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CATALYTIC NANOMOTORS

Synthetic nanomotors are propelled by catalytic decomposition of hydrogen peroxide fuel

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The use of catalysis to convert chemical energy into motion on the nanometer scale is widespread in nature. The synthesis of adenosine triphosphate in living cells, for example, relies on the power of enzymes to pump protons across membranes inside the cells.

Two groups of chemists, working independently, have now demonstrated that catalytically driven motion on the nanoscale is possible outside biological systems. The new synthetic systems consist of suspensions of nanorods, composed of two or more metallic segments, in aqueous hydrogen peroxide. One of the metals catalyzes the decomposition of the hydrogen peroxide, liberating oxygen, which provides thrust to propel the nanorods through the solution.

PIVOTING Gold-nickel nanorod tethered to silicon wafer precesses like a top in hydrogen peroxide solution when oxygen is generated at the nickel end.

ADAPTED FROM IMAGE BY LUDOVICO CADEMARTIRI

The first example of such a system, dubbed a "catalytic nanomotor," was described last year by Ph.D. student Walter F. Paxton, chemistry professors Ayusman Sen and Thomas E. Mallouk, physics professor Vincent H. Crespi, and coworkers at Pennsylvania State University [*J. Am. Chem. Soc.,* **126,** 13424 (2004)]. The nanomotors are rod-shaped particles, 370 nm in diameter, consisting of 1-µm-long platinum and gold segments. The platinum catalyzes the decomposition of hydrogen peroxide and formation of oxygen. The rods move at speeds of up to 10 body lengths per second.

"The dimensions of the rods and their average speeds are similar to those of multiflagellar bacteria such as *Bacillus cereus,*" Sen notes. "Control experiments establish that purely Brownian motion occurs in the absence of the hydrogen peroxide fuel.

"Catalytically driven nanomotors are autonomous in that they do not require external electric, magnetic, or optical fields as energy sources," he adds. "Instead, the input energy is supplied locally and chemically."

The second example involves gold-nickel nanorods. The gold ends are tethered to the surface of a silicon wafer. The nickel catalyzes the hydrogen peroxide decomposition and generates oxygen, which causes the nanorods to rotate like propellers. The work was published a couple of months after the Penn State paper by chemistry professors Ian Manners and Geoffrey A. Ozin and their coworkers at the University of Toronto [*Chem. Commun.,* **2005,** 441].

Both groups synthesized the nanorods electrochemically in the nanochannels of alumina membranes.

NANO HOT RODS **Penn State group developed a catalytic nanomotor fueled by hydrogen peroxide. From left: (top) postdoc Paul E. Lammert, Catchmark, Crespi, Sen; (bottom) Ph.D. student Yanyan Cao, Kline, Subramanian, Paxton, Mallouk.**

COURTESY OF AYUSMAN SEN

"THESE PAPERS describe a clever use of chemistry and nanomaterials to realize a new class of nanostructures that are chemically addressable by virtue of catalytic properties that have been designed into them," comments Chad A. Mirkin, a chemistry professor at Northwestern University. "The work is going to inspire others to come up with all sorts of new methods for effecting and using controlled nanostructure movement in anything ranging from power generation to nanorobotics."

Harvard University chemistry professor George M. Whitesides points out that a lot of work has already been done on synthetic noncatalytic molecular systems in solution in which one part moves relative to another part. "Much of the previous work on what have been called 'molecular motors' has not really described 'motors,' " he says. "Although there are molecules that change conformation when oxidized or reduced or when irradiated, they have generally been systems that were not able to do work in the thermodynamic sense and thus are not, in my opinion, really motors. The nanorod systems are motors and, very elegantly, motors with no moving parts. There is a fuel--aqueous hydrogen peroxide--and there is directed, even controlled, movement."

In 2002, Whitesides and coworkers showed that catalysis can be used to power the autonomous movement of millimeter-sized objects on the surface of an aqueous solution of hydrogen peroxide [*Angew. Chem. Int. Ed.,* **41,** 652 (2002)]. Their system consists of a small piece of platinum-covered porous glass pinned to a hemicylindrical polydimethylsiloxane (PDMS) plate.

The Harvard authors suggest that assemblies of autonomously moving components could find technological applications and could help to understand the behavior of other complex systems characterized by a large number of autonomously moving interacting components such as schooling fish and swarming bacteria.

The propulsion mechanism of the millimeter-scale system described by Whitesides and coworkers is probably different from that of the Penn State and Toronto nanoscale systems. The energy required for surface movement of the floating PDMS plate in the millimeter-scale system comes from the recoil force of the liquid as the oxygen bubbles burst.

