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Electrochemical Actuation of Growing Copper Dendrimers in Water

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We report the observation of electrochemical actuation in growing dendritic fibers made of self-assembled copper nanostructures (of 100 nm or less in diameter), on the metallic cathode of an ordinary aqueous electrochemical cell. This could be achieved when a copper anode and another metal cathode is placed in aqueous solution of either dilute HCl or $CuSO_4$, or $CuCl_2$, or H_2O, and upon application of a DC voltage in the range of 1.5−12.0 V. The actuation could be observed with an on−off cycle of the applied voltage in the above range. The phenomenon was also observed with the growth of bimetallic structures using a number of electrolytes such as $Ag(NO_3)$, $Pb(NO_3)_2$, $CoCl_2$, $NiCl_2$, $CdCl_2$, $ZnCl_2$, and $HAuCl_4$. The fibrous structures remained stretched as they grew longer with time in the presence of an applied voltage. The extent of actuation was dependent on the applied voltage, the concentration of Cu^{2+} ions in the solution, and also on ions such as Na^+, which did not get deposited at the cathode. The observed phenomena under different conditions have been explained on the basis of electrocapillarity.

Introduction

One of the primary focuses of nanotechnology based devices[1,2] is the fabrication and operation of nanoscale actuators, which could be controlled by internal as well as external handles. Solution-based actuators assume significance in the wake of observation of actuation of nanoscale structures with electrical[3−5] or self-generated forces[6] and of devices such as the single molecule torsional pendulum made of carbon nanotubes.[7] In addition, there has been a recent surge in efforts in making polymer based actuators.[8] Also, there have been reports of observation of actuation in fluidic devices.[9] Further, autonomous movements have been induced into self-assembled structures[10] using gas bubbles generated by decomposition of H_2O_2. Although, there have been several reports of the generation of metal nanofibers, including electrochemical generation,[11−14] there is no report of actuation of mono or bimetallic fibrous structures in aqueous solution, which are important in the generation of futuristic devices. These structures would be significant as they can be self-assembled from hybrid materials and would exhibit actuation in the presence of appropriate electromagnetic waves, magnetic and electric fields, and due to specific molecular and ionic interactions in a solution.

We report the unprecedented observation of electrochemical actuation in growing dendritic fibers[15] made of self-assembled copper nanostructures, on the cathode of an ordinary aqueous electrochemical cell, with a copper anode and any common metal cathode, upon application of a DC voltage in the range of 1.5−12.0 V, and in the presence of one of the species such as dilute HCl, $CuSO_4$, $CuCl_2$, H_2O, or a host of other salts. Typical scanning electron microscopic images of fibers grown identically on glass slides, exhibited dendritic fibers consisting of self-assembled Cu structures of 100 nm or less in diameter. In addition, the fibers generated in the three-dimensional cell also had similar structures and components. The presence of a non-copper metal cation in the solution resulted in bimetallic fibers consisting of Cu (from Cu^{2+} released by the anode) and the other metal from solution. The fibrous structures remained stretched as they grew longer with time. The extent of actuation was dependent on the applied voltage, the concentration of Cu^{2+} ions in the solution, and also on ions such as Na^+, which did not get deposited at the cathode. The observed angle of actuation with voltage is consistent with the Lippmann equation, based on electrocapillarity.[16]

Experimental

Silver (Ag), Aluminum (Al), Gold (Au), Copper (Cu) wires and stainless steel (SS) plates used in the experiments were obtained from commercial sources. HCl (∼ 11.3 M), $CuSO_4\cdot 5H_2O$, $CuCl_2\cdot 2H_2O$, $CdCl_2$, $CoCl_2\cdot 6H_2O$, $Pb(NO_3)_2$, $AgNO_3$, $ZnCl_2$, $NiCl_2\cdot 6H_2O$ used herein were obtained from Merck (India) and $HAuCl_4$ (Hydrogen tetrachloroaurate (III), 17 wt. %,) was procured from Sigma-Aldrich. For cathode we used either commercially available Ag wire (∼2 mm diameter) or Al wire (∼2 mm diameter) of typically 5 cm in length or SS plate (cross section of 1 cm × 3 cm). Aqueous solution of HCl, $CuSO_4$, $CuCl_2$, $CdCl_2$, $CoCl_2$, $Pb(NO_3)_2$, $AgNO_3$, $ZnCl_2$, $NiCl_2$, $HAuCl_4$, or milli-Q water was used as the electrolyte. While the cathode metal and the electrolyte were varied, the anode was always the same in all the experiments, i.e., a 2 mm diameter and 5 cm length Cu wire. The two electrodes were placed in the electrolyte; about 2 cm apart in a 100 mL beaker containing 100 mL of the solution and a potential difference was applied across the electrodes using an ordinary DC eliminator. When the concentration of the electrolyte was kept at or below 5.0×10^{-4} M, self-assembled dendritic fibrous structures grew on the cathode. This concentration is an upper limit for the observation of dendritic growth, above which an ordinary deposition of bulk metallic copper on the cathode was observed. Furthermore, we could observe fibrous growth of the

