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REPORT

Transferring vertically aligned carbon nanotubes onto a polymeric substrate using a hot embossing technique for microfluidic applications

A. Mathur, S. S. Roy* and J. A. McLaughlin*

Nanotechnology and Integrated Bio-Engineering Centre, School of Electrical and Mechanical Engineering, University of Ulster, Newtownabbey BT37 0QB, UK

We explored the hot embossing method for transferring vertically aligned carbon nanotubes (CNTs) into microfluidic channels, fabricated on poly-methyl-methacrylate (PMMA). Patterned and unpatterned CNTs were synthesized by microwave plasma-enhanced chemical vapour deposition on silicon to work as a stamp. For hot embossing, 115°C and 1 kN force for 2 min were found to be the most suitable parameters for the complete transfer of aligned CNTs on the PMMA microchannel. Raman and SEM studies were used to analyse the microstructure of CNTs before and after hot embossing. The PMMA microparticles with dimensions (approx. 10 μm in diameter) similar to red blood cells were successfully filtered using laminar flow through these microfluidic channels. Finally, a microfluidic-based point-of-care device for blood filtration and detection of bio-molecules is drawn schematically.

1. INTRODUCTION

Motivated by the remarkable properties of carbon nanotubes (CNTs), researchers have been immensely interested in their processing, integration and applications. The incorporation of CNTs onto polymeric substrates provides a wide range of applications in various areas such as microfluidics, flexible microdevices, field emission and micro/nanoelectronics, etc. The main obstacles to the implementation of CNT-based

Authors for correspondence (s.sinha-roy@.ulster.ac.uk; jad.mclaughlin@ulster.ac.uk).

microfluidic devices lie in the proper integration of CNT arrays with polymer platforms. The CNTs in the microfluidic channel can be incorporated in two ways: firstly, synthesizing CNTs in the microfluidic channel, and, secondly, transferring the as-grown CNTs to the microfluidic channel by any novel technique. Owing to the low glass-transition temperatures of most of the polymers, it is extremely difficult to synthesize high-quality CNTs directly onto them. On the other hand, various techniques like solution-based processing, soft lithography, casting into PDMS and hot embossing have been developed in recent years for incorporating CNTs onto polymers (Jacobs & Whitesides 2001; Barry *et al.* 2003; Blanchet & Rogers 2003; Meitl *et al.* 2004; Sun & Rogers 2004; Allen *et al.* 2006). Among these techniques, hot embossing has demonstrated the ability to transfer CNTs onto polymers with critical dimensions down to 10 μm (Allen *et al.* 2006; Sunden *et al.* 2006).

The CNTs in the microfluidic devices can be used as micro/nanoparticle filtering elements and/or as sensing material (An & Simon 2006). The CNTs, with their unique properties, dimensions and a huge surface-to-volume ratio, have great potential as a filtration, separation and concentration medium for various chromatographic applications. A common approach for microfluidic filtering has been the creation of polymer pillar structures or flow restrictions (He *et al.* 1999; Andersson *et al.* 2001). The limitation of these methods is the resolution of the patterning technique employed. Fabrication of submicron patterned structures using e-beam lithography would be expensive. Recently, there have been some interesting reports (Jeon *et al.* 2004, 2005) on the fabrication of a three-dimensional nanostructure, as small as 50 nm, using the optical technique, and those nanoscale channels could be very useful in various applications in the microfluidic system. Patterning CNT arrays in specific parts of a microfabricated device allows easy submicron particle filtration and eliminates the need for nanolithography. A comprehensive study on transferring CNTs onto polymer and their application in biological particle filtering has not yet been reported.

In this paper, we present a hot embossing method for transferring vertically aligned CNT arrays onto poly-methyl-methacrylate (PMMA). We also demonstrate that the CNTs can be used as blood particle filtering elements. Finally, we propose the application of these CNT arrays as a filter in a point-of-care (PoC) device, using electrical impedance spectroscopy (EIS) transducers.

