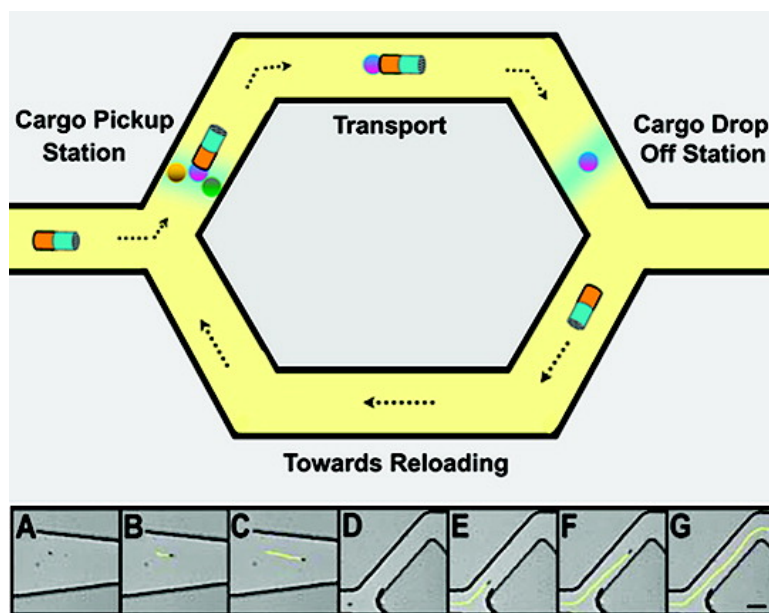


## Can Man-Made Nanomachines Compete with Nature Biomotors?

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# Can Man-Made Nanomachines Compete with Nature Biomotors?

Joseph Wang\*

Department of Nanoengineering, University of California, San Diego, La Jolla, California 92093

**ABSTRACT** Biological nanomotors have evolved over million years to perform specific tasks with high efficiency. The remarkable performance of biomotors is inspiring scientists to create synthetic nanomachines that mimic the function of these amazing natural systems. This review discusses the challenges and opportunities facing artificial nanomotors and summarizes recent progress toward the development of such man-made nanomachines. Particular attention is given to catalytic nanowire motors propelled by the electrocatalytic decomposition of a chemical fuel. While artificial nanomotors pale compared to nature biomotors, recent advances indicate their great potential to perform diverse applications and demanding tasks. Such advances include significant improvements in the velocity, motion control, cargo-towing force, and lifetime of such catalytic nanomotors. As a result, artificial nanomotors can have velocities as large as 100 body lengths per second and relatively high powers to transport a “heavy” cargo within complex microchannel networks. Despite this impressive progress, man-made nanomachines still lack the efficiency, functionality, and force of their biological counterparts and are limited to a very narrow range of environments and fuels. Improved understanding of the behavior of catalytic nanomotors will facilitate the design of highly efficient and powerful artificial nanomachines for complex operations in diverse realistic environments, leading to practical nanoscale applications in the not-so-distant future.

**KEYWORDS:** nanomachines · nanomotors · nanowires · motion · biomotors · nanoscale transport · propulsion · microsystems

The use of nanomotors to power nanomachines and nanofactories is one of the most exciting challenges facing nanotechnology. Nanomotors are nanoscale devices capable of converting energy into movement and forces. Nature has created efficient biomotors through millions of years of evolution and uses them in numerous biological processes and cellular activities. Such biomolecular motors have been the subject of several excellent review articles.<sup>1–3</sup> Nanoscale biomotors rely on spontaneous reactions of energy-rich biomolecules, such as hydrolysis of the biological fuel adenosine triphosphate (ATP). The energy released from the ATP hydrolysis results in linear or rotational movement induced by small conformational changes. Such efficient conversion of chemical energy into mechanical work makes biological nanomachines the active

workhorses in cells and enables numerous functions, ranging from intracellular transport of organelles and vesicles to large-scale muscle contractions. Due to the remarkable performance of biological motors, extensive research efforts are currently being devoted toward utilizing them in artificial microscale systems.<sup>3</sup> Most of the research in this area has focused on using the linear motor kinesin as a “molecular shuttle” in microfluidic devices.

