Fuel for Thought: Chemically Powered Nanomotors Out-Swim Nature's Flagellated Bacteria

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ABSTRACT Half a century ago, Richard Feynman envisioned tiny machines able to perform chemistry by mechanical manipulation of atoms. While this vision has not yet been realized in practice, researchers have recently discovered how to use chemistry to drive tiny engines and to operate tiny machines in the liquid phase, in much the same way Nature uses biochemistry to power a myriad of biological motors and machines. Herein, we provide a brief Perspective on the rapidly growing research activity in the emerging field of chemically powered nanomotors and nanomachines, consider some of the challenges facing its continued rapid development, and imagine a future in which these tiny motors and machines can get down to doing some serious work.

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Humans have always had a fascination with the challenge of reducing the size of things that exist in the macroscopic world into miniature replicas, often being motivated by efficiency or simply the importance and satisfaction of fabricating, manipulating, or visualizing things at smaller and smaller length scales.

In 1907, Paul Wentz was thinking small when he engraved the Lord's Prayer on the head of a brass pin with a diameter of 2 mm, an early example of human ingenuity and endurance. (The pin can be viewed in the Historical Society of Pennsylvania.) In 1915, Geoffrey Lundberg further reduced the scale of the Lord's Prayer on the head of a gold pin by a factor of 3. His handiwork was displayed at the 1915 Panama-Pacific Exposition in San Francisco.

In Richard Feynman's 1959 prescient "There's Plenty of Room at the Bottom" speech, he foresaw tiny yet powerful computer systems able to manipulate and to store data, and to deliver output in a constructive format, and high-magnification microscopes able to see objects that were at the time at unimaginably small scales. He also imagined tiny machines that could manipulate atoms and perform chemistry in a predetermined way. In this vein, the skilled craftsman William McClellan rose to one of Richard Feynman's miniaturization challenges and constructed a working motor at 1/1000 the scale of its macroscopic parent, and Stanford graduate Tom Newman built a machine that could reduce the information on the page of a book by 1/25000.

The Ever Shrinking Size of Things: Tiny Motors and Machines. In this Perspective, we ask the following question: Rather than building tiny machines that can do chemistry by mechanical manipulation of atoms in the way that Feynman envisioned, why not use chemistry to drive tiny engines and operate tiny machines in the liquid phase, in much the same way that Nature has been using biochemistry to power a myriad of biological motors and machines?

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The sophistication of currently available nanomachines has been dramatically increasing over the past 5 years. Researchers have created nanoscale objects that can be induced to undergo autonomous motion in the vicinity of a chemical fuel. Understanding the origin of the motion and control of the speed and the direction of the motion of chemically powered nanomotors have been some of the key points of investigation in this field.

The development of a new class of miniaturized chemically propelled micromotors by Wang and co-workers[1] presented in this issue of *ACS Nano* has addressed many of the parameters that need to be considered in the realization of self-propelled objects,

including shape and compositional distribution of various materials within the moving structure.

Chemical Power: Where It All Began. Forty-three years after Richard Feynman's speech, the Whitesides group made the first step toward miniaturized self-propelled objects, which were able to convert chemical energy from hydrogen peroxide in their environment into dynamic, autonomous motion.[2] The centimeter-sized "floats" decorated with a Pt component on their "stern" were propelled at the air/water interface in the presence of hydrogen peroxide. The oxygen bubbles that formed as a product of the peroxide decomposition on the Pt surface pushed the floats around through a recoil mechanism. Two years later, the first reported examples of chemically powered nanoscale motors emerged from the research groups of Tom Mallouk[3] at The Pennsylvania State University and Geoffrey Ozin[4] at University of Toronto. They independently and simultaneously discovered that Pt−Au and Ni−Au bimetal nanorods, synthesized by templated sequential electrodeposition of the respective metal segments in the confines of a nanochannel membrane, showed autonomous self-propulsion in aqueous hydrogen peroxide fuel. When anchored to a substrate or free to move in solution, the nanorods displayed rotary and linear motion, respectively. Others have demonstrated nanorod motion based on external fields (*e.g.,* electrical, magnetic)[5] and often these are combined with chemical motion, but autonomous movement represented a great step forward for these devices.