2. EXPERIMENTAL DETAILS

2.1. Growth of carbon nanotubes on silicon substrate and transferring them on poly-methyl-methacrylate substrate

The CNTs were produced using a microwave plasma-enhanced chemical vapour deposition (MPECVD) system, which is described in detail elsewhere (Chhowalla *et al.* 2001). The maskless UV lithographic technique was employed for the production of the microstructures on a silicon surface. These microstructures were fabricated using the metal lift-off method

on a silicon wafer. A thin layer of cobalt (approx. 2 nm) was used as a catalyst for CNT growth. These substrates were then transferred to the MPCVD chamber for nanotube growth (Mathur *et al.* 2009*a*,*b*). Scanning electron microscopy of these nanotubes revealed that they are aligned vertically on the top of the surface. Micro-Raman studies were also performed on the samples before and after hot embossing. Three spectra were recorded from three different spots on each sample. Raman parameters were evaluated from the average of three values obtained from spots. Errors in the Raman fitting parameters appear to be mainly due to the non-uniformity of spots and base-line correction, and a suitable background function can minimize the error. We should mention that, in our experiments, the error in the Raman fitting parameters was negligible and did not have any influence on the trends of Raman parameters before and after hot embossing. The spectrometer was calibrated with a silicon substrate, and the sharp first-order Raman shifts of silicon were accurate to $\pm 1 \text{ cm}^{-1}$.

The nanotubes grown on Si work as a stamp and are placed over the top of a PMMA sheet, which is then heated above its glass transition temperature. Experiments were carried out in the temperature range $110-120°C$ and pressure range $0.5-2$ kN to optimize the effect of temperature and pressure. We noticed that the temperature of $115°C$ and pressure of 1 kN was the most reliable for reproducible and non-destructive transfer of CNTs onto the polymer substrate. The vertically aligned patterns of CNTs grown on Si (acting as a master template) were placed in contact with a smooth 500 μm thick PMMA substrate, and then heated to $115°C$, and embossed into the polymer at a pressure of 1 kN. After cooling to room temperature, the load was released and the master removed from the substrate. Nearly all of the CNTs were transferred, and exceptional pattern replication was achieved. The total cycle time was between 20 and 30 min.

2.2. Construction of the filtering system using the above carbon nanotubes on poly-methyl-methacrylate

The microfluidic channels with a depth of approximately $30-50 \text{ μm}$ were fabricated on a separate PMMA substrate using the hot embossing method. The length and width of the channel were 15 and 5 mm, respectively. The vertically aligned CNTs (VACNTs) on PMMA were bonded with the above PMMA microfluidic channel with appropriate inlets and outlets (Mathur *et al.* 2009*a*,*b*). In this case, the direct bonding technique between PMMA sheets was employed. The vertically aligned patterns of CNTs grown on PMMA were placed in contact with a PMMA substrate (containing the microchannel), and then heated to $95°C$, and embossed into the polymer at a pressure of 5 kN. For any devices, channel depths were chosen slightly higher (approx. 2 μm) than the CNT height on PMMA. This allowed us leakage-free direct bonding between PMMA substrates. Finally, the filtering system was tested with 10 μm PMMA

particles in DI water with red dye (to simulate blood conditions) for flow characterizations.

3. RESULTS AND DISCUSSION

Various, vertically aligned CNTs and patterned CNTs were grown on a Si substrate using MPCVD and successfully integrated onto PMMA without affecting the nanotube structure and alignment using the contact transfer method (Zhu *et al.* 2008). Two representative images obtained from SEM are shown in figure 1. Figure 1*a* shows the CNTs on Si (i.e. before hot embossing) with the CNT pillars of 100 μm width and 100 μm spacing. The height of the CNT pillars was approximately 50 μm. Although figure 1*b* shows CNTs on PMMA (i.e. after hot embossing), the vertical alignment was almost intact with the same dimensions as the CNTs on Si, and the height of the CNTs on PMMA was nearly 40 μm, suggesting that part of the CNTs was buried under the PMMA. Figure 1*b* also confirmed the integrability of CNT films with PMMA.

