Fabrication and electrical conductivity of suspended carbon nanofiber arrays

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ABSTRACT

We demonstrate a simple, efficient and novel self-assembly based method to fabricate arrays of suspended polymeric nanofibers of polyacrylonitrile and SU-8 negative photoresist by electrospinning on micro-fabricated posts of resorcinol–formaldehyde (RF) gel. The suspended electrospun nanofibers together with the RF gel posts were subsequently pyrolyzed in an inert atmosphere to yield large area monolithic structures of suspended glassy carbon nanofibers (CNF) integrated on RF gel derived carbon posts. The electrospun nanofibers self-assemble to connect the posts owing to a stronger electric field on their tips, obviating the need for positioning and integration of carbon nanowires with the underlying microstructures and paving the way for fabricating novel carbon based micro and nanoscale devices. The fabrication technique also allowed measurements of electrical conductivity of a single suspended CNF between carbon electrodes using I–V characteristics and comparison of the carbon nanowire conductivities for the CNF derived from different polymer precursors.

1.   Introduction

One-dimensional (1D) nanostructures, such as carbon nanotubes (CNT) and metal nanowires have received a lot of attention due to their unique features such as large surface to volume ratios and plasmonic and quantum confinement effects. Some of these 1D nanostructures also hold tremendous potential as interconnects in nano-devices [1–6]. As a result, fabrication of metallic, semiconducting and insulating 1D nanostructures continues to be an active area of exploration [1–12]. Among these, glassy carbon nanofibers (CNF) [13–17] with excellent mechanical, electronic, electrochemical, biocompatible and functional properties [18,19] find numerous applications ranging from active filters, catalysts, nanowire-sensors, to energy storage devices.

In view of a huge potential of 1D nanostructures in general, and of CNF in particular, efficient methods of micro/nano fabrication are required for a precise positioning and integration of carbon nanowires with underlying microstructured platforms, which is not easily achieved over large areas by the top-down methods. Further, measurements of single wire properties also require a fabrication technique which minimizes the problems of contact resistance and proper positioning between the electrodes. Thus, it is important to develop a precise control over the process of manufacturing suspended polymeric and carbon nanowires between two electrodes, e.g., carbon posts. A self-assembly based method guided by an applied field should thus be more suitable for fabricating large arrays of suspended nanofibers with the possibility of addressing these wires individually. As sus-

pended CNT are free of any intermolecular or surface interactions with the substrate, they may be useful for integration in electrical, mechanical, and electromechanical measurements [20] and in building blocks of micro/nanoelectromechanical systems (MEMS/NEMS), nano-sensors and other microfabricated devices.

There are some techniques reported for the fabrication of suspended polymeric and other nanowires [1–15,21], including in situ catalyzed growth of silicon [1], CNT wires [1–6,21] and direct drawing and peeling of polymer solutions [10–12]. Liu et al. [8] and Kameoka et al. [9] used a scanning electrospinning source with a rotating target to fabricate suspended nanowires of silicon dioxide and polyaniline. Suspended CNT were grown by chemical vapor deposition and have also been used as interconnects [2–7]. Positioning of an individual CNT or an array of CNT was done either by patterning metal catalysts [2–7] or dielectrophoresis [2–4]. Thus, positioning involves multiple steps such as e-beam lithography, dry-etching, wet-etching and selective metal deposition.

There have been few attempts using the top-down techniques for the fabrication of suspended glassy carbon microstructures between electrodes, such as by e-beam writing in SU-8 followed by pyrolysis [20]. A modified UV lithography has also been used to assemble suspended polymer strings between the tops of SU-8 posts [22,23]. However, these methods produce rather thick micrometer size wires with somewhat variable reproducibility in fabrication. There is however no previous study on fabrication of free hanging glassy carbon nanowires integrated with MEMS platforms and measurement of their electrical properties. Here, we present a technique that employs self-organized formation of polymeric nanowires of ~100 nm diameter to directly connect an underlying array of microstructure, thus allowing a seamless positioning and integration of nanostructures with a MEMS platform. Further, we demonstrate fabrication of both single suspended polymer and carbon nanofiber, as well as arrays of such free hanging nanofibers. The far field electrospinning method employed here allows the versatility of choosing from many different electro-spinnable polymers and a variety of electrospinning strategies that already exist for the control of electrospun fiber thickness. To illustrate the technique, we have chosen two different polymer precursors to make carbon wires through carbonization: PAN and an epoxy based negative photoresist, SU-8. PAN is one of the primarily used precursors for the synthesis of CNF, while SU-8 is a widely used deep UV, high aspect ratio photoresist. Upon pyrolysis SU-8 yields an amorphous carbon having very similar characteristics to that of glassy carbon [22,23]. The electrical conductivity of glassy carbon is tunable to a wide range depending on the polymer precursor and its pyrolysis temperature. Therefore, suspended glassy CNF derived by pyrolysis of polymers may provide more flexibility in applications ranging from interconnects to sensors. The use of SU-8 is also motivated by its compatibility with the widespread photolithographic techniques which allows for the facile integration of glassy carbon nanowires with underlying Carbon-MEMS and Bio-MEMS platforms. To the best of our knowledge, fabrication of suspended glassy CNF derived from SU-8 pyrolysis has not been reported. Finally, we have measured the electrical conductivity of individual suspended glassy CNF that will

