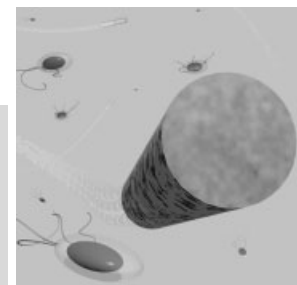


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Dream Nanomachines**

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Locomotion on the nanoscale through a fluid environment is one of the grand challenges confronting nanoscience today. The vision is to synthesize, probe, understand, and utilize a new class of motors made from nanoscale building blocks that derive on-board or off-board power from in-situ chemical reactions. The generated mechanical work allows these motors to move through a fluid phase while simultaneously or sequentially performing a task or series of tasks. Such tiny machines, individually or assembled into designed architectures, might someday transport medicine in the human body, conduct operations in cells, move cargo around microfluidic chips, manage light beams, agitate liquids close to electrode surfaces, and search for and destroy toxic organic molecules in polluted water streams. Are these just “nanomachine dreams”, or “dream nanomachines”? Some very recent exciting developments suggest that a world of amazing chemically powered nanomachines will be the way the story unfolds in the not-too-distant future!

1. Nanomachine Challenge

Visionary physicist Richard Feynman, in his prescient 1959 Caltech speech “There’s Plenty of Room at the Bottom”, issued a public challenge and a thousand-dollar prize to the first person to create an electrical motor “smaller than one sixty-fourth of an inch”.^[1] Soon thereafter, and much to Feynman’s surprise, William McLellan built such a tiny motor tediously yet meticulously by hand using just an optical microscope and fine tweezers.

Since Feynman’s prophetic speech, pertinent questions about tiny motors and machines, invisible to the naked eye, include: How small can they be and still function? What external or internal energy sources can be used to drive them? What are the forces responsible for the locomotion? What power can they generate? Finally, what tasks can they undertake? In this Research News paper, we will take a brief look at how the field has evolved post-McLellan and what the future holds for these tiny mechanical contraptions.

2. MEMS and NEMS

The Feynman–McLellan episode seems to have inspired research into microelectromechanical systems (MEMS), a field that emerged in the mid-eighties. This led to the development of micromotors orders-of-magnitude smaller than McLellan’s handmade creation. They are now being mass produced to manufacture fascinating products, such as digital projectors composed of millions of electrically driven micromirrors and airbags in automobiles deployed by micromotion sensors.^[2] MEMS, an integration of top-down semiconductor processing and engineering physics, enables tiny machines to be sculpted from smaller components on the scale of millimeters to micrometers. Downsizing MEMS represents the futuristic realm of

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nanoelectromechanical systems (NEMS): the world of the tiniest machines, sensors, and computers, now considered to be an achievable goal as Moore's law races towards 70 nm feature sizes on chips by 2010. However, it is not yet clear whether NEMS will be fashioned from bulk materials by refining top-down nanofabrication methods to go even smaller, or rather by adopting a radically different strategy which entails self-assembling them from the bottom-up using nanoscale building blocks with controlled size and shape, surface structure, and chemical functionality.^[3] One thing is certain: the bottom-up approach has attractive advantages over its rival when considering Nature's bionanomachines.

3. Nature's Bionanomachines

We see self-assembly at work in Nature's impressive biomolecular motors and machines that manufacture and transport biochemicals in the cytoplasm and provide motility to cells.^[4,5] A classic example of a biomolecule factory is the ribosome, an RNA and protein composite that uses a temporary transcript in the form of messenger RNA to assemble proteins from amino acids, which can then proceed to other tasks. An impressive case of biological locomotion is the kinesin protein, a linear processive motor that transports chemical payloads along microtubules in the cell. In addition, there are also non-processive motors, including myosin and the dynein protein family, which detach from the track and subsequently re-attach, and therefore can be seen as hopping along the track instead of walking. It is hard for nanoscience to compete with the flagella biological motor in bacteria like *Escherichia coli*—an assembly of proteins embedded in cell membranes that decomposes adenosine triphosphate (ATP) for energy, and, through a whip-like rotary motion, provides motility to bacteria in a liquid. Forward translation occurs when

the thrust provided by flagella rotation overcomes opposing forces of viscous drag on the *E. coli* body, while the attainable speed depends on the size and shape of the cell.

This is a cursory glance at just a few bionanomachines created from the bottom-up by Nature's self-assembly biochemistry. To emulate this impressive skill in the laboratory is one of the grand challenges of contemporary bionanoengineering.

