



AFRL-OSR-VA-TR-2013-0627

SELF-MOVING CATALYTIC NANOMOTORS

AYUSMAN SEN

PENNSYLVANIA STATE UNIVERSITY

12/11/2013

Final Report

DISTRIBUTION A: Distribution approved for public release.

**AIR FORCE RESEARCH LABORATORY
AF OFFICE OF SCIENTIFIC RESEARCH (AFOSR)/RSA
ARLINGTON, VIRGINIA 22203
AIR FORCE MATERIEL COMMAND**

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

| | | | | | |
|--|--------------------------|---------------------------------------|---|--|--|
| 1. REPORT DATE (DD-MM-YYYY) 05-12-2013 | | 2. REPORT TYPE Final Report | | 3. DATES COVERED (From - To) September 15, 2010 - September 14, 2011 | |
| 4. TITLE AND SUBTITLE Self-Moving Catalytic Nanomotors | | | | 5a. CONTRACT NUMBER FA9550-10-1-0509 | |
| | | | | 5b. GRANT NUMBER | |
| | | | | 5c. PROGRAM ELEMENT NUMBER | |
| 6. AUTHOR(S) Sen, Ayusman | | | | 5d. PROJECT NUMBER | |
| | | | | 5e. TASK NUMBER | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Pennsylvania State University Department of Chemistry 104 Chemistry Building University Park, PA 16802 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research, Molecular Dynamics and Theoretical Chemistry Program Manager: Dr. Michael R. Berman | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | |
| 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release. | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT Work performed during the 3-year grant period includes the following: (a) The design of an efficient, bubble-free, nanoscale motor consisting of a copper-platinum segmented rod that operates as a nanobattery in dilute aqueous bromine or iodine solutions. (b) The fabrication of motors driven by both catalytic polymerization and depolymerization reactions. The former were observed to exhibit chemotaxis when placed in a monomer gradient. Scaling down to sub-nm scale, enhanced mobility for single catalyst molecules was also observed during substrate turnover. (c) The identification of a new mechanism for producing self-generated flows. This involves auto diffusio-osmosis due to the dissolution of a wide variety of minerals. Further, the diffusio-osmotic mechanisms was employed to design proof of principle crack sensing and repair systems, as well as to drive flows in and out of dead-end channels. (d) The design of a polymeric material that is self-powered, operates as a non-mechanical fluid pump in response to molecular level inputs, and "remembers" the presence of the signal to which it was exposed, even when the signal is fleeting. | | | | | |
| 15. SUBJECT TERMS Nanotechnology, nanomotors, micropumps, self-powered, catalysis, crack detection, crack repair | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT UU | 18. NUMBER OF PAGES 11 | 19a. NAME OF RESPONSIBLE PERSON Ayusman Sen |
| a. REPORT UU | b. ABSTRACT UU | c. THIS PAGE UU | | | 19b. TELEPHONE NUMBER (include area code) (814) 863-2460 |

PI Name and Contact Information:

AYUSMAN SEN

Department of Chemistry

The Pennsylvania State University

University Park, PA 16802

Phone: (814) 863-2460; FAX: (814) 863-5319

E-mail: asen@psu.edu

During the 3-year grant period, we have made significant progress in the design of catalytic systems that couple sensing with directional motion. Below, we summarize the most important aspects of our work. The details on these and related work can be found in the referenced publications.

1. Self-electrophoretic Mobility.

We have confirmed the generality of self-electrophoresis as a mechanism for micro/nanomotor movement and the results suggest that virtually any redox reaction occurring asymmetrically on an appropriate micro/nanostructure can be employed in the design of self-powered systems.

Our original platinum/gold rods constituted a bipolar electrochemical system in which anodic and cathodic reactions are catalyzed at separate locations on a segmented nanorod (or patterned micro-gear) (Figure 1). In this case the fuel is a reducing/oxidizing agent pair which does not react in the absence of the appropriate electrocatalysts. A more efficient and bubble-free system that we discovered during the current grant period is shown in Figures 2 and 3.[1] As expected, for a given rod length, both the velocity and the current density were found to increase linearly with bromine or iodine concentration (Figure 3). In 0.5 mM Br₂ or 1.1 mM I₂, the resulting current density between the Cu and Pt electrode is around 0.01 mA/cm², which is very similar to the current density observed from the Au and Pt electrode system in 180 mM H₂O₂. Thus, the latter motor system is significantly more efficient than the previously described Au-Pt motor in H₂O₂. In the case of H₂O₂, a significant fraction of the fuel is wasted due to its rapid catalytic decomposition on the Pt-end alone.