These and subsequent studies, with the continued use of aqueous hydrogen peroxide as a propellant, established that the rotation and translation speed of the bimetal nanorods depended upon a number of factors including the overall dimension of the nanorods, size of the metal segments, choice of metals, concentration of fuel, viscosity

of the solvent, surfactant additives, and pH and ionic strength. From the results of these investigations an understanding of the basic science of chemically powered nanoscale locomotion emerged.

Fortunately, in these experiments the different reflectivity of the segments of the bimetal nanorods enables the nanorod motion to be tracked in two-dimensional (2D) space and time using an inverted optical microscope coupled to a video camera. This setup enables real-time observation of the motional dynamics and determination of the velocities and diffusion constants for a statistically meaningful sample of nanorods.

The motion of the nanorods stems from their anisotropic shape and chemically generated thrust, which overcomes the opposing hydrodynamic forces of frictional drag and Brownian motion. The nanoparticles effectively diffuse through a 2D fluid at the substrate−solution interface, where hydrodynamic coupling of the particle to the surface of the substrate occurs, resulting in mobility retardation due to frictional surface interactions, which might dominate the diffusional behavior of these nanorods. Related studies on swimming microorganisms in the vicinity of surfaces have indicated that the balance between the flow induced from force dipole and any image flow fields has a direct effect on the orientation of the microswimmer with respect to the substrate.[6] Parallel orientation results in propulsion, whereas reorientation in the perpendicular direction with respect to the substrate causes rotational motion.[6] An insightful study explored how viscous drag in the proximity of the solution−substrate interface impacts the movement of hydrogen-peroxide-powered nanorods. The strategy employed was to investigate how chemical functionalization of the substrate using self-assembled monolayers (SAMs) with varying terminal groups would influence nanorod motion, confirm-

ing the presence of a dominating particle−substrate interaction that led to lower than expected diffusion coefficients.[7]

Origin of Motion. Attempts to understand the mechanism responsible for the motion of the nanorods have not been without controversy; however, the general consensus is that movement is induced by the catalytic conversion of hydrogen peroxide in aqueous solution into water and oxygen gas. While $2H_2O_2 \rightarrow 2H_2O + O_2$ looks like a superficially simple reaction, the mechanistic details of how it works at the solution−Pt interface is not well understood. Unravelling the relationship between the stored chemical potential and the velocity of the nanorod has presented a formidable challenge for experiment and theory alike.

One can imagine a number of mechanisms to explain the chemically powered motion of the nanorod, including bubble recoil, bubble implosion, Brownian ratchet, thermal gradient, interfacial tension, and bipolar electrophoresis (electrokinetic motion). It is likely that all of these mechanisms contribute to different extents to the observed motion, and there continues to be scholarly debate in the literature as to which mechanisms dominate. To establish which of these mechanisms operates, at least two main criteria must be satisfied. First, the magnitude of the generated thrust must be sufficient to overcome viscous drag and thereby create motion. Second, the observed direction of the motion must be consistent with the model for generating thrust.