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structures in as low as 1.0×10^{-7} M concentration of the electrolyte, although it took typically 1 h to achieve a 10 mm length fibrous structure when a potential of 12 V was maintained. On the other hand, under identical conditions, but with higher electrolyte concentration of 1.0×10^{-4} M, it took about 5 min to grow a fiber of similar length. In practice, there is no lower limit of concentration as we find that the fibrous growth of copper could also be obtained with only milli-Q (Millipore) grade (resistivity 18.2 MΩ/cm) water as the electrolytic medium and copper as the anode. However, the deposition was slow, taking about 1 h to grow to a length of about 10 mm at a deposition voltage of 12 V and when only 25 mL of milli-Q water was used as the electrolyte. This observation is consistent with report of similar dendritic silver growth from water using Ag as the anode.[11] It is to be noted that fibers grown at lower concentrations are thinner and more fragile than those grown at higher concentrations of the electrolyte. In addition, we find that small amounts of gaseous product evolve at the cathode (possibly H_2) and the anode (possibly O_2 and/or Cl_2). We find that gaseous evolution at the electrodes is greater at lower concentrations of electrolyte and negligible at higher concentrations of the electrolyte used in our experiments.

Composition of the Dendritic Fibrous Structure Grown in Different Electrolytes. Scanning electron microscopic (SEM) and energy-dispersive X-ray (EDX) analysis was pursued for the composition analysis of various fibers. The dendritic fibers were grown on a glass slide using a drop of the respective electrolyte and applying a DC voltage of 6.0 V across the electrodes immersed in the drop. Depending on the electrolyte being used, the dendritic fibers with graded composition may be grown. We have studied a variety of metal salts as electrolytes and find that only those metal cations whose standard reduction potential is less than that of water ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, $E° = -0.83V$) yield the bimetallic fiber. For the salts of these metals (other than Cu^{2+}), in each case, we obtained graded bimetallic dendritic fiber formation (see Table SI-1 in the Supporting Information—I). In addition, we have collected fibers from the three-dimensionally grown fibers in regular cell and studied them under SEM.

Results and Discussion

When the salt concentration was kept at a value equal to or less than 5.0×10^{-4} M and copper metal anode was used dendritic fibrous structures continuously grew on the cathode. Scanning electron micrographs (SEM) of such structures grown on a glass slide with cathode and anode clamped firmly to the surface of the glass slide and using a drop of the electrolyte, such that the "as grown" structure is preserved when recording SEM, revealed the dendritic growth with assembly of particles that have typical dimensions in the range of 100 nm or less (Figures 1a). The close proximity of the glass slide in this setup interferes with appropriate and controlled actuation, possibly due to the role played by the additional interfacial forces, even though we did observed movements of the fibers at the time of the growth on the slides. Hence the actuation results were all recorded on a regular electrochemical setup. It is to be noted that because the dendritic structures grown in a normal electrochemical cell had to be lifted off to be observed under SEM, the overall symmetry of the dentritic structure (Figure 1b) could have been disturbed in the process. However in this case despite the sample handling, we find that the structures are composed of assembly of particles with dimensions typically in the range of 100 nm very similar to those in Figure 1a (inset). This suggests that the mechanism of growth of dentritic fibers is probably similar in the two different electrochemical cells. The actuation could be observed without any hindrance in the normal electrochemical cell as the glass walls were well separated from the growing dentrictic structures. We also mention here that the structures in the regular cell (as well as on glass slides) could be grown at any applied voltage between 1.5 and 12.0 V and they remained stretched perpendicular to the electrode as long as the potential was applied. Although, the fibers were made up of assemblies of nanoscale structures