Movement in the nanoscale system occurs in the opposite direction--that is, toward the platinum ends of the rods. The Penn State chemists point out that oxygen is generated uniformly and selectively on the platinum segments of the nanorods. They attribute the direction of motion to an oxygen concentration gradient that occurs from the platinum/gold junction to the end of the gold segment of each nanorod. The oxygen bubbles pinned to the hydrophobic gold surface create a liquid/vapor interface. As the oxygen concentration decreases, the interfacial tension gradient at the liquid/vapor interface increases, causing the nanorod to be propelled in the direction of the platinum end.

"The nanorods move along their long axis with the platinum end forward," Sen explains. "Forward movement is preferred because the drag force is minimized in this direction and the catalytic reaction takes place on only one end. The direction of movement is opposite to that expected if oxygen generated by the platinum segment impelled the rod by momentum recoil or through a pressure increase."

Although the motion of the nanorods is predominantly linear, rotary motion is also possible.

"When two rods collide and stick together, one acts as the motor and the other as the inertial stator to give the rotary motion," Mallouk explains. "Alternatively, when one end of a rod sticks to a surface, the force is directed along the rod axis. Any asymmetry in the rod probably causes it to spin on its head like a top."

Sen, Mallouk, Paxton, and Ph.D. student Timothy R. Kline have also shown that the linear movement of nanorods with five segments--platinum/nickel/gold/nickel/gold--in aqueous hydrogen peroxide can be directed by using an external magnetic field [*Angew. Chem. Int. Ed.,* **44,** 744 (2005)].

"The nickel segments are ferromagnetic and can be magnetized to control the direction of rod movement," Sen says. "The calculated magnetic moment of the rods is comparable to that observed for magnetotactic bacteria. The axial velocity is essentially unaltered by the magnetic field, thereby demonstrating that the field only aligns the rods and neither impedes nor enhances the axial motion."

The group suggests that, in principle, tethering these magnetically controlled, catalytically driven nanoengines to other objects could result in new classes of nanomachines or micromachines.

Whereas the work described by the Penn State group focuses on the linear motion of their nanorods, the Toronto group's paper reports investigations into the rotary motion of nanorods. "We synthesized gold-nickel rod-shaped nanobuilding blocks, about 500 times smaller than the width of a human hair," Ozin says. "When the rods are placed in a hydrogen peroxide solution, they self-propel in a roughly linear trajectory. However, when the nanorods touch and anchor to the surface of a silicon wafer, they do not migrate but rotate instead."

Preliminary studies by the group indicate that the angular velocity of the rotating nanorods can be controlled by varying the concentration of the hydrogen peroxide solution and the length of the nickel segment.

"THIS WORK is a beautiful demonstration of how a designed nanoscale object can undergo a rotary movement powered by a chemical fuel," comments molecular motor expert Ben L. Feringa, a chemistry professor at the University of Groningen, in the Netherlands. "Although there are many challenges regarding precise positioning and control of the movements, it is clear that these findings offer fascinating opportunities to ultimately build nanomachines."

Ozin points out that nanomachines need more than just a nanorotor. "We need to assemble and integrate our synthetic nanorotors into more complex architectures so that the rotary motion can be harnessed to accomplish a variety of tasks," he explains. "Although nanorods are used in our study, there are a multitude of other nanobuilding blocks such as nanospheres, nanorings, and nanotubes, which could be powered with a chemical fuel. There are also a number of ways in which these dynamic nanomachines could be interconnected."

Other examples of synthetic catalytically driven machinery, albeit on the microscale, are already beginning to emerge. In recent work, for example, Sen, Ph.D. student Shyamala Subramanian, and research associate Jeffrey M. Catchmark at Penn State used microfabrication techniques to prepare gold gearlike objects specifically designed to exhibit catalytically driven rotational movement [*Small,* **1,** 202 (2005)]. The gear has a diameter of around 100 µm.

"Each tooth in the gear has platinum coated on one face," Sen explains. "This geometry generates interfacial tension forces across each tooth.

"We fabricated the gear by a combination of optical lithography, evaporation, and electroplating on a silicon substrate," he continues. "We then released the gears from the surface by wet chemical etching and suspended them in aqueous hydrogen peroxide. The gear rotates an order of magnitude faster than the nanorod."

A large number of metals, metal complexes, and enzymes catalyze reactions that can be used to generate chemical gradients at the surface of nanoscale objects, Sen notes. "By appropriate design, these gradients can be translated into anisotropic body and/or surface forces," he points out. "Depending on the shape of the object and the placement of the catalyst, different kinds of motion can be achieved. The resulting nanomotors can, in principle, be tethered or coupled to other objects to act as the 'engines' of nanoscale assemblies."

Whitesides remarks that the conversion of chemical energy into motion by a heterogeneous catalytic reaction is unquestionably interesting. "What remains to be done is everything else--coupling the motion to some useful task and controlling the system," he says. "There is also a core question: What is the problem that requires having a nanomotor?"

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