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Horizontal Carbon Nanotube Alignment

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Abstract

The production of horizontally aligned carbon nanotubes offers a rapid means of realizing a myriad of self-assembled near-atom-scale technologies - from novel photonic crystals, to nanoscale transistors. The ability to reproducibly align anisotropic nanostructures has huge technological value. Here we review the present state-of-the-art in horizontal carbon nanotube alignment. For both *in-* and *ex-situ* approaches, we quantitatively assess the reported linear packing densities alongside the degree of alignment possible for each of these core methodologies.

Keywords - carbon nanotubes, horizontal alignment, *in-situ*, *ex-situ*, solid-state extrusion, electric field, magnetic field, gas flow

I. INTRODUCTION

Carbon nanotubes (CNTs) have proven potential in a wide range of mechanical, optical and electrical devices whose function is often predicated on the ability to align the nanotubes. Indeed, the capacity to align, *en masse*, via extremely highly parallelised processes has resulted in the demonstration of a variety of unique devices whose function is dramatically improved relative to their unaligned counterparts. CNT-based optical polarizing media have shown a clear correlation in the magnitude of the polarization selective absorption with the degree of alignment, the typical failure strain in aligned CNT films has been improved by up to an order of magnitude following CNT alignment¹, and thin film transistors based on aligned single-walled CNTs show mobilities up to 40 times higher than randomly orientated devices^{2,3}. With the continued maturity of carbon nanotube growth and deposition techniques, an extensive variety of horizontal *in-situ* and *ex-situ* alignment techniques have been developed, including, most commonly; roll, scratch, density and field alignment. The ability to rationally synthesis truly self-assembled nanoscale channels, novel optical devices and next generation integrated circuit interconnects has never been closer.

CNTs can be aligned (**Figure 1**) via; (i) *ex-situ*, also termed post-synthesis, alignment, where external forces such as electric fields (i.e. dielectrophoresis)^{4,5} orientate the nanotubes once dispersed onto a substrate, often by means of a liquid medium; or via (ii) aligned synthesis (*in-situ*) where the aligning fields are imposed during nanotube synthesis. Herein we provide a review and comparative meta-analysis of these various alignment techniques.

II. EX-SITU ALIGNMENT

A number of *ex-situ*, or post-synthesis alignment techniques have been developed to mediate *en masse* parallel bulk alignment, though these *ex-situ* techniques often experience significant inter-tube interactions which often reduces the degree of alignment. Vertically aligned nanotube forests can be compressed, rolled and sheared⁶; though often only approximate directionality is achieved. Such techniques are largely inaccurate and suffer from poor reproducibility. A wide variety of *ex-situ* shearing techniques have been developed; from loading at a predetermined angle, to stretching and compressing vertically aligned CNT forests. This technique shows some of the highest packing densities recorded (at the thin film surface at least). Bulk assessment remains challenging, though alignment in this technique is dependent on the angle of shear for the pressing technique and is strongly dependent on the user. When compressed from a fixed axis of rotation, sometimes misalignment is introduced, however if the press is moved translationally forward as it rotates the alignment can be dramatically improved.

Nano-manipulation is another increasingly common method, though the processing is serial and requires time-consuming electron microscopy techniques⁷. Spin and drop casting of nanotube suspensions have shown moderate success^{8,9}. Nevertheless, despite the nanotubes in-plane alignment they have little or no linear directionality, which is to say that there is no controllable way to define the mean azimuth and that they are merely randomly orientated within the plane. Wei *et al.*¹⁰ demonstrated the use of dielectrophoresis exploiting the weak nanotube dipole. An electric field, of the order of $\sim 10 \text{ V}/\mu\text{m}^{11-14}$, was used to align solution dispersed nanotubes, whereas only $\sim 1 \text{ V}/\mu\text{m}^{15-17}$ has been shown to align the nanotubes during synthesis. In contrast, *ex-situ* E-Field alignment requires no fixing agent and allows for immediate burning of metallic tubes, should the application call for this. *Ex-situ* E-field approaches often produce varied results, with a degree of alignment less than comparable shear methods. This is likely

due to the use of suspending CNTs within a liquid, with viscous and surface tension largely determining the degree of CNT alignment. Packing density with this technique was strongly dependent on the ink concentration used prior to alignment.

Ex-situ B-Field alignment samples are often relatively poorly aligned. Usually suspended within a composite or epoxy, the slowing of the CNTs paramagnetic alignment is critical, as is a fixing agent making the technique impractical for some applications.

