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Ultrafast Catalytic Alloy Nanomotors**

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The use of nanomotors to power nanomachines and nanofactories is one of the most exciting challenges facing nanotechnology.[1,2] Recent efforts have demonstrated the continuous autonomous non-Brownian movement of bimetal nanowires (Au-Pt, Au-Ni) propelled by electrocatalytic decomposition of hydrogen peroxide fuel.[3,4] Efficient energy transduction is crucial for the successful use of such catalytic nanomotors as power-generating engines for nanoscale devices. Most bimetal nanowires known to date can move at speeds of up to 10–20 $\mu m\,s^{-1}$.[5] We reported recently that the speed of nanomotors can be accelerated up to 51 $\mu m\,s^{-1}$ by incorporating carbon nanotubes (CNTs) into the platinum segment.[6] Bioelectrochemical propulsion has also been reported but in connection with larger (mm-long) enzyme-functionalized carbon fibers.[7]

Herein, we demonstrate a dramatic acceleration of bisegment nanowire motors to over 150 $\mu m\,s^{-1}$ by using a cathodic Ag/Au alloy instead of a gold segment. Alloys have been used for several decades for improving the catalytic activity of electrodes.[8] Ag/Au alloys were shown earlier to enhance the electron transfer reactions of hydrogen peroxide compared to silver or gold alone.[9,10] However, to the best of our knowledge there are no reports on using alloy segments to dramatically enhance the speed and power of fuel-driven nanomotors. As the alloy segment is prepared by simultaneous electrodeposition of its metal constituents, the ultrafast speed and high efficiency of the new Ag/Au-Pt nanomotors are achieved without compromising the simplicity of the template-guided nanowire preparation route.

Figure 1 shows typical tracking lines and moving distances of Au-Pt (A) and Ag/Au-Pt (B) nanowire motors for 1 sec in the presence of 15 wt% hydrogen peroxide. The Au-Pt motors travel over a distance of circa 10 μm, whereas the Ag/Au-Pt nanowires moved over 110 μm during this period. The corresponding videos (see the Supporting Information) clearly illustrate the dramatically faster motion of the alloy-containing nanowires. These nanomotors display a well-defined directional motion with their platinum end forward and maintained their speed during the entire 15 min tracking experiment. Speed distribution profiles (for over 50 nanomotors during a 10 sec period; Figure 1 C), indicate average speeds of 10.2 and 113.6 $\mu m\,s^{-1}$ for the Au-Pt and Ag/Au-Pt nanowires, respectively. About 5% of these alloy wires display speeds higher than 150 $\mu m\,s^{-1}$, corresponding to over 75 body-lengths/s and approaching the speed of the most efficient biomotors (e.g., flagellated bacteria).[11] CNT-containing nanowires have an average speed of 51 $\mu m\,s^{-1}$ using the same fuel composition.[6] The data of Figure 1 indicate that the energy conversion and output power of the alloy nanomotors are significantly higher than that of Au-Pt nanomotors, reflecting the substantially higher fuel decomposition rate. Considering that the output power varies as the square of velocity[6] and the 11-fold speed enhancement, the new alloy wires offer approximately 121 times higher output power compared to conventional nanowire motors.

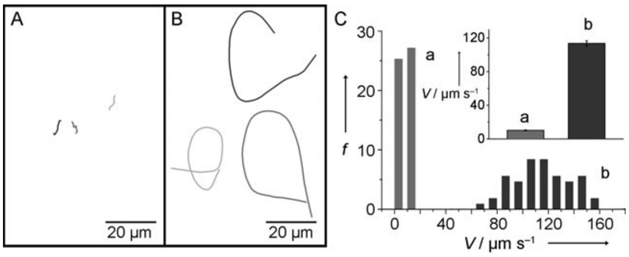

Figure 1. A,B) Tracking lines of nanomotors illustrating the distances traveled by A) Au-Pt and B) $Ag_{75}Au_{25}$-Pt nanomotors in 1 second in 15 wt% H_2O_2 solution. C) Histograms representing the speed distributions of a) Au-Pt and b) $Ag_{75}Au_{25}$-Pt nanomotors obtained from tracking a set of over 50 nanowires during a 10 s period. The inset shows a comparison of the average speeds of the catalytic nanomotors and the corresponding error (90% confidence intervals).