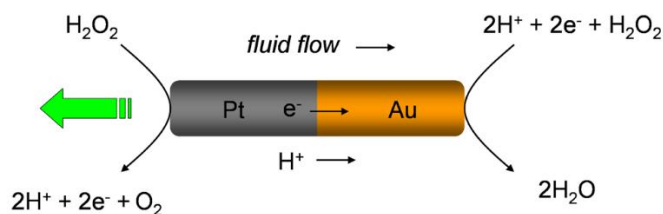


Figure 1. Schematic illustrating auto-electrophoresis. Hydrogen peroxide is oxidized to generate protons in solution and electrons in the wire on the platinum end. The protons and electrons are then consumed with the reduction of H_2O_2 on the gold end. The resulting ion flux induces an electric field and motion of the particle relative to the fluid, propelling the particle towards the platinum end with respect to the fluid.

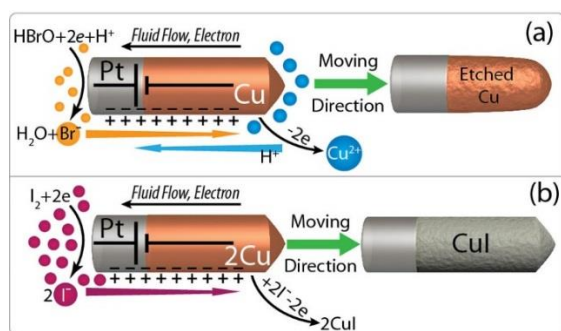


Figure 2. Mechanism of self-powered nanomotor motion in (a) aq. bromine and (b) aq. iodine.

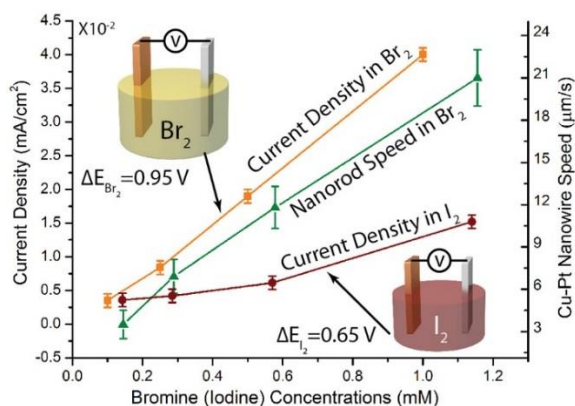


Figure 3. Steady-state short-circuited current densities for Cu and Pt electrodes in different concentrations of bromine (orange square) and iodine (brown circle) solutions, as well as the speed of Cu-Pt nanorods versus bromine concentration (green triangle). (The Cu-Pt nanorods

were synthesized by electrodepositing copper at -3 mA/cm^2 for 10 min, and then platinum at -1 mA/cm^2 for 45 min.)

2. Motility from Non-Redox Reactions.

We have also demonstrated that motion can be powered by catalysis of non-redox reactions, including both polymerization (Figure 4) [2] and depolymerization (Figure 5) [8]. As with the self-electrophoresis mechanism, the polymerization motor speed (and thus apparent diffusivity on a longer timescale) increases with increasing substrate concentration. More interestingly, the motors were observed to display the phenomenon of chemotaxis when placed in a monomer gradient; an extremely rare example outside biology.

