NANO
LETTERS

2008
Vol. 8, No. 4
1169-1173

Fabrication of Very High Aspect Ratio Metal Nanowires by a Self-Propulsion Mechanism

Rona Sharabani, Saada Reuveni, Gilad Noy, Eyal Shapira, Shira Sadeh, and Yoram Selzer*

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

Received December 31, 2007; Revised Manuscript Received February 8, 2008

ABSTRACT

A novel synthesis method of very high aspect ratio metal nanowires is described. The synthesis utilizes a nanoporous membrane as a template and self-electrophoresis as a directed force that continuously push formed nanowires out of the pores in a rate that is identical to the rate of their elongation. As a result, while the pores of membranes are only 6 μm long, the formed nanowires could be more than 100 μm long.

Metal nanowires (MNWs) hold great promise for a large variety of applications in areas such as biomedicine, lithography, plasmonics, and bioanalysis as well as for technological applications such magnetoresistive memories and thermoelectric devices.[1–8] This large diversity of possible applications has motivated a surge of research in recent years to devise synthesis methods of MNWs.

Since metals typically have a highly symmetric cubic crystalline structure, the synthesis methods of wires seldom require template-based methodologies. Hard templates, such as nanoporous membranes[1] or carbon nanotubes,[9] physically constrain crystal growth. Soft templates, such as surfactants,[10] polymers,[11] or ionic species,[12] modify the kinetics of atoms assembly on the growing colloids to generate shapes other than the thermodynamically favored spheres.

Template-based methods suffer however from several drawbacks. In the case of hard templates, the resulting MNWs are typically polycrystalline, and removal of the templates requires chemical steps that could damage the MNWs.[3] In the case of soft templates, synthesis of wires often requires elevated temperatures[13] and the yield of high aspect ratio (length/diameter >1000) wires is usually rather poor.

It would be highly beneficial if a synthesis method that combines only the advantages of the above template methods could be devised. One possibility is a membrane-based method that allows precise control over the aspect ratio of the MNWs, with the additional advantage of spontaneous release of the MNWs from the template, eliminating any possible damage by template removal. Here we demonstrate realization of such a method by conveying autonomous motion capability to the formed MNWs which, as will be shown, drives them out of the pores, to form colloidal suspensions. While some characterization of the resulting MNWs will be shown, the emphasis in the presented data below is on the unique nanoscale mechanism by which they are formed.

Recent studies have demonstrated that autonomous motion of nanoscale objects is feasible for applications such as self-assembly of superstructures, roving sensors, and drug delivery.[14–17] Motility in these systems is made possible by conversion of locally available chemical energy into mechanical energy.

One possible mode of a self-generated force in these systems is self-electrophoresis, i.e., the migration of a particle in an electric field that is generated by the particle itself. This idea was first suggested as a mode of transport for microorganisms[18,19] and has recently been invoked to explain the autonomous movement in solution of asymmetric two-segments nanowires that catalyze an oxidation reaction on one of their ends and a reduction reaction on the other, generating an ion gradient parallel to their long axis which drives their movement with respect to the fluid.[17]

Such a reaction asymmetry along a MNW composed of one type of metal can be imparted if it is embedded within the pores of a membrane that physically separates between two half-reactions: oxidation of a reducing agent on one side, and reduction of metal ions to form the metal MNWs itelf on the other side (see Figure 1). The steady-state redox reaction across the membrane and through the MNWs can prevail only if electroneutrality is preserved, which can be maintained by migration of ions through the pores of the

---

* Corresponding author, selzer@post.tau.ac.il.