The most intuitive model to account for nanorod motion is the bubble recoil mechanism, where bubbles of oxygen generated from hydrogen peroxide oxidation at the Pt end undergo expansion during evolution and provide thrust to the nanorod, causing it to move in the opposite direction with the Au end leading (Figure 1). The bipolar electrophoresis or electrokinetic model
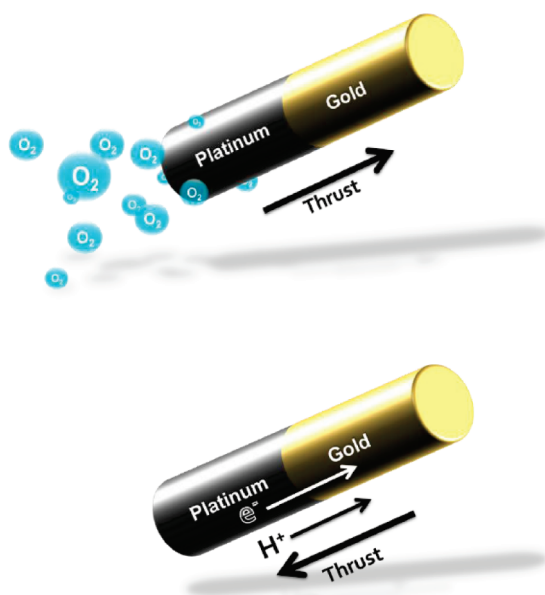
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Figure 1. (Top) Bubble propulsion mechanism and **(bottom)** bipolar electrophoresis (electrokinetic) mechanisms considered responsible for hydrogen peroxide driven motion of bimetal nanorods in water. The illustration is courtesy of Chris Wilmer.

for motion invokes the operation of a short-circuited electrochemical cell where anodic oxidation and cathodic reduction of hydrogen peroxide occurring at the Pt and Au ends, respectively, causes electronic charge to move from anode to cathode within the nanorod. This is synchronous with the migration of charge-balancing protons and water of hydration at the nanorod−solution interface, causing the nanorod to move in the other direction (Figure 1).[8]

It is interesting to note that two recent nanorotor systems favor the bubble propulsion mechanism based upon the observed direction of rotation of an asymmetric Pt−Au nanorod[9] and a bent Pt−Si nanorod,[10] neither of which needs to invoke the bipolar electrophoresis mechanism as a significant contributor to the motion. Similarly, the mobility of single-component Pt nanorods observed by Kovtyukhova suggests that built-in bimetallic asymmetry is unlikely a necessity for self-propulsion at the nanoscale.[11] As for most micrometer- and centimeter-scale propelled objects, the oxygen-bubble propulsion mechanism has been used to describe the motion of bimetallic coni-

cal microtubes fabricated by Wang.[1] Despite the findings that the electrokinetic mechanism and motion induced by bubble recoil appear to be the most dominant explanations for the motility of nano- and microscale objects, understanding their interconnectedness and relative magnitudes depending on the particular system will be the key to future research.

Advantages of bubble-recoil motors compared to bipolar electrophoretic ones include the lack of dependence of the motion on ionic strength and, for practical applications, also include the targeted delivery of payloads to specific locations on microfluidic chips or disease sites in the human body.

Speed. Understanding the principles behind the catalyzed locomotion at the nanoscale allows further insight into regulating nanoscale object speeds, which ultimately can affect performance attributes of nanomotors such as acceleration and maximum load. High power output nanomotors would have the ability to carry heavier cargo for longer distances, whereas higher speeds would facilitate transport at the nanoscale. In the current literature, material composition and ar-

chitectural design were considered in the realization of nanomotors that have displayed enhanced speeds compared to the original self-propelled bimetal nanorods.

By templating different degrees of porosity into the Pt segment of a Pt−Au nanorod, a correlation was found between the surface area and surface roughness of the Pt and the velocity of the nanorod, enabling the earlier speed record to be broken.[12] A further significant enhancement in the velocity of nanorod motion was discovered by incorporating carbon nanotubes (CNTs) into the Pt segment of a Pt−Au nanorod.[13] By this means, the aqueous hydrogen peroxide powered nanomotor speed record was elevated from ∼20 to 50 μm/s, and the addition of hydrazine raised the bar to an impressive 200 μm/s, leaving all other nanorod motors behind in the dust and challenging some of the fastest flagellated microbial swimming machines!