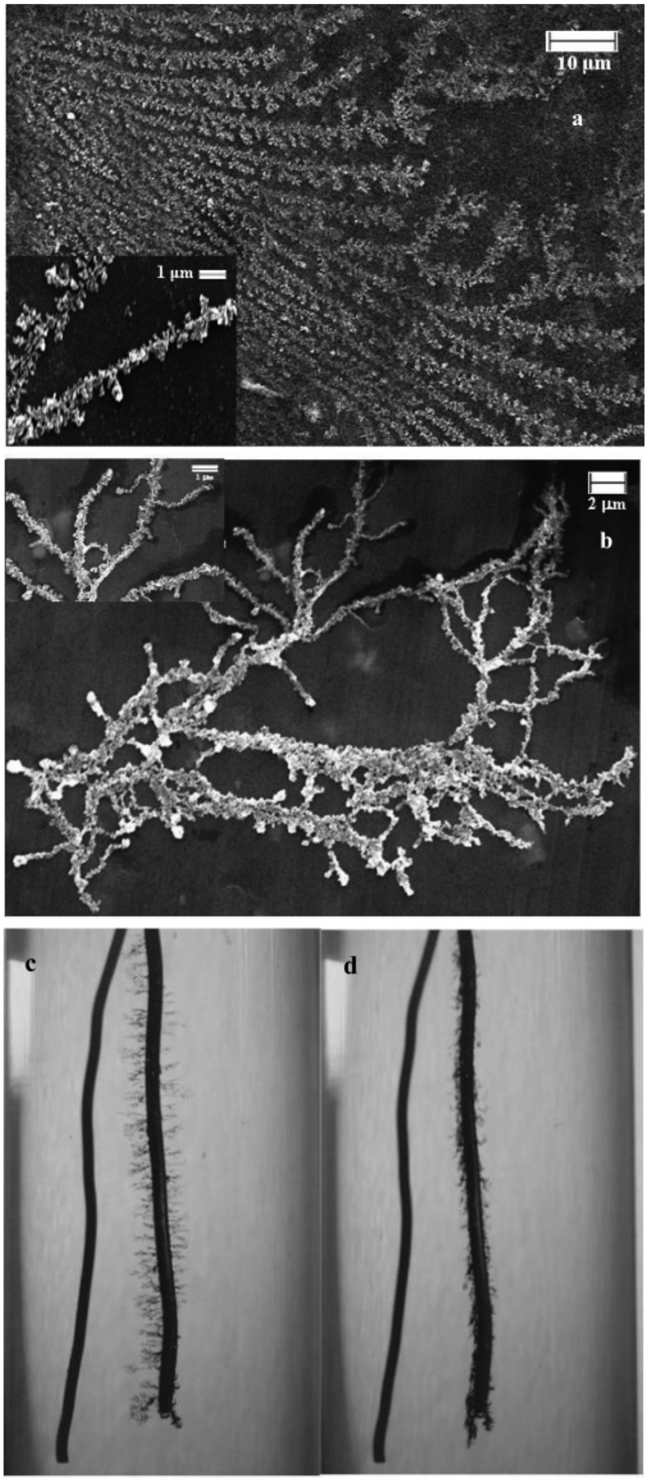

Figure 1. (a) Scanning electron micrograph of dendritic Cu grown on a glass slide with an expanded view in the inset. (b) Scanning electron micrograph of dendritic Cu grown in a regular electrochemical cell with an expanded view in the inset. (c) Actuation of fibers at the cathode with field on at 6.0 V and subsequent relaxation with the field off (d).

the final diameters of the fibers were of micrometer sizes and hence the actuation of the fibers could easily be observed by naked eye.

Turning off the voltage turns off the actuation (i.e., the fibers switch to relaxed position along the electrode). The actuation process was reversible as long as the time during the voltage “off” position did not exceed typically 7−9 s. If the time exceeded this limit, the fibrous dendritic structure agglomerated, which prevented further actuation in the next voltage “on” cycle. A typical on−off cycle of actuation is shown in Figures 1c and 1d (refer to the Supporting Information−II for video).

Electrochemical deposition of dendritic metal fibers is known to occur at rather low electrolytic concentrations, where the reaction is diffusion controlled.[16] This occurs via preferential growth at the tip in comparison to stunted growth across the length of the fiber due to kinetic factors. Thus, the fibers grow longer and assume dendritic structures at the cost of thickness of the deposited structures. Under these conditions the length of the growing fiber would act as a polarizable electrode where changes in interfacial tension, γ, is related to the changes in applied potential and to changes in solution composition:[9,16] and is governed by

$$d\gamma = -q_{\mathrm{M}}dV - \frac{q_{\mathrm{M}}}{z_{\mathrm{j}}F}d\mu_{\mathrm{j}} - \sum \Gamma_{\mathrm{i}}d\mu_{\mathrm{i}} \tag{1}$$

where, $d\gamma$ is the differential interfacial tension at the polarizable electrode;

q_{M}, the charge density on the electrode,

$$q_{\mathrm{M}} = \frac{\epsilon}{4\pi d}V \tag{1a}$$

dV is the differential applied voltage, μ_{j} is the chemical potential of species j which are released at the electrodes, z_{j} is the charge on the species j, $d\mu_{\mathrm{i}}$ is the chemical potential of species i which react on the unpolarizable electrode(s), Γ_{i} is the surface excess of ith species; $\Gamma_{\mathrm{i}} = c_{\mathrm{i}}/A - c_{\mathrm{i}}^{o}/A$, $c_{\mathrm{i}}^{\mathrm{o}}$ is bulk concentration of i, c_{i} is concentration of species i at the electrode, and A is the cross sectional area of the electrode.

