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Capillary force assisted fabrication of DNA templated silver wires

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We demonstrate for the first time formation of micron scale conductive silver (Ag) wire induced by capillary forces through scribed micro-cuts on deoxyribonucleic acid-silver nanoparticles (DNA-AgNPs) film. The "writing" flexibility based on the physical re-arrangement of the particles may prove prominent towards fabrication of conductive wires.

Deoxyribonucleic acid or DNA has in the last few decades been increasingly studied as a smart electronic material with highly complementary base pair specificity[1,2]. Fuelled by "technological aggravations" caused by predictions of Moore's Law, DNA electronics promises nano-scaled dimensions of tuneable electronic properties. The main interest lies in the fact that DNA molecular constituents enable specific bindings with metallic nanoparticles allowing flexible nano-templating abilities. Not surprising, DNA assisted metallic wire deposition has been studied for its potential use in electronics by various groups[1,2]. DNA was chosen primarily for its self-assembly and selective metallic templating properties. It has been reported that metals evenly distribute along the phosphate backbone of DNA[3,4]. These properties in turn can be utilized to selectively bind inorganic materials such as silver (Ag) along the DNA strands. The last two decades showed much progress in these aspects[5], yet the challenge still remains to establish a flexible, practical and cost effective methodology.

In 1997, Deegan et al[6] observed higher particulate concentrates at the edge of a drying drop as a result of evaporation influenced capillary forces. This phenomenon, known as the coffee-ring effect, involves movement of particles from the interior of the drop towards the edge. Particles are also re-distributed back to the interior by means of the Marangoni effect[7]. By addition of surfactants, which drastically reduces the surface tension of the droplet, this effect could be drastically reduced[7]. In this communication, we employed these capillary forces to displace DNA strands templated with Ag nanoparticles (NPs) along a micro-cut, which acts as the edge through where evaporation occurs. Continuous evaporation towards the edge results in the metal loaded DNA molecules to aggregate and form long micro-wires on both sides of the edges. As demonstrated by Deegan et al in their coffee ring experiment, migration of the molecules is influenced by the outward flow within the droplet containing the molecules, which is driven by the evaporation induced solvent loss through the cut edges. According to them, this is further determined by the geometrical constraint of the boundary of the shape of the DNA-AgNPs droplet.

Fabrication of the proposed silver microwires involves three major stages; self-assembly of DNA-AgNPs suspension, scribing process and material rearrangement. A silicon (Si) wafer (single side polished, <100>, n-type, undoped) with a dimension of 2.0 inch x 0.5 mm bought from Sigma, UK was used as a substrate for the microwire formation. The sample used in this work was used only once and fresh from the supplier, as such no further cleaning was necessary. Indium tin oxide (ITO) (KINTEC, Hong Kong) slides for the Field Emission Scanning Electron Microscope (FESEM) imaging meanwhile was first sonicated for 15 minutes in detergent. The slides were then rinsed with deionized water, followed by acetone, isopropyl alcohol and deionized water. Finally, the slides were purged with nitrogen gas prior to usage. An aliquot of 0.5 ml of deionized water (18.2 MΩ.cm) was mixed with the vial containing lyophilized pBR322 DNA (MW $2.9x10^6$ Da) from *Escherichia coli* RR1 (Sigma, UK). 400.0 µL of this DNA solution was mixed with 400.0 µL of AgNPs dispersion (10 nm particle size, 0.02 mg/mL, Sigma, UK) in aqueous buffer and sodium citrate as stabilizer. The solution was then incubated overnight to allow metallic silver aggregates to bind to the DNA molecules. A micropipette was then used to displace 50.0 µL of the DNA-AgNPs solution onto the silicon wafer. 15 minutes later a drop of ethanol (10.0 µL) was applied onto the droplet and left to dry in air overnight. Ethanol concentrates and dehydrates the DNA, which renders them mechanical stability[8]. A gel-like residue was observed after evaporation of water molecules.

