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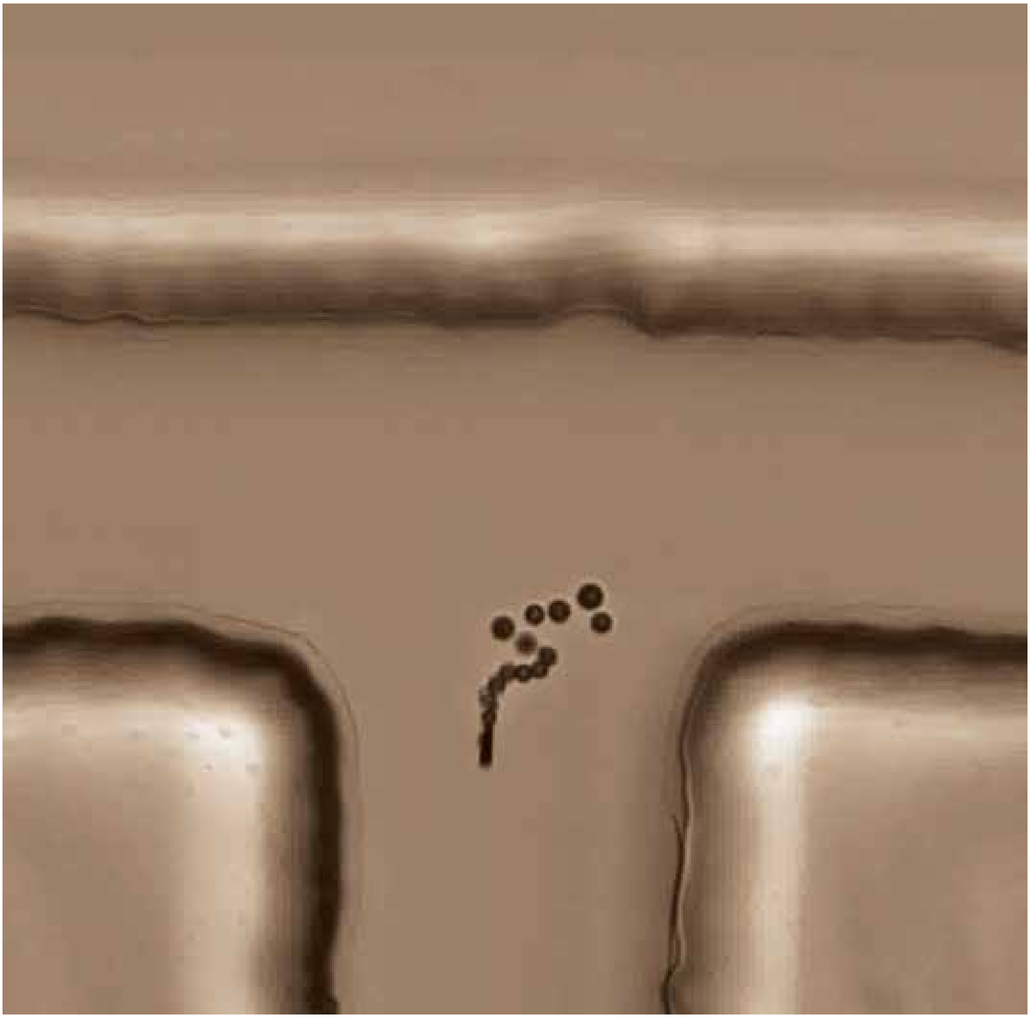
Electroanalysis at the Nanoscale



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PAPER

Template electrodeposition of catalytic nanomotors

Joseph Wang*

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The combination of nanomaterials with electrode materials has opened new horizons in electroanalytical chemistry, and in electrochemistry in general. Over the past two decades we have witnessed an enormous activity aimed at designing new electrochemical devices based on nanoparticles, nanotubes or nanowires, and towards the use of electrochemical routes – particularly template-assisted electrodeposition – for preparing nanostructured materials. The power of template-assisted electrochemical synthesis is demonstrated in this article towards the preparation and the realization of self-propelled catalytic nanomotors, ranging from Pt–Au nanowire motors to polymer/Pt microtube engines. Design considerations affecting the propulsion behavior of such catalytic nanomotors are discussed along with recent bioanalytical and environmental applications. Despite recent major advances, artificial nanomotors have a low efficiency compared to their natural counterparts. Hopefully, the present *Faraday Discussion* will stimulate other electrochemistry teams to contribute to the fascinating area of artificial nanomachines.