At constant composition, the second and third terms are zero. Hence

$$d\gamma = -q_{\mathrm{M}}dV \tag{2}$$

is the Lippmann equation.[16]

The solution leads to

$$\gamma = \gamma_{\max} - \left(\frac{\epsilon}{8\pi d}V^2\right) \tag{2a}$$

where, $d = \chi^{-1}$ is the Debye separation of double layer for a plane electrode, at 25 °C,

$$\chi^{-1} = \sqrt{\frac{\epsilon kt}{8\pi {e_0}^2 \sum n_i {z_i}^2}}$$

For 10^{-4} M $CuCl_2$ solution, $\chi^{-1} = 13.1$ nm

10^{-6} M $CuCl_2$ solution, $\chi^{-1} = 131$ nm, 10^{-8} M $CuCl_2$ solution, $\chi^{-1} = 1310$ nm, $V =$ applied potential difference, $\epsilon =$ permittivity of bulk water $= 6.9 \times 10^{-10}$ C^2/Nm^2

or permittivity of structured water (at the electrode−electrolyte interface)[17] $= 5.31 \times 10^{-11}$ C^2/Nm^2, $\gamma_{\max}$ for Cu = 0.03 N/m and is the potential when γ for copper electrode is maximum. Thus

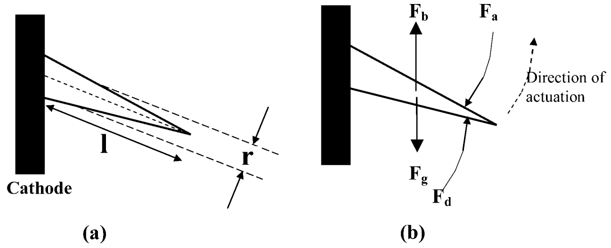

Figure 2. (a) Cone shaped nanofiber suspended at one of its end from the cathode of an electrochemical cell. (b) Qualitative representation of the forces acting on the fiber. F_{b} is the buoyancy force, F_{g} the gravitational force, F_{d} is the viscous drag force, and F_{a} is the force required for actuation.

$$\Delta\gamma = \gamma - \gamma_{\max} = -\left(\frac{\epsilon}{8\pi d}V^2\right) \tag{2b}$$

Thus the applied electrical potential would lead to changes in the interfacial tension, which in turn, would produce actuation of the fibers as explained below.

Actuation of the fiber could possibly be understood to occur in a manner similar to the wetting and de-wetting characteristics of a drop of liquid on a flat substrate surface. The drop spreads or recoils to minimize the surface free energy as governed by surface tension of the liquid drop, the surface tension of the substrate surface and the interfacial tension between the liquid and the substrate surface. In a similar fashion when a microscopic fiber is subjected to different interfacial stresses the result will be the actuation of the fiber as it cannot move, being bound to the surface of the electrode. A model calculation shown below indicates that, when a small fiber attached to an electrode (in the present case Cu fiber on cathode) is subjected to an applied voltage, to minimize the interfacial tension across the electrified interface the fiber will actuate and will tend to remain perpendicular to the electrode at a relatively high voltage. The extent of deflection would depend on the magnitude of the applied voltage, bulk solution ionic strength of an electrolyte and concentration of depositing species and shape and size of the fiber. However, this can happen only if the cations (in the present case) get continuously deposited at the tip of the fiber, while a kinetic barrier prevents the growth across the length of the fiber thus creating the situation of a polarizable electrode. For simplicity of calculation and to be in line with the above argument we consider the fiber to be conical in shape, with the base diameter fixed at 100 nm and the length at 1 cm. The fiber is considered to be made up of Cu metal deposited at the cathode from an aqueous solution of $CuCl_2$ and the copper anode. A pictorial representation of the fiber is shown in Figure 2a. The forces acting on the fiber are represented qualitatively in Figure 2b.

Assumptions:

Length of the conical fiber, $l = 1$ cm, and its base radius, $r = 100$ nm,

$\rho_{\mathrm{Cu}} = 8230$ kg m^{-3} (same as for bulk copper)

The fiber is polarizable along its length with deposition occurring at the tip only.