Figure 1*c* shows the micro-Raman spectra before and after hot embossing. Raman spectra showed that the nanotubes were highly graphitic and SEM showed that the CNTs were predominately multi-walled. Raman spectra of the CNTs were compared before and after the transfer. The peaks at approximately 1350 and approximately 1572 cm^{-1} can be seen for both samples, which correspond to D and G bands in CNTs. The G peak corresponds to the tangential stretching (E_{2g}) mode of highly oriented pyrolytic graphite, which indicates the presence of crystalline graphitic carbon in the CNTs. The origin of the D peak has been explained as disorder-induced features due to the defect and finite particle size effect. The ratio of the intensity of the D peak (I_D) to the intensity of the G peak (I_G) is a measure of the amount of disorder in the CNTs. The I_D/I_G ratios of the CNTs in this experiment are all smaller than 1, which suggests less defect content in the CNTs (Wilhelm *et al.* 1998). The I_D/I_G ratio on the transferred CNTs was nearly similar to that of the as-grown structures, indicating that the crystalline quality of CNTs was maintained after the transfer. We observed an increase in the D peak width after hot embossing. After the hot embossing process, Raman spectra were taken from the base ends of the tube. The sample edge can always be considered as a defect. The hot embossing process may introduce edge-plane-like defects on the tube ends. The increase in the D peak width and I_D/I_G ratio was due to the introduction of the edge plane defect and/or disorder created by hot embossing (Mathur *et al.* 2009*a*,*b*; Sanchez *et al.* 2009). The G peak position moved to 1579 from 1577 cm^{-1} after hot embossing. The shape of the G line and the dispersion of CNTs depend on various factors such as film thickness, deposition condition, substrate stress, laser wavelength and to some extent on instrumental precision. In the literature, the G band shifts linearly to a higher wavenumber with the increase in stress in carbon thin films and CNT/polymer composites. In our study, the depth of the laser was around 5 μm; so we have not probed CNTs buried under the polymer. We believe
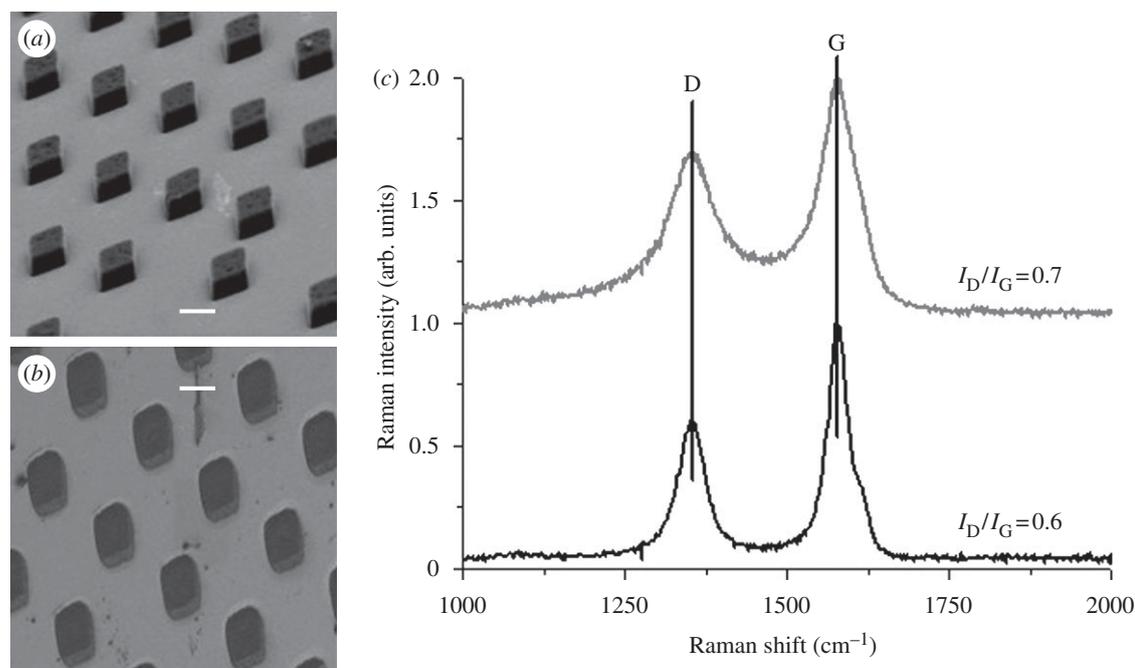
Figure 1. SEM images of CNTs: (*a*) before and (*b*) after hot embossing (SEM scale bar showing 100 μm). (*c*) A comparative Raman spectrum of CNTs before (black line) and after (grey line) hot embossing.

that the hot embossing process introduces a slight strain in the nanotubes as well as creates edge-plane-like defects, which in turn changes the G peak position.

