Platinum Nanowire Actuator: Metallic Artificial Muscles

Shaoxin Lu, Kousik Sivakumar and Balaji Panchapakesan*

Delaware MEMS and Nanotechnology Laboratory, Department of Electrical Engineering, University of Delaware, Newark, Delaware, 19716, USA, * Email: baloo@eecis.udel.edu

ABSTRACT

In this paper, we report the fabrication of platinum nanowires using single wall carbon nanotubes as templates and their application as an electro-chemical actuator. Two regimes of actuation were seen in this actuator. In the "low" charge injection regime, quantum mechanical effects introduced by electrochemical double layer charge manipulation were the dominant actuation mechanism. Strain of about 0.04% without significant hysteresis was readily achieved. In the "medium" charge injection regime, electrostatic effect is believed to be the dominant mechanism producing strain of 0.22% which is much larger than those of the commercial piezoelectric materials.

Keywords: platinum nanowire, actuator, carbon nanotube

1 INTRODUCTION

The direct conversion of electrical energy to mechanical energy is of importance in many applications such as robotics, artificial muscles, optical displays and micro-mechanical devices and many material systems have been introduced as actuators to accomplish the energy conversion. Piezoelectric ceramics, shape memory alloys, magnetostrictive materials are well known conventional actuation materials and in recent years polymer actuators [1-3] have been proposed to be attractive alternatives. More recently, as new emerging materials, nano material systems such as carbon nanotubes [4-6] and metallic nano-particles [7, 8] have also been proposed as promising candidates for actuation technologies. Both these actuators from nano materials pose the form of electro-chemical actuator and actuate by means of an electrochemical double layer charging processes at the SWNTs (platinum nanoparticles) /electrolyte interface. It is well known that nano materials such as SWNTs and nanoparticles have extremely large surface area to volume ratio, which makes a large volume fraction of materials to be surface or interface atoms. In electrochemical actuators, the large electrochemically accessible surface area of these nano materials and the nanometer scale separation of charges between nano materials and electrolyte render the actuator a giant capacitance. The charge injection, when applying a voltage, will in turn modify the surface charge density and related surface properties causing the actuation. Strain values larger than 0.2% in SWNT actuator and 0.15% in platinum nano particle actuator (due to quantum mechanical effects induced by electrochemical double layer charging process) could produce dimensional changes large enough to do mechanical work [8]. This implies that nano material systems may open the way for better actuation technologies especially in the nano scale [9].

In this paper we demonstrate the electrochemical actuation of a new nanowire material—platinum nanowire. Single wall carbon nanotubes were used as templates for the fabrication of platinum nanowires. Then thin sheets of platinum nanowires were made to demonstrate the actuation. This actuator has the advantages of metallic nanowires such as high temperature endurance, chemical stability and low operating voltage of only a few volts. Due to the excellent mechanical properties of the inner SWNT templates, the actuator could have long-time stability against mechanical fatigue and defects, which are desired for many actuation applications such as artificial muscles. These platinum nanowires are also suitable candidates for nano scale actuators such as nano grippers due to their one-dimensional structure.

2 EXPERIMENTAL AND DISCUSSION

Commercially obtained carbon nanotubes made by pulsed laser ablation process were used in this work as templates for the fabrication of nanowires. Dihydrogen Hexachloroplatinate ($H_2PtCl_6 \cdot 6H_2O$), purchased from Alfa Aesar, was used as the platinum source. The platinum nanowires were synthesized by procedures described in reference [10], following which a nanowire sheet was made using vacuum filtration of the resulting platinum nanowire solution [4]. After subsequent rinsing with iso-propyl alcohol and DI water, the nanowire sheet was dried at 80ºC for 20 minutes to remove the remaining solution and organics in the sheet and further annealed in argon ambient at 750°C for 30 minutes to enhance the mechanical strength of the sheets. The resulting sheet had an average thickness ranging from 15µm to 75µm, depending on the amount of nanowires used, and a density of ~ 5.1g/cm^3. Figure 1(a) is the SEM image of the platinum nanowires after annealing. The nanowires have diameters ranging from 60nm to 100nm and form highly entangled nanowire bundles. These sheets were used to examine the actuation properties without further optimization. The TEM image in Figure 1 (b) gives a better view of an individual platinum nanowire, showing that the nanotube templates were coated with layers of platinum nanoparticles. The inset shows a high-resolution image of the platinum nanoparticles with an average diameter of 8nm. This would result in a surface to volume ratio even higher than nanowires with a smooth

coating of platinum, which is essential for actuation applications.