Protein biomotors can be produced at extremely low cost and modified using modern biotechnological tools. A major drawback of biomolecular motors is their limited lifetime *in vitro* and the narrow range of environmental conditions that they are able to tolerate. Such limitations reflect the rapid protein degradation outside biological environments.

The remarkable performance of biomotors (along with their *in vitro* limitations) has provided an inspiration for the development of man-made nanomachines, operating on locally supplied fuels and performing various tasks.<sup>4–8</sup> Such artificial nanomachines are currently the subject of intense interest due to their potential applications in nanomachinery, nanomedicine, nanoscale transport and assembly, nanorobotics, fluidic systems, and chemical sensing. Some of these potential activities (*e.g.*, transport and assembly) are not very different from the cellular activities of biomotors. Transforming the concept of biological motors into engineered man-made nanomachines would require detailed understanding of the basic principles of operation of biomotors.<sup>9–11</sup> This is particularly challenging since biological motors are so efficient, small, and complex that they are currently beyond achievable by synthetic means.

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\*Address correspondence to [josephwang@ucsd.edu](mailto:josephwang@ucsd.edu).

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This review article summarizes recent progress toward the development of artificial nanomotors based on chemically powered catalytic nanowires, describes the vision of applying them for demanding activities, and discusses the challenges facing the realization of such operations. Other artificial nanotube-based rotary nanomotors<sup>12</sup> or mass conveyors<sup>13</sup> or synthetic molecular-level machines<sup>14</sup> or rotors,<sup>15</sup> performing various tasks *via* mechanical motion, fall outside the scope of this review. The goal is to encourage more researchers to tackle the challenges and share the excitement of nanomotor development and to use nature as a guide for designing future man-made nanomachines with greater sophistication.

Accordingly, in the following sections, we will address several key questions related to the development of synthetic nanomotors:

- Can we transform the basic principles of biomotors for designing powerful man-made nanomachines?
- Can artificial nanomotors compete with biological motors?
- In what environments can they function? What fuels can they use?
- Can synthetic nanomotors be powerful, versatile, and “smart” enough to perform demanding tasks and complex self-regulating operations?
- Can we integrate our nanoengines with more complex architectures, performing multiple functions?

### CATALYTIC NANOWIRE MOTORS

One promising route for creating synthetic nanomachines involves fuel-driven bimetal (*e.g.*, Au/Pt) catalytic nanowire motors.<sup>4–8,16,17</sup> Such bi-segment nanowires are prepared by template-directed electrodeposition within the cylindrical nanopores of a porous membrane followed by the template removal. This template-assisted electrochemical synthesis allows convenient preparation of multisegment nanowires of a variety of sizes or compositions. The sequential deposition of the platinum and gold segments thus leads to asymmetric nanowires with spatially defined catalytic zones. Such asymmetry is essential for generating a directional force. The resulting nanomotors are propelled by electrocatalytic decomposition of the hydrogen peroxide fuel (on both ends of the wire), with oxidation of the peroxide fuel occurring at the platinum anode and its reduction to water on the gold cathode. This leads to a random autonomous non-Brownian movement at speeds around 10–15  $\mu\text{m/s}$  toward their platinum end.<sup>6,16,17</sup>

Precise motion control of nanomotors is essential for performing various tasks and diverse applications. A directed motion has been accomplished by incorporating a ferromagnetic nickel segment and aligning the magnetized nanowires remotely using an external magnetic field.<sup>17</sup> Modulating between weak and strong magnetic fields can be used for initiating and stopping

the motion, respectively, with high spatial and temporal resolution.<sup>18</sup> Precise steering is accomplished by controlling the orientation of the magnetic field. Catalytic nanowire motors display a chemotactic behavior in the presence of a gradient of the fuel concentration, with a directed movement and increased speed toward higher peroxide concentrations.<sup>19</sup> Such behavior resembles the movement of living organisms toward a chemical attractant. Controlling and modulating the local fuel level may thus be used for guiding, initiating, or slowing the motion. Recent efforts have demonstrated the use of light<sup>20</sup> or heat<sup>21</sup> to initiate and control the motion.