have potential applications in development of suspended carbon wire nanosensors.

2. Experimental section

2.1. Fabrication of arrays of suspended CNF

Before describing the fabrication of suspended CNF, we briefly describe the electrospinning process. A schematic of electrospinning set up is shown in Fig. 1. During electrospinning, a high voltage (typically 5–30 kV) is applied to a syringe needle that acts as a positively charged electrode and a polymer solution dispensed through the needle is attracted to a negatively charged grounded collector electrode. Beyond a threshold voltage, an electrically charged jet of the polymer solution ejects, stretches under the action of electric field, dries by solvent evaporation and deposits on the grounded collector in the form of a fiber. In this study, we have electrospun two different polymers as precursors to CNF. A 8 wt.% solution of PAN (Sigma Aldrich, India) was prepared in N,N-dimethyl formamide (Rankem Chemicals, India). Another polymer used in this work is a commercially available negative photoresist, SU-8 2015 solution (MicroChem Corp., USA), which was used directly for electrospinning. We have recently reported the optimized conditions for synthesizing long and continuous SU-8 based CNF on surfaces [16,17]. Here, we describe the use of electrospinning to make self-organized suspended wires connecting a MEMS structure.

To fabricate an array of suspended polymeric fibers, we have electrospun these polymers onto specially designed three-dimensional (3D) collector electrodes (e.g., an array of posts on a collector substrate). These electrodes were made of an organic resorcinol–formaldehyde (RF) based xerogel by using the micro replica-molding technique [24]. It is to be noted that this organic RF xerogel is also a suitable precursor to carbon [24,25]. The details of the synthesis of RF xerogel are also reported elsewhere [24,25]. The far-field electrospinning conditions such as applied voltage, inter-electrode distance and the duration of spinning were optimized in order to produce suspended polymeric nanofibers positioned on top of the micro-electrodes forming an array.

To obtain suspended CNF arrays from the suspended polymer wire arrays, the PAN based suspended nanofiber array
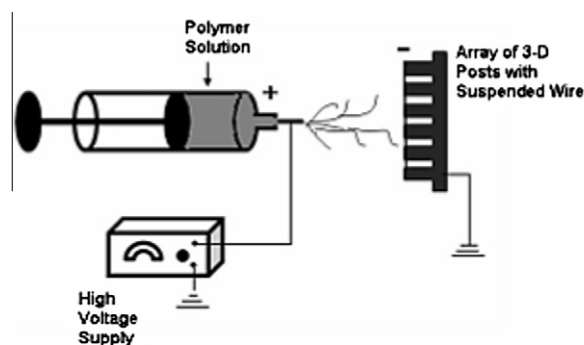

Fig. 1 – Schematic of electrospinning setup used for suspending nanofibers on a micro-patterned electrode.

was first thermally stabilized [26] at 250 °C in an oxygen atmosphere before pyrolysis. In the case of SU-8, the SU-8 nanofibers were crosslinked by UV exposure for 5 min prior to pyrolysis. Finally, the suspended polymeric nanofiber arrays were heated at 900 °C in an inert atmosphere (N_2 flow rate 0.2 lpm) to yield suspended CNF arrays.

A confocal micro-Raman microscope (CRM 200, WiTec, Germany with λ = 543 nm) was used to record the first order Raman spectra of the suspended CNF at a 2.0 cm^{-1} resolution. Raman spectra were excited from an argon ion laser at 15 mW under ambient conditions. This technique allowed the characterization of the types of bonds between the elements constituting the material.

### 2.2. Measurement of I–V characteristics

For measuring the electrical conductivity of a single CNF between two electrodes, two micro-pillars with square geometry were fabricated by the usual photolithography process [17] using a photopatternable mixture of SU-8 2015 and carbon black powder (Sigma Aldrich, India). The addition of latter was observed to make the positioning of nanofibers on the micro-posts more efficient. To suspend a single nanofiber, the polymer solution was electrospun for a short duration of 1 s. Upon UV crosslinking followed by pyrolysis, we obtained a single CNF suspended freely between the two carbon micropillars. Electrical contacts were made to the two carbon micro-pillars using sharp tip probes and I–V characteristics were measured using a Keithley 6517A digital electrometer.