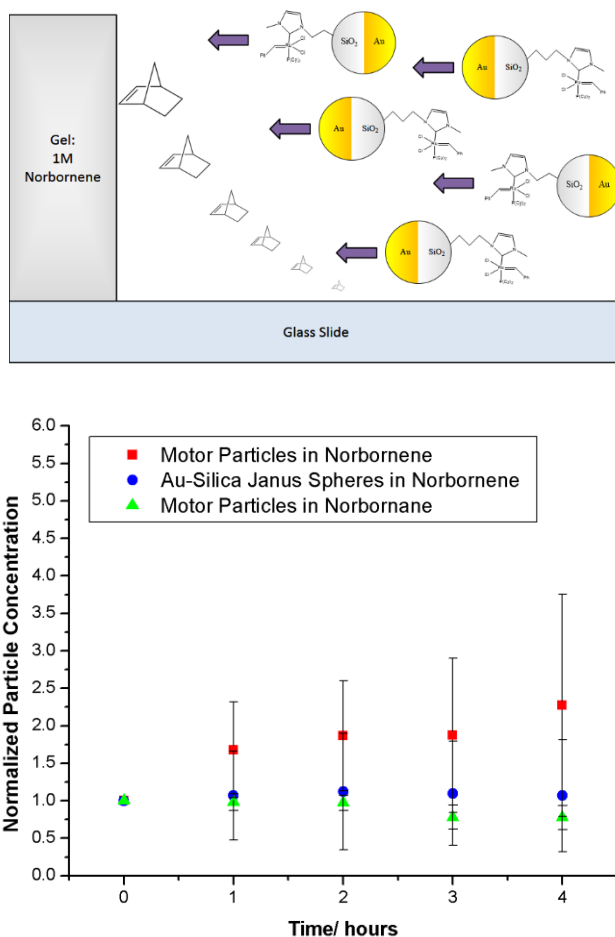


Figure 4. Catalytic motors fabricated by the attachment of Grubbs' catalyst asymmetrically to gold-silica Janus microspheres. These motors show increased diffusion when placed in solutions

of the monomer (norbornene). The motors were also observed to exhibit chemotaxis when placed in a monomer gradient. Lower plot shows normalized particle population at the gel edge as a function of time. The populations were normalized so that the initial population is taken to be 1. The motor particles in a norbornene gradient (red) exhibit a higher average agglomeration at the gel over both unfunctionalized Au-Silica Janus spheres in norbornene gradient (blue) and motor particles in a norbornane (non-monomer) gradient (green).

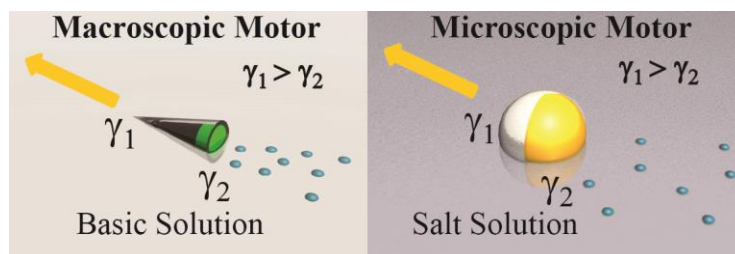


Figure 5. Schematic of motors driven by base-catalyzed depolymerization of poly(2-ethylcyanoacrylate) (PECA). The generated depolymerization products lower the local interfacial tension near one side of the motor, resulting in directed motion towards the region of higher interfacial tension. (γ_1 , γ_2 are the interfacial tension coefficients at the sides).

Scaling down to sub-nanoscale, we have observed that the diffusive movement of a molecular ruthenium-based Grubbs' catalyst increases during ring-closing metathesis as a function of the substrate concentration (Figures 6 and 7).[6] This is one of the smallest single molecule motors to exhibit catalytically-driven motion.

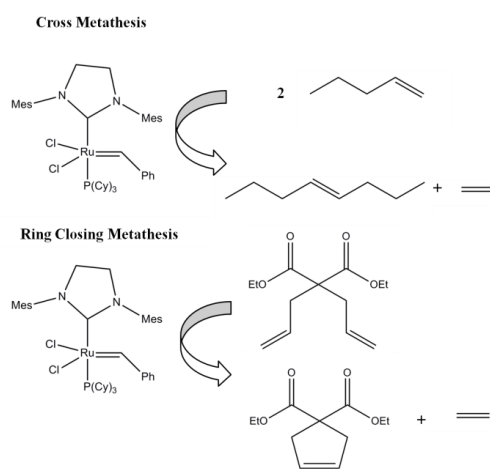


Figure 6. Structure of Grubbs' 2nd generation catalyst and reaction scheme for the cross metathesis (CM) of 1-pentene and the ring closing metathesis (RCM) of diethyl diallylmalonate (DDM).