Various mechanisms have been proposed for the self-propulsion of bimetallic catalytic nanomotors,<sup>5,8,22</sup> the most accepted one being an electrokinetic self-electrophoresis.<sup>22</sup> This mechanism suggests that in addition to the hydrogen peroxide reduction the cathodic reaction on the gold segment involves also the four-electron reduction of oxygen to water. These cathodic reactions, along with the oxidation of the peroxide fuel at the platinum segment, result in electron flux within the wire (toward the gold cathode) and generation of an electric field (Figure 1). These lead to electromigration of protons in the electrical double layer (surrounding the nanowire) from the platinum end to the gold end and to self-electrophoresis and propulsion of the nanomotors. Such mechanism suggests good correlation between the mixed potential difference and the speed of bimetallic nanowires. This self-electrophoresis mechanism has been reviewed re-

**VOCABULARY: NANOMACHINE** – a nanoscale device that performs a task • **NANOMOTOR** – a nanoscale device capable of converting energy into movement and forces • **BIOMOTOR** – a biological molecule capable of converting energy into motion and perform a function • **NANOWIRE** – a one-dimensional nanostructure having a lateral size constrained to tens of nanometers (or less) and an unconstrained longitudinal size • **PROPULSION** – a force causing movement • **LAB-ON-A-CHIP** – a microchip device that integrates several laboratory functions

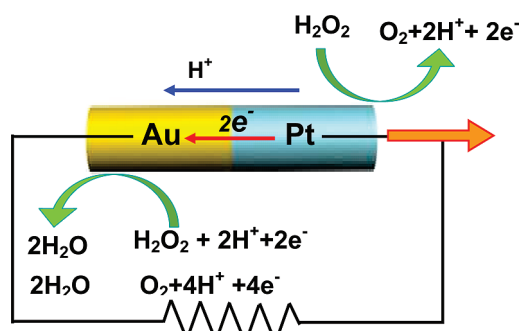
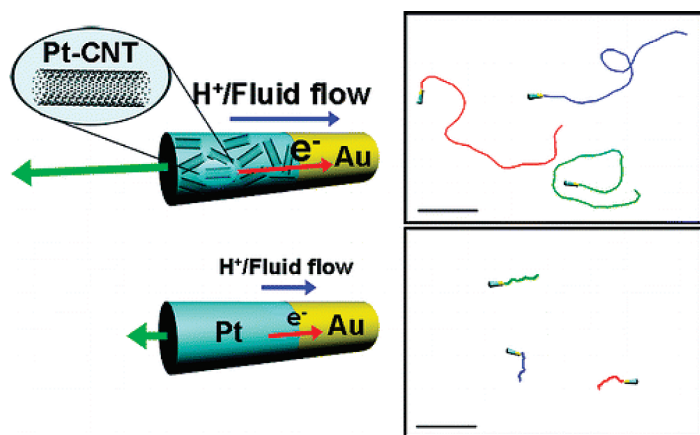


Figure 1. Self-electrophoresis (bipolar electrochemical) mechanism for the propulsion of catalytic nanowire motors in the presence of hydrogen peroxide. The mechanism involves an internal electron flow from one end to the other end of the nanowire, along with migration of protons in the double layer surrounding the wires.