The fabrication of the filtering system is discussed in detail in the experimental section. In order to demonstrate the filtering capability of nanotubes, we used a mixture of PMMA spheres of 10 μm diameter (in DI water with red dye) that were passed through the channel using capillary flow. The reason for choosing 10 μm particles was that the size of red blood cells (RBCs) and white blood cells in real blood is also in this region (Crowley & Pizziconi 2005). Figure 2 shows the PMMA beads concentrated at the CNT filter. The nanotube patches were a few tens of microns long and sufficient for filtering, and there were a number of PMMA spheres clearly visible before the CNT membrane, whereas only one or two spheres (figure 2, inside red circle) were visible after passing through the CNT membrane. Ideally, we expected no particles at the outlet; the resulting one or two particles at the outlet may have escaped through any structural defect in the sidewall/lid. The filling time (meniscus displacement time from inlet to outlet) of the fluid flow inside the channel was measured as 16 s, whereas without CNTs it was approximately 5 s. This could be the effect of surface energies as the CNTs are highly hydrophobic. The water contact angle of CNTs was approximately 110°, whereas that of PMMA was approximately 67°, measured using sessile drop measurements. Studies are currently underway to quantitatively characterize the hydrodynamic resistance of the filters as well as to determine the minimum size of the particle that can be filtered in our devices. Acid solution can be used to create three-dimensional nanostructures on the surfaces of the aligned multi-wall carbon nanotubes (MWCNTs) (Correa-Duarte *et al.* 2004). However, at this stage, we are not totally sure
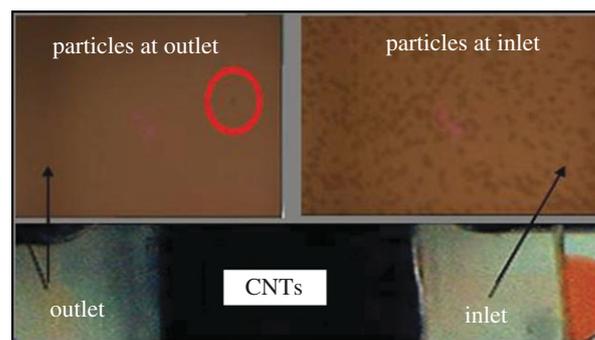

Figure 2. An experimental demonstration of CNTs as a filter in the microfluidic channel. Top two optical microscopy images with a magnification ×10 clearly revealed microparticle filtration.

about the dyed water/microparticle interaction with the side wall of the nanotubes. From the fundamental point of view, it will be interesting to study the surface chemistry and the nature of particle trapping by the tube.

The passive capillary flow technique was exploited in the filtering system. The capillary filling process was based on momentum conservation. In the passive capillary filling process, the overhead pressure is zero. It is mainly a surface-tension-driven filling process in which momentum change is balanced by the surface tension force and wall viscous force (Saha *et al.* 2009). Surface tension of a liquid meniscus provides sufficient pressure to push water into the channel. It is difficult to estimate the capillary pressure for a general channel shape with any width and height. However, the capillary pressure (P) at the entrance can be roughly estimated from the relation $P = 2\sigma \cos\theta \ (1/h + 1/w)$, where w is the width of the channel, h its height, σ is the surface tension of water and θ is the contact angle. In our studies,
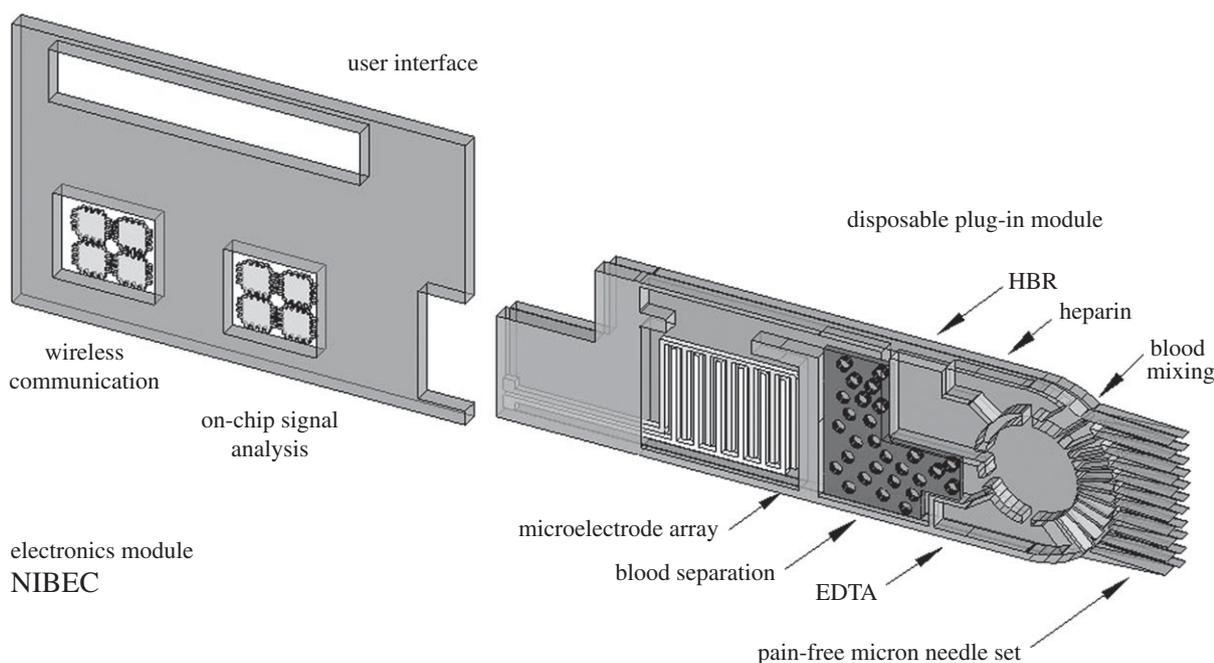
Figure 3. A schematic drawing of the proposed PoC device.