The speed of the new alloy nanowire motors is strongly affected by the composition of the Ag/Au segment. Histograms and graph bars (Figure 2) illustrate that the speed increases in a nearly linear fashion upon increasing the silver level in the growth solution from 0 to 75%(v/v) (a–d). Whereas motors based on the pure gold segment display an average speed of 9.9 $\mu m\,s^{-1}$ (A), average speeds of 35.9, 63.6, and 87.2 $\mu m\,s^{-1}$ are observed in 5 wt% H_2O_2 solution for alloy segments prepared in plating solutions containing 25 (b), 50 (c), and 75 (d)%(v/v) of silver, respectively (labeled here as $Ag_{25}Au_{75}$, $Ag_{50}Au_{50}$, and $Ag_{75}Au_{25}$). The motion of the Ag/Au alloy segments decreased rapidly to around 7 $\mu m\,s^{-1}$ at a higher silver content (85% by volume), and nearly came to a stop for a pure silver segment (not shown). Such behavior is consistent with early reports on extremely high hydrogen peroxide decomposition rates at Ag/Au alloys compared to the pure silver catalyst,[8] with faster reaction rates upon raising the silver content in the alloy,[9] except when the silver

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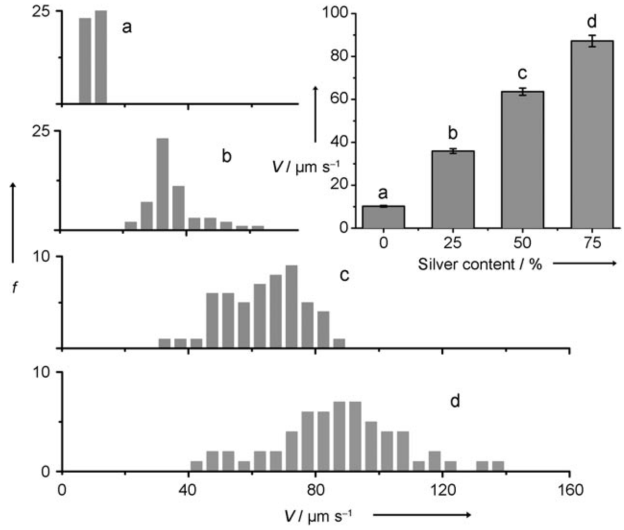

Figure 2. Histograms of the speed distributions of a) Au-Pt, b) $Ag_{25}Au_{75}$-Pt, c) $Ag_{50}Au_{50}$-Pt, d) $Ag_{75}Au_{25}$-Pt nanomotors in a 5 wt% H_2O_2 solution. For each nanomotor composition, the histograms are based on 50 or more nanomotors.

content approaches unity.[8] Our EDX data indicate that alloy plating solutions containing 25 and 75%(v/v) silver lead to alloy nanowires containing 81 and 95 wt% silver, respectively (not shown). Overall, the speed of alloy nanowires can be tailored by controlling the alloy composition (Figure 2). Such tunable speed could be exploited for designing novel nanowire barcodes based on motion as a new mode of identification (orthogonal to composition-based readout).

The attractive behavior of the new catalytic alloy nanomotors reflects the marked increase in the fuel decomposition rate compared to the pure metals, which is associated with the formation of adsorbed OH^- species and the minimization of catalyst loss.[9,12] The self-electrophoresis (electrokinetic) mechanism of bisegment catalytic nanomotors suggests that the speed of such nanomotors is proportional to the mixed potential difference (ΔE) of the corresponding segment materials in the fuel.[5] Tafel plots of the hydrogen peroxide reaction, used for obtaining the ΔE values, using Pt, Au, $Ag_{25}Au_{75}$, $Ag_{50}Au_{50}$, and $Ag_{75}Au_{25}$ alloys are given in Figure 3. A gradual potential shift from 243 to 274 mV is observed upon raising the silver content in the Ag/Au alloys, which leads to larger $\Delta E_{\mathrm{Ag/Au\text{-}Pt}}$ values (67 to 98 mV) compared to 56 mV for the pure metals. Such increase of the $\Delta E_{\mathrm{Ag/Au\text{-}Pt}}$ value with the silver content is consistent with the speed-composition data of Figure 2.

In conclusion, we have demonstrated a dramatic increase of the speed of fuel-driven nanowire motors to over 150 $\mu m s^{-1}$ using a cathodic Ag/Au alloy segment instead of a pure gold segment. As ultrafast speeds are achieved without any additives or accelerators, even further acceleration of the alloy nanomotors can be expected using mixed fuels (e.g., peroxide–hydrazine) or upon incorporation of carbon nanotubes within the platinum segment. Tailoring the alloy composition, including the spatial distribution of the metals within the cathodic segment, could also be used for optimizing the catalytic activity and efficiency of the new nanomotors.