4. Artificial Bionanomachines

One approach to create artificial bionanomachines is to transfer biotechnology from Nature and integrate biomolecules with man-made nanostructures. Inspired by the flagella rotary motor, a hybrid bionanomechanical rotary device has been assembled from ATP synthase and a nickel propeller.^[6] ATP synthase, also called ATPase, is an assembly of proteins anchored in the cell lipid bilayer responsible for the synthesis of ATP, the biological energy currency, and is powered by a proton gradient across the membrane created by nearby proton pumps. Every time an ATP molecule is synthesized, the head of ATPase rotates by 120°, making this protein a very small and very efficient nanopropeller. Inspired by this ability, ATPase has been chemically anchored via a histidine linkage on its underside to a lithographically defined nanoscale nickel pillar on a substrate, and via a biotin-streptavidin linkage on its topside to a nanoscale nickel propeller, also made by lithography. When fed with ATP, the ATPase enzyme provides the energy to cause the propeller to rotate (Fig. 1).

A first step towards a muscle-powered bionanomachine has been realized by self-assembling muscle fibers, comprising comb-like arrays of protein actin filaments having myosin protein rods interdigitated between the teeth of the combs,

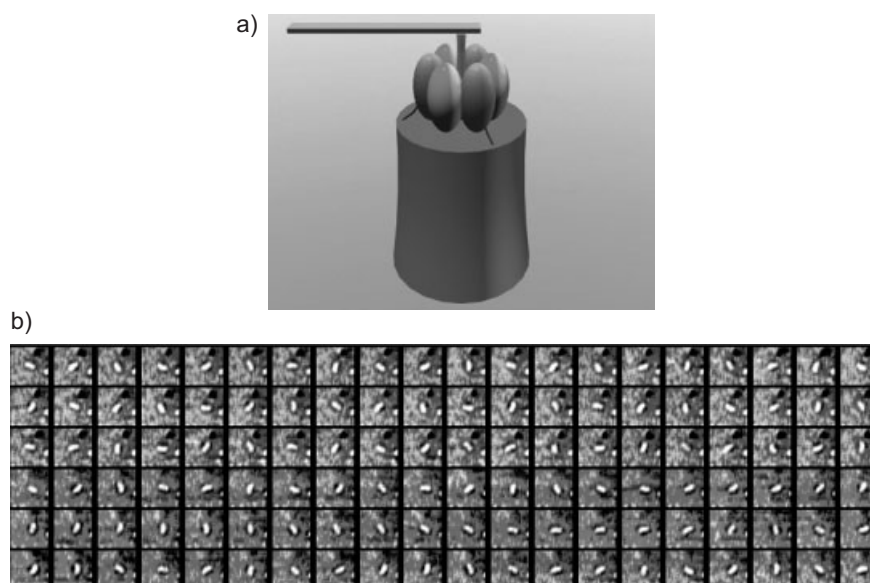


Figure 1. Schematic of a hybrid organic-inorganic propeller powered by the ATPase enzyme (top), and consecutive frames of a video image showing the synthetic propeller fed ATP as an energy source (bottom). Reprinted with permission from [6]. Copyright 2000 AAAS.

with a NEMS device and feeding it glucose biofuel.^[7] The glucose causes molecular motors located at the termini of the myosin filaments to step along the actin filaments, causing deeper interpenetration of the myosin rods into the actin filaments and thereby inducing the muscle fiber to contract. This hybrid biochemomechanical system has been shown to perform as a force transducer for measuring the mechanical properties of muscle; moreover, it functions as a mechanical device with muscle-powered movement.

In another study, it was demonstrated that chemical control could be exerted over the adhesion in specific numbers and orientations of motile, living *E. coli* bacteria to patterned, functionalized self-assembled monolayer (SAM) surfaces that had structural features of a pre-determined size and shape.^[8] This represents a step towards bacteria-powered nanomachines, whereby surface-confined bacteria could be harnessed for performing specific machine tasks, like delivering a chemical or physical payload to a targeted destination or powering a device.

Continuing with the theme of size and shape, filamentous cells of *E. coli*, when spatially confined and allowed to grow in microchambers patterned by soft lithography in nutrient-soaked agarose, have been found to adapt their form to the shape of the microchamber.^[9] Crescent-, zigzag-, sinusoidal-, and spiral-shaped *E. coli* with flagella motors created in this way have been observed to retain these shapes when released into solution. Moreover, their swimming style depends on the shape of the adapted cell. Just as the growth and form of a myriad of non-living materials exemplified by crystals, colloidal crystals, and block copolymers can be controlled by the geometrical and spatial constraints of surface-relief patterns,^[3] so too can living bacteria like *E. coli* be directed to adopt a shape commensurate with the container in which they grow. In the context of bionanomachines, this paradigm provides a valuable platform for understanding and optimizing the relationship between shape and locomotion of self-propelled cells of bacteria. Such studies will generate a body of information that may assist with the design of man-made nanomachines that perform a useful task (as discussed below).

