytosol, mitigating the potentially toxic effects of excess aldehyde and limiting the loss of carbon by diffusion



Microcompartment architectures. (A) Model of the ethanolamine utilization (Eut) microcompartment. (B) Model of the carboxysome microcompartment. (C) Shell structure of *T. maritima* encapsulin (PDB: 3DKT). (D) Shell structure of *B. subtilis* lumazine synthase (PDB: 1RVV). (E) Three-dimensional reconstruction of bovine pyruvate dehydrogenase complex [derived from (6) with permission from the National Academy of Sciences, USA]. (F) Structure of human ferritin (PDB: 2HFA). Structures in (C), (D), and (F) were generated with the molecular graphics program Chimera, with the indicated PDB files.

Department of Chemistry and Biochemistry and Center for Bio-Inspired Nanomaterials, Montana State University, Bozeman, MT 59717, USA. E-mail: tdouglas@chemistry.montana.edu



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David J. Cole-Hamilton (December 31, 2009)

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