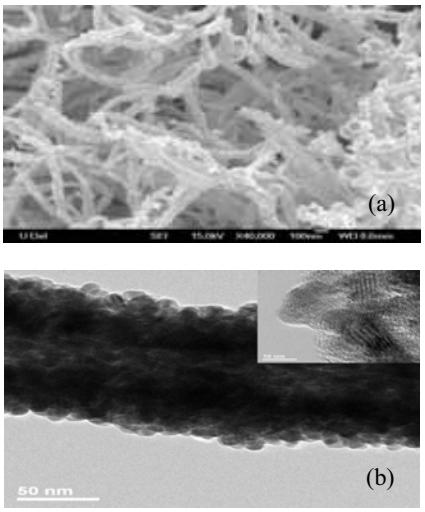

Figure 1: (a) SEM image and (b) TEM image of platinum nanowires. The inset in (b) shows platinum nanoparticles of size ranging from 5nm to 10nm.

A set up shown in Figure 2 was used to characterize the strain of the nanowires. A platinum nanowire sheet with dimensions of 20mm×2mm×50µm was attached to a strip of PVC of dimensions 50mm×3mm×100µm, which is vertically anchored to the bottom of the beaker. Another platinum nanowire sheet of much larger size than the actuator was used as the counter electrode. The bending of PVC strip was recorded using a digital camera mounted on a microscope and this displacement data was further used to characterize the strain of platinum nanowires. A third Ag/AgCl reference electrode was also inserted in the solution and all the voltages were measured versus the reference potential. 1M KOH solution was used as the testing electrolyte.

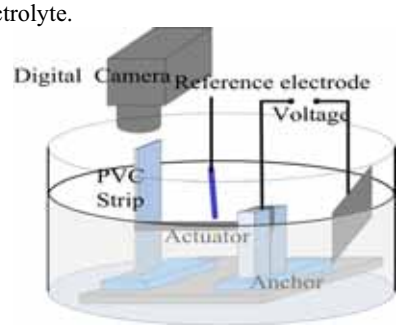

Figure 2: Experimental setup used to characterize the strain of platinum nanowires.

When platinum nanowires are biased, a potential difference forms at the interfaces between the nanowires and the solution. Thus an electrochemical double layer forms at the interface due to the capacitive charging processes, which is similar to those in SWNT [4] and platinum nano particle electro-chemical actuators [7]. It was suggested by Baughman [4, 8] and Weissmuller [7] that at "low" charge injection levels, quantum chemical effects lead to a strain and hence actuation in their actuators. The large surface area to volume ratio and the small dimensions of both the SWNTs and platinum nano particle networks that make the electrolyte-accessible area very large, together with the nanometer scale separation of charges at the interface between nano materials and electrolytes, lead to super capacitance in the actuator, which is the key factor for achieving high actuator strains at low voltages [8]. Similarly, super capacitance could also result in our platinum nanowire actuator from the electrochemical double layer due to the high surface area of these one-dimensional nanowires.

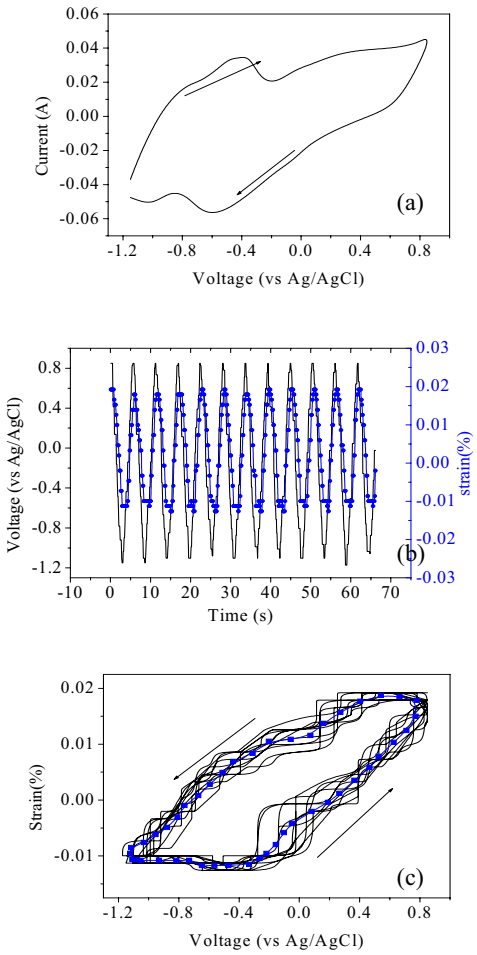

Figure 3: (a) In situ cyclic voltammograms of current measured during actuation. (b) Actuation responses versus time and applied voltage (c) Strain response of actuator versus the applied potential.