Gravitational force:

$F_{\mathrm{g}} = \pi \mathrm{r}^2 \mathrm{l} \rho_{\mathrm{Cu}}$ x $9.81 = 2.54 \times 10^{-11}$ N

Buoyancy force:

$F_{\mathrm{b}} = \pi \mathrm{r}^2 \mathrm{l} \rho_{\mathrm{H2O}}$ x $9.81 = 3.08 \times 10^{-12}$ N

The viscous drag force acting on fiber during its movement is (using Stokes equation)

$F_{\mathrm{d}} = 3\ \pi\eta \mathrm{U} d_{\mathrm{e}}\kappa$

TABLE 1: Actuation Velocity of a Typical Fiber[a]

concentration of electrolyte (M)	applied voltage (V)	length of the fiber (mm)	angular deflection	time required for the deflection (s)	velocity (m/s)
1.03×10^{-4}	6	5.0	45°	7.0	5.61×10^{-4}
1.03×10^{-4}	6	5.0	45°	7.5	5.23×10^{-4}
1.03×10^{-4}	6	5.0	45°	9.0	4.36×10^{-4}
mean velocity:					5.07×10^{-4}m/s

where, κ = convection factor for a fiber of uniform cross section = 1.25 to 1.5

$\eta_{H2O} = 8.905 \times 10^{-2}$ N/sec m^2

d_e = effective diameter = $((6/\pi)$ x volume of fiber$)^{-1/3}$

For the present fiber, $d_e = ((6/\pi) \text{ x } \pi(100 \times 10^{-9})^2 \text{ x } 0.01)^{-1/3} = 8.4 \times 10^{-6}$ m

The measured velocity of the fiber, $U = rd\theta/dt = 5.07 \times 10^{-4}$ m/s (Table 1)

$\therefore$ $F_d = 3.57 \times 10^{-9}$ N (when $\kappa = 1.25$).

At a constant composition of 1.0×10^{-4} M $CuCl_2$, the Debye length d = 13.1 nm and at an applied potential of V = 6.0 V eq 2b provides

$\Delta\gamma = 7.54 \times 10^{-2}$ N/m for bulk water,

$\Delta\gamma = 5.80 \times 10^{-3}$ N/m for structured water.

The force due to interfacial tension at the polarizable electrode = electrocapillary force = actuation force = F_a

$\therefore$ $F_a = \Delta\gamma \times$ (half circumference) $= \Delta\gamma$ x πr

where r is the radius of the fiber base.

$\therefore$ $F_a = 0.0754 \times \pi r = 2.37 \times 10^{-8}$ N, for bulk water,

and similarly, $F_a = 1.82 \times 10^{-9}$ N, for structured water.

From the above calculation of forces F_d, F_g, and F_b, acting on the actuating fiber, it is abundantly clear that buoyancy and gravity forces are insignificant as compared to the drag force. Moreover, Coulombic interaction between two fibers, which are separated in the present case by millimeters, is too small (on the order of 10^{-17} N)[18] to make a meaningful contribution to actuation and hence discounted in the discussion altogether. Also, the magnitude of actuation force is greater than the dominant drag force, and hence the actuation of fiber occurs due to interfacial tension at the polarizable electrode.

Further, we show here that actuation can be upward or downward depending on the original direction of orientation of the fiber during growth. Consider two orientations of the fiber in Figures 3a (initially pointing downward) and 3b (initially pointing upward). The fiber shown in Figure 3a would ideally remain attached to the cathode such that axis of the fiber (dotted line) is directed down along the cathode, i.e., $\theta_1 = 0°$ when the applied voltage $V = 0$. When this fiber actuates it moves upward under the application of external voltage i.e., $\theta_1 > 0°$ when $V > 0$. On the other hand the fiber shown in Figure 3b would ideally remain attached to the cathode such that axis of the fiber (dotted line) is directed up along the cathode, i.e., $\theta_1 = 0°$ when the applied voltage $V = 0$. And the fiber would actuate and move downward under the application of external voltage i.e., $\theta_1 > 0°$when $V > 0$. The corresponding vector (force) diagrams are schematically shown in Figures 3c, 3d, 3e, and 3f.

The relation between interfacial tension (γ) and contact angle (θ) for the electrified interface formed by the fiber and the surrounding fluid layer is

$$\gamma = \frac{rhg\Delta\rho}{2\cos\theta} \qquad (3)$$

where, r = radius, h = height of fluid, $\Delta\rho$ = difference of densities between the copper fiber and the fluid forming the electrified interface, and g is the gravitational acceleration.

In the present system assuming growth is slower than actuation, r, h, $\Delta\rho$, and g can be set constant, and hence, $\gamma \propto 1/\cos\theta$

In both cases shown in Figure 3, $\theta_2 > \theta_1$, such that average angle θ of actuation of the filament is as follows:

$$\theta = \left(\frac{180° + \theta_1 - \theta_2}{2}\right)$$

In absence of an applied field the net actuation force is zero. This means the summation of γ_1 and γ_2 is equal to 0. This is possible when the fiber is relaxed, i.e., $\theta_1 = 0°$ and $\theta_2 = 180°$. So, $\gamma_1 = (rhg\Delta\rho/2)$ and $\gamma_2 = -(rhg\Delta\rho/2)$ and thus the resultant force $F_1 + F_2 = 0$, cannot move the fiber away from main electrode. Thus the fiber remains relaxed.