In a continuing quest to enhance the efficiency of transduction of chemical energy to translational kinetic energy in catalytic nanorod motors, it was discovered that replacing the pure Au segment in a bimetal Pt−Au nanorod with an alloy of Ag and Au (*e.g.,* Pt−Ag_xAu_{1-x}) enabled another leap in nanorod speed, from ∼20 μm/s to over 150 μm/s.[14] A significant result was the linear increase of the speed of the alloy nanomotors with the atomic fraction of Ag, by using alloy segments that ranged in Ag composition from $Ag_{25}Au_{75}$, $Ag_{50}Au_{50}$, and $Ag_{75}Au_{25}$ to pure Ag. This phenomenon was rationalized in terms of the improved catalytic activity of Ag_xAu_{1-x} alloy electrodes and superior electron transfer and decomposition rates to hydrogen peroxide compared to Ag and Au alone. A correlation between the potential differences of Pt and Ag_xAu_{1-x} and the speed-composition of the alloy nanorods provides insight into the origin of motion (Figure 2). It is anticipated that further improvements in the speed of the nanomotors

could be achieved by using mixed hydrogen peroxide–hydrazine fuels, incorporating CNTs in the Pt segment, and tailoring the spatial distribution of Ag and Au in the alloy segment.

Fuel. While the obsession with hydrogen peroxide as fuel continues to dominate the emerging nanomotor field, there have been a few reports that hydrazine can also function as the energy-rich propellant, and it is expected that other fuels, such as methanol, formic acid, diazomethane, azides, hydrides, and organic peroxides, will be explored in the not too distant future. In the search for biologically friendly fuels, initial steps have been taken recently where carbon fibers decorated with glucose oxides and bilirubin oxidase enzymes were propelled in the presence of a glucose solution.[15]

Shape. Optimization of the motor geometry, including variations in shapes and dimensions, is an absolute necessity for the design of nanomachines where the maximization of inertial propulsion and minimization of viscous drag is to be realized.

There are some examples that examine the effect of shape on the motion of nanoscale motors or swimmers. In an attempt to learn from natural systems such as bacteria flagella, artificial chiral structures that are capable of helical motion have been reported in the literature.[16,17] One group has reported on magnetic particles of different sizes and shapes including bars, rods, and boomerangs.[18] Another serendipitous discovery involved the hydrogen peroxide powered motion of bent Ni–Au nanorods, which displayed an amazing bubble-recoil driven spiral trajectory in the presence of surfactant additive.[19] Further shape studies involved a nanosphere heterodimer comprising a noncatalytic silica nanosphere joined to a catalytic Pt nanosphere with motion fueled by hydrogen peroxide (Figure 3).[20] This study quantitatively
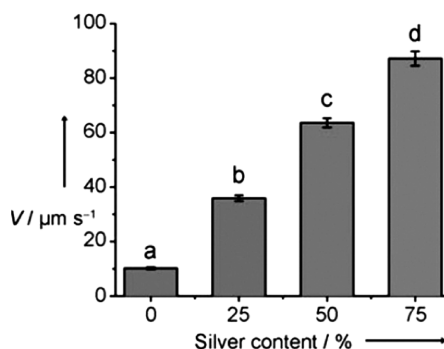

Figure 2. Dependence of the speed of hydrogen peroxide powered Pt–Ag$_x$Au$_{1-x}$ alloy nanomotors with silver content of the alloy segment. Reprinted with permission from ref 14. Copyright 2008 Wiley Science.

defined the dependence of the dynamics of the nanosphere dimer upon the relative sizes of its catalytic and noncatalytic nanosphere components. Using large-scale molecular dynamics and mesoscopic multiparticle collision dynamics incorporating hydrodynamic interactions, it was possible to simulate the rotational and translational dynamics of the catalytic nanosphere heterodimer in the solution phase and at the interface between the solution and substrate.