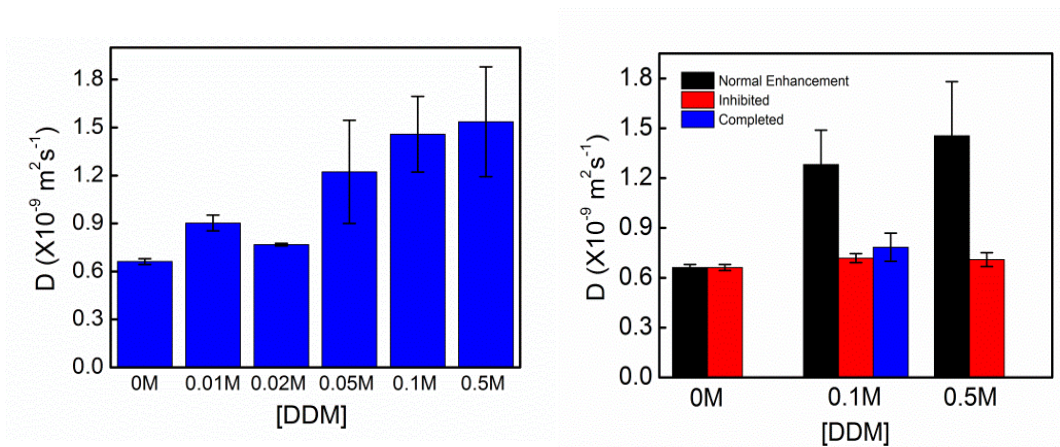


Figure 7. (Left) Diffusion coefficients of Grubbs' catalyst over a range of concentrations of diethyl diallylmalonate (DDM). The diffusion increases as the concentration is increased saturating at around 0.1 M. (Right) Diffusion coefficient of the catalyst with the addition of an inhibitor and after the reaction has reached equilibrium. The diffusion coefficient is reduced to the base value in presence of the inhibitor and when the reaction reaches equilibrium.

In addition to self-electrophoresis, the motion of particles can also be directed by an external ion gradient. We have employed this phenomenon to design a proof of principle crack sensing and repair system (see Figures 8 and 9).