On the other hand under the application of a potential the net force is nonzero and the actuation of fiber occurs, which is possible if $\Delta\gamma$ is nonzero when voltage is applied.

When actuation occurs, then $\theta > 0°$, $\Delta\gamma$ is negative and the resultant force is in the direction of actuation, as explained with an example below:

If $\theta_1 = 60°$ and $\theta_2 = 110°$, then $\theta = 65°$ with the fiber sloping downward (Figure 3a). Then $\gamma_1 = 2.00$ x $(rhg\Delta\rho/2)$; $\gamma_2 = -2.92$ x $(rhg\Delta\rho/2)$ and R, the resultant force lifts the fiber during actuation (Figures 3e and f).

Similar arguments can be extended to a fiber which is originally directed upward (Figure 3b) and it can be shown in that case also the fiber actuates in the direction of increasing θ. This is because, in both cases, we are assuming the fiber has two-half surfaces: lower and upper. Because of the symmetry of a fiber, the maximum actuation for any fiber occurs when the surface tension ($\therefore$ contact angle) above and below the fiber

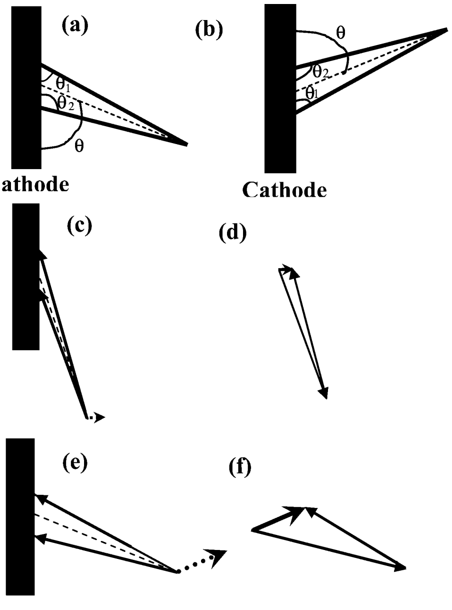

Figure 3. Schematic illustration of the orientation of fibers (a and b) with angles relative to the cathode. Schematic illustrations of the direction of actuation of fibers with corresponding vector diagrams (c, d, e, f).

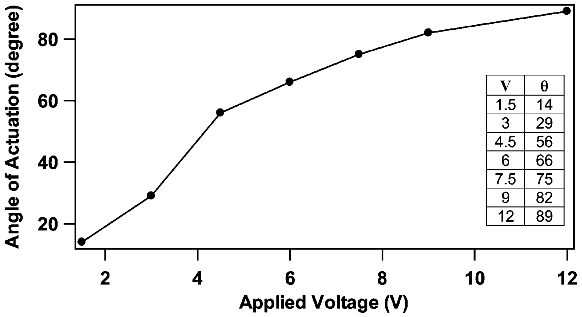

Figure 4. Plot of angle of actuation verses applied voltage. The applied voltages and the corresponding θ values are in the table (inset).

are equal, i.e., 90°. During actuation, more of the surface is exposed (similar to spreading of the drop on a flat substrate due to the favoring of interfacial tension in the system). The copper metal is not a fluid, but is composed of assemblies of nanoparticles so it responds to this electrocapillary induced stress by actuating the fiber at various possible junctions. When the voltage is turned off, $\gamma \approx \gamma_{\max} \approx 0$ (for Cu) and hence the actuation force is zero and the fiber relaxes. However, when voltage is applied, then $\gamma < \gamma_{\max}$ and fiber actuate as explained above.

The above model presents a simple yet realistic account for the actuation of a fiber by taking into account the driving and opposing forces of actuation. Additionally, the actuation of the branched dendritic structure observed in our study could be explained by the same model, where a fiber is attached in a branched fashion to a main fiber. The branched fiber actuates on the main fiber, in just the same way as the main fiber actuates on the cathode, upon the application of voltage. Further, the calculation of drag force for a branched fiber would be more involved. One can also extend the argument to the whole length of a long and flexible fiber by considering that it is composed of multiple small fibers of increasingly thinner average cross section from its base to its tip. The approximations involved are that the fibers are all of identical shapes and sizes. It is to be noted that the conical shape used in our model is a representative shape and is chosen just to demonstrate the various forces acting on the fiber. Similar conclusions can be obtained by choosing a differently shaped fiber as long as the fiber is polarizable along its length. For simplifying the model formulation, interaction between the adjacent fibers is neglected and it is assumed that there is no growth of fiber during the measurement of actuation.