A related but distinct shape study has been reported for the hydrogen peroxide powered motion of Janus microspheres composed of Pt-SiO$_2$ halves.[21] On the basis of a detailed study of the effect of concentration of the fuel and surface tension on the speed of the microsphere motor, the researchers concluded that the bubble recoil mechanism also dominates in this system.[21]

At a larger scale, there have been two recent reports of hydrogen peroxide fueled, micrometer-scale, funnel-shaped, Pt-lined/Au-coated, tubular microjet engines that exhibit exceptionally high-speed motion. This motion has been shown to originate from an oxygen bubble recoil mechanism involving the production of oxygen bubbles at the front of the funnel and expulsion from the rear.[22] The first of these microjet engines to be reported was prepared by a complex top-down nanofabrication procedure that required deposition of multimetallic layers onto a sacrificial photoresist with designed internal stresses, which spontaneously rolls up into a microtubular structure upon lift-off.[22]

Wang has taken the geometrical design of anisotropic nanomotors to a new level with the development of a novel template-assisted method for the fabrication of tubular microjet engines.[1] The much
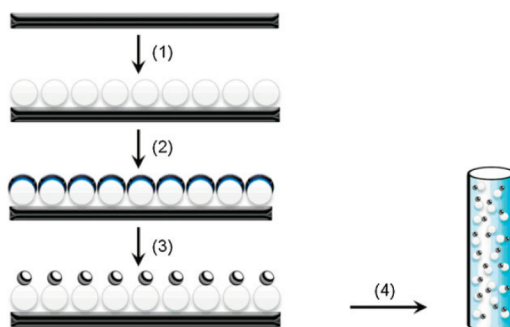

Figure 3. Bottom-up synthesis of catalytic sphere dimer nanomotors: (1) formation of silica sphere submonolayer on substrate, (2) deposition of metallic half-shell over silica spheres wherein a 5 nm Cr adhesion layer was sputter-deposited followed by a thicker Pt layer, (3) thermal annealing at 900 °C for 3 h, (4) redispersion of sphere dimers in water by sonication. Reprinted with permission from ref 20. Copyright 2010 Wiley Science.

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simpler bottom-up synthetic strategy can be employed to achieve the same goal as the complex top-down nanofabrication procedure. It involves the electrodeposition of controlled-thickness Pt and Au layers onto the surface of a sacrificial Ag wire template that had been prepatterned by nitric acid etching into conical segments.[1] By dicing the wire and etching the Ag core one can obtain Pt−Au funnels with predetermined size and shape (Figure 4), a great asset when attempt-

ing to design microfunnel parameters that optimize the performance of the bubble recoil microjet engine. The resulting jet engines were propelled forward at a speed of ~456 μm/sec (corresponding to ~3 body lengths/sec) as a result of bubbles being ejected from the larger opening of the microcone (Figure 5).

Direction. Typically, directional control of nanoscale locomotion has been achieved through the incorporation of a magnetic Ni segment, as in the initial report on Pt−Ni−Au−Ni−Au nanorods, where guided motion of a chemically powered nanomotor by an external magnetic field was first achieved.[23]

In his design of self-propelled microjets, Wang integrated a magnetic Ni layer between that of the internal catalytic Pt and external noncatalytic Au layers. This technique not only proved to direct the motion of the microjet engine with an external magnetic field, but also to coerce the engine to pick up a 100 μm diameter magnetic microsphere payload along the way.[1]

Recent efforts have also employed the use of thermal energy[24] for the control of nanoscale locomo-

tion, as well as the implementation of a fuel gradient. Bimetal nanorod motion in a gradient of fuel has been investigated, which can be considered a mimic of chemotaxis whereby bacteria have learned to survive by directing their motion toward the highest concentration of food (chemoattractive) or away from poisons (chemorepellant).[25] Experiments of this type are readily conducted in the microchannels of microfluidic chips. One can imagine bimetal nanorods racing down parallel microchannels in pursuit of a source of fuel where the nanorod design, composition and type of fuel determine the winner.