**Figure 2.** CNT-induced high-speed catalytic nanomotors. (Right) Tracking lines illustrating a typical motion and moving distances of Au/Pt (bottom) and Au/Pt–CNT (top) nanomotors during a period of 4 s in the presence of 15 wt % hydrogen peroxide fuel. Scale bar = 45  $\mu\text{m}$ . (Left) Schematic representation of the self-electrophoresis mechanism of Au/Pt (bottom) and Au/Pt–CNT (top) bipolar nanomotors.<sup>18</sup>

cently.<sup>22</sup> A bubble-driven mechanism was considered by Ozin's group at Toronto that observed a rotary motion of Ni–Au nanowires with the gold end of the nanowire anchored to a substrate.<sup>16</sup> Such motion was attributed to the evolution of oxygen nanobubbles at the nickel end. The contribution of gravitational forces, associated with such bubbles' evolution, to the self-propulsion of metallic nanowires was also considered recently.<sup>23</sup> Other mechanisms proposed for the self-propulsion of catalytic nanomotors include an interfacial tension mechanism<sup>6</sup> and a Brownian ratchet mechanism in which the oxygen evolved on one segment decreases the local viscosity.<sup>24</sup>

### TOWARD HIGHLY EFFICIENT AND POWERFUL SYNTHETIC NANOMOTORS

Efficient energy conversion is crucial for extending the scope of catalytic nanomotors to diverse operations and realistic conditions. Recent efforts have illustrated the ability to increase the velocity, force, lifetime, and versatility of synthetic nanomotors by exploring new motor and fuel compositions.<sup>18,25</sup>

For example, we demonstrated that the incorporation of carbon nanotubes (CNT) into the platinum segment of catalytic nanowire motors leads to a dramatically enhanced speed and power (Figure 2).<sup>18</sup> The resulting nanomotors are capable of moving autonomously at speeds approaching 100 body lengths per second, representing the world's fastest synthetic nanomotors.<sup>26</sup> Such improvement reflects the increased electrochemical reactivity of the CNT component toward the hydrogen peroxide fuel.

We also illustrated a dramatic increase of the speed of fuel-driven nanowire motors to over 100  $\mu\text{m/s}$  using a cathodic Ag–Au alloy segment (instead of a pure gold one).<sup>25</sup> The speed of these al-

loy nanowire motors is strongly affected by the composition of the Ag–Au segment, with a nearly linear dependence upon changing the silver level in the growth mixture solution from 0 to 75% (v/v). Such behavior is attributed to the marked increase in the fuel decomposition rate associated with the enhanced electrochemical reactivity of Ag–Au alloys (compared to silver or gold alone).

Tailoring the fuel composition has also facilitated a dramatic speed enhancement. For example, adding a second component (hydrazine) to the peroxide fuel solution greatly increases the average speed of the Au/Pt–CNT nanowires to over 94  $\mu\text{m/s}$ .<sup>18</sup> Other hydrazine-derived fuels indicate great promise to power nanomotors.<sup>27</sup>

While magnetized nanowires have been used earlier for a precise motion control,<sup>17,18</sup> more complex movement patterns (mimicking those of biomotors) are essential for a variety of demanding nanoscale applications. Recent studies by Mirkin<sup>28</sup> and Zhao<sup>29</sup> demonstrated the ability to control the asymmetric forces involved in fuel-driven catalytic nanomotors by exposing only one side of the catalytic metal segment or coating one face of Si nanowires with the catalytic material, respectively. Such asymmetric character of the resulting nanowires leads to rotation in the peroxide fuel bath.

