

# Electrospray deposition of carbon nanotubes in vacuum

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Here we report on a novel and effective technique for the deposition of carbon nanotubes onto surfaces in vacuum directly from a liquid suspension. The technique, based on in-vacuum electro-spray ionisation, has the potential to bridge the gap between high resolution techniques requiring ultra-high vacuum conditions, and non-volatile molecules and nanostructures such as carbon nanotubes. Atomic force microscopy of double-walled nanotubes deposited onto silicon surfaces in vacuum show individual nanotubes and low density bundles.

## I. INTRODUCTION

Heralded amongst the most promising building blocks for nanoscale devices (1) carbon nanotubes exhibit extraordinarily useful electronic and structural properties (2; 3). Gaining an understanding of nanotubes at their most fundamental level requires an ability to probe their electronic densities of states and map their molecular orbitals. For smaller fullerenes such as  $C_{60}$ , photoemission and scanning tunnelling microscopy continue to provide unprecedented insights (4–6), but the crucial obstacle in extrapolating these techniques to carbon nanotubes is that they cannot be deposited by sublimation in vacuum. In an important step towards the in-situ deposition of non-volatile molecules and nanostructures, we have developed a novel and effective technique for the deposition of carbon nanotubes onto surfaces in vacuum directly from a liquid suspension. The advantage this approach is that it opens up the possibility of preparing well-defined substrates under UHV conditions, without the need for subsequent exposure to the ambient conditions of ex-situ deposition techniques commonly used for carbon nanotubes and other non-volatile nanostructures.

Deposition from liquids in ambient conditions forms the basis for virtually all methods currently used to disperse nanotubes onto surfaces. In their non-functionalised state, however, carbon nanotubes have remarkably low solubility and hence only suspensions, rather than solutions, are formed. Fortunately, due to their relatively inert nature, a myriad of solvents can be used, but rigorous sonication is still needed in order to suspend the nanotubes individually. Even then, strong van der Waals interactions between carbon nanotubes induce rapid re-aggregation into bundles, and this causes the suspensions to be unstable in time. Functionalisation (7), or the use of surfactants, overcomes this problem but also chemically alters the nanotubes. Therefore, concentrating on deposition methods that can encompass both pristine and functionalised nanotubes is highly desirable. The most common methods currently employed

include spin-casting, drop-drying and (quasi)-Langmuir-Blodgett (8) methods, generating fairly random films. Alignment during deposition can be further aided by the use of electric (9) or magnetic (10) fields, or gas flow techniques (11). As stated above, a common feature of current deposition techniques is that they are all performed in air. This poses a considerable frustration for the study of carbon nanotubes on surfaces because while we can routinely prepare well-characterised single crystal substrates under UHV conditions, these would not survive subsequent exposure to ambient conditions. Since liquids are generally not compatible with vacuum because of their extremely high vapour pressures, in-situ deposition of carbon nanotubes remains a significant experimental hurdle to overcome in applying ultra-high vacuum analysis techniques to these systems. Electrospray ionisation, a method used extensively in mass spectrometry to get fragile biomolecules into the gas-phase (12), offers one of the most promising solutions. Here we show that double-walled carbon nanotubes can be deposited on a surface in vacuum using a relatively simple and novel implementation of vacuum electrospray. The resulting surfaces are characterised using atomic force microscopy (AFM) to show the degree of dispersion and carbon nanotube morphology.

## II. EXPERIMENTAL METHOD

Electrospray essentially involves drawing a liquid through a highly charged capillary such that the strength of the electric field at the tip overcomes the surface tension of the liquid resulting in a jet of highly charged liquid droplets. These droplets quickly undergo successive Coulomb fission events and solvent evaporation to produce progressively smaller droplets and in some cases ionized single molecules. The process is generally carried out at ambient pressure with subsequent extraction of the charged plume into vacuum. This approach has indeed recently been extended to the deposition of molecules including conjugated polymers (13), clusters and biomolecules (14) in vacuum. However, the very low flow rates in electrospray, on the order nanolitres per minute, enable the electrospray event to take place already in