10.1021/nl073410v CCC: $40.75

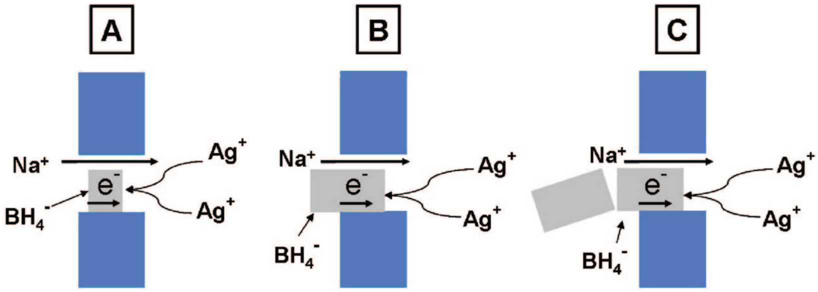

Figure 1. A schematic presentation of the processes involved in the synthesis of MNWs, shown here for Ag wires. (A) The reacting solutions intermix within the 6 μm long pores of the membrane to form metal crystals that progressively become wires. (B) Once MNWs are formed in the pores, Ag^+ reduction takes place only in the pores by electron transport through the MNWs. While growing, the MNWs move toward the $NaBH_4$ solution as a result of electroosmotic flow of the Na^+ ions toward the $AgNO_3$ solution. (C) Once the length of the MNWs is longer than some critical value defined by their mechanical stability, the MNWs start breaking into solution while the process continues via the remaining fragments in the membrane. With time, more MNWs accumulate in the $NaBH_4$ solution to form a diluted colloidal suspension. In all steps, electroneutrality is preserved by transport of Na^+ ions; see text for details.

membrane. We claim as will be discussed later, that the electroosmotic flow accompanying the migrating ions results in a fluid movement in one direction with respect to the embedded MNWs. This movement by Galilean invariance is equivalent to movement of the MNWs through the fluid in the pores in the opposite direction, leading in parallel to their elongation, to their protrusion out of the pores where they tend to break into fragments once their protruding length becomes longer than some critical value determined by their mechanical stability (see Figure 1).

We demonstrate the synthesis process by Ag MNWs. Although several efficient synthesis methods for these wires have been presented in the past several years,[20–26] the decision to use Ag^+ ions here is mainly due to the simplicity of the growth process once this monovalence ion is used. It is important to note though that the proposed method appears to be quite general and has already been applied to fabricate Au, Ni, Bi, and Fe MNWs as well.

The experimental system is comprised of a 6 μm thick porous polycarbonate membrane (GE Osmonics) with a monodisperse distribution of $6 \times 10^8/\text{cm}^2$ pores with average diameter of 40 nm positioned in a U-shaped tube between two aqueous solutions, one containing $AgNO_3$ (typically 20 mM) and the second the reducing agent $NaBH_4$. The latter reagent is used for the synthesis of all metals. The two solutions intermix within the pores of the membrane and react to form MNWs according to the following two half-reactions:

$$8Ag^+ + 8e^- \rightarrow 8Ag \qquad (1a)$$

$$BH_4^- + 8OH^- \rightarrow H_2BO_3^- + 5H_2O + 8e^- \qquad (1b)$$

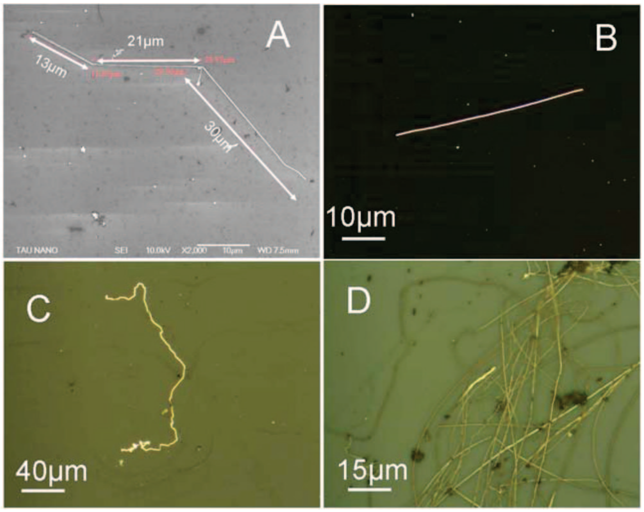

Figure 2. Representative Ag MNWs. (A) A scanning electron micrograph of a ~64 μm long wire. (B, C) Optical images of ~40 and ~200 μm long wires, respectively. (D) A bundle of ~100 μm long wires.