Although local electric and magnetic fields have been shown to be promising, the demanding electrode and catalyst patterning processes limits scalability, both in terms of nanotube length and mass production. Practical devices require larger scales. Recently, Cole *et al.*¹⁸ reported fabrication of freestanding alternative, capable of producing significant lengths of free-standing thin films consisting of aligned multi-walled carbon nanotubes *without* the use of a binder or any supporting substrate. Such structures are often very-well aligned and afford a high linear packing density. There are broadly two types of solid state extrusion that are largely alignment independent; namely those being drawn from vertically aligned CNT forests and those from less orientated aerogels. Little variation in alignment was noted between these.

III. IN-SITU ALIGNMENT

Density alignment was achieved by depositing the catalyst material on the vertical face of a sputtered SiO₂ protrusion using angled physical vapour deposition. Low-density catalyst particles permit random alignment during growth. This produces the classic entangled spaghetti-like networks. In some instances, it is possible to use such thermal randomisation to deposit in-plane nanotubes by careful consideration of the catalyst, diffusion barrier and growth conditions. In-plane alignment is possible, though in-plane directional control is not. Instead, the application of forces during growth can be used to align the nanotubes in plane.

Figure 2 shows SEM micrographs of various reported *in-situ* alignment techniques including: graphoepitaxy¹⁹⁻²¹, gas flow²²⁻²⁶ and electric field^{12, 15, 17}. Although clear divisions can be discerned between alignment techniques in practice many groups have exploited combinations of these in order to optimize the alignment in terms of linear packing density and degree of alignment.

Nanotubes graphoepitaxially align to surface nanofacets during growth. The technique is surface critical which limits the broadness of the technique. Nevertheless, researchers have built impressive rudimentary computational devices based on these aligned horizontal architectures²⁷. High degrees of alignment and uniformity have been evidenced through the production of highly linear, regular and periodic arrays^{21, 28}. Despite this, the process involves time-consuming substrate preparatory processes and requires expensive substrates, such as sapphire or quartz. Rational substrate design, using elevated Si pillars, offers another approach²⁹. Here the nanotubes grow between elevated pillars. The micrometer pillars limit the practicality of

the technique as well as restricting the maximum packing density. As a result, techniques based on electric field and gas flow alignment show perhaps the most promise. They are rapid, parallel processes that offer simplicity and the ability to fabricate high density arrays.

During CVD-synthesis it is also possible to align using the growth gases. Here the growth and carrier gases flow parallel to the catalyst-carrying substrate and it is this flow which induces the alignment during the growth. Huang²⁵, Xin²⁶, and Jin *et al.*²⁴ demonstrated gas flow alignment with varying degrees of success. Xin *et al.*²⁶ showed, in a gas flow cell, free stream velocities of up to 9 cm/s were necessary for aligned growth, though the SiO₂ surfaces nonetheless ultimately passivated the growth irrespective of the flow rate. The gas flow can both enhance and degrade the degree of alignment; turbulent flow has been seen to degrade the alignment in otherwise high-packing density well-aligned samples. The magnitude of the forces relating to the turbulent flow may very well dominate those associated with the underlying catalysis, ~0.5 μN for nominally 45° misalignment¹⁶. The flow regime must therefore be critically considered via a chambers specific Reynolds number, which is principally dictated by the chambers characteristic dimension of the flow-perturbing feature, the free-stream flow velocity and the kinematic viscosity of the growth gaseous species. Based on Sun *et al.*³⁰, at 700°C and for a predominately NH₃ flow at 5 mBar, where the etchant gas had a much higher flow rate than the carbon precursor, for most cold-walled reactors with a central heating stage of the order of 5 cm in size, a predominately laminar flow is viable. Nevertheless, few have pursued this avenue in practice, likely in part associated with the challenging issue of micro-eddy formation which places strict upper limits on the degree of alignment.

Law *et al.*¹² found, for electric field alignment, that plasma induced self-biasing and the resultant surface charging effects on metallic electrodes were sufficient to align the nanotubes, whereas Zhang¹⁶ and Ural *et al.*¹⁵ reported similar alignment effects ascribed to globally applied electric fields of the order of 0.5-4.0 V/ μm . They argued that the nanotubes highly anisotropic polarisability induces large dipole moments when they interact with the local electric field. This interaction produces large aligning torques which governs the resulting growth orientation. Blažek *et al.*³¹ estimated the electric field aligning force to be of the order of 10⁻⁵ nN, a force approximately four orders of magnitude greater than the weight of the catalyst particle. Hertel *et al.*³² estimated that a 10 nm wide nanotube experiences a per unit length Van der Waals surface binding force of the order of 35 nN, supporting the observed nanotube termination in many density alignment experiments.