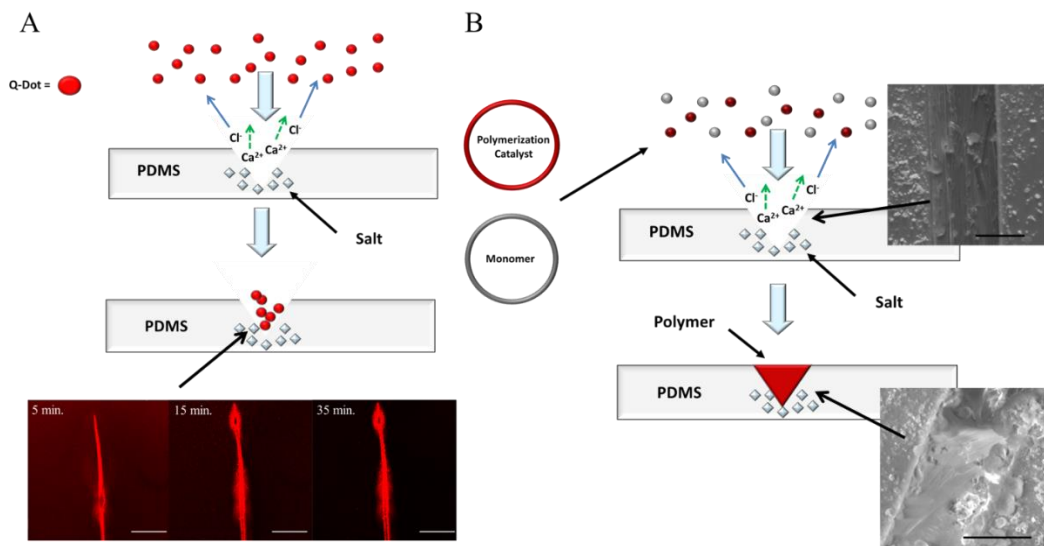


Figure 8. Diagrams of (A) crack sensing and (B) repair systems. The calcium salt (CaCl_2) is mixed into a polymer (polydimethylsiloxane, PDMS) layer and sealed with a thin layer of PDMS. The surface is cracked, exposing the calcium salt to the water causing ion leaching and formation of ion gradient. (A) The quantum dots (Q-dots) begin to aggregate at the crack (scale bar = $325\mu\text{m}$) through electrophoresis. (B) The separate emulsions containing catalyst (red) and monomer (grey) move toward the crack by electrophoresis. At the crack (scale bar = $50\mu\text{m}$) the emulsion stability is decreased due to the high ionic strength, and the emulsions begin to break apart resulting in mixing of catalyst with monomer and polymer deposition at the crack.

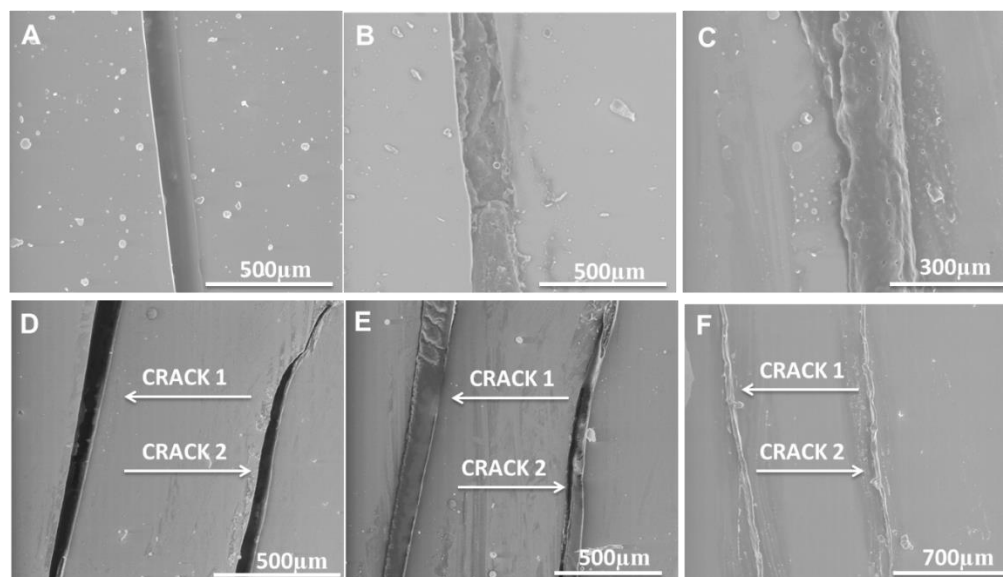


Figure 9. ESEM images of the cut showing polymer deposition. The strategy works well for both single (A-C) and multiple cracks (D-F). **A, D)** The image of cut polymer with no salt after 1 hr. exposure to emulsions. **B, C, E, F)** PDMS/CaCl₂ in inverted setup after 1 hr. exposure to emulsions.

The observation of ion gradient-driven transport has wide implications. For example, geologic formations that are disturbed by natural or artificial phenomena will often release ions into surrounding water through dissolution of their component minerals. The resulting ionic gradients can drive spontaneous diffusiophoretic movement of reservoir fluids and suspended particles, generating microflows at rock surfaces and in pores much more efficiently than pressure-driven flows. We demonstrated and study diffusiophoretic-driven microflows using a model system of calcium carbonate microparticles dissolving near a glass substrate (Figure 10), and extended the work to other common geologic minerals.[5] The flows generated by the release of ions from these materials has broad implications for natural and artificial geologic processes, even on short timescales and distances.