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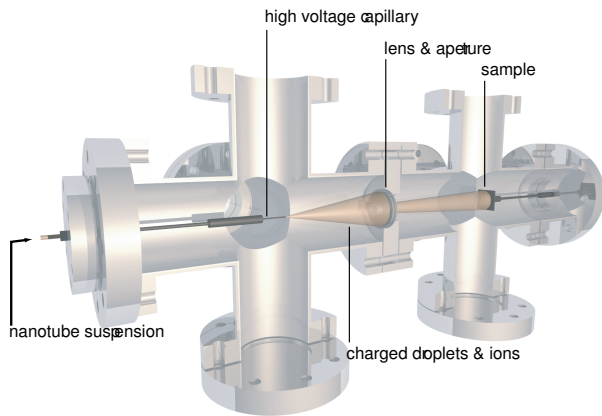


FIG. 1 Schematic representation of the electro spray deposition system. The nanotube suspension in ethanol is fed through a narrow liquid feedthrough into a  $20\ \mu\text{m}$  diameter high voltage capillary. The resulting electro spray plume of charged droplets and ions is extracted through a small lens aperture into the differentially pumped deposition chamber where they impinge on a sample surface.

a region of high vacuum (15) as illustrated in figure 1. This procedure has advantages not only in terms of the overall gas-load and cleanliness of the system, but also in the way the droplets of suspension behave in vacuum. With a significantly increased mean free path, the emitted droplets undergo fewer collisions with gas molecules and typically hit the sample surface as nanoscale liquid droplets. Impact desolvation has recently been successfully used in mass-spectrometry (16), where despite the droplets travelling at several kilometres per second, the impact energy is largely dissipated by the surrounding droplet providing a soft-landing for the deposited molecules.

The electro spray and deposition chambers are both pumped continuously by  $70\ \text{Ls}^{-1}$  turbomolecular pumps. The differential pumping achieved by the 6 mm lens aperture which connects the two chambers results in a base pressure in the deposition chamber in the  $10^{-7}$  mbar range. The system can therefore be coupled to an ultra-high vacuum system such as a scanning tunnelling microscope (STM), a photoelectron spectrometer, or the end-station of a synchrotron beamline. Moreover, many samples of interest, such as oxides can be transferred to this pressure without undergoing excessive contamination or reconstruction. During electro spray deposition the pressure increases to around  $10^{-4}$  mbar in the current configuration, with the additional pressure being due solely to the high vapour pressure of the liquid ethanol in which the carbon nanotubes are suspended. The pressure was measured using an ion gauge situated approximately 10 cm below the sample.

The electro spray emitter, a  $20\ \mu\text{m}$  internal diameter stainless steel capillary (Proxeon) is held at a potential of  $+2.6\ \text{kV}$ . The emitter is connected to a pressurised liq-

uid reservoir through a custom-built liquid feedthrough and  $160\ \mu\text{m}$  internal diameter PEEK capillary tubing on both the vacuum and air sides. A typical flow rate of  $500\ \text{nLmin}^{-1}$  is achieved with a backing pressure of 2 bar. CVD-grown double-walled nanotubes (Nanocyl), characterized as having lengths ranging from  $1\text{-}10\ \mu\text{m}$  and an average diameter of  $3.5\ \text{nm}$ , were suspended in pure ethanol by sonication without further purification. A  $2\ \mu\text{m}$  frit filter (Valco) at the inlet prevents large bundles of nanotubes, long tubes and particulates from entering the capillary. The liquid reservoir can be removed from the inlet for further sonication without ending the deposition or venting the system. This allows the surface coverage to be built up, in principle, to any coverage. Since the droplets and nanotubes impinging on the surface are charged by the electro spray process, the deposition current can be measured on the sample and, at least qualitatively, correlated to the amount of material deposited. Three 15 minute deposition periods at an average target current of  $\sim 1\ \text{nA}$  were used to prepare the low surface coverages of carbon nanotubes presented here.

### III. RESULTS

Isolated nanotubes are observed on the surface following the deposition as shown in Figure 2 (b and c). The lengths of isolated nanotubes on the surface ranged from  $0.2$  to  $1.8\ \mu\text{m}$ , with heights (corresponding to their diameter) of  $1.5$  to  $3.5\ \text{nm}$  consistent with the diameters specified for the double-walled nanotubes used. The absence of longer nanotubes and large bundles is for the most part due to the  $2\ \mu\text{m}$  inlet filter. However, this further suggests that either the carbon nanotubes do not aggregate significantly in the inlet capillary of the system or that the electro spray process is able, at least to some degree, to re-segregate bundles that have formed inside the capillary. It is, of course, not possible to distinguish which of these processes contributes most. It is also worth noting that within the observed low-density bundles there is a degree of separation between the nanotubes which might suggest that the impact of the charged bundle-containing droplets, (or conversely desolvated bundles) with the surface plays a role in further separating out the nanotubes to some degree.