1 Introduction

The first Royal Society Discussion Meeting held under the name "Faraday Discussions", was held in 1947, and was devoted to the topic of "Electrode Processes".[1] This Introduction is intended to provide some background to the topic of the present *Faraday Discussion* 164 on Electroanalysis at the Nanoscale, starting with a short history of the subject. The trend to miniaturization of electrodes started in the mid 1970s, prior to the nanotechnology boom. Leading electrochemists have recognized for a long time that the miniaturization of working electrodes has obvious practical advantages, and opens up fundamentally new possibilities.[2–4] Ultramicroelectrodes have been widely used for over three decades for local electrochemical investigations, and particularly for *in vivo* monitoring of neurotransmitters.[2,4] The emergence of nanotechnology, and the introduction of nanoparticles, nanotubes or nanowires and in the 1980s and 1990s, has opened new horizons for designing new electrochemical devices and electroanalytical strategies. Over the same periods we have witnessed

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Department of NanoEngineering, University of California, San Diego La Jolla, CA 92093, USA. E-mail: josephwang@ucsd.edu; Fax: +1 (858) 534 9553; Tel: +1 (858) 246 0128

considerable efforts in the use of electrochemical routes for preparing nanostructured materials. The field of nanoscale electrochemistry has thus been growing very fast.

2 Use of nanomaterials in electroanalysis and electrochemistry

Major efforts, starting in the 1980s, have greatly improved the way of making, assembling, positioning and imaging nanomaterials of different compositions with controlled sizes, shapes and functionality. The unique properties of nanoscale materials have paved the way to new and improved electrochemical sensing devices.[5,6] The range of nanomaterials used in electrochemistry is wide and diverse. Nanomaterials such as carbon nanotubes, gold nanoparticles, or silicon nanowires have thus made a major impact on the field of electrochemical biosensors, ranging from glucose enzyme electrodes to DNA hybridization sensors.[5–7] For example, various nanoparticles have been used towards effective electrical communication between the redox proteins and the electrodes or as amplification tags for ultrasensitive electrochemical bioaffinity assays.[8,9] Nanomaterial–biomolecule hybrid systems have also led to the development of new and improved biofuel cells. Electrocatalytic sensing and energy-conversion applications have also benefited from the ability to vary the size, composition and shape of nanomaterials, and hence tailoring their electrochemical reactivity. The newest nanoscale carbon material, graphene, has already been shown to be extremely useful for enhancing greatly a wide range of electrochemical sensing and energy storage applications.[10] Considerable attention has been given recently to understanding the various factors and parameters that affect the electrochemical reactivity of nanoscale carbon materials, owing to uncertainties associated with the source or quality of these nanomaterials.[11]

3 Use of electrochemical methods for preparing nanostructured materials

Electrochemical deposition has been shown to be extremely useful for preparing nanomaterials. In particular, the membrane-template electrosynthesis method, introduced by Charles Martin in the mid 1990s, has been one of the most widely used electrochemical routes for preparing nanostructured materials.[12] Such template-assisted electrochemical growth of different nanowires involves electrodeposition into the cylindrical void nanopores of a host porous membrane template, followed by dissolution of the template.[13,14] Nanoporous membranes (*e.g.*, track-etched polycarbonate, anodized alumina), with a wide range of pore diameters (0.03–10 μm) and pore densities (10^5–10^9 pores cm^{-2}), are available commercially from companies such as Millipore or Whatman, and are the most widely used sacrificial template.