as the fluid and substrate were fixed, channel geometry has a huge influence on capillary pressure. In the present study, the flow rate was higher at the entrance and slowed down owing to the viscous effect. The flow rate can be controlled by the channel geometries, its surface energy and the liquid used.

The system (figure 2) was filled by adding an approximately 5 µl droplet to the channel inlet, although 2 µl was enough to fill the device. In our study, the particle concentrations were varied from 60 to 180 000 counts μl^{-1}. In this range, no clogging was observed. The particle filtration efficiency in the system was always greater than 99 per cent. To date, we have tested the filtering system to its maximum for six weeks and found it to be working well. In future, we will address the long-term durability of the filtering system. In particular, temperatures above 90°C should be avoided for PMMA-based devices. The filter has been designed keeping in mind that it will be used for blood filtration afterwards as a part of the project (figure 3); therefore, we consider this device to be suitable for single use or to be disposable.

There are huge challenges in microfluidic chip technology in the development of new generation sensor devices by incorporating nano- and microelectronic materials into a single chip-sized substrate. We are also engaged in this challenging research and are hoping to develop a novel CNT-based microfluidic device for blood filtration and detection of bio-molecules for a lab-on-a-chip application. Figure 3 shows the schematic of the proposed PoC device with gold inter-digitated electrodes and other electronics. The new device consists of microlitre sampling, integrated microfluidic and electrochemical sensing systems, with wireless communications that can be used in new and evolving multi-frequency-based EIS transducers. Moreover, label-free sensing offers the possibility of detecting analytes with a high sensitivity and molecular

selectivity, in parallel, rapidly and at a low cost (Linder 2007).

Integration of the EIS sensor technology with suitable microfluidics will ensure good signal detection using only micro- or pico-litre amounts of a patient's blood sample. The nanostructured fluidics system must filter out RBCs, preventing adhesion and distortion of the detection system. *In situ* fine filtering of the serum will be obtained via micro- and nanoscale pillars with optimized geometry and surface chemistry (figure 3). Thermoplastic imprinting/bonding will allow the definition of the capillary features in bonded devices, and the use of low-cost printing/fabrication processes will enable the manufacture of inexpensive, disposable sensor arrays (Mathur *et al.* 2009*a*,*b*). Remote processing and 'smart analysis' will be realized with the integration of telemetry, microprocessors and embedded software, allowing the lab-on-a-chip platform to achieve the ultimate goal of multi-analyte blood monitoring, enabling continuous and remote patient monitoring (figure 3).

4. CONCLUSIONS

In this paper, we have reported a simple process for the transfer of CNTs, in any geometry and size, from the original grown surface to PMMA sheets using the hot embossing technique. This technique is non-destructive and could easily be replicated on a large area. The SEM and Raman studies showed excellent physical/mechanical bonding of the CNTs on the polymeric substrate. The laminar flows through CNT-based microchannels were highly controllable and reproducible. The CNTs were very effective for microparticle filtration. With the optimization of the transfer process (CNTs to microfluidic chip) and real blood flow behaviour studies, it will be possible to achieve a microfluidic platform for

filtration and detection of blood analytes. Here, we outlined a PoC device to provide a true PoC monitoring system to allow a blood sample to be rapidly analysed for a range of applications.

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