Figure 3(a) shows the recorded in situ cyclic voltammograms of current during the actuation when the applied voltage was swept from -1.15V to 0.85V at a scan rate of 710mV/s (0.18Hz), which is a typical curve for the actuator in different operation conditions. The strain response of the actuator during actuation is shown in Figure 3 (b) where the applied voltage and corresponding strain are plotted as a function of time. The cycles are quite repeatable with nearly the same amplitude and durations. When the strain response is plotted versus the applied voltage, a hysteric curve results as shown in Figure 3(c).

Comparing with the actuation response of platinum nanoparticles [7], the strain in platinum nanowires follows nearly the same pattern, indicating that the strain obtained from the platinum surface dominates over the inner carbon nanotube template. With an arbitrary zero strain point, a total strain of about 0.03% was acquired when the applied voltage is swept from -1.15V to 0.85V at scan rate of 710mV/s (0.18Hz). This obtained strain value is smaller than that of platinum nano particle actuator [7], however, the scan rate is more than 700 times faster (compared to less than 1mV/s rate in [7]), which is crucial in deciding the strain value as will be addressed later in this paper.

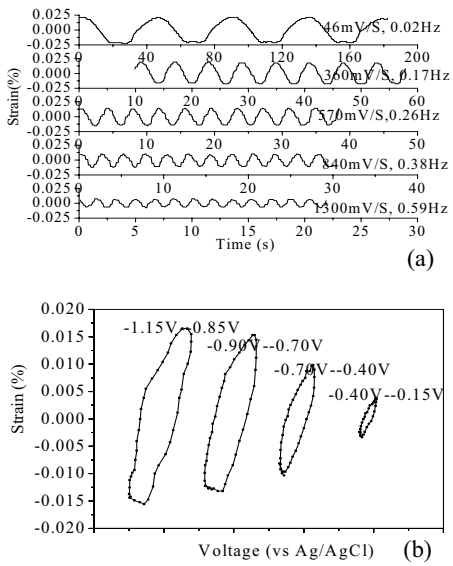

Figure 4: The dependence of strain on (a) potential scan rate (frequency response) and on (b) potential sweeping range.

To investigate the frequency dependence of the actuator, the voltage sweeping range was set to be constant from -0.7V to 0.4V (vs Ag/AgCl), and the strain responses measured at different voltage scan rates or different frequencies. As shown in Figure 4 (a), when the voltage scan rates varied from 1300 mV/s (0.59Hz) to 840 mV/s (0.38Hz), 570 mV/s (0.26Hz), 360 mV/s (0.17Hz) and 46 mV/s (0.02Hz), the total strain increased from 0.014% to about 0.042%, three times lager than the high frequency values. This negative frequency dependence of strain was also witnessed at other voltage sweeping ranges when operated at different frequencies, which means that the strain of platinum nanowires is not saturated under faster scan rate or high frequencies. If the quantum mechanical effect induced by modulation of surface charge density is responsible for the strain, the more the modulation by means of electrochemical double layer charging, which needs more time to accomplish under same driving voltage, the more will be the resulting strain. Consequently, larger strain will be acquired under longer charging time as in the case of low frequency actuations.

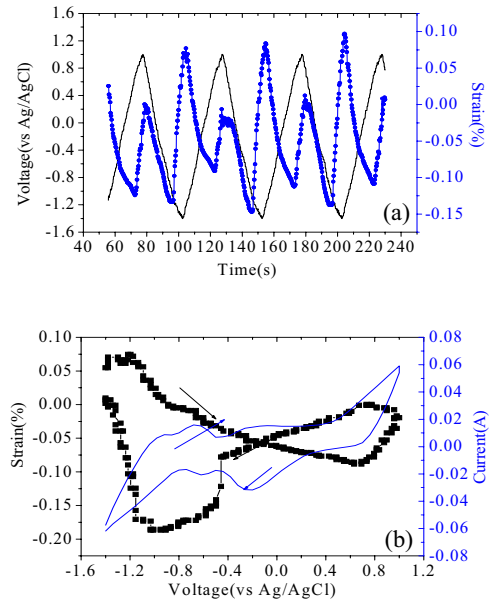

Figure 5: Actuation response at "medium" charge injection level. (a) Actuation responses versus time and applied voltage. (b) The strain is plotted as a function of applied potential (left) and current measured during actuation (right). The arrows indicate the direction of sweeping.