The template electrodeposition method is very general as it entails synthesis of the desired material within the cylindrical pores. The method has thus been extremely useful for preparing nanowires with broad range of chemical compositions, including metallic, polymeric and semiconductor nanowires. This is accomplished by depositing first a thin film of metal on one side of the template to create the working electrode and electrical contact. The membrane is then assembled in an electrochemical cell with the open pores facing a plating bath to allow deposition of the wire segments. Applying a potential to this metal film contact in the presence of an electrolyte containing the metal ions or monomer to be deposited thus results in controlled bottom-up growth of nanowires in the pores of the template. Nanowires of tailor-made lengths can be obtained by controlling the charge passed during synthesis. Microstructures of different shapes, including cylindrical microtubes, conical, double-conical or bilayer microtubes or core–shell microwires, have also been realized by the template-assisted electrochemical route. Multi-segment nanowires have been prepared through sequential electrodeposition of several materials, with different pre-determined lengths, into the pores of the template (Fig. 1).[15] Such multisegment nanowires have found important applications as product barcodes[16] or tags for multiplexed biodetection.[17,18]

The power and versatility of template-assisted electrochemical syntheses is demonstrated in the following sections towards the realization of self-propelled catalytic nanomotors of different designs and propulsion mechanisms.

4 Template synthesis of self-propelled catalytic micromotors

Template electrodeposition has been shown to be extremely attractive for preparing catalytic nanowire and microtube motors.[15,19,20] Locomotion of small scale objects through fluid environments is one of the most exciting areas of nanotechnology.[19,21,22] Man-made nano/microscale catalytic motors represent a major step towards the development of practical nanomachines. Such synthetic motors have received considerable recent attention over the past decade owing to their great potential for diverse applications ranging from directed drug delivery to environmental remediation.[23–25] Particular attention has been given to the design of efficient synthetic micro/nanoscale motors that convert chemical energy into autonomous motion, based on the decomposition of hydrogen peroxide fuel.

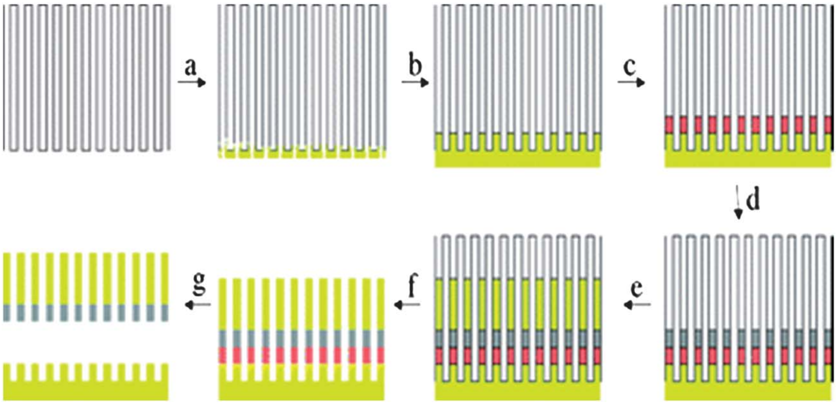

Fig. 1 Template-assisted electrodeposition of multi-segment nanowires: (a) Gold sputtering onto the alumina membrane template. (b) Electrodeposition of gold plugs. (c) Electrodeposition of a sacrificial layer of copper. (d) Electrodeposition of nickel segment. (e) Electrodeposition of gold segment. (f) Dissolution of alumina. (g) Dissolution of copper. (Reproduced from ref. 15.)