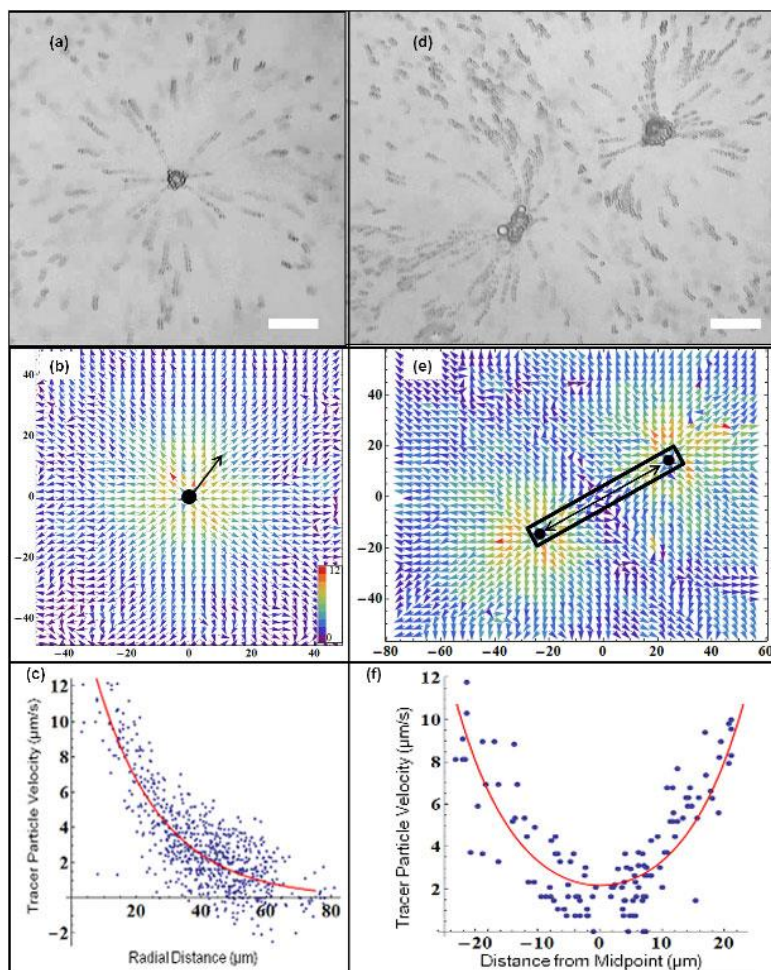


Figure 10. Microflows for one single CaCO_3 particle micropump and two interacting micropumps. These systems contained only calcium carbonate pumps and $1.4 \mu\text{m}$ sulfate-functionalized polystyrene latex tracer particles (sPSL) in DI water. **(a,d)** Time-lapse images. The videos were filmed on a bare glass substrate using an inverted microscope. Optical microscopy time-lapse images were taken at $40\times$ magnification with overlays every 0.2 s . Scale bars in these images are $10 \mu\text{m}$. In the vector field plots, axes are distance in μm . **(b, e)** Vector field. The black circles represent the location of the micropumps, and the vector arrows represent the tracer particle direction and speed in $\mu\text{m/s}$ at the substrate surface. The plots were generated by tracking the movement of 750-1000 particles over 0.3 seconds. **(c, f)** Radial speed plots. In (c), the radial speeds of all sPSL tracers sampled in (b) are plotted against the distance of those tracers from the center of the lone calcium carbonate micropump. In (f), the radial speed of tracer particles within 6 microns of the line between the two micropumps in (e) (boxed

area shown) is plotted against the distance of those tracers from the midpoint between the two pumps. In both cases, curves have been added to guide the eye.

Finally, we recently described a new type of polymeric material with an unusual combination of functional capabilities. This material responds to specific external chemical and physical signals, is self-powered, performs a macroscopic response to molecular level inputs (i.e., it operates as a non-mechanical fluid pump), and it “remembers” the presence of the signal to which it was exposed, even when the signal is fleeting (Figure 11).[7] This ability to “remember” allows the material to continue operating as a non-mechanical pump, even when the signal is no longer present. The key elements to this new type of material are (i) recognition units that are integrated into the polymers to cause the material to respond selectively to a pre-defined stimulus, and (ii) “memory” units that initiate a continuous, self-propagating reaction within the material once the recognition unit responds to the applied stimulus.