While there are a large number of solvents that can be used for electro spray ionisation under ambient conditions, there are relatively few suitable for in-vacuum electro spray. We found that ethanol is the most suitable for the electro spray deposition of carbon nanotubes in terms of the quality of suspension and the stability of the spray in vacuum. A mixture of methanol and water (75:25 ratio) is also highly suitable for electro spray in vacuum in terms of spray stability, however this did not produce such a high quality suspension of nanotubes, resulting in poor transfer efficiency of nanotubes to the electro spray emitter. Other solvents, such as toluene were found to freeze at the emitter tip in vacuum and are therefore not

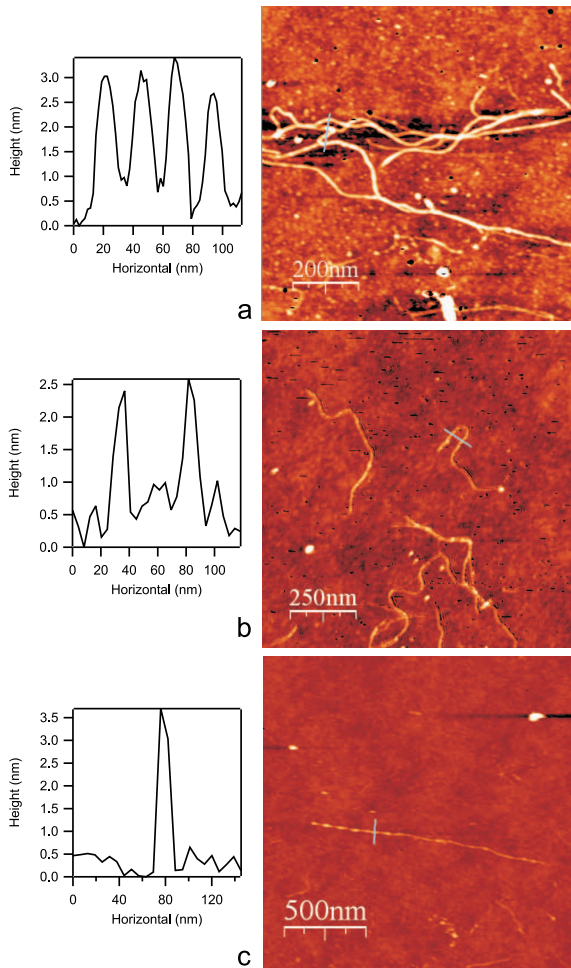


FIG. 2 AFM images of double-walled carbon nanotubes deposited onto the native oxide of Si(111) at a pressure of  $10^{-4}$  mbar from an ethanol suspension. Low density bundles (a), and isolated nanotubes ranging from 0.2 and 1.8  $\mu\text{m}$  in length are observed (b and c). Height traces suggest diameters between 2.5 and 3.5 nm for the indicated cross-sections.

suitable for this technique.

#### IV. CONCLUSIONS

We have demonstrated the use of vacuum electrospray for the deposition of carbon nanotubes on surfaces under high vacuum conditions. The resulting depositions contain a substantial number of individual isolated nanotubes which will allow high resolution STM and scanning tunnelling spectroscopy (STS) studies of individual nanotubes to be carried out on well-defined, low contamination surfaces in UHV. The portability of the system will enable in-situ deposition of carbon nanotubes at synchrotron facilities for soft-x-ray investigations. As we begin to synthesise more complex nanotube-related molecular architectures such as 'peapods' or filled nanotubes (17), the desire for clean deposition without the use of chemical functionalization is inevitable. In these

cases vacuum electrospray will play a key role in transferring these molecular architectures to well-defined surfaces for UHV characterization. We are currently exploring ways to extend the technique to promote alignment of the deposited nanotubes on the substrate surface which will enable measurements of their directional electronic and magnetic properties with electron and x-ray spectroscopic techniques.

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