Few comprehensive attempts have been made in the literature to explain the orientation mechanism involved; challenges arise in decoupling the evident catalysis with the alignment mechanisms. Indeed, low gas flow rates (< 2 cm/s) are often used to avoid turbulent interactions. Chen *et al.*³³ proposed a so-called kite growth mechanism. Here the catalyst particle,

located, in this instance at the nanotube apex, is forced in the direction of the prevailing electric field (or gas flow) at a largely uncontrollable angle from the substrate. When the growth terminates the nanotubes fall to the substrate, where it subsequently becomes strongly bound. Huang *et al.*²² presented a similar mechanism, whereas Yu *et al.*³⁴ postulated that charged species form bonds along the electric field direction and that the nanotubes can only grow if they align to the electric field. Tanemura *et al.*³⁵ suggested that the alignment effect may be a result of an excess of electrostatically attracted positive charge ions at the nanotube tips. They concluded that the ions, radicals and excited molecular species in the incident plasma play a decisive role in the alignment by reducing the lateral mechanical stress exerted on the nanotubes. The combined findings of^{15, 16, 36, 37} indicate that an electric field in the range of 0.1-2.0 V/ μm is necessary for *in-situ* electric field alignment. Note, also, that Jang *et al.*¹⁷ reported negligible improvements in the alignment 'quality' for fields >2.0 V/ μm , whilst Ural *et al.*¹⁵ found an optimal field of 0.1 V/ μm .

Other than the low-linear densities, a significant limitation to local electric-field alignment is the requirement for micro and macro electrodes, patterned directly on the planar substrate; this certainly limits the approach to those technologies that have few metallic features on the substrate to be coated, such as anisotropic optical media. Such structures interfere with post-growth processing and device fabrication. Substrate independent electrodes obviate the limitations of the patterned electrode. The electric field can then be applied across the entire sample. Such an approach has been widely demonstrated in a vertical context; however, to the best of the author's knowledge, no one has hitherto demonstrated such alignment convincingly in plane.

It has been widely postulated that, as for vertical nanotube growth, alignment is achieved by anisotropic torque induction within a narrow plasma sheath³⁸. This sheath exists in the narrow glow region, ~ 3 mm wide, adjacent to the biased cathode. For typical process conditions, in a Child's Law like plasma in a quasi-neutral Maxwellian regime, the local charge carrier population $n_e = 2.5 \times 10^{17} \text{ m}^{-3}$ and $T_e = 0.7 \text{ eV}$; values which show excellent agreement with those reported by Blažek *et al.*³¹. The electron density linearly increases with plasma power³⁹ and quadratically decays with pressure. The electron temperature is independent of plasma power and exponentially decays with increasing reactor pressure. Sheath elongation, and hence an increase in the alignment length is therefore possible by decreasing the plasma power, where it is also worth noting that the electron density and temperature decrease with increasing reactor pressure^{39, 40}.

Figure 3 shows the variation in the qualitative degree of alignment as assessed via the Herman's Orientation Factor (f) as a function of the linear packing density (LPD) for the various *ex-situ* and *in-situ* techniques discussed. If not stated, the LPD was quantitatively determined via grey-scale image analysis using ImageJ. to calculate the Herman's Orientation Factor we first process the Fast Fourier Transform (FFT) on the square-cropped collective SEM imagery. From the resulting power

spectrum, we extract the azimuthal average to obtain the intensity (I) - azimuthal angle (δ) distribution, which is subsequently used to calculate the Herman's orientation factor (f), as given by;

$$f = \frac{3 \langle \cos^2 \delta \rangle - 1}{2} \quad (1)$$

where, I_Δ is the intensity and;

$$\langle \cos^2 \delta \rangle = \frac{\int_0^{\pi/2} I_\Delta \cos^2 \delta \sin \delta d\delta}{\int_0^{\pi/2} I_\Delta \sin \delta d\delta} \quad (2)$$

The f -factor takes values in the range of $-0.5 \leq f \leq 1.0$. For $f = 1.0$ the nanotubes are perfectly aligned to the azimuth, $f = 0$ denotes a random orientation, and $f = -0.5$ for alignment perpendicular to the azimuth. No images produced $f < 0$ as, in all cases, for ensured compatibility, all images were aligned with their primary axis parallel to the azimuth. All processing was conducted in the Origin Pro 8 environment.