Our major finding is depicted in Figures 2 and 3, which shows typical MNWs found in small extractions *taken out of the $NaBH_4$ solution,* several hours after the above reaction had been initiated. In each extraction (a few microliters) a very large number of MNWs could be found. As will be shown below, statistics and analysis are based on several tens of nanowires from each sample. While the diameter of the MNWs appears to be comparable to that of the pores with well-ordered crystal strcuture (Figure 3), their length could be as long as a few hundreds of micrometers (Figure 2), much longer than the thickness of the membrane in which they were formed (6 μm). This extraordinary result is also surprising because it is well-known that when MNWs are electrochemically grown in a membrane template, once they are long enough to protrude out of the pores into the metal ions solution, coalescence of the diffusion layers to the individual pores results in a metal film that covers the entire membrane.[27] Thus in our case, once the wires become longer than 6 μm (the thickness of the membrane) it is expected that their growth process would stop as a result of metal film formation on the $AgNO_3$ side of the membrane. We claim that this is not happening[28] because the MNWs are continuously pushed in the pores *away from the $AgNO_3$ solution toward the $NaBH_4$ solution* and that this movement is at the same rate as the reduction process of Ag^+ ions, forcing the latter to take place only within the pores of the membrane. The argument is detailed in the following.

To verify that the pores are essential for the formation of MNWs, we determined the resulting composition of a solution prepared by mixing the reacting solutions without a separating membrane. MNWs could not be found, and

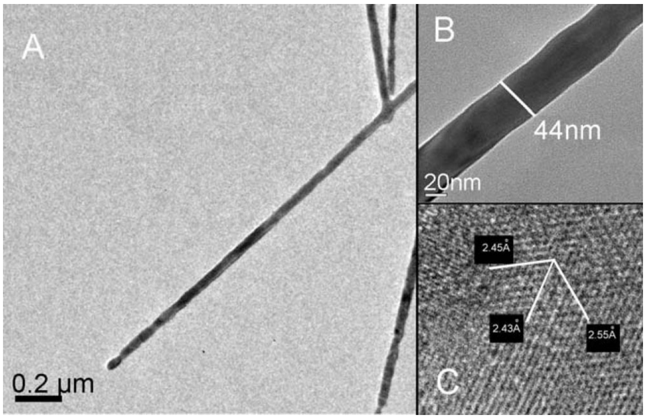

Figure 3. (A) A TEM image of a few MNWs. (B) The diameter of the MNWs is comparable to that of the pores in the membrane. (C) High-resolution lattice image at the atomic scale of a MNW depicting the ⟨111⟩ directions and the spacing between planes.

instead only colloids or large crystals of Ag with irregular morphologies were formed.

With a separating membrane, no wires were found in the $AgNO_3$ solution, establishing that the protrusion of the MNWs out of the membrane is not random and is governed by a force that is directed from the $AgNO_3$ side of the membranes toward the $NaBH_4$ solution.

Figure 4 shows the length distribution of MNWs found in small extractions taken out of the $NaBH_4$ solution after 5, 14, and 19 h of reaction. Two important facts emerge from this figure. First, while on the average the length of MNWs indeed increases with time, the distribution of lengths is wide, and it becomes wider as a function of time as determined by their standard deviation (see also Figure 5). Second, a large fraction of the wires after prolonged reaction times, 14 and 19 h, has a characteristic length of $\sim$30 μm, suggesting limited structural stability of the MNWs once their aspect ratio is greater than $\sim$1000.