As well as directing the growth and form of *E. coli* in geometrically and spatially confined microcontainers, their motion has also been directed by microchannels fashioned in a patterned master placed on top of and in conformal contact with a substrate.^[10] By manipulating the dimensions of the microchannels, the material properties of the microchannel ceiling and side walls, the chemical nature of their surfaces, and the nutrients and additives contained therein, conditions could be found that coerced the *E. coli* to “drive on the right”. In a series of ingenious experiments, this preference could be traced to the flagella-driven motion of the body of the cell, thrusting and twisting forward, and how the differential resistance of the ceiling and side walls of the microchannel (glass and plasma-oxidized polydimethylsiloxane) and the substrate (agarose) influence the direction and sense of movement. This innovation points the way to bacteria-powered microfluidic devices and analysis systems.

But the assembly and action of these bionanomachines still has “more than a little help from Nature”—to operate, they all rely on active biomolecular components and energy-rich biofuels. Can we do better? Can we outsmart Nature? Can we create nanomachines from the bottom-up that derive their power from simple solution-phase or surface chemical reactions that do not make use of complex biological molecules?

5. Autonomous Self-Assembly

Self-assembling synthetic systems are usually built by chemically pre-programming components to form a specific structure.^[3] But what if we provide the components with autonomous movement capabilities? This idea was demonstrated using chemically powered, asymmetrically shaped macroscale objects sculpted from polydimethylsiloxane, endowed with hydrophilic and hydrophobic regions.^[11] They float at an air/water interface and can self-assemble through capillary interactions. Platinum was applied to these objects at a specific location, and, when floated on an aqueous solution of hydrogen peroxide, the surface-catalyzed evolution of oxygen from the platinum propelled the objects, causing them to move about and collide. Through complimentary hydrophobic interactions, these chemically driven colliding objects formed dimers bearing two platinum motors. Isomers of a like kind formed dimers with motors at opposite ends and looped around at the air/water interface. In contrast, isomers of the opposite kind formed mirror-image dimers with motors at the same end and displayed linear motion. *Eureka, the race for nanoscale chemically powered motors had begun!*

6. Man-Made Nanomachines

Some of the most dramatic recent examples of synthetic nanomachines, some with moving parts, are based upon creative devices made of carbon nanotubes, metal, or semiconductor nanowires, and mainly driven by an electrical source of energy. An exception is a nanoscale thermometer based on a single-walled carbon nanotube that converts thermal energy into expansion of a nanocolumn of liquid gallium imbedded within the body of the nanotube, thereby registering temperature.^[12] A nanorotor based on a suspended-beam carbon nanotube and an attached silicon nanoplate between two electrodes converts electrical energy into rotary motion of the plate.^[13] Such tiny rotors might find utility as nanoscale stirrers for agitating liquids in confined spaces like microchannels, or near electrode surfaces to enhance diffusion processes, or as optical switches for directing light beams. A metal nanowire, suspended in a droplet of water located between microelectrodes having a specific geometry to which alternating current voltages with a particular frequency and phase are applied, has been coerced to undergo linear and rotary types of motion.^[14,15] The force responsible for the locomotion is dielectrophoresis, which arises from the interaction between the

polarized conduction electrons in the nanowire and the applied electric field. Velocity, rotation speed, rotation sense, and degree of rotation of the nanowires are all under electrical control. Magnetic and non-magnetic nanowires and carbon nanotubes have been manipulated in this way, moving freely in solution and chemically anchored to a substrate. Also, a micromotor based upon the movement of a dust particle by a bent, rotating metal nanowire was demonstrated.

Going even smaller, an electrically driven nanocrystal linear nanomotor has been assembled in an electron microscope from an indium nanocrystal ram between two carbon-nanotube lever arms (Fig. 2).^[16] Another indium nanocrystal is attached to one of the lever arms, and through electromigration of indium atoms along the surface of the nanotubes, serves as a continuous supply of indium atoms.^[17] The voltage bias applied to the lever controls the direction of flow of indium atoms between reservoir and ram, making the ram grow or shrink, and thereby prying the lever arms apart or allowing them to relax together. Individual or crossed inorganic nanowires made of common semiconductors like silicon, gallium arsenide, cadmium sulfide, and zinc oxide can function as electrically activated transistors or diodes, light-emitting diodes, or lasers. For example, the electrical-switching action of a field-effect transistor built from a silicon nanowire with a surface-tethered alkoxy silane can have a terminal amine group that is sensitive to pH or a molecular recognition group that is responsive to specific biomolecules, although these nanowire sensors have no moving parts.^[18]

Scanning probe microscopes are also a class of nanomachines, where an electrically driven and piezoelectrically positioned nanoscale tip attached to the end of a microcantilever, besides imaging at the nanoscale, can also manipulate and write with nanometer precision atoms and molecules, macromolecules and biomolecules, and clusters and surfaces. Millions of these fine tips on microcantilevers are now being used to deposit a wide range of molecules and materials into functional nanopatterns by dip-pen nanolithography, as well as to make patterns of nanoindentations in polymer surfaces. Such nanoindentations can be used to encode vast quantities of information and erased by thermally consolidating the nanoindentation, as has been demonstrated by the IBM Milli-

pede—a MEMS-based nanomechanical system that has achieved data-storage densities of more than one terabit (1000 gigabits) per square inch (1 inch=2.54 cm). This is equivalent to storing the contents of 25 digital video discs (DVDs) on an area the size of a postage stamp.^[19]