Scribing was then carried-out using a surgical blade, which created a visual separation. Due to the gel-like nature of the film, some flexible material mobility can be observed with the Ag loaded DNA molecules influenced by the capillary force to occur towards the edge of the cut. Prior to imaging, the prepared sample was left overnight to allow maximum displacement at the edges. The balance between the coffee-ring[6] and the Marangoni[7] effects governs the kinetics of the particles (AgNPs/DNA) dispersion within the droplet. By allowing long enough time, evaporation process at the meniscus of the droplet may allow the deposition of a higher amount of AgNPs/DNA molecules at the edges. After which, Atomic Force Microscope (AFM) surface and conducting AFM (cAFM) electrical imaging (Veeco Dimension 3100, Department of Chemical Engineering and Biotechnology, University of Cambridge) was carried-out using two separate modules; AFM probe with tapping mode tip (NSC15 from µmasch) and conducting AFM (cAFM) probe with contact mode tip (Model SCM-PIC with Antimony (n) doped Si). The cAFM was utilized in contact mode for measuring current against a dc voltage bias of 300 mV.

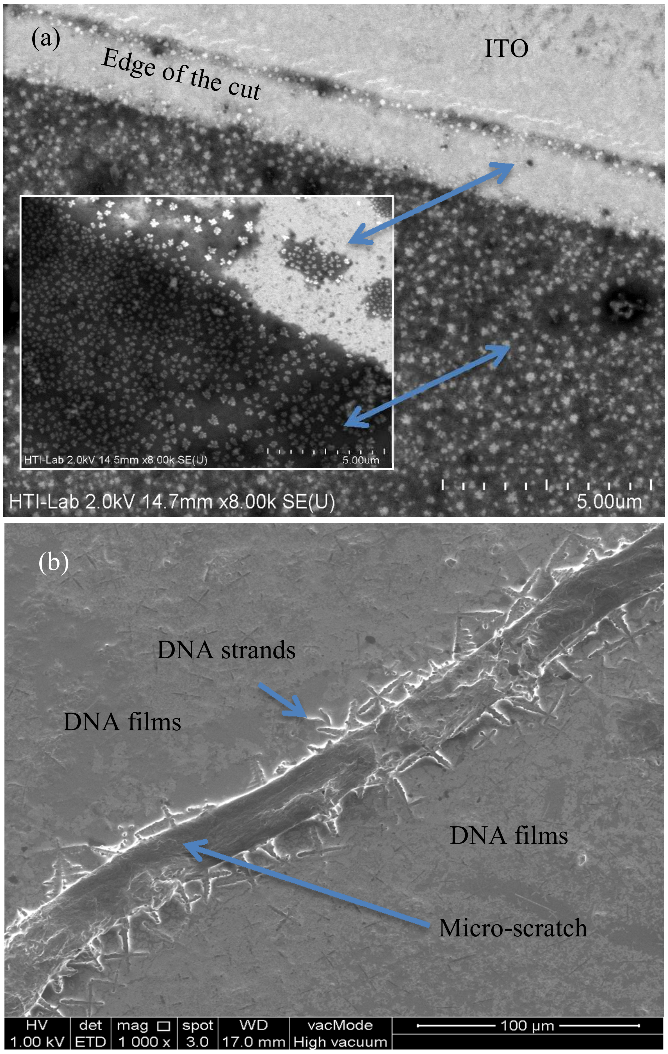

Fig. 1 FESEM images showing (a) densely populated DNA strands at the edge of the cut while the inset allows better visual inspection of the bright-white edge and (b) well-connected chain of individual DNA strands aligned along the incision at a higher magnification.

Investigation of particle mobility towards the edge of the cut was carried-out using a DNA-only solution (0.02 mg/mL, isolated from *Mimosa pudica*) on ITO were allowed to self-assemble overnight before scribing the next day prior to the FESEM investigations. Higher effective mobility can be seen at the edges of both sides of the cut, showing a higher concentration towards the edges as shown by the FESEM (Quanta FEG-450, Department of Physics, University of Malaya), image in Figure 1a. This observation agrees well with the coffee-ring effect observed with drying drops of solutions[6] and may be utilized to enable the DNA molecules to "drag" the AgNPs to the edges of the cut. The nature of the interaction between the DNA, and the AgNPs is considered to be purely electrostatic, where the alternating pentose and phosphate groups forming the polyanionic backbone of DNA bind to the AgNPs through *d-p* orbital bonding[9].

Closer inspection of DNA arrangement on a scratch was carried-out using another preparation of DNA-only solution on ITO. Here, connected individual DNA strands can be seen clearly aligned along the cut (Figure 1b). Deposition of the Ag loaded DNA occurs as capillary force channels the molecules to move towards the edge much like the diffusion of particles in drying drops[6,10]. The metal-DNA complex formed is strong enough to maintain the Ag bound to the DNA during this move. This results in the formation of a well defined and continuous wave-like wire formation observed along the cut and shown in Figure 2. A granular exterior (Figure 2c) similar to the wire structure achieved by Braun et al[1] was also seen. The granular structure in our case, as also deduced by them, could be indicative of the aggregation of Ag particles along the wire. However, unlike the limited wire patterning abilities of this and other methods[11,12], the current work may allow a more controlled and flexible method of printing conductive wires.