### TOWARD AUTONOMOUS MICROSYSTEMS: DIRECTED TRANSPORT AND CARGO MANIPULATIONS WITHIN MICROCHANNEL NETWORKS

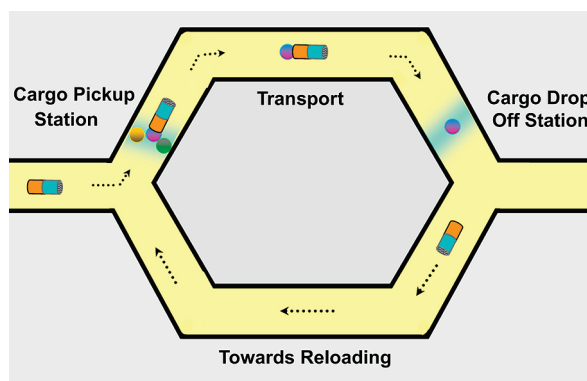
The greatly improved velocity, motion control, cargo-towing force, and lifetime of modern catalytic nanomotors offer great promise for creating powerful on-chip microsystems powered by autonomous transport. By transporting analytes or cargo without bulk fluid flow, such nanomotors may eliminate the need for external pump or power common to pressure-driven or electrokinetic flow-based microfluidic devices and may address the challenge of fluid transport in nanofluidic systems. Biological motors, such as kinesin-powered biomolecular shuttles, have shown considerable promise for enhancing the functionality of laboratory-on-a-chip devices.<sup>30,31</sup> Increasing efforts are currently being devoted for designing nanoscale transport (shuttle) systems driven by motor proteins.<sup>9,30</sup> These biomotors exert forces in the range of 1 to 10 pN, sufficient to move large objects. Directional microchip transport of microtubules<sup>30</sup> or quantum dot nanocrystals<sup>32</sup> throughout microfabricated channels coated with kinesin has thus been demonstrated. Yet, biomotor-based microchip operations suffer from a low speed transport and a limited lifetime and require biomolecular patterning to guide the motion.

We are currently designing similar chip-based nanoscale transport and distribution systems that are

driven by nonbiological nanomotors (Figure 3). Such engineered transport highways will rely on directed motion of nanowire motors and cargo manipulations (e.g., precise loading and release) along predetermined traffic tracks. The improved power and speed of our catalytic nanomotors have enabled demanding microchip applications.<sup>33</sup> For example, in an initial proof of concept, we demonstrated the magnetically guided nanomotor motion within microchannel networks, its selective sorting in microchip intersections, and the pickup and transport and release of “heavy” cargo along predetermined paths (Figure 4, video 1). The latter relied on the incorporation of magnetic segments to enable dynamic loading and transport of magnetic-sphere cargo.

Sen's group also reported recently on the movement of sphere-loaded functionalized Pt–Au–Ni–polymer nanowires in free hydrogen peroxide solutions.<sup>34</sup> Coupling of the cargo spheres onto the nanomotors was accomplished through an electrostatic force between a negatively charged polypyrrole segment and a positively charged polystyrene sphere, or *via* a more selective linkage of a streptavidin-coated microsphere to nanowire functionalized with biotin-terminated disulfide (Figure 5). Other common biomolecular interactions, such as DNA hybridization, aptamer or antibody protein binding, or a nickel-histidine linking, could be employed for on-demand pickup and release of selected functional cargo. By exploiting differences in the binding strengths, such schemes should facilitate the autonomous loading/unloading of cargo without external stimuli. For example, aptamer-functionalized nanomotors could be used for selective loading of protein cargo along with the use of nucleic acid hybridization for controlled release (Figure 6). Such attachment and release mechanisms may require overcoming the high salt limitation of catalytic nanomotors. Photosensitive linkers could also be used for a light-induced cargo release. Different surface chemistries could be used for functionalizing the nanomotor and facilitating the fixation of nano/microscale cargo. The template synthesis of nanowire motors allows selective functionalization of the gold end (e.g., Figure 6), as desired for carrying cargo with minimal drag force (while the nanomotor moves in the direction of the platinum end). Such functionalization could also facilitate an on-demand capture and release of a fuel-consuming enzyme (e.g., peroxidase) and hence a reversible stop-and-go operation.

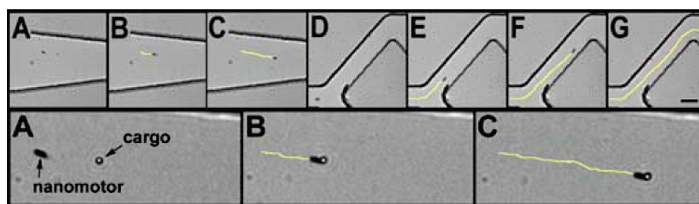
Microchip based on artificial nanomotors and active transport offers considerable promise for enhancing the analytical capability of laboratory-on-a-chip devices. Controlled manipulations of cargo within microchannel networks (with high temporal and spatial precision) hold considerable promise for a wide range of microchip applications, including separation and enrichment of different materials. Indeed, active