Factors Affecting the Actuation of Fibers. We have studied in detail the dependence of actuation on various factors such voltage, concentration of electrolyte, concentration of other ions, etc. These are reported below.

Extent of Deflection Versus Applied Voltage. It was observed that the extent of deflection increased with applied voltage. The results in Figure 4 demonstrate such a trend for a single dendritic fiber of 2.0 mm length, initially grown at 12 V in a 1.0×10^{-4} M $CuCl_2$ electrolytic solution and then subjected to various applied voltages. Unfortunately, a relation between the angle of actuation and dγ is not straightforward and depends on the exact growth conditions due to the reasons explained in preceding paragraphs. However, our results in Figure 4 are consistent with the Lippmann equation (eq 2). The plot of 1/cos θ is found to vary linearly with the square of applied voltage (V^2), where θ is the experimentally observed angle of actuation, consistent with that predicted by Lippmann equation (refer to part B of the Supporting Information—I).

TABLE 2: Cu^{2+} Concentration Dependent Actuation of the Fiber

concentration of $CuCl_2$ (M)	applied voltage (V)	angle of deflection
5.00×10^{-5}	6.0	14°
5.02×10^{-5}	6.0	17°
5.04×10^{-5}	6.0	56°
5.06×10^{-5}	6.0	63°
5.08×10^{-5}	6.0	90°

TABLE 3: Tabulated Data of Concentration of Cu^{2+} with Deposition Time

time (min)	concentration of Cu^{2+} (M)
0	4.21×10^{-4}
5	4.28×10^{-4}
10	3.82×10^{-4}
15	3.91×10^{-4}
20	3.49×10^{-4}
25	2.85×10^{-4}
30	3.12×10^{-4}
134	8.18×10^{-5}

Extent of Actuation at a Constant Voltage Versus Concentration of $CuCl_2$. We found that the final actuation angle was higher when the concentration of $CuCl_2$ electrolyte was higher (Table 2). When 2.0 mm dendritic structures were grown at a $CuCl_2$ concentration of 5.00×10^{-5} M then an actuation of 90° could be observed at an applied voltage of 12.0 V. After this when the voltage was stepped down to 6 V the angle of actuation reduced to 14°. Upon gradual addition of a concentrated solution of $CuCl_2$ to the actuated system, the angle of actuation increased gradually and reached a value of 90°at a final concentration of 5.08×10^{-5} M of $CuCl_2$. The maximum actuation angle is as always 90°. For example, when a much higher concentration of $CuCl_2$ solution was used (1.0×10^{-4} M) at an applied voltage of 6 V the angular deflection was still 90°. Similar results were obtained when $CuSO_4$ was used as the electrolytic medium instead of $CuCl_2$.

When $CuCl_2$ is added at constant applied voltage, the condition of electro-neutrality reduces eq 1 to[16]

$$d\gamma = -\Gamma_{-}\, d\mu \tag{4}$$

Where Γ_{-} is surface excess of anions at the anode and $d\mu$ is the chemical potential change of the electrolyte. At higher $CuCl_2$ concentrations $d\mu$ is more positive as compared to when concentration of $CuCl_2$ is lower. Hence addition of $CuCl_2$ makes $d\gamma$ more negative. As a result, more actuation is observed with increasing concentration of $CuCl_2$ at constant applied voltage.

Unfortunately, in this experiment, a relation between the angle of actuation and $d\gamma$ is not straightforward and depends on the exact growth of the fiber. There are additional issues, such as the extent of polarizability of the surface of the fibers and the rate of growth of the fiber tips, which need to be taken into account to quantify the effect.

Observed Variation of Concentration of Cu^{2+} Ions in the Solution as a Function of Time of Electrodeposition. Concentration of Cu^{2+} was monitored by measuring the optical density of the copper ammine complex at 605 nm after addition of ammonia to a part of the electrolytic solution. The concentration of copper ion reduced with the time allowed for electrodeposition of the copper dendritic structures (Table 3 and Figure 5). When milli-Q water and no additional salt was used as the electrolyte along with copper anode, then the concentration of Cu^{2+} reached a steady-state value of $\sim 6.6 \times 10^{-5}$ M (after 50 min. of deposition at 12 V), which is close to the limiting concentration of 8.18×10^{-5} M achieved after a 134 min of deposition using $CuCl_2$ (Table 3).