3. Results and discussion

Fig. 2 illustrates the suspended carbon nanowire arrays over a relatively large area (few cm^2) as derived from two different polymer precursors on two different geometries of the collector electrode arrays. Fig. 2a and b shows the RF xerogel based 3D post arrays used for suspending the electrospun nanofibers. Two different geometries of the posts used for these arrays were cross-shaped (Fig. 2a) and cylindrical (Fig. 2b). It has recently been demonstrated that in the MEMS involving ionic transport, the cross-shaped design performs better than a cylindrical one because of the shorter diffusion lengths [27]. This design has also a higher second moment of inertia which is important for the high aspect ratio 3D posts to survive during pyrolysis.

Fig. 2c and d shows the SU-8 derived CNF suspended between the cross-shaped 3D carbon posts. Similarly, we were able to suspend SU-8 derived CNF between cylindrical RF gel derived carbon posts (Fig. 2e–g). The optimized electrospinning parameters for SU-8 were as follows: voltage: ∼20 kV, distance between source and collector: ∼10 cm, flow rate: 3 μl/min, which were consistent with an earlier study [16]. The average diameter of the suspended nanofibers as shown in Fig. 2g is 180 ± 24 nm.

Similarly, PAN derived CNF could also be organized to connect the carbon posts. An example of this is shown in Fig. 2h in which a PAN derived CNF is suspended between cross shaped 3D carbon posts. The optimized electrospinning parameters in this case were: voltage: 12 kV, distance between
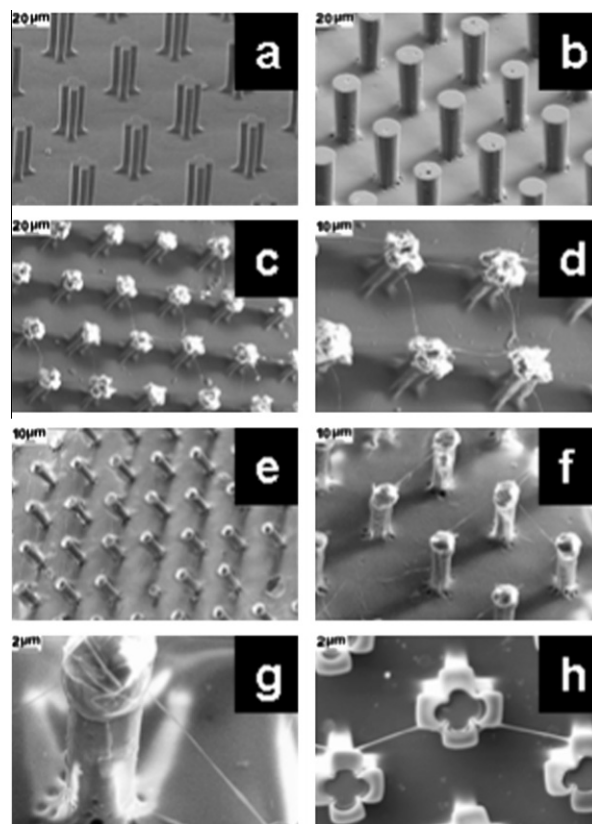
Fig. 2 – SEM images of RF gel derived 3D carbon posts: (a) cross-shaped geometry; (b) cylindrical geometry; (c) SEM image showing suspended SU-8 derived CNF on cross geometry 3D carbon posts; (d) higher magnification image of (c); (e) SEM image showing suspended SU-8 derived CNF on cylindrical geometry 3D carbon posts; (f) higher magnification image of (e); (g) higher magnification image of (f) showing an individual suspended CNF; (h) PAN derived suspended CNF on RF gel derived 3D cross geometry carbon posts.

source and collector: 10 cm, flow rate: 3 μl/min. The average diameter of PAN derived CNF under these conditions shown in Fig. 2h is 340 ± 19 nm.