Considering this information and also the fact that, as shown in Figure 2, extremely long MNWs with an aspect ratio of $\sim 10^5$ could also be found (although very rarely), it is plausible to assume that some of the MNWs sampled from each batch are only fractions of longer wires. For this reason in addition to the average length of MNWs as a function of reaction time, Figure 5 also plots the longest MNW found in each collected batch, as these wires may better approximate the maximal growth rate that could be achieved from the system under ideal conditions. Without any information on the mechanical properties of the MNWs, we analyze our results based on the averaged data.

The curves in Figure 5 can be divided into three parts: (i) up to $\sim$8 h, where the apparent growth rate of the MNWs is $\sim$1.5 μm/h; (ii) between 8 and 14 h, where the average growth rate is $\sim$8 μm/h; and (iii) after more than 14 h, where no substantial increase in length is observed.

We explain each part separately, starting with the growth behavior observed between 8 and 14 h. The average growth rate of $\sim$8 μm/h can be converted into a current of $\sim 8 \times 10^{-11}$ A that flows through each MNW as it is formed according to

$$I = \pi a^2 F(\text{growth rate})/MV_{\text{Ag}} \tag{2}$$

where a is the radius of a pore (20 nm), F is the Faraday constant, and MV_{Ag} is the molar volume of Ag (10.27 cm^3). This current per pore can be theoretically rationalized if we assume, after considering the standard potential of the two involved half-reactions, and the stoichiometry of the overall reaction (each BH_4^- reduces eight ions of Ag^+)[29] that the MNWs are formed in a diffusion-controlled rate determined by the diffusion of Ag^+ ions to the pores. Under this assumption and by considering the geometry of the process (see Figure 1), the current through a MNW under steady state should be identical to the diffusion controlled current of the Ag^+ ions to a disk electrode defined by the pore which is described by

$$I = 4nFDCa \tag{3}$$

where n (=1) is the number of electrons in the reduction process of Ag^+, D is the diffusion coefficient of Ag^+ (5×10^{-6} cm^2/s), C is the concentration of Ag^+, and a is the radius of the pore (20 nm), resulting in $I = 8 \times 10^{-11}$ A, in excellent agreement with the experimental result.

According to our model (see Figure 1), electron transfer from the BH_4^- side to the Ag^+ side of the membrane could be accompanied by either cation (Na^+) transfer in the same direction of the electron or anion transfer (NO_3^-) in the reverse direction. However, since based on our observations the MNWs move into the $NaBH_4$ solution, electron transfer is probably mainly accompanied by Na^+ transfer. The resulting electrophoretic flow from the $NaBH_4$ solution toward the $AgNO_3$ solution results in electrophoretic movement of the MNWs in the reverse direction. The rate of Na^+ transfer is thus expected to quantitatively be equivalent to the growth rate of the MNWs. To test this, we have used atomic absorption to trace the changes in Na^+ concentration in the $NaBH_4$ solution at various time intervals after mixing. The change in concentration is found to be $\sim$0.0007 M/h. Since the volume of the $NaBH_4$ solution in these experiments was 30 mL, the above rate can easily be translated to a Na^+ ion current of $\sim 10^{-12}$ A through each of the 10^8 pores of the membrane. This value is within reasonable agreement with the growth current through each pore described above. The difference can be explained by a smaller ionic flux (NO_3^- in the other direction), which has not been measured.

The ion flux brings about MNWs migration with a velocity that scales with the Helmholtz−Smoluchowski equation[30]

$$U_{\text{ep}} = \mu_e J/\kappa \tag{4}$$

where μ_e is the electrophoretic mobility of the MNWs, J is the current density due to the electrochemical reaction, and κ is the conductivity of the solution in the pores. This simple equation holds under steady-state conditions, where κ is assumed to be constant. Thus, the propagation of MNWs (toward the $NaBH_4$ solution) in the pores is effectively synchronized with and proportional to the growth rate (elongation) of the wires. This coupled process of elongation and protrusion is continuous, and as the MNWs are protruding into the $NaBH_4$ solution, they randomly break to give fragments with a broad distribution of lengths as seen in Figure 1c and Figure 5. Based on this mechanism, it is