4.1 Template prepared catalytic nanowires

Initial efforts in this direction, pioneeered by Sen and Mallouk at Pen State University[26] and Ozin's group in Toronto,[15] have led to the introduction of catalytic nanomotors based on bisegment (Pt–Au) nanowires. The sequential deposition of the platinum and gold segments thus leads to asymmetric nanowires with spatially defined catalytic zones, with the oxidation and reduction of the hydrogen-peroxide fuel occurring preferentially at the Pt anode and Au cathode. Such asymmetry is essential for generating a directional force and movement through a self-electrophoretic propulsion mechanism. The speed of the bimetallic nanowire motors is proportional to the mixed potential difference (ΔE) of the fuel at the corresponding metal segments. Tafel plots of the anodic and cathodic reactions on the corresponding electrode materials can be used for obtaining the ΔE.

We demonstrated the ability to increase the velocity and force of synthetic bimetallic nanowire motors by exploring new motor compositions. For example, we illustrated that the incorporation of carbon nanotubes (CNT) into the platinum segment of catalytic nanowire motors leads to a dramatically enhanced speed and power.[27] The resulting nanomotors are capable of moving autonomously at speeds approaching 100 body lengths per second, reflecting the greatly increased fuel decomposition rate at the anodic Pt–CNT segment. We also demonstrated a dramatic increase of the speed of nanowire motors to over 100 $\mu m\ s^{-1}$ by replacing their cathodic gold segment with a Ag–Au alloy segment.[28] Such behavior is attributed to the substantially enhanced electrochemical reactivity of Ag–Au alloys, compared to silver or gold alone. The speed of these alloy nanowire motors is strongly affected by the composition of the Ag–Au segment, being nearly linearly proportional the silver level in the growth mixture solution from 0 to 75% (v/v). Such dependence is attributed to the influence of the Ag–Au alloy composition upon the reduction process of the peroxide fuel.

Guiding the movement of catalytic nanowire motors and regulating their speed are essential for diverse future applications of catalytic nanomotors. Most commonly such motion control is accomplished by adding a nickel segment[29] to allow guided movement along preselected paths as well collective motion of multiple nanomotors through alignment with an external magnetic field. Speed control of catalytic nanowire motors has been realized through a temperature control. Balasubramanian *et al.*[30] demonstrated the use of heat pulses for modulating rapidly the speed of catalytic nanowire motors. Such temperature control reflects the controlled reaction kinetics, analogous to that observed in thermoelectrochemistry at heated electrodes.

4.2 Template prepared catalytic microtube engines

Bubble-propelled microtube engines (‘microrockets’) have been developed to address the limitation of catalytic nanowire motors to low ionic-strength media.[31,32] As desired for diverse practical applications, the oxygen-bubble propulsion mechanism of microtube engines (in the presence of hydrogen peroxide fuel) leads to efficient locomotion in salt-rich solutions and real-life environments.[33] These tubular microengines thrust forward in discrete increments, reflecting the release of the individual oxygen microbubbles (generated at their inner catalytic surface) through the larger opening of the microcone. The speed of the tubular microengine corresponds to the product of the bubble radius and expelling frequency.

Tubular microengines were prepared initially by Mei and Schmidt using a rolled-up lithographic fabrication route.[31,32] Our team described a simplified template-membrane based electrodeposition synthesis of highly efficient and smaller (8-μm long) polymer/Pt bilayer conical microtube engines, illustrated in the SEM images of Fig. 2.[20,34] These peroxide-driven bubble-propelled microrockets have been electrosynthesized using the conical polycarbonate membrane template. Such a template directed route involves sequential deposition of the polymeric and catalytic metal tubular layers within the conical-shaped micropores of the membrane. The nucleation and growth of conducting polymer microtubes within such conical micropores involve electrostatic and solvophobic interactions between the polymers and pore wall.[35] An inner catalytic platinum tubular layer is subsequently plated inside the resulting polymeric microtube. The influence of the composition and electropolymerization conditions upon the propulsion of new template-prepared polymer-based bilayer microtubular microbots has been investigated. Such investigations examined the effect of different electropolymerized outer layers, including polyaniline (PANI), polypyrrole (PPy), or poly(3,4-ethylenedioxythiophene) (PEDOT) (Fig. 2), and of various inner catalytic metal surfaces (Ag, Pt, Au, Ni–Pt alloy), upon the movement of such bilayer microtubes.[34] Such polymeric layers were selected owing to their inherent chemical stability. Electropolymerization conditions, such as the monomer concentration and medium (*e.g.*, surfactant, electrolyte) or plating parameters (*e.g.*, charge) have a profound effect upon the exact morphology of the resulting polymer/metal bilayer microtubes and hence upon their propulsion behavior. The most efficient propulsion was observed using PEDOT/Pt microengines that offer a remarkable speed of over 1400 body lengths s^{-1}, which is the fastest relative speed reported to date for man-made micro/nanomotors. Such ultrafast nanomotor speed corresponds to a large force and power essential to execute different cargo-towing and delivery tasks. Magnetic guidance of such template-prepared microengines is achieved through the deposition of an intermediate Ni layer. In addition to the polymer–Pt microtube bilayer, it is possible to achieve bubble propulsion using template-assisted deposition of bimetallic Cu–Pt microjects.[36]