It may be observed from Fig. 2d and g that different segments of a typical single electro-deposited nanofiber were attracted by the neighboring posts and were anchored on them. Interestingly, the excess length of the fiber frequently formed a coil on the post so that a taut suspended bridge like structure was formed between the posts. The selective positioning and integration of the nanowires with the posts may owe its genesis to higher charge accumulation and stronger electric field on the tips during the electrospinning process. The more detailed mechanistic steps for the directed wire formation are currently under investigation. It appears that charge accumulation and stronger field strengths on the protruding microelectrodes, adhesion between the electrospun polymer thread and the pillar, whipping and bending of jets in a non-uniform field, geometry of the nozzle and collector, charges in the polymer solution and viscoelastic properties of the polymer may all play some role. The last three factors are common

to all electrospinning processes, whereas the first three are specific to the situation of fiber deposition on a topographically patterned substrate that may engender localized field heterogeneities. It is important to note that the time for electrospinning should be very short in order to obtain suspended individual nanowires. In all the cases reported here, this time varied from 1 to 5 s. For larger electrospinning times, fiber deposition was copious and random with multiple connections between the posts and deposition in the intervening substrate-patches as shown in Supplementary data.

The method presented here for fabricating suspended glassy CNF array is simple, fast and reproducible. Based on the electrode design, the technique also allows addressing a single hanging nanofiber. With this approach, one can fabricate an array of suspended nanofibers with a large number of electro-spinnable polymers which makes this technique versatile.

Fig. 3 summarizes the conductivity measurements performed on individual hanging CNF. As described earlier in the experimental section, polymer fibers were electrospun between two measuring electrodes made by a photopatternable mixture of SU-8 and carbon black. Fig. 3a and b shows the SEM images of an individual SU-8 based CNF (average diameter 198 ± 11 nm) and PAN based CNF (average diameter 217 ± 14 nm), respectively, suspended between the electrodes. I–V characteristics as shown in Fig. 3c were measured using two probes contacting the electrode posts. The linear behavior of I–V curve in both cases implies an ohmic contact between the electrodes and the suspended CNF. This is facilitated by a close integration of the wire with its base during pyrolysis to produce a carbon monolith. The testing voltage ranged from −20 to 20 V, with step variations of 0.1 V. To ensure the repeatability of the results, the tests were repeated at least three times for a suspended nanofiber.

Table 1 summarizes the electrical properties obtained for suspended PAN derived and SU-8 derived CNF, respectively. The conductance was calculated by measuring the slope of linear I–V curves. From the Table 1, we observe that electrical conductivity of a PAN derived CNF was (1.30 ± 0.11) E 04 S/m. This value is consistent with what has been reported by Wang et al. ($\sim$1.70 E 04 S/m) [14]. The conductivity of the SU-8 derived CNF was calculated to be (1.84 ± 0.31) E 03 S/m, which is almost an order of magnitude less compared to that of PAN derived CNF. The bulk conductivity of SU-8 derived carbon film ($\sim$1.87 E 04 S/m) as reported in the literature [22,23] is about an order of magnitude higher than that of the nanofiber.