Functionality. Departure from the classic one-dimensional (1D) nanomotors comprising Au, Pt, and Ni segments has been noted as the quest for specific functionalization of swimming nano-objects continues. Other nanorod designs with unique compositional and architectural attributes are beginning to enter the nanomotor fray, exemplified by a Pt−Si nanorod powered by hydrogen peroxide that provides clues on the mechanism of the motion.[10] A nanorod made entirely of Au but with Pt deposited on one side and at one end displayed rotary motion.[9] Flexible nanorods (e.g., Pt · · · Pt and Pt · · · Pt · · · Pt) have been synthesized by sacrificial etching of the Au segments from layer-by-layer polyelectrolyte coated Pt−Au−Pt and Pt−Au−Pt−Au-Pt multisegment nanorods. These flexible nanorods displayed bending motions in aqueous hydrogen peroxide and might serve as chemically powered mimics of the bacterial flagellar motor.[26]

Ultimately, the goal is to design "intelligent" nanomotors that display completely self-dependent motility while performing useful tasks at the nanoscale. Attractive characteristics such as pick-up and drop-off of cargo as well as gathering information about the surrounding environment in the form of sensing are currently being explored. Autonomous self-navigation
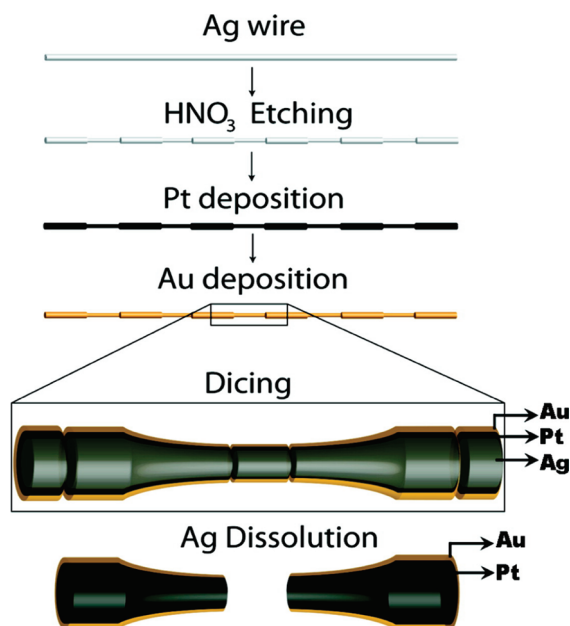

Figure 4. Bottom-up synthesis strategy for making funnel-shaped platinum−gold microjet engines. Reprinted from ref 1. Copyright 2010 American Chemical Society.

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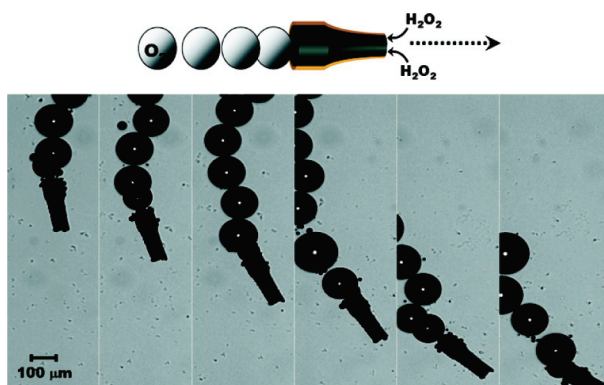

Figure 5. Oxygen bubble recoil mechanism for the propulsion of a hydrogen peroxide powered funnel-shaped microjet engine. Reprinted from ref 1. Copyright 2010 American Chemical Society.

and coherent performance of challenging duties by a collection of nanomotors can be envisioned as one of the future steps in the employment of "smart" nanomotors.