7. Man-Made Nanochemomechanical Systems (NCMS)

While biomolecular motors can drive nanomechanical systems, they are complex and constrained to functioning under physiological conditions. In contrast, a chemically powered motor could, in principle, be constructed from nanoscale building blocks having a myriad of compositions, sizes, and shapes, with different surface structures and functionalities, and powered by a diversity of environmentally friendly on-board fuels.^[4] One of the main challenges to reduce this idea to practice is to figure out how to interface nanoscale objects with internal or external chemical power sources which can endow them with a particular type of motion.

The idea that anisotropic forces can be created on the body of a nano-object by an on-board chemical motor raises the exciting possibility of discovering whole new classes of entirely synthetic nanomachines which can be “pre-programmed” by synthesis and “designed” through surface chemistry to perform specific tasks. Such bottom-up chemically powered nanomachines could provide the basis of a new genre of nanochemomechanical systems, denoted NCMS, placing them in context with well-documented top-down, electrically driven, engineered silicon-based nano-electro-mechanical systems known as NEMS.

It is well recognized that surface-stress changes caused by chemical processes in molecules anchored to microcantilevers can induce bending of the lever. Coupling species to the microcantilevers capable of molecular recognition enables the development of a novel class of ultrasensitive chemical and biological sensors that can operate in air and in water with detection capability in the parts-per-billion to parts-per-trillion range. By building a surface-stress change in the microcantilever, caused by either a redox or a photoinduced conformational change of a molecule attached to one side of the microcantilever, bending can be induced, thus raising the possibility of developing novel kinds of nanochemomechanical devices.

Nanochemomechanical-induced bending of an array of microcantilevers has recently been reduced to practice by a redox-powered linear molecular rotaxane motor that had been chemically attached via thiol linkers to the surface of a microcantilever (Fig. 3).^[20] Cycles of chemical oxidation and reduction of the tethered rotaxane molecule induce a contractile strain in the surface of the microcantilever, causing it to flex. This is an impressive example of how a molecular analogue of mus-

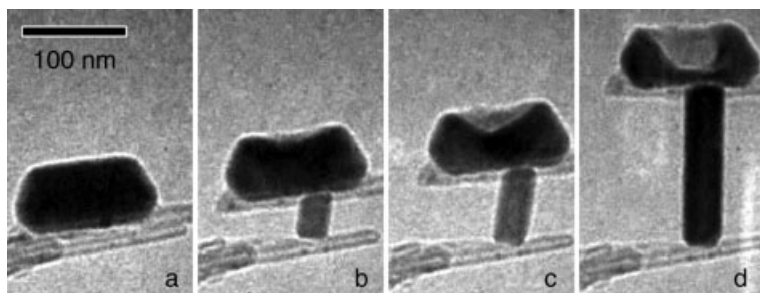


Figure 2. Electrically driven linear nanomotor made from an indium nanocrystal and a carbon nanotube lever. Reprinted with permission from [16]. Copyright 2005 American Chemical Society.

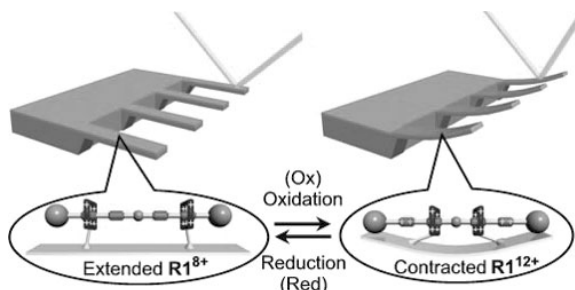


Figure 3. Nanochemomechanical devices based on a redox-active rotaxane tethered to a microcantilever, which causes reversible beam flexing in chemical oxidation–reduction cycles. Reprinted with permission from [20]. Copyright 2004 American Institute of Physics.

cle filaments can be tethered to a cantilever and chemically stimulated to make it bend.

In a related vein, nanophotochemomechanical-induced bending of a microcantilever has also been achieved by trans-cis photoisomerization of an azobenzene molecular motor that had been chemically anchored to the gold surface of a cantilever via a thiol linker (Fig. 4).^[21] In this case, bending occurs because of surface stress induced by the photochemically induced change in the dimension of the molecule tethered to the cantilever. This stress is transmitted to the surface of the cantilever, forcing it to bend.