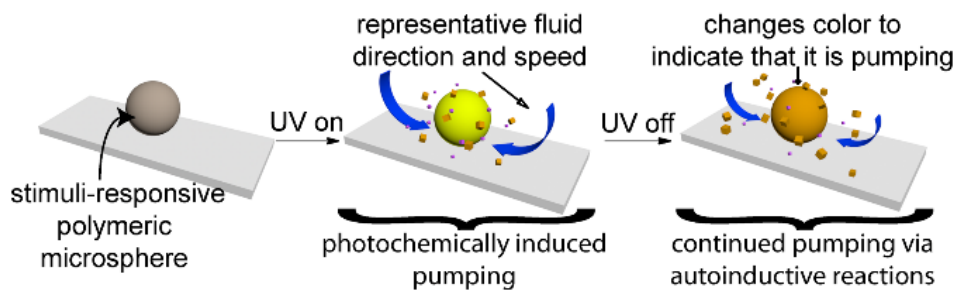


Figure 11. Schematic of a polymer microsphere pump that induces the movement of fluid that surrounds the pump in response to a specific stimulus, even after the stimulus has been removed. The blue arrows represent the direction of fluid movement, and the size of the arrows illustrate an approximation of the relative magnitude of fluid flow when the signal is present or absent.

While this work is in its early stages, the ability of a self-powered material to “remember” a specific signal to which it was exposed (and continue to perform a macroscopic function) offers a new and unusual set of capabilities to smart polymeric materials. In the present example, the polymeric material pumps the fluid surrounding the material towards the material when exposed to a specific stimulus. Macroscopic responses other than pumping also can be envisaged, including plastics that continually and actively release a specific payload once exposed to a specific, pre-defined signal.

Publications:

1. “Autonomous Nanomotor Based on Copper-Platinum Segmented Nanobattery,” Ran Liu and Ayusman Sen, *J. Am. Chem. Soc.*, **2011**, *133*, 20064.
2. “A Polymerization-Powered Motor,” Ryan A. Pavlick, Samudra Sengupta, Timothy McFadden, Hua Zhang, and Ayusman Sen, *Angew. Chem., Int. Ed.*, **2011**, *50*, 9374.
3. “Scalable Manufacturing of Plasmonic Nanodisk Dimers and Cusp Nanostructures Using Salting-out Quenching Method and Colloidal Lithography,” Bala K. Juluri, Neetu Chaturvedi, Qingzhen Hao, Mengqian Lu, Darrell Velegol, Lasse Jensen, and Tony Jun Huang, *ACS Nano*, **2011**, *5*, 5838
4. “Controlled Synthesis of Heterogeneous Metal-Titania Nanostructures and Their Applications,” Ran Liu and Ayusman Sen, *J. Am. Chem. Soc.*, **2012**, *134*, 17505.
5. “Self-Generated Diffusioosmotic Flows from Calcium Carbonate Micropumps, ” Joseph J. McDermott, Abhishek Kar, Majd Daher, Steve Klara, Gary Wang, Ayusman Sen, and Darrell Velegol, *Langmuir*, **2012**, *28*, 15491.
6. “A Catalytically-Driven Organometallic Molecular Motor,”
Ryan A. Pavlick, Krishna K. Dey, Andrew Sirjoosingh, Alan Benesi, and Ayusman Sen, *Nanoscale*, **2013**, *5*, 1301.
7. “A Self-Powered Polymeric Material that Responds Autonomously and Continuously to Fleeting Stimuli,” Matthew S. Baker, Vinita Yadav, Ayusman Sen, and Scott T. Phillips, *Angew. Chem., Int. Ed.*, **2013**, *52*, 10295.
8. “Depolymerization-Powered Autonomous Motors Using Biocompatible Fuel,” Hua Zhang, Wentao Duan, Lei Liu, and Ayusman Sen, *J. Am. Chem. Soc.*, **2013**, *135*, 15734.

9. “Enhanced Electrophoretic Motion Using Supercapacitor-Based Energy Storage System,”
Ran Liu, Flory Wong, Wentao Duan and Ayusman Sen, *Adv. Mater.*, **2013**, 25, in press.