These results can be explained from a Raman spectrum analysis of SU-8 and PAN derived carbons as shown in Fig. 3d and e, respectively. After background subtraction, the Raman spectra for both SU-8 and PAN derived carbon were de-convoluted into two Gaussian peaks [28]. In case of SU-8 derived carbon, we observe two peaks centered around 1342 cm^{-1} (width 111.2 cm^{-1}) and 1596 cm^{-1} (width 109.6 cm^{-1}) corresponding to D- and G-band, respectively. For PAN derived carbon, D and G bands are observed at 1357 cm^{-1} (width 91.2 cm^{-1}) and 1576 cm^{-1} (width 108.2 cm^{-1}). These D- and G-bands are associated with the vibrations of sp^2 carbon atoms with dangling bonds. The peak intensity ratio (defined as I_D/I_G) corresponds to the disorder present in the carbon fiber [29].
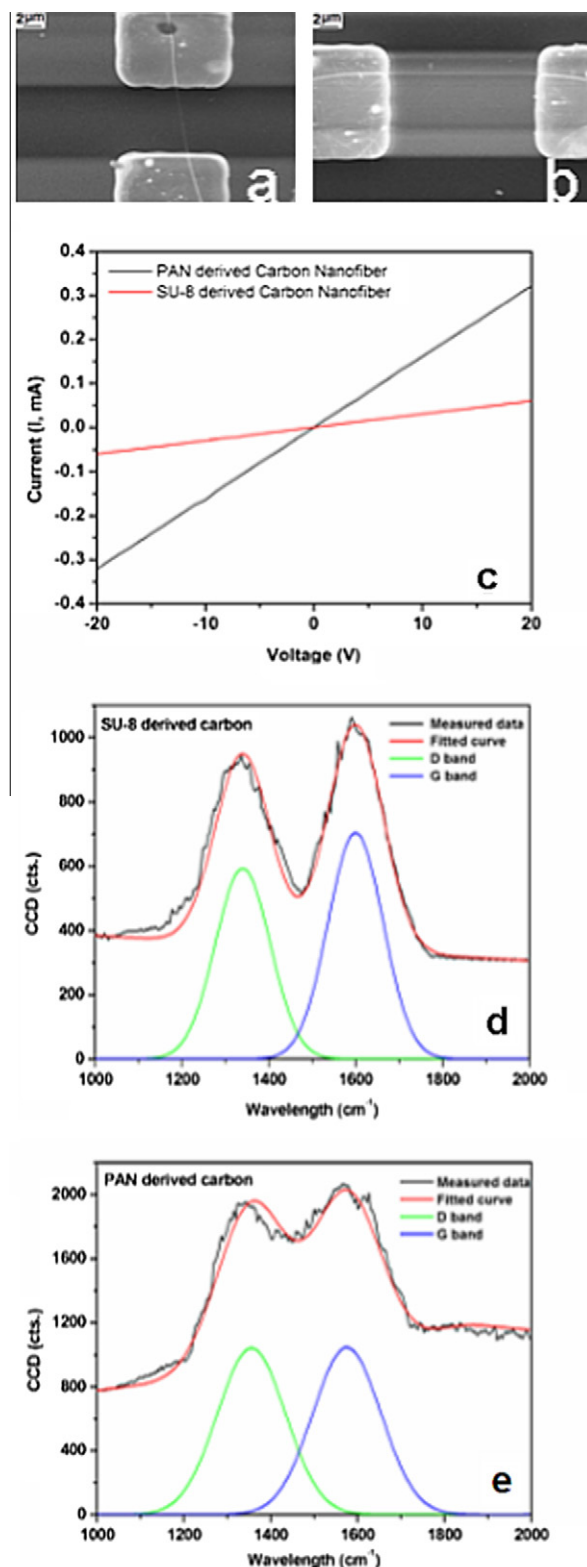
Fig. 3 – SEM images of single suspended nanofiber between two electrodes (a) SU-8 derived; (b) PAN derived; (c) I–V curve for single suspended CNF for both cases; Raman spectra of (d) SU-8 derived carbon; (e) PAN derived carbon, respectively.

This ratio (I_D/I_G) was found to be 0.98 and 0.74 for SU-8 and PAN derived carbon fibers, respectively. The lower the value

Table 1 – Electrical properties of suspended single CNF as measured by I–V curve.

Samples	Slope of I–V curve (conductance) (S)	Length of the fiber (l) (μm)	Average diameter of the fiber (d) (nm)	Cross-sectional area of the fiber (A) (m^2)	Conductivity (k) (S/m)	Resistivity (ρ) (ohm m)
SU-8 derived carbon nanofiber	2.99 E-06	19.0	198	3.08 E-14	1.84 E 03	5.42 E-04
PAN derived carbon nanofiber	1.60 E-05	30.1	217	3.70 E-14	1.30 E 04	7.68 E-05

of I_D/I_G, the higher the crystallinity or the lower the amorphous nature of carbon is. In other words, PAN derived CNF is more graphitic in nature as compared to SU-8 derived CNF and thus exhibits higher conductivity. This is further supported by observing the intensity of Raman scattered light. Since Raman spectrum is more sensitive to sp^2 hybridization as compared to sp^3 hybridization [28], larger intensity of Raman scattered light in case of PAN derived carbon may be attributed to more graphitic nature of it. As is shown below, electrical conductivity of the more ordered carbon nanofiber derived from PAN is indeed higher than the SU-8 derived carbon fiber.

The knowledge about the electrical conductivity of suspended CNF derived from different polymer precursors gives us another means of controlling the resulting suspended carbon nanowires and this is vital for various applications. The versatility of this method not only makes it attractive tool for developing suspended nanowire array based electronic devices such as switches, memory elements but also for fabricating single nanowire based sensing devices. These CNF may, for example, be functionalized to interact with specific biomolecules. In all these cases conductivity, wire thickness, mechanical strength, etc. will be different.

4. Conclusions

A simple yet versatile method is presented for the fabrication of integrated polymeric and glassy carbon MEMS/NEMS platforms by field induced self-assembly of hanging nanowires onto the tips of the underlying MEMS structures. The method is highly reproducible and portable across a variety of polymers that can be electrospun. This includes a large number of bio-polymers, conducting polymers, ceramics, carbon precursors, etc. with a wide spectrum of functionalities. Additionally, the flexibility of interfacing suspended nanowire with microfabricated posts of various size and shape is also demonstrated.

5. Supplementary data

For larger electrospinning time, SEM image showing the fiber deposition is provided as supplementary data.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.12.058.

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