Inner biocatalytic layers can serve as attractive alternatives to electrocatalytic metals for propelling peroxide-driven nano/microscale motors.[34,37] Template electrodeposition of the polymer–Au microtube can lead to a very rough gold surface suitable for immobilizing large amounts of the enzyme catalase through a mixed alkanethiol monolayer and EDC coupling.[34] The resulting catalase-powered microengines propel favorably in the presence of a low peroxide level (0.5% H_2O_2).

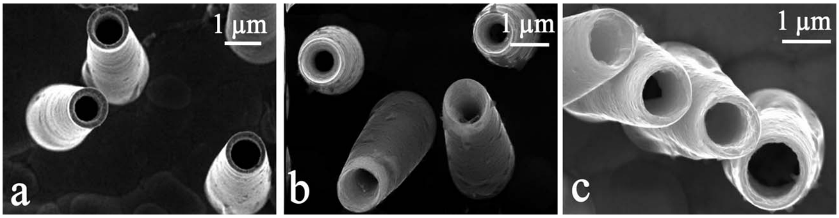

Fig. 2 SEM images of three template-prepared polymer/Pt bilayer microtube engines based on different outer polymeric layers: (a) PANI/Pt; (b) PPy/Pt; (c) PEDOT/Pt. (Reproduced from ref. 34.)

The template electrodeposition can be used for preparing microtube engines based on other fuels. For example, Gao *et al.*[38] described the efficient acid-driven propulsion of polymer/zinc bilayer microrockets. The effective propulsion of the zinc-based microtubes in acidic media reflects the continuous thrust of hydrogen bubbles generated by the spontaneous redox reaction occurring at the inner Zn surface. The exploration of new alternative fuels, through studies of new motor materials and reactions, should expand the scope of operation and environments of catalytic nanomotors.

4.2.1 Recent applications of template-prepared microtube engines. Various bioanalytical ('Capture–Transport') separation applications of catalytic microtube engines have been accomplished by functionalizing their outer surface with an immobilized bioreceptor.[39] For example, we have also demonstrated the rational functionalization of tubular microengines with different bioreceptors, such as antibodies or oligonucleotide probes (Fig. 3). This has been accomplished *via* a mixed self-assembled monolayer (SAM) chemistry on a sputtered gold surface (Fig. 3) or through carboxy groups on the outer (PEDOT–carboxy) polymer layer. Such surface modification procedures ensure efficient binding processes while minimizing nonspecific binding, and have a minor effect upon the propulsion efficiency in biological media. The resulting functionalized microenegines have been shown to be extremely useful for capturing, transporting, isolating and detecting a wide range of target bioanalytes. The 'on-the-fly' isolation of cancer cells,[40] proteins,[41] or DNA targets[42] from complex raw biological matrices has thus been accomplished. The unique features of these motion-driven bio-isolation protocols make them an extremely attractive alternative for current sample processing protocols in connection to microfabricated lab-on-chip microsystems.