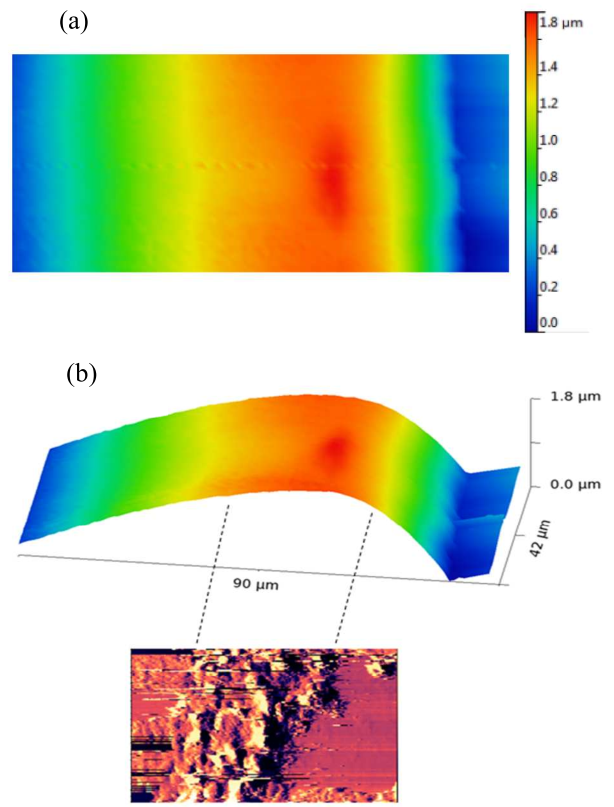

Fig. 2 Tapping-mode AFM imaging illustrating; (a) height profile and (b) 3-dimensional wave-like granular structure of the Ag wire.

Figure 3 shows the current profile of the silver wire fabricated using this method. A portion of the wire measuring about 9.0 µm in length was profiled and analysed. From the image, current was measured around 2-4 nA (0.3 V bias voltage) for the 10.0 µm peak width and 1.0 µm peak height wire. Line graphs represent current fluctuations in three different regions; bulk (i), center of the wire (ii), and silicon wafer (iii). Comparative values demonstrate lowest current when scanned across the wafer substrate (iii) while the bulk region indicates weaker conductivity (i) in respect to the wire backbone.

Although a higher particles density can be deduced from the observation, particles, which may consist of AgNPs, DNA and DNA-AgNPs, are also clearly seen (Figure 1a). These could be attributed to influence of the Marangoni effect. According to Hu et al[7], non-uniform evaporation rate leads to non-uniform distribution of temperature along air-liquid (DNA-AgNPS suspension), which results in non-uniform surface tension driving a thermal Marangoni flow. This flow may cause the re-distribution of the Ag loaded particles back into the droplet's' interior resulting in the weaker electrical conductivity observed here (i). The higher conductivity shown at the wire backbone (ii) demonstrates the higher net retention along the edge of the cut as predicted by the coffee ring effect. However, almost no current fluctuations are observed in the cut region (iii), which illustrates non-metallic deposition.

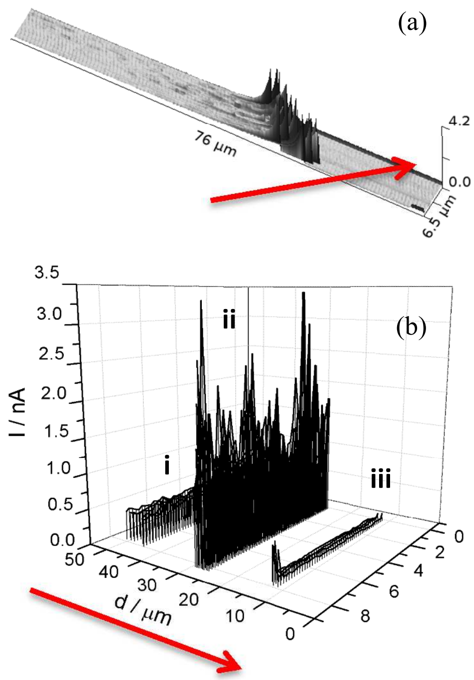

Fig. 3 (a) A section of the silver wire profiled to illustrate the peak current generated at 300 mV bias-potential. (b) The line graph shows current fluctuations at three different positions along the direction of the arrow across the wire. Position i represents the interior or bulk bulk region, ii is the region on the silver wire and position iii is the region on the cut.