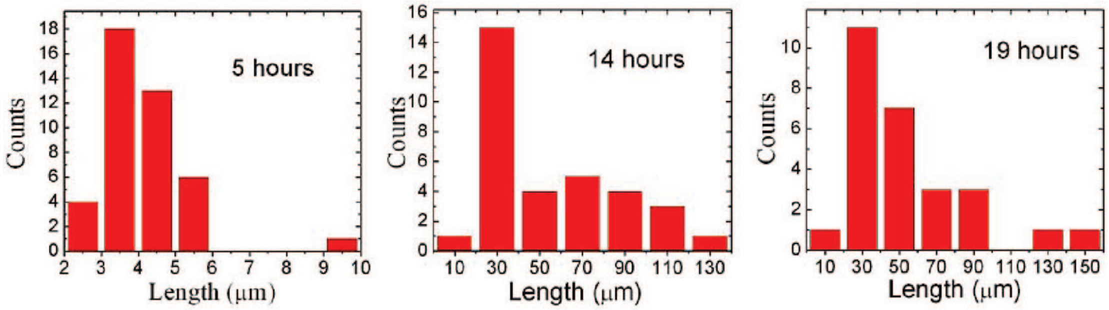

Figure 4. Length distribution of Ag MNWs found in small solution extractions taken out of the $NaBH_4$ solution at the designated time intervals after mixing.

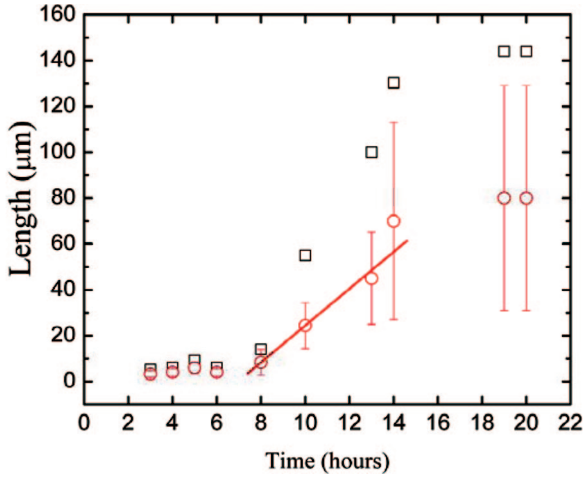

Figure 5. Average length (circles) of MNWs as a function of reaction time. The longest MNW found in all batches as a function of time is shown as well (squares). The apparent average reaction rate determined by the linear fit is ~8 μm/h.

possible to understand the apparent growth in Figure 5 at short and long times after mixing. Since in our system the pH of the BH_4^- solution is ~10, BH_4^- is not stable and slowly hydrolyses to become inactive as a reducing agent, according to the following reactions:[29]

$$BH_4^- + H_2O \rightarrow BH_3OH^- + H_2 \tag{5}$$

$$BH_3OH^- + H_2O \rightarrow BO_2^- + 3H_2 \tag{6}$$

As a result after approximately 14 h the length of sampled MNWs is not changing with time as effectively hardly any reaction takes place anymore. At short times (less than ~6 h), the apparent slow growth rate (~1.5 μm/h) results also because of the above two reactions which hinder the diffusion of BH_4^- into the pores by hydrogen evolution.