Seeing is Sensing. An intriguing selective Ag ion enhancement effect on the speed of hydrogen peroxide powered Au–Pt motors has provided a novel motion-based protocol for detecting trace Ag ions in aqueous solution with a sensitivity of about 10^{-9} M.[27] One simply uses an optical microscope to visualize the speed of the nanowire motors performing the useful task of chemical sensing. The pronounced selectivity in the acceleration of the speed for Ag ions compared to 11 other metal cations, all as aqueous nitrate salts at the same 100 μM concentration, can be easily recognized by inspection of the length of the tracks of five randomly selected nanomotors and a histogram of their speeds (Figure 6). Clearly Ag ions are special, and a number of ideas were explored in this study to define the origin of the Ag effect. The favored mechanism was related to the underpotential deposition of Ag on both Au and Pt segments of the Au–Pt nanorods, defined by energy dispersive X-ray analysis. This mechanism proposed that the deposited Ag(0) rather than Ag(I) in solution was responsible for the acceleration. As described above for Ag_xAu_{1-x}–Pt alloy nanorods,[14] the enhanced speed was found to originate in the increased electrochemi-

cal potential between the anodic and cathodic segments, and it was surmised that a similar effect was operating for Au–Pt nanorods with a coating of Ag metal. The ability to sense Ag ions in solution by visualizing the speed of a chemically powered nanorod motor can be considered an important step toward the

practical realization of nanomachines performing a task.

Swimming the Channel. Another important step toward controlled motion of chemically powered nanomotors in microfluidic channels with the ability to load, transport, and unload a cargo has recently been accomplished.[28] This impres-
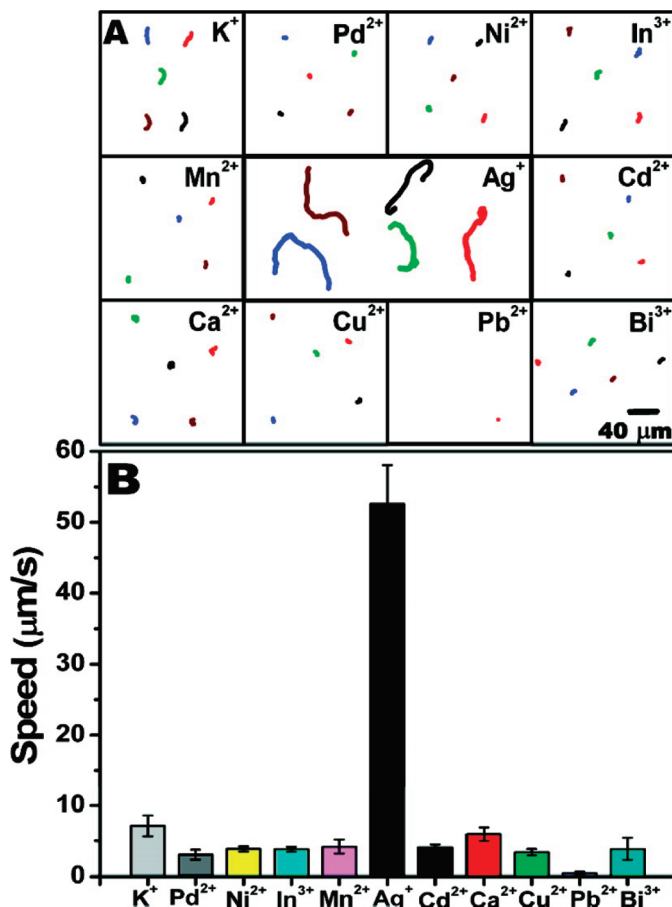