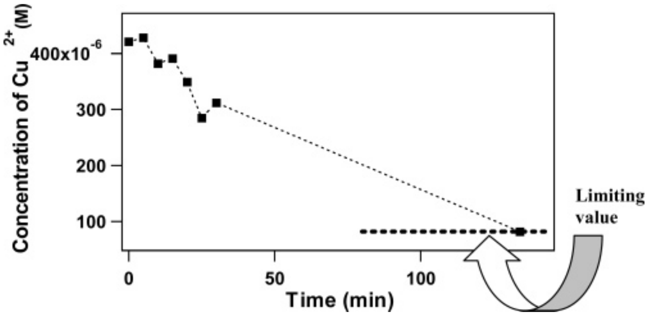

Figure 5. Graphical plot showing the approach to a steady-state concentration of Cu^{2+}

TABLE 4: Effect of NaCl on the Actuation of the Fiber

concentration of NaCl (M)	applied voltage (V)	angle of deflection
0	12 V	90°
5.0×10^{-5} M	12 V	21^0
1.0×10^{-4} M	12 V	0^0

The Effect of Addition of NaCl on the Extent of Actuation of Fiber. When a few drops of concentrated NaCl was added to a growing and actuated (with 90° deflection) copper fiber electrolytic system (with 1.0×10^{-4} M $CuCl_2$ electrolytic solution and grown at 12.0 V till fibers were 1.5 mm long) the maximum angle of actuation dropped (Table 4). Similar results were obtained if Na_2SO_4 was added instead of NaCl.

The decrease in actuation of fibers on addition of NaCl can be rationalized on the basis of ionic strength effects. Addition of a nonreactive salt at constant applied voltage implies that eq 1 simplifies to

$$d\gamma = -\frac{q_M}{z_j F} d\mu_j \tag{5}$$

where, $z_j = +2$ for Cu^{2+} ions.

Initially the system is at a steady state with constant applied voltage V, prior to the addition of NaCl. So the composition is fixed and as per eq 1, dγ is constant and the fiber remains actuated at a constant angle. The presence of additional nonreactive ions (NaCl or Na_2SO_4) increases the ionic strength (I) of the solution thus making $d\mu_{Cu}{}^{2+}$ more negative in eq 5. This leads to more positive $d\gamma$ and reduction of the net actuation force in the presence of NaCl. Higher the concentration of NaCl lesser the actuation.

Effect of Anode Material on Growth of Dendritic Structure of Copper Nanofiber. We found that when the anode was made of metals other than copper, dendritic copper did not grow on the cathode, even when the electrolyte was a copper salt. On the other hand, if after growing a copper fiber using copper anode we replaced the anode with any other metal, such as Ag or stainless steel; we found that the growth as well as the actuation stopped. This observation is important and suggests that the origin of actuation is not due to the applied potential drop as such across the two electrodes. On the other hand the continuous growth of the fiber was observed to be a prerequisite for actuation.

Conclusion

Herein we have been able to demonstrate electrochemical actuation of growing dendritic mono and bimetallic fibers with nanoscale structures in aqueous solutions. We have been able to account for the actuation based on electrocapillary forces (Lippmann equation), produced by changes in interfacial tension at the electrified interfaces. An externally applied potential induces a gradient in interfacial tension on two opposite sides of the fiber resulting into its actuation. The actuation of fibers could also be controlled by controlling the applied potential and the concentration of electrolytes. This work is expected to propel further research work in the field of micro and nano electromechanical systems.

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Note Added after ASAP Publication. Due to a production error in the version posted ASAP on October 20, 2006, an error occurred in the corresponding author footnote, eq 2b, and Table 1. The correct version was published ASAP on October 24, 2006.

Supporting Information Available: Tables, figures, and a video showing further details of the analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) $\epsilon = K \text{ x } \epsilon_o$, where K is the dielectric constant of the medium; ϵ is the permittivity of the medium; and ϵ_o is the permittivity of vacuum where (a) $K = 78$ for bulk water and $K = 6$ for structured water; O’M Bockris, J.; Reddy, A. K. N. *Modern Electrochemistry*, 1st ed.; Plenum Publishing Corporation: New York, 1973; Vol. 2, p. 757, and (b) $\epsilon_o = 8.85419 \times 10^{-12}$ C^2N^{-1}m-2; Atkins, P.; Paula, D. *Atkins’ Physical Chemistry*, 7th ed.; Oxford University Press: New York, 2006

(18) The electrolytic cell is considered as a parallel plate capacitor, where the cathode and anode are separated by a distance (d) of 2.0 cm and the two consecutive fibers (that actuate) on the cathode are 1.0 mm apart (R). Under an applied potential (V) of 6.0 V, the charge density on the cathode, $\sigma = \epsilon V/d$, where ϵ = permittivity of the medium between the two plates (electrodes) that is of water here. If one considers the radius of the fiber to be 100 nm and length 1 cm, then the charge on a fiber q= σ x 3.14×10^{-9} C. The electrostatic force between the two consecutive fibers is then $F = q^2/4\pi\epsilon R^2 = 4.87x10^{-17}N$, for bulk water and $F = 3.74x10^{-18}N$ for structured water.