Once the MNWs are long enough to protrude into the $NaBH_4$ solution, i.e., after ~6 h (see Figure 6), BH_4^- ions do not need to diffuse/migrate into the pores to react, but instead can transfer electrons by interacting with the exposed surface of the MNWs in their solution, shifting the process from being rate determined by hindered slow diffusion of BH_4^- into the pores to be rate determined by diffusion of Ag^+ ions, as described above. Importantly, although between 8 and 14 h the total surface available for BH_4^- oxidation is continuously increasing, the apparent growth rate is approximately constant, since the increase in metal surface is

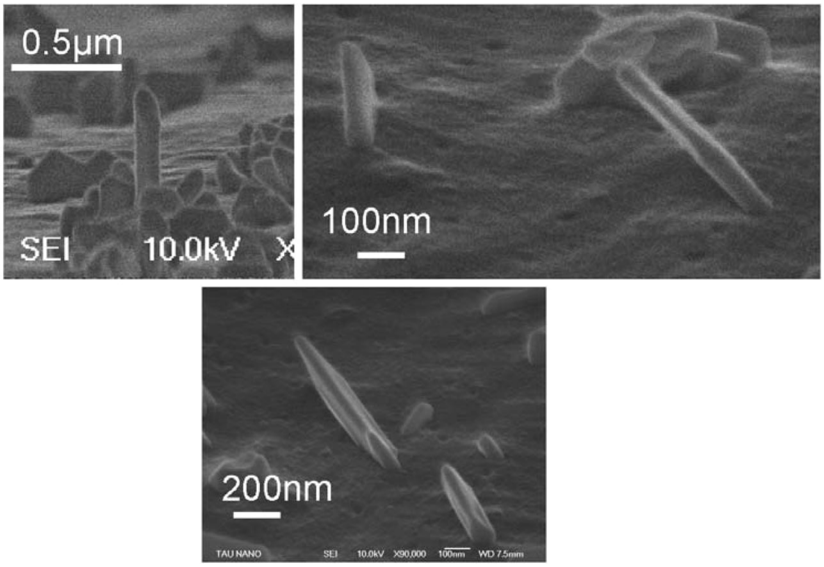

Figure 6. Scanning electron micrographs showing Ag wires starting to protrude out of a membrane. The length of the protruding wires is not uniform as the growth reaction proceeds at each pore in a different rate.

balanced by the hydrolysis of BH_4^- which decreases the growth rate of the MNWs.

Our model implies that the transfer of charge-compensating ions takes place through metal-filled pores. Electroosmotic flow through open pores obviously cannot lead to electrophoretic movement of the MNWs. Detailed inspection of the membranes by scanning electron microscopy does not reveal empty pores, and it seems that the growth of MNWs is uniform. Thus, Na^+ ions must be transferred at the interface between the metal MNWs and the walls of the pores. This squeezing of ions is essential for lubrication of the pores to enable MNWs movement. When we tried to eject short MNWs (<6 μm long) out of membranes by imposing a few atmospheres of osmotic pressure on them, the MNWs remained inside the pores. However, when the same membrane was placed at the interface between a $NaBH_4$ and $Fe(NO_3)_3$ solutions, the MNWs could be released from the membrane into the former solution. The operating mechanism is probably also self-electrophoresis (note that as before the same ions, i.e., Na^+ and NO_3^- have been used); however, since in this case Fe^{3+} is mainly reduced to Fe^{2+} (with some residual formation of Fe), no significant deposition of metal takes place on the MNWs, and they maintain almost their initial length while simply pushed out of the membrane.

Electron transfer through the MNWs appears to be a necessary driving force for Na^+ ions penetration into the pores. Only in their presence the friction between the metal MNWs and the polycarbonate is lowered enough to enable sliding of the wires. The role of charged lubricants has been suggested recently in other systems.[31]

It seems plausible that Na^+ ions are transported through the pores, across the membranes, at the interface between the metal MNWs and the polycarbonate, essentially on the walls of the membranes. If we assume a typical surface conduction value[30] of $\sigma \sim 3 \times 10^{-9}$ S, it is possible to calculate the electric field that is needed to drive the ionic current according to $E = J/\sigma$, where J is the surface flux in a pore calculated by $J = (Na^+$ ionic current/circumvent of a pore$) = (1 \times 10^{-12})/(2\pi(20 \times 10^{-7})) = \sim 8 \times 10^{-8}$A/cm. The field E is then $\sim$25 V/cm, which for a 6 μm thick membrane corresponds to a potential drop of 15 mV. Thus a very small potential drop is needed to drive the ionic current, making this process feasible under the experimental conditions.