Recently, we introduced new microtube engines possessing a 'built-in' recognition capability within their outer polymeric layer itself, hence eliminating the need for an additional receptor functionalization step.[43,44] These included nanomotors for recognizing monoscharides based on a poly-3-aminophenylboronic acid (PAPBA) outer layer,[43] and nanomotors based on a molecularly imprinted polymer (MIP) outer layer that contained artificial receptor cavities.[44] The latter involves introduction of the imprinted recognition sites for the target protein (FITC-labeled avidin) template, by adsorption on the walls of the micropores, during the electropolymerization of the outer PEDOT layer (Fig. 4). Direct extraction and isolation of Av-FITC from raw serum and saliva samples has thus

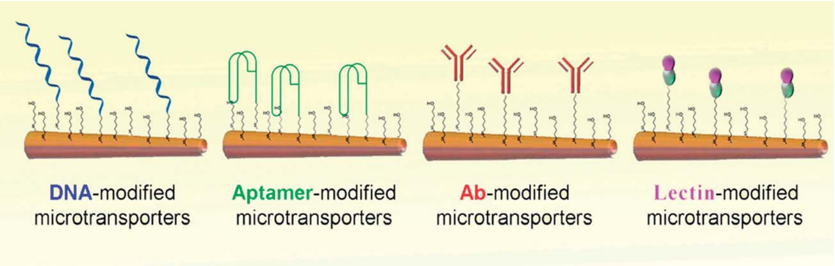

Fig. 3 Microtube engines functionalized with ss-DNA (a), aptamer (b), antibody (Ab), and lectin (d) receptors, for the 'on-the-fly' isolation of nucleic acids, proteins, cancer cells and bacteria, respectively, from unprocessed biological media (Reproduced from ref. 39.)

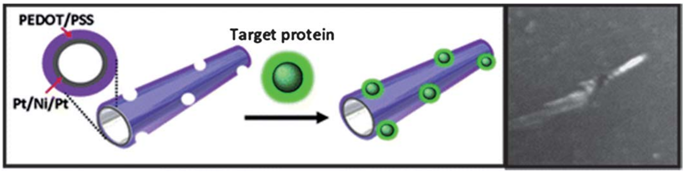

Fig. 4 Scheme illustrating the preparation and characterization of the MIP-based microtube engine, containing artificial receptor cavities within its outer layer, along with the strategy for capture and transport of the target protein. Also shown (right) is an image of the MIP-based microengine after movement in a solution containing the fluorescent-tagged analyte. (Reproduced with permission from ref. 44.)

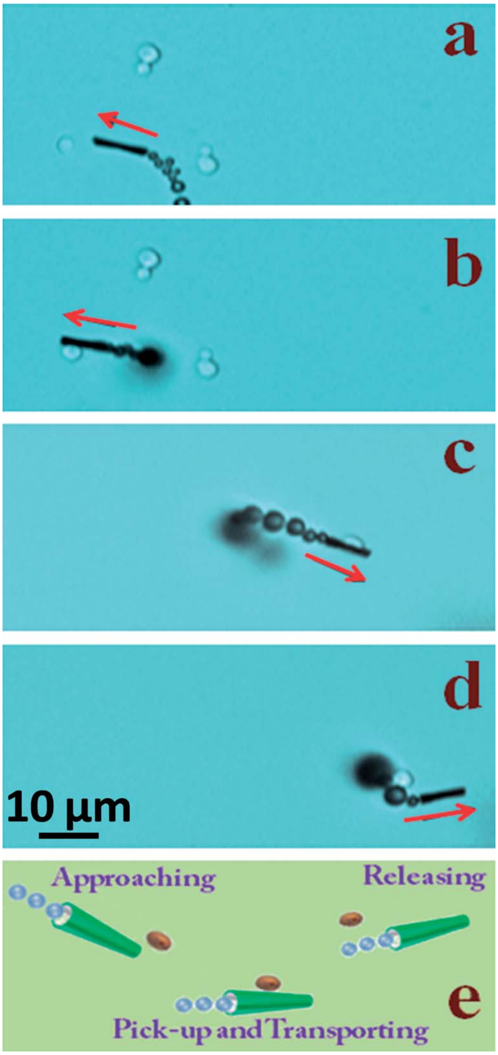

Fig. 5 'Capture–Transport–Release' of yeast cells using a PAPBA/Ni/Pt tubular microengine approaching (a), capturing (b), transporting (c) and releasing (d) the yeast cell. (e) Schematic representation of the 'Capture–Transport–Release' process. (Reproduced with permission from ref. 43.)