**Figure 3.** Nanoscale transport highway based on directed motion of artificial catalytic nanomotors and cargo manipulation (loading, transport, and delivery) along predetermined microfabricated tracks.

transport (analogous to the one occurring in cells) represents a potentially powerful separation mechanism. Such analyte binding and manipulation capabilities should lead to enhanced microchip detection efficiency. The higher speed of our new catalytic nanowires ( $\sim 50\text{--}100$  vs  $1\ \mu\text{m/s}$  of the kinesin nanomotor) indicates promise for short analysis times. Future nanomotor-based analytical microsystems could benefit also from the use of motion as a new readout (transduction) mechanism. Here, the recognition of the target analyte will trigger the release and movement of an anchored nanomotor through a displacement reaction. This should lead to remarkable sensitivity, reflecting the ability to detect single-binding events. Proper attention to the high ionic strength limitation of catalytic nanomotors is crucial for realizing such exciting bioanalytical opportunities.

Synthetic nanomachines pave the way to integrated functional microdevices powered by autonomous transport and perform a series of tasks. Yet, the very few microchip demonstrations of artificial nanomotors have not been integrated into useful functional devices. Such devices would require completely autonomous and intelligent nanomotors which constantly gather information about their surroundings while navigating themselves from point A to point B within complex nanochannel (“traffic lane”) networks. Current efforts in our laboratory are aimed at developing such self-controlled “smart” (environment-sensing) nanomotors based on enzyme logic-controlled motion (through



**Figure 4.** Optical microscopy images of the dynamic loading of a Au/Ni/Au/Pt–CNT nanomotor with a  $1.3\ \mu\text{m}$  diameter magnetic sphere cargo (A–C) and transport it through microfabricated (PDMS) microchannels (D–G). Scale bar in (G) =  $25\ \mu\text{m}$ . Bottom: magnified ( $\times 3.5$ ) images (A–C) of the top images (A–G).<sup>33</sup> Video 1 is available in the html version of this paper.

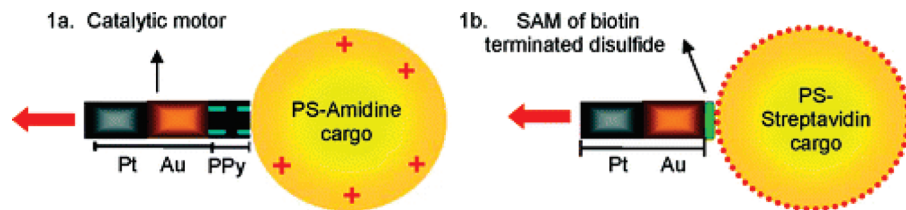


Figure 5. Cargo motor attachment by (a) electrostatic interaction between the negative polypyrrole (PPy) end of a Pt–Au–PPy motor and a positively charged polystyrene (PS) amidine microsphere; (b) biotin–streptavidin binding between the Au tips of Pt–Au rods functionalized with a biotin-terminated disulfide and streptavidin-coated cargo.<sup>34</sup>

control of the localized fuel concentration and movement toward high fuel levels). The decision to move through certain microchannels and the pass-code to enter into specific segments/channels will be controlled by multiple chemical signals (received from their surrounding environment), logically processed by the bio-computing system. In addition to self-adaptive navigation, the logic-controlled operation could be used for “deciding” which cargo to select, load, and deliver (e.g., Figure 3).

#### EXTENDED SCOPE: TOWARD NEW ENVIRONMENTS AND FUELS

Chemically powered catalytic nanomotors currently operate only within a very narrow range of environments (low ionic strength aqueous solutions) and limited fuels (hydrogen peroxide, hydrazine). This limitation currently precludes many potential applications of artificial nanomotors, particularly biomedical ones. Extending the scope of synthetic nanomotors to diverse operations and wide range of environments would require the identification of new fuel sources and further improvement in the power and efficiency. The literature on fuel cells contains energy-rich reactions and redox-

active fuels which can be tailored to achieve locomotion. Alternately, one may induce motion using biomolecules present in body fluids as potential fuel precursors. For example, the high (mM) concentration of glucose in body fluids can be coupled with glucose-oxidase-functionalized motors for biocatalytic generation of the peroxide fuel. Appropriate surface coatings may facilitate operation in media of higher ionic strength. The substantial improvement in power and efficiency of catalytic nanomotors should extend their scope to diverse and demanding operations and realistic conditions.