In conclusion, the novel synthesis method of metal nanowires presented here proceeds in what could be termed as a "meat grinder" process in which, as the nanowires are growing inside a porous membrane, they continuously move out of the membranes into the surrounding solution by means of a self-electrophoretic process. As a result, while the membranes are only 6 μm thick, the resulting nanowires could be 2 orders of magnitude longer. This new synthetic approach is important first because it is intriguing in terms of the fundamental processes involved, and second because it opens new routes to fabricate very high aspect ratio one-dimensional nanoscale materials.

Acknowledgment. Y.S. is grateful to the Israel Science Foundation (ISF Grant No. 1305/04) and to Clal Biotechnology Industries for support of this research.

References

(1) Martin, C. R. *Science* **1994**, *266*, 1961.
(2) Qin, L. D.; Park, S.; Huang, L.; Mirkin, C. A. *Science* **2005**, *309*, 113.
(3) Kline, T. R.; Tian, M. L.; Wang, J. G.; Sen, A.; Chan, M. W. H.; Mallouk, T. E. *Inorg. Chem.* **2006**, *45*, 7555.
(4) Pearce, M. E.; Melanko, J. B.; Salem, A. *Pharm. Res.* **2007**, *24*, 2335.
(5) Qin, L. D.; Park, S.; Huang, L.; Mirkin, C. A. *Science* **2005**, *309*, 113.
(6) Qin, L. D.; Zou, S. L.; Xue, C. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 13300.
(7) Shapira, E.; Tsukernick, A.; Selzer, Y. *Nanotechnology* **2007**, *18*, 485703.
(8) Piraux, L.; Renard, K.; Guillemet, R.; Mátéfi-Tempfli, S.; Mátéfi-Tempfli, M.; Antohe, V. A.; Fusil, S.; Bouzehouane, K.; Cros, V. *Nano Lett.* **2007**, *7*, 2563.
(9) (a) Ajayan, P. M.; Iijima, S. *Nature* **1993**, *361*, 333. (b) Ugarte, D.; Chatelain, A.; de Heer, W. A. *Science* **1996**, *274*, 1897.
(10) Yu, Y. Y.; Chang, S. S.; Lee, C. L.; Chris Wang, C. R. *J. Phys. Chem. B* **1997**, *101*, 6661.
(11) Zhang, D.; Qi, L.; Ma, J.; Cheng, H. *Chem. Mater.* **2001**, *13*, 2753.
(12) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957.
(13) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, *2*, 165.
(14) Paxton, W. F.; Kistler, K. C.; Olmeda, C. C.; Sen, A.; St. Angelo, S. K.; Cao, Y.; Mallouk, T. E.; Lammert, P. E.; Crespi, V. H. *J. Am. Chem. Soc.* **2004**, *126*, 13424.
(15) Paxton, W. F.; Sen, A.; Mallouk, T. E. *Chem. Eur. J.* **2005**, *11*, 6462.
(16) Wang, Y.; Hernandez, R. M.; Bartlett, D. J., Jr.; Bingham, J. M.; Kline, T. R.; Sen, A.; Mallouk, T. E. *Langmuir* **2006**, *22*, 10451.
(17) Paxton, F. W.; Baker, P. T.; Kline, T. R.; Wang, Y.; Mallouk, T. E.; Sen, A. *J. Am. Chem. Soc.* **2006**, *128*, 14881.