been accomplished following short navigation times. The images of Fig. 5 illustrate the use of the PAPBA/Pt microtube engine 'on-the-fly' binding and transport of yeast cells (containing sugar residues on their wall), along with the fructose-triggered release of the cells. Such use of the recognition polymeric layer does not hinder the efficient propulsion of the microengine in aqueous and physiological media.

Environmental applications. Catalase-powered microtube motors have been used for rapid water-quality testing based on changes in their propulsion behavior and lifetime in the presence of common pollutants[45] Enzyme-powered biocompatible polymeric (PEDOT)/Au-catalase tubular microengines have thus offered highly-sensitive direct optical visualization of changes in the swimming behavior in the presence of common contaminants (toxins) and hence a direct real-time assessment of the water quality. Such real-time tracking of the toxin-induced hindered movement and life expectancy of the tubular microengine ('artificial microfish') mimics common live-fish water testing and relies on the toxin-induced inhibition of the enzyme catalase, responsible for the biocatalytic bubble propulsion of these microengines.

We also illustrated how the deliberate modification of the rough outer surface of microtube engines with highly hydrophobic long-chain self-assembled alkanethiol monolayers (SAM) can be used for the capture, transport and removal of oil droplets from contaminated water samples.[25] This motor-based environmental remediation method relies on the strong interaction of the SAM-modified microtubular engine with oily liquids *via* adhesion and permeation onto its long alkanethiol coating. The resulting superhydrophobic microswimmers thus offer a rapid and highly efficient collection and transport of oil droplets in aqueous environments, as well as considerable promise for the isolation of hydrophobic molecules or for transferring target analytes between liquid–liquid immiscible interfaces, and hence great potential toward diverse practical applications.

Conclusions

The papers included in this volume illustrate the tremendous impact that nanoscale materials have had on modern electroanalysis. For over two decades, electroanalysis has been taking advantage of the new possibilities that nanomaterials offer. The unique properties of nanomaterials have thus been exploited successfully to enhance the performance of electroanalytical devices. There is no doubt that the new materials offered by nanoscience will continue to have a profound impact upon electroanalytical techniques. Considerable efforts are required for gaining a better understanding of how these nanoscale materials affect the electrochemical reactivity. Such studies should involve a careful characterization of the corresponding materials (using high resolution imaging techniques) and proper control experiments.

The template-directed electrodeposition has been shown to be extremely useful and versatile approach for preparing catalytic nanomotors, ranging from Pt–Au nanowires to polymer/Pt microtube engines. The template-assisted electrochemical growth can also be used for preparing externally-powered (fuel-free) nanowire motors, which are particularly suitable for *in vivo* biomedical applications.[46,47] A wide range of other useful nanoobjects can be prepared by the template electrodeposition technique, and by electrochemical methods in general.

The use of synthetic nanomotors to power nanomachines is one of the most exciting challenges facing nanotechnology. Microscale catalytic motors, converting chemical energy into autonomous motion, have been redesigned over the past decade for faster movement, larger force, and for enhanced functionality. Despite of these major recent advances, both catalytic nanowires and microtube motors still have a low efficiency with which they convert the free energy stored in chemical fuel to mechanical energy.[48] Accordingly, I hope that this article will stimulate other electrochemistry groups to bring their expertise and talent to address the important challenge of powering artificial nanomotors and to accelerate the pace of developing functional nanomachines for meeting future societal needs.

Acknowledgements

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