Further works are however necessary before the realization of high-precision nanoscale dimensions of DNA templated metallic wires. For example, Ag adhesion to the substrate can be improved by specific surface treatment such as plasma etching[13] or annealing[14]. Resolution can also be improved and manipulated with ease by using cutting or writing instruments with nanometer widths such as electron beam nanolithography or other techniques[15-17].

Conclusions

The technique suggested could provide control of high-precision wire printing using the DNA-templated circuits. Further optimizations of the AgNPs suspension concentrations, process temperature, control of suppression of the Marangoni effect and the effective residual DNA removal is also needed for fabrication of smoother and thinner dimensions of conductive wires. Ultimately, process improvements and optimization will lead to fabrication of enhanced flexibility and cost-effective conductive wires from metallic NPs templated to DNA molecules.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
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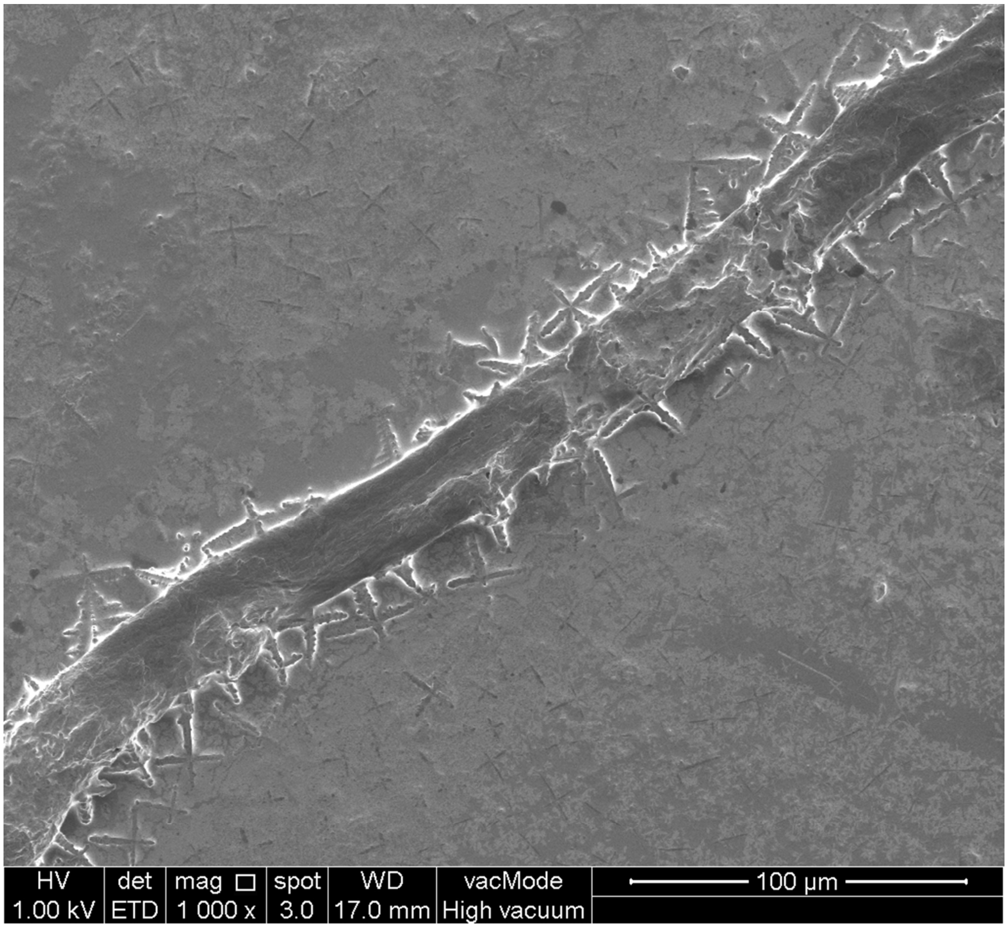

Re-arrangement of DNA molecules along micro-scratches assisted by capillary force.