To investigate the voltage dependence of strain, the scan rate was set constant at 900mV/s and the strain of the actuator measured under the following voltage sweeping ranges: -0.4V to 0.15V, -0.7V to 0.4V, -0.9V to 0.7V and -1.15V to 0.85V. Figure 4(b) shows the strain response of different voltage sweeping range under the constant scan rate of 900mV/s. It can be seen when the voltage sweeping range was increased from -0.4V-0.15V to -1.15V-0.85V, the total strain (arbitrary zero point for strain value) increased from 0.008% to 0.033%, more than 4 times its value at smaller voltage sweeping range, which also led to the occurrence of hysteresis at the same time. As the potential sweeping range increases, the interfacial electrical

field between platinum nanowires and electrolyte becomes stronger and causes increased charge injection and surface charge modulation. This increased charge injection consequently leads to a higher strain in the nanowire sheet. Further, under constant voltage scan rate, larger voltage sweeping range means longer time of sweeping, which would also cause an increase in charges injected and hence resulting in greater strain values.

From these results, at small voltage sweeping range (normally smaller than -1V to 0.8V) or fast scan rate (normally larger than 150mV/s), the charge injection level in electro-chemical double layer is relatively low due to the insufficient driving voltage or insufficient time for charging. The strain due to the quantum mechanical effect is proportional to the charge injection and is a dominant mechanism for the actuation [4, 7, 8]. In order to probe the actuation response at higher charge injection levels, which can be realized by increasing the voltage sweeping range or by decreasing the voltage scan rate, we measured the strain response of the actuator at an increased voltage sweeping range of -1.4V to 1V and a small voltage scan rate of 96mV/s. Figure 5 (a) shows the actuation responses (right) and the applied voltage (left) versus time. An important difference between this curve and that in "low" charge injection level is the double peaks in every cycle, which is a typical feature in actuation in this charge injection regime. It is known that strain due to the quantum mechanical effects will change sign when the charge injection changes sign [4, 8, 11, 12]. Due to this only one peak is obtained in every cycle. Instead, if the electrostatic effect dominates the actuation, then the strain value would go close to zero with minimum dimension change of actuator when it is at the potential of zero charge (PZC), and either positive or negative charge injection would cause expansion of the actuator resulting in strain peaks at both ends of the voltage sweeping range [4, 7, 8, 13]. As a result double strain peaks form during every cycle. Based on our experimental result, we believe that strain from electrostatic effect is dominant beyond a certain charge injection level and quantum mechanical effects are suppressed. Three cycles of actuation is shown in Figure 5(a) to be quite repeatable with nearly the same strain amplitude of ~0.22%. This strain value is much larger than the maximum strain of 0.15% obtained from platinum nanoparticles actuator [7]. Figure 5 (b) plots the strain response as a function of applied potential. The cyclic voltammograms of current is also shown in the graph for reference. The two strain peaks in a cycle are not symmetrical with a much larger peak amplitude at negative potential end and smaller peak amplitude at positive potential end. The reason for this asymmetry is not clear. One possible reason could be due to the unique structure of the nanowires made of platinum nanoparticles on SWNTs templates. The platinum nanowires could have an inherent Schottky barrier at the nanotube – platinum interface. Under moderate negative bias, more electrons may gain sufficient energy and reach the nanotubes through tunneling or thermal emission across the Schottky barrier. This injection of negative charges could lead to a quantum mechanical expansion of the nanotubes and add to the electrostatic strain experienced by the platinum coating to result in a bigger strain. Whereas, under positive bias, charge injection leads to shrinkage of the nanotubes and the overall effective strain of the nanowire (the platinum surface would still expand under positive bias due to electrostatic effect) is reduced resulting in a smaller peak under positive bias.

To the best of our knowledge, the platinum nanowire actuator reported here is the first nanowire actuator that exhibits strain comparable to commercial piezoelectric materials while requiring only a few volts to operate. The work explained here is only a preliminary demonstration of the actuation capabilities of the nanowire actuator. There is a lot of scope for improvement to obtain better actuation. Platinum nanowires of smaller diameters would have higher surface to volume ratio leading to higher surface charge modulation and hence larger strain. A better control of nanowire thickness can be achieved by more efficient separation of carbon nanotube templates in the solution [14]. We believe that with proper control over synthesis, nanowires as small as 10nm can be repeatably fabricated [15]. Moreover, in order to obtain better strain values, it is desirable to use directional, oriented platinum nanowires instead of the highly entangled ones for the construction of nanowire sheets, which could suppress the overall strain response. SWNT sheets grown with good directionality using CVD processes [16] can be used for the fabrication of platinum nanowire sheets. The use of proper electrolytes with wider stability window such as organic solutions is also an important factor in improving the performance of the actuator [5].

3 ACKNOWLEDGEMENTS

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