#### LOOKING TO THE FUTURE

The developments (described in previous sections) indicate that catalytic nanomotors offer great promise for creating self-powered practical nanomachines and provide the building blocks for realizing advanced nanoscale transport and assembly systems. Despite this impressive progress, current man-made nanomachines are still primitive compared to their biological counterparts, leaving much room for improvement. In particular, artificial nanomotors lack the sophisticated functionality of biomotors and are limited to a very narrow range of environments and fuels. Extending the scope of such motors to high ionic strength media is particularly crucial for realizing exciting biomedical opportunities. The energy-conversion efficiency of artificial nanomotors is significantly smaller (by orders of magnitude) than the energy transduction of biomotors.

In addition, synthetic nanomotors require further increase in force and versatility, along with substantial size reduction. Current efforts toward achieving such improved performance involve the exploration of novel energy-rich chemical reactions, different wire compositions, geometries, and various coatings. To extend artificial nanomachines to perform more complex tasks would require an autonomous self-adaptive operation with machines cooperating and communicating with each other and making “decisions” depending on environmental conditions. The implementation of such autonomous self-regulated nanomotors and their integration into functional microdevices

#### Loading/releasing of protein cargo linked nanomotor

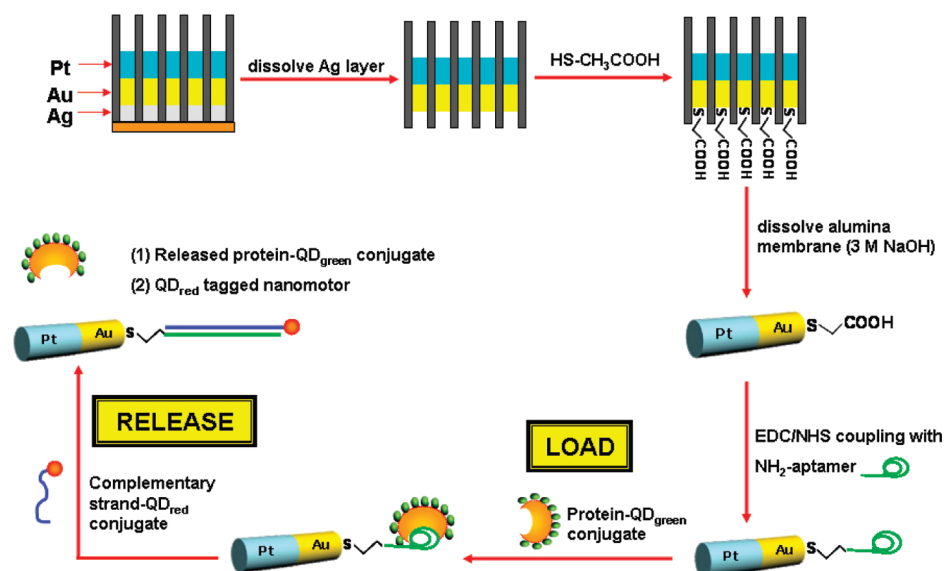


Figure 6. Use of aptamer-functionalized nanowire motors for selective binding, transport, and release of a protein cargo.

could lead to a new generation of laboratory-on-a-chip systems with unprecedented capabilities.

The improved efficiency, power, functionality, and scope of chemically powered artificial nanomotors could pave the way to exciting and important applications and to sophisticated nanoscale devices performing complex tasks. In the not-so-distant future, we expect to see self-regulated nanomachines delivering drugs or destroying toxic pollutants, motion-based ultrasensitive biosensing of disease markers or chemical agents, or nanorobots cleaning out clogged arteries. These and other exciting future applications of man-made nanomachines will be limited only by our imagination.

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