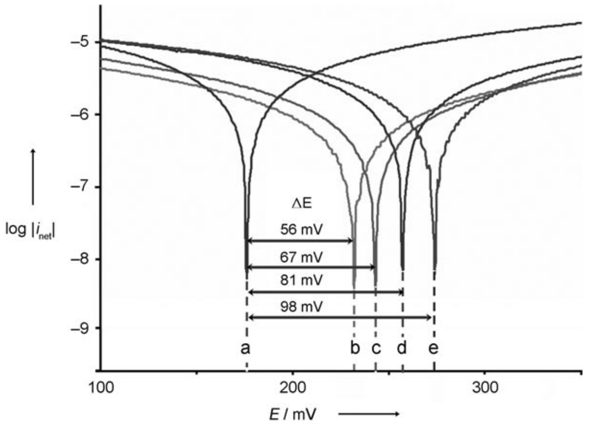

Figure 3. Tafel plots of a) Pt, b) Au, c) $Ag_{25}Au_{75}$, and d) $Ag_{50}Au_{50}$, and e) $Ag_{75}Au_{25}$ in a 5 wt% H_2O_2 solution. The mixed potential differences (ΔE, Pt vs. Au/Ag alloys or pure Au) are also indicated in the figure.

Improved understanding of the electrochemical reactivity of alloys (including potential synergistic effects), and of the role of various fuel and motor additives, would thus enable the design of energy efficient nanomotors to perform complex tasks.

Experimental Section

The bi-segment nanomotors were prepared by sequential electrodeposition of the silver/gold (Ag/Au) alloy segment and of the pure platinum segment into a porous alumina membrane template (Catalogue no. 6809–6022; Whatman, Maidstone, U.K.). A sacrificial copper layer was first electrodeposited into the branched area of the membrane using a 1M cupric sulfate pentahydrate solution ($CuSO_4 \cdot 5H_2O$; Sigma–Aldrich, St. Louis, MO), a total charge C = 10 Coulombs and a potential of V = −1.0 V (vs. Ag/AgCl; a platinum wire as a counter electrode). Subsequently, Au or Ag/Au alloys were electrodeposited at −0.9 V. In the case of Au-Pt nanomotors, the gold segment was plated from a gold plating solution (Orotemp 24 RTU RACK; Technic Inc., Anaheim, CA). Various compositions of Ag/Au alloys were plated from silver/gold alloy plating solutions containing 25, 50, and 75% v/v of the silver plating solution (1025 RTU@4.5 Troy/Gallon; Technic Inc) until an alloy segment length of 1 µm was reached. Platinum was then deposited galvanostatically using a current of −2 mA for 50 min from a platinum plating solution (Platinum RTP; Technic Inc). The sputtered gold layer and the copper layer were removed simultaneously by mechanical polishing and the membrane was dissolved in 3M NaOH for 30 min. These nanowires were collected by centrifuging the solution at 10000 rpm for 5 min and washed repeatedly with nanopure water (18.2 MΩ cm) until a neutral pH was achieved. All nanowire solutions were stored in nanopure water at room temperature and their speed was tested on the same day of synthesis.

Details of the procedure used for tracking nanomotor movement and of the statistical analysis of sampling data were reported earlier.[6] An optical microscope (Nikon Instrument Inc., Eclipse80i, Melville, NY) was employed along with a Photometrics CoolSnap CF camera (Roper Scientific, Duluth, GA) and a MetaMorph 7 software (Molecular Devices, Sunnyvale, CA, USA).

Tafel plots were used to obtain the mixed potential established at electrode materials corresponding to the individual nanomotor segments (Au, Ag/Au, and Pt) in a 5 wt% hydrogen peroxide solution. Gold-, platinum- and Ag/Au-alloy-coated glassy carbon electrodes (CH Instruments, Austin, TX) were used as the working electrode in these electrochemical measurements. Cyclic voltammetry of 5 wt% aqueous hydrogen peroxide (without any electrolyte) was performed using CH Instrument Model CHI630C at a scan rate of 50 mV s^{-1} and over a potential range of 0.1 to 0.4 V (vs. Ag/AgCl), using a platinum wire as the counter electrode. Further details have been previously reported.[6]

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