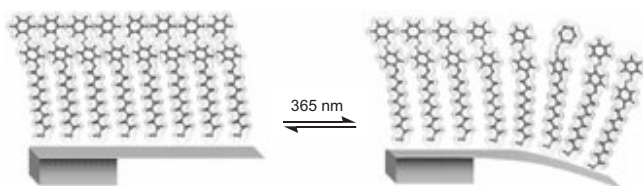


Figure 4. Nanophotochemomechanical-induced bending of a microcantilever induced by trans–cis photoisomerization of an azobenzene chemically anchored to the gold surface of a cantilever via a thiol linker [21]. Reproduced by permission of the Royal Society of Chemistry.

Similarly, a photocatalytic microengine has recently been described whose motion is fuelled by surface photo-oxidation of hydrocarbons on a thin titania film deposited on the silicon nitride side of a gold/silicon nitride bimorphic microcantilever.^[22] The observed reversible bending of the microcantilever occurs at room temperature and was explained in terms of a four-step process involving adsorption, photo-ignition, heat generation, and desorption of the hydrocarbon fuel on the surface of the titania. An analogy was drawn between this hydrocarbon-fuelled photocatalytic microengine and a four-stroke internal-combustion engine based on fuel intake, compression, combustion, and exhaust. The elegance of this photochemically powered self-cleaning microengine is its simplicity, which lends itself to the future development of large-scale motors comprising massively parallel microcantilever arrays that convert solar photons and hydrocarbons into mechanical work.

Towards the end of last year, it was independently reported by materials chemistry groups at Toronto and Penn State^[23,24] that chemically powered linear motion of a gold/platinum nanorod could be achieved in solution,^[24] and that rotational motion of a gold/nickel nanorod could be realized when tethered at one end to a surface (Fig. 5).^[23]



Figure 5. Illustration of rotary motion of a gold/nickel nanorod anchored via the gold end to a silicon surface and propelled into a circular orbit by oxygen nanobubbles evolved from the catalytic decomposition of hydrogen peroxide fuel to water and oxygen at the nickel end [23].

In these experiments, segmented nanorods were made by electrochemical deposition of the respective metals into a nanochannel alumina membrane, followed by sacrificial etching of the membrane and release of the nanorods into solution. In these first examples of chemically driven nanolocomotion, it was surmised that movement was provided by nanobubbles formed from the decomposition of hydrogen peroxide to oxygen and water generated at a catalytic nickel or platinum segment of a bimetal nanorod. However, it is still unclear whether the origin of the nanobubble-induced motion is something like gas propulsion or surface-tension gradients, or something else entirely.

This question of “something or something else” will be the subject of intense scrutiny in future studies. One aspect that deserves attention is the hydrodynamics of nanobubble collapse. Very recent molecular dynamics simulations show collapse to be very fast (on the order of picoseconds), creating high local temperatures and a large free-energy change.^[25] Therefore, the force associated with nanobubble implosions might be another contribution to nanorod motion. The production, size, and location of nanobubbles on the nanorod need to be defined.

These nanorod nanomotor results were expanded upon in a demonstration that an external magnetic field could enable guided motion of gold/nickel/platinum nanorods in an aqueous solution of hydrogen peroxide, whereby nanobubble-induced mobility of the nanorod is directed by the magnetic lines of force acting on the ferromagnetic nickel segment of the nanorod.^[26]

While much needs to be clarified concerning the specific forces responsible for the mobility of these chemically powered nanorods, the possibilities for extending this concept are limitless. These include new nanorod compositions, segmented architectures, surface functionalities, chemical fuels, and catalytic reactions. Individual nanorods or nanorods anchored in pre-defined geometries to other nanorods or nano-objects (biological or non-biological) can be set into motion while freely suspended in solution; chemically tethered to surfaces; confined at liquid/liquid, liquid/solid, or gas/liquid interfaces; contained within microfluidic channels; or guided by director-field patterns of liquid-crystalline hosts.

In a follow-up study to the nanorod nanomotors, a lithographically defined gold microgear having platinum deposited asymmetrically on one side of the teeth of the gear was driven to rotate by oxygen-nanobubble formation from the platinum-catalyzed decomposition of an aqueous hydrogen peroxide solution.^[27]

An important extension of the nanorod and microgear work makes use of a binuclear manganese cluster (a mimic of the binuclear manganese catalase enzyme) chemically anchored to the surface of a silica microsphere that, in the presence of aqueous hydrogen peroxide, causes catalytic formation of oxygen nanobubbles that send the sphere into motion.^[28] The significance of this work is that it represents an example of a molecular-based system in which autonomous movement of micrometer-scale spheres has been powered by catalytic conversion of chemical to mechanical energy. Whether the propulsion mechanism stems from oxygen nanobubbles, an interfacial-tension gradient, or something else has yet to be defined. Needless to say, an extension to chemically propelled nanospheres will enable a cornucopia of interesting tasks to be performed, like dynamic self-assembly of colloidal aggregates and crystals, or delivery of an active payload to a targeted destination.