(18) Anderson, J. L. *Annu. Rev. Fluid. Mech.* **1989**, *21*, 61.
(19) Lammert, P. E.; Prost, J.; Bruinsma, R. J. *Theor. Biol.* **1996**, *178*, 387.
(20) Shen, Q.; Sun, J.; Wei, H.; Zhou, Y.; Su, Y.; Wang, D. *J. Phys. Chem. C* **2007**, *111*, 13673–13678.
(21) (a) Sun, Y. G.; Yin, Y. D.; Mayers, B. T.; Herricks, T.; Xia, Y. N. *Chem. Mater.* **2002**, *14*, 4736. (b) Wei, G.; Nan, C. W.; Deng, Y.; Lin, Y. H. *Chem. Mater.* **2003**, *15*, 4436. (c) Zhang, S. H.; Jiang, Z. Y.; Xie, Z. X.; Xu, X.; Huang, R. B.; Zheng, L. S. *J. Phys. Chem. B* **2005**, *109*, 9416.
(22) (a) Behrens, S.; Wu, J.; Habicht, W.; Unger, E. *Chem. Mater.* **2004**, *16*, 3085. (b) Zong, R. L.; Zhou, J.; Li, Q.; Du, B.; Li, B.; Fu, M.; Qi, X. W.; Li, L. T. *J. Phys. Chem. B* **2004**, *108*, 16713. (c) Wu, Y. Y.; Livneh, T.; Zhang, Y. X.; Cheng, G. S.; Wang, J.; Tang, J. F.; Moskovits, M.; Stucky, G. D. *Nano Lett.* **2004**, *4*, 2337.
(23) (a) Jana, N. R.; Gearheart, H.; Murphy, C. J. *Chem. Commun.* **2001**, 617. (b) Zhang, D. B.; Qi, L. M.; Ma, J. M.; Cheng, H. M. *Chem. Mater.* **2001**, *13*, 2753. (c) Zhang, J. L.; Liu, Z. M.; Han, B. X.; Jiang, T.; Wu, W. Z.; Chen, J.; Li, Z. H.; Liu, D. X. *J. Phys. Chem. B* **2004**, *108*, 2200.
(24) (a) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353. (b) Mohanty, P.; Kang, T.; Kim, B.; Park, J. *J. Phys. Chem. B* **2006**, *110*, 791.
(25) (a) Liu, X.; Luo, J.; Zhu, J. *Nano Lett.* **2006**, *6*, 408. (b) Kline, T. R.; Tian, M.; Wang, J.; Sen, A.; Chan, M. W. H.; Mallouk, T. M. *Inorg. Chem.* **2006**, *45*, 7555. (c) Tian, M.; Wang, J.; Kurtz, J.; Mallouk, T. E.; Chan, M. H. W. *Nano Lett.* **2003**, *3*, 919. (d) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, *2*, 165. (e) Hu, J.-Q.; Chen, Q.; Xie, Z.-X.; Han, G-B.; Wang, R.-H.; Ren, B.; Zhang, Y.; Yang, Z.-L.; Tian, Z.-Q. *Adv. Funct. Mater.* **2004**, *14*, 183. (f) Caswell, K. K.; Bender, C. M.; Murphy, C. J. *Nano Lett.* **2003**, 667.
(26) Mohanty, P. *J. Am. Chem. Soc.* **2007**, *129*, 9576.
(27) Schonenberger, C. *J. Phys. Chem. B.* **1997**, *101*, 5497.
(28) Some build up of a metal film is observed. However, it is not uniform and it also appears by SEM to be porous, enabling diffusion of species to the pores of the membrane.
(29) Mirkin, M. V.; Yang, H.; Bard, A. J. *J. Electrochem. Soc.* **1992**, *139*, 2212.
(30) *Interfacial Electrokinetics and Electrophoresis*; Degado, A. V., Ed.; Marcel Dekker: New York, 2002.
(31) Raviv, U.; Glasson, S.; Kampf, N.; Gohy, J. F.; Jerome, R.; Klein, J. *Nature* **2003**, *425*, 163.

NL073410V