Figure 6. The effect of metal cations on the speed of 5% hydrogen peroxide powered Au–Pt nanorods. Reprinted with permission from ref 27. Copyright 2009 American Chemical Society.
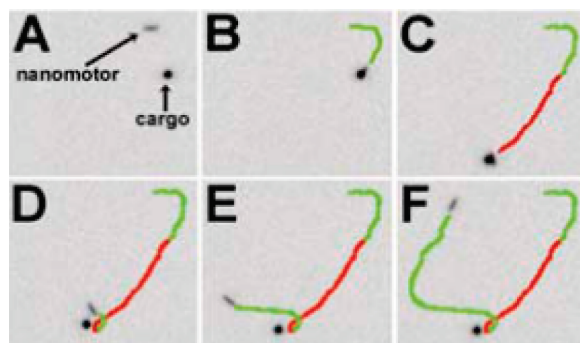
Figure 7. Series of time lapse images depicting sequential magnetically directed hydrogen peroxide powered nanomotor operations comprising (A) seek, (B) load, (C) transport, (D) rapid turn and drop off of a magnetic microsphere cargo, and (E,F) ending with the movement of the unloaded nanomotor away from the released cargo. Reprinted with permission from ref 28. Copyright 2008 American Chemical Society.

sive advance in the field of nanomotors bodes well for the intelligent design of integrated microdevices powered by chemistry rather than having to employ pressure or electricity to induce motion. In this study, to achieve high cargo-towing forces and directed motion within the microchannel, an ultrafast Au−Ni−Au-Pt/CNT nanorod was employed, where the Ni segment under magnetic field control determined the direction of movement while the CNT-Pt composite segment of the nanorod provided the accelerated speed. Furthermore, the magnetic segment enabled the nanorod to pick up a magnetic microsphere cargo, deliver it to a specific location, and drop off the cargo at the location by means of a rapid change in direction (Figure 7). Provided the viscous fluid drag on the microsphere was greater than the magnetic force between the nanorod and the microparticle, the cargo was released on demand.[28]

Wang and co-workers have also illustrated these capabilities of magnetically controlled motion and cargo transport along predetermined paths in connection with tubular microengines.[1] As the propelled microtube picked up and transported a large magnetic-sphere cargo (75 μm in diameter), the speed of the microengine was not compromised, reflecting the impressive propulsion power. This is the second example of cargo transport in the nanomotor literature. Sen and co-workers demonstrated transport of polystyrene microspheres attached by electrostatic interactions or by biotin-streptavidin binding.[29]

What Is Next? Five years after the discovery of the first examples of chemically powered nanomotors it is instructive to examine the challenges that face the continued development of the field and how can we get these tiny nanomotors to do useful work. One challenge facing the field is reproducible methods to synthesize catalytic nanomotors with a desired size and perfect shape so that these parameters can be assessed with regard to their effects on motion. Another challenge involves understanding the factors that control long-term chemical stability of nanomotors in the liquid phase in that, as with their macroscopic analogues, surface corrosion and contamination deleteriously affect motion. Further, discovery of fuels beyond hydrogen peroxide and hydrazine will be necessary, especially those that can be used in chemically or biochemically sensitive environments and do not interfere with the collection and delivery of different kinds of payloads. Besides expanding the portfolio of energy-rich fuels, it will be important to examine other ways of powering nanomotors based on photocatalytic oxidation, like photoisomerization, plasmonic photothermalization, galvanic displacement, and living polymerization, to name but a few. And finally and perhaps most importantly it will be necessary to coerce these tiny engines to perform practical tasks in the maze of channels and cavities found on microfluidic chips or within the intravascular or cellular spaces found in the human body. More strategies to pick up, to transport, and to release cargo on demand are needed, as current methods rely on specialized interactions between the cargo and the nanomotor.

Perhaps one of the most useful forms of employment one will find for these nanomotors will be as analytical nanomachines where they report directly on the activity of a chemical or catalytic solution phase reaction simply by visualization of their speed. One can imagine a combinatorial mode using a library of chemically powered nanomotors such as bimetal nanorods, each with a different catalytic segment, each adapted to provide direct information on the kinetics of a catalytic polymerization or methanol oxidation or azide decomposition. The movement of chemically powered nanomotors in confined spaces and at solid−liquid interfaces found within those spaces will need to be carefully assessed; otherwise, these motors will certainly stray off their desired paths or get stuck before they find their designated targets.

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