On-board chemical power was also applied to a conductive carbon microfiber that was coated at one end with a bioelectrocatalyst for the oxidation of glucose (glucose oxidase, GOx, anode) and at the other with a catalyst for the reduction of oxygen to water (bilirubin oxidase, BOD, cathode).^[29] This innovative construction creates a shorted biofuel cell in which the net bioelectrochemomechanical power-generating reaction of aqueous glucose and oxygen is directly converted into propulsive mechanical power of the fiber (Fig. 6). The origin of the locomotion appears to stem from a pH gradient, whereby protons generated at the anode and their associated hydrogen-bonded water molecules, together with charge balancing electrons, migrate cooperatively from the anode to the cathode in this pH gradient. It is purported that the ion flux around the fiber induces fiber motion at the solution/air interface.

8. Nano Locomotion—A Few Thoughts

Hopefully, this brief glance at nanoscale motors and machines, moving around in a fluid environment and driven by

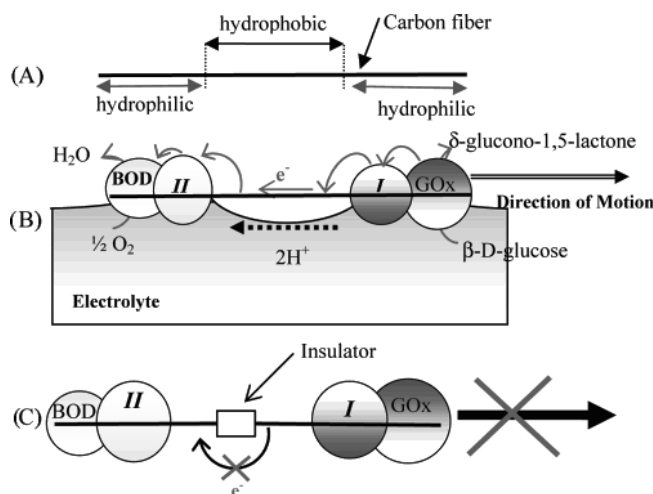


Figure 6. Illustration of a self-propelled carbon-fiber-based bioelectrochemical motor driven by the reaction of glucose and oxygen. Reprinted with permission from [29]. Copyright 2005 American Chemical Society.

on-board or off-board chemical power sources, makes it clear that fantastically interesting challenges lie ahead with respect to not just making them work, observing their motion, and using them to perform a task, but, at a more fundamental level, understanding what forces are at work to make them tick. This enquiry will take us into the world of fluid dynamics at the nanoscale, the regime of low Reynolds numbers where viscosity is a dominant theme—an unfamiliar world for many materials chemists, but one that has been quite well trodden by physicists and engineers, especially those with a bent towards biology and interested in how microorganisms like *E. coli* swim, so there are plenty of lessons to learn.^[30]

To expand slightly, for locomotion of nanoscale objects in water, one is in the realm of very low Reynolds numbers (10^{-5}), defined as the ratio of inertial to viscous forces and shown by Osborne Reynolds more than a century ago to be given by the equation $Re = Lv\rho/\eta$, where L is the dimension of the nano-object, v is the velocity, ρ is the density of the fluid, and η is the viscosity. In this regime, viscous forces dominate inertial forces, and to induce motion on the nano-object the force F must overcome the viscous drag D . This is usually expressed as $ma = F - D$, where m is mass, a is acceleration, and $D = 3\pi\eta LS$, where S is a shape parameter.

In the case of a nanorod motoring around in a fluid, one can get an idea of what controls motion by noting that, for constant or zero F , $m/D \sim 2a^2\rho/\eta$, where a is the radius of the nanorod and ρ' is the density of the nanorod. This simple analysis brings forth the inescapable realization that to move nanorods in a small Reynolds number environment, using on-board or off-board energy-rich chemical fuels, large forces will have to be applied to the nanorods because of the opposing large viscous drag.

This then begs the question whether or not such forces can be generated on a nano-object with a chemically powered motor. The optical microscopy visualization of the nanobub-

ble-driven nanorod nanomotors mentioned above provides direct evidence that they work,^[23,24,26,27] so either the inertial forces generated on the nanorod from the nanobubbles (e.g., surface-tension gradient, propulsion, implosion) are sufficient to overwhelm the opposing viscous forces, or there is something else at work that has yet to be recognized. Possibly, nanorod movement occurs partly or completely at the interface between air and water, where viscous drag will be reduced. Maybe the motion is facilitated by the reduction in viscous skin friction that is anticipated to arise for nanorod movement, with nanobubbles located at the interface between water and the hydrophobic gold segment of the nanorod.^[31] In other words, a translating nanorod, partly or wholly coated in nanobubbles, may experience less hydrodynamic drag than one free of nanobubbles. Detailed studies of nanobubbles formed in the surface-catalyzed decomposition of hydrogen peroxide to water and oxygen by nanorods are underway (see below).^[32]

9. Nanomachine Dreams

In the not-too-distant future, it is possible that completely synthetic chemically propelled nanoscale motors and machines will be developed to a point of sophistication that they will impact certain areas of nanotechnology. Is this a realistic or imaginary vision?

Cells in Nature, whose nanoscale-machine operations are powered by chemical reactions, provide an existence proof that synthetic mimics are feasible in the laboratory. Recall the philosophy of Jean-Marie Lehn: “*if it exists, it can be synthesized!*” While Nature’s biomolecular machines are indeed hard to copy, recent reports of chemically powered nanomotors constructed from nanorods with energy-rich chemical cargoes provide evidence that powering nanoscale machinery through chemistry in the liquid phase is now a practical proposition.

Our latest experiments have been chemically orchestrated using surfactant additives to enable recording in real-time video of the hydrogen peroxide fueled motional dynamics of aqueous-phase nanorod nanomotors, and at the same time capturing images of the accompanying oxygen-nanobubble propulsion.^[32] In these movies (see Supporting Information), one can literally see “racing nanorods” with linear- and corkscrew-type motion, and even nanorods “orbiting” around a micrometer-size bubble, giving the impression of “egg fertilization”. Amazingly, the observed nanobubble “nanojet-stream”, emanating from one end of the nanorod, suggests a propulsion mechanism whereby the thrust on the nanorod stems from the nanobubbles themselves rather than a nanobubble-induced surface-tension gradient. One can imagine a “synthetic mimic of the proverbial nanosubmarine”: see the corkscrew motion presented in Figure 7 in the movie provided as Supporting Information.

Nanomachine enthusiasts, experimentalists, and theoreticians have been waiting a long time for such a break-

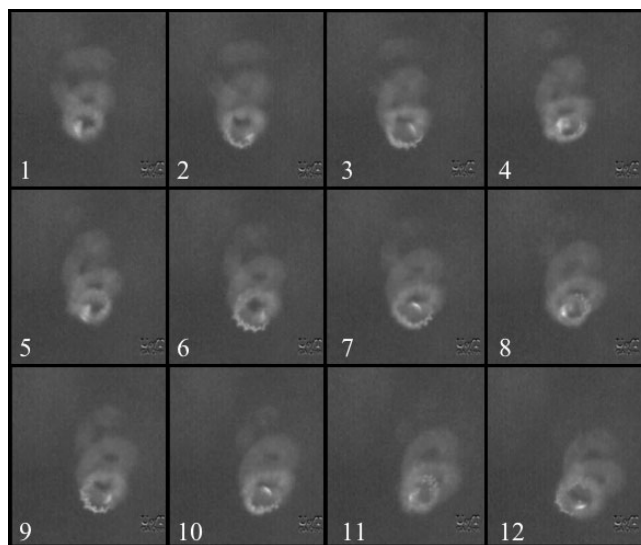


Figure 7. Sequence of time-lapse microscope images of aqueous-phase corkscrew motion of a chemically driven Ni-Au barcode nanorod nanomotor capturing both the nanorod dynamics and the nanobubble jet stream emanating from the decomposition of hydrogen peroxide at the catalytically active nickel end of the nanorod [32].

through.^[5] What is appealing about the discovery of the chemically propelled nanorod nanomotor is that it is elegant in its simplicity, powerful in its scientific ramifications, and extraordinary in that nobody thought of doing it a long time ago. The nanorod building blocks are straightforward to make, and many simple solution-phase and surface-energy-rich chemical reactions, found in basic chemistry textbooks, can be formulated to achieve nanoscale locomotion. Beyond nanorods, a diversity of other kinds of building blocks can be synthesized whose bulk and surface structure and composition, size, and shape are under strict chemical command.^[3] The simplicity of these “bottom-up” nanomotors will enable deeply analytical and synergistic experimental and theoretical investigations geared towards determining how they work and how they may be adapted to nanoscale machinery.

Perceived benefits undoubtedly will be the fundamental nanoscience accrued. As the new nanoscience becomes clear over the next few years, new nanotechnology will blossom. It could be the biomedical and pharmaceutical, analytical, and environmental sectors that will eventually benefit from nanomotors and nanomachines that perform useful tasks. Only doing the research will answer these questions and enable “*nanomachine dreams*” to become “*dream nanomachines*”!

- [1] a) R. P. Feynman, *Engineering and Science (California Institute of Technology)* **1960**, 23, 22. b) R. P. Feynman, *There's Plenty of Room at the Bottom: An Invitation to Enter a New World of Physics*. <http://www.zyvex.com/nanotech/Feynman.html> (accessed August 2005).
- [2] M. Roukes, *Phys. World* **2001**, 14(2), 25.
- [3] G. A. Ozin, A. Arsenault, *Nanochemistry: A Chemical Approach to Nanomaterials*, Royal Society of Chemistry, London **2005**.

- [4] C. Mavroidis, A. Dubey, M. L. Yarmush, *Annu. Rev. Biomed. Eng.* **2004**, *6*, 1.
- [5] G. M. Whitesides, *Sci. Am.* **2001**, *285*, 78.
- [6] R. K. Soong, D. Bachand, H. P. Neves, A. G. Olkhovets, H. G. Craighead, C. D. Montemagno, *Science* **2000**, *290*, 1555.
- [7] J. Xi, J. J. Schmidt, C. D. Montemagno, *Nat. Mater.* **2005**, *4*, 180.
- [8] S. Rozhok, C. K. F. Shen, P. L. H. Littler, Z. Fan, C. Liu, C. Mirkin, R. C. Holz, *Small* **2005**, *1*, 445.
- [9] S. Takeuchi, W. R. DiLuzio, D. B. Weibel, G. M. Whitesides, *Nano Lett.* **2005**, *5*, 1819.
- [10] W. R. DiLuzio, L. Turner, M. Mayer, P. Garstecki, D. B. Weibel, H. C. Berg, G. M. Whitesides, *Nature* **2005**, *435*, 1271.
- [11] R. F. Ismagilov, A. Schwartz, N. Bowden, G. M. Whitesides, *Angew. Chem. Int. Ed.* **2002**, *41*, 652.
- [12] Y. Gao, Y. Bando, *Nature* **2002**, *415*, 599.
- [13] A. M. Fennimore, T. D. Yuzvinsky, W.-Q. Han, M. S. Fuhrer, J. Cumings, A. Zettl, *Nature* **2003**, *424*, 408.
- [14] D. L. Fan, F. Q. Zhu, R. C. Cammarata, C. L. Chien, *Appl. Phys. Lett.* **2004**, *85*, 4175.
- [15] D. L. Fan, F. Q. Zhu, R. C. Cammarata, C. L. Chien, *Phys. Rev. Lett.* **2005**, *94*, 247 208.
- [16] B. C. Regan, S. Aloni, K. Jensen, R. O. Ritchie, A. Zettl, *Nano Lett.* **2005**, *5*, 1730.
- [17] B. C. Regan, S. Aloni, R. O. Ritchie, U. Dahmen, A. Zettl, *Nature* **2004**, *428*, 924.
- [18] Y. Cui, Q. Q. Wei, H. K. Park, C. M. Lieber, *Science* **2001**, *293*, 1289.
- [19] P. Vettiger, M. Despont, U. Drechsler, U. Durig, W. Haberle, M. I. Lutwyche, H. E. Rothuizen, R. Stutz, R. Widmer, G. K. Binnig, *IBM J. Res. Dev.* **2000**, *44*, 323.
- [20] T. J. Huang, B. Brough, C. H. Hoa, Y. Liu, A. H. Flood, P. A. Bonvallet, H.-R. Tseng, J. F. Stoddart, M. Baller, S. Magonov, *Appl. Phys. Lett.* **2004**, *85*, 5391.
- [21] H. F. Ji, Y. Feng, X. Xu, V. Purushotham, T. Thundat, G. M. Brown, *Chem. Commun.* **2004**, 2532.
- [22] M. Su, V. P. Dravid, *Nano Lett.* **2005**, *5*, 2023.
- [23] S. Fournier-Bidoz, A. C. Arsenault, I. Manners, G. A. Ozin, *Chem. Commun.* **2005**, 441.
- [24] W. F. Paxton, K. C. Kistler, C. C. Olmeda, A. Sen, S. K. St. Angelo, Y. Cao, T. E. Mallouk, P. E. Lammert, V. H. Crespi, *J. Am. Chem. Soc.* **2004**, *126*, 13 424.
- [25] F. Lugli, S. Hofinger, F. Zerbetto, *J. Am. Chem. Soc.* **2005**, *127*, 8020.
- [26] T. R. Kline, W. F. Paxton, T. E. Mallouk, A. Sen, *Angew. Chem. Int. Ed.* **2005**, *44*, 744.
- [27] J. C. Catchmark, S. Subramanian, A. Sen, *Small* **2005**, *1*, 202.
- [28] J. Vicario, R. Eelkema, W. R. Browne, A. Meetsma, R. M. La Crois, B. L. Feringa, *Chem. Commun.* **2005**, 3936.
- [29] N. Mano, A. Heller, *J. Am. Chem. Soc.* **2005**, *127*, 11 574.
- [30] E. M. Purcell, *Am. J. Phys.* **1977**, *45*, 3.
- [31] A. Agrawal, J. Park, D. Y. Ryu, P. Hammond, T. R. Russell, G. H. McKinley, *Nano Lett.* **2005**, *5*, 1751.
- [32] S. Fournier-Bidoz, G. A. Ozin, unpublished.