Though set-to-set comparison is challenging, variations of f within individual production techniques is revealing. Though coarse assignment is possible, we stress that intentional and unintentional combinations of alignment processes have been developed and unavoidably included herein, making it challenging to demarcate well-defined zones, as does some non-commensurate real-space length scale variations within images. Nevertheless, we stress here that the aim of Figures 3(b) and (c) is not to draw strict relationships between f and the LPD. Indeed, for some techniques there appears little correlation; a testament to the alignment techniques robustness towards variation as a function of LPD. Despite this, and though somewhat noisy, there does appear to be, in the case of the *ex-situ* techniques, a modest positive correlation between f and LPD; the higher the LPD the greater the f , suggesting that packing effects play at least some role in enhancing alignment in most of the alignment techniques. Such a correlation is yet to be clearly identified in the case of *ex-situ* B-field alignment, likely due to a lack of source data. It is evident that shear alignment, and other mechanical approaches such as solid-state extrusion, proffer the highest LPD, with correspondingly high f (~ 0.7), making them well-suited for the formation of mechanically anisotropic components, though *in-situ* techniques exploiting lattice faceting, such as graphoepitaxy *via* thermally derived and artificially patterned facets, are clearly making significant headway towards high alignment ($f \sim 0.6$), though with typical LPDs at least an order of magnitude less than *ex-situ* shearing. Both *in-situ* and *ex-situ* E-field alignment appear deficient in terms of alignment, with LPDs ranging from 10^2 - 10^1 CNT/ μm . There appears a similarity in the approximate f -LPD space for *ex-situ* E- and B-field techniques, with the f of both likely strongly influenced by other factors local to the deposition, such as Brownian motion within the carrier solution. Indeed, we also note similar f -LPD zoning for both *in-situ* and *ex-situ* E-field alignment, largely testifying to the reduced robustness of the approach towards local

environmental variations, which, in the case of *in-situ* CVD approaches are a product of local and transient turbulence in the growth gases and potentially significant thermal spatial and temporal variations. Further variation in the LPD distribution for *in-situ* gas aligned samples is largely attributed to the predetermined catalyst loading and the resultant heterogeneous catalysis therein. Nonetheless, both *ex-situ* E- and B-field techniques fail to compete with *in-situ* graphoepitaxy, *ex-situ* shearing and *ex-situ* solid-state extrusion. Solid-state extrusion, though having perhaps the highest mean f , some 10% or so more than shearing, is particularly competitive, especially given its substrate independent formation. Indeed, solid-state extrusion also appears, at present, to be one of the most reproducible techniques, showing some of the lowest variation in LPD of all the techniques considered (6-50 CNTs/ μm). Given the high cost of suitable graphoepitaxy substrates and the time consuming thermal pre-processing required to derive suitable lattice facets, shearing and solid-state extrusion approaches appear the most commercially attractive approaches to date, with some of the highest yields and lowest costs. Nevertheless, the need for high packing density and vertical CNT synthesis, which is becoming increasingly common place and is readily achieved by many using simple low-cost growth reactors, is critical, as is improved reproducibility in the alignment processes, without which such approaches will fail to gain industrial traction.

IV. OUTSTANDING CHALLENGES

Not all applications require high LPD. *In-situ* approaches are evidently well-suited for such technological needs. However, there are, at the time of publication, very few dedicated commercial growth reactors designed specifically to mediate horizontal CNT growth and certainly none that allow for synthesis at industrially viable scales, albeit at high LPD or otherwise. There is a dramatic gap in the commercial space. Much progress has nonetheless been made in the attaining high f with correspondingly high LPDs, making the use of carbon nanotubes in advanced electronics and optics more viable than ever before.

Though horizontal alignment has been demonstrated by many this has almost exclusively been focused on alignment across entire arrays. To date very little has been reported on the development of *ad hoc*, adjustable in-plane CNT alignment, either *in-situ* or *ex-situ*. Indeed, the ability to controllably align the in-plane angle of CNTs, across entire arrays, or more localized directional control within an array, will open up a huge variety of technologies that have hitherto required the use of high-resolution lithographic processing as well as multiple nanotube transfers based on often complex and cumbersome processes. Though some reports have evidenced bi-directional serpentine-like in-plane growth⁴¹, as a result of spontaneous and largely uncontrolled facet alignment, the ability to accurately control the alignment direction remains a particularly difficult research topic to broach.

As required by many applications, the desirably high catalyst density, and hence nanotube linear density results in zones of misalignment due to strong randomising inter-nanotube interactions. Reductions in catalyst density would certainly be

favorable, though potentially at the expense of final device functionality. For example, such a methodology may produce CNT-FETs with superiorly aligned channel regions, though at the cost of fewer transport routes within the channel. Nevertheless, to fully exploit aligned nanotubes in many applications, it is certainly evident that significantly longer nanotubes are necessary, as is concurrent high alignment and high LPD, necessitating the development of various time-consuming repeat-growths or repeat-transfer (most likely polymer-mediated), as recently reported²⁷. The effects of such repeat transferring on the underlying transport remain largely unclear, though the effects seem somewhat functionally marginal.

In the present study we have focused exclusively on the horizontal alignment of CNTs. In the case of the *in-situ* techniques it is important to note that though there is a significant interplay between the growth conditions and the degree of alignment, there too exists an interaction between the growth processes and the nanotube length, chirality, and type, along with other critical physical and technological characteristics of the synthesised material. All are central design parameters and must be considered independently and with care in order to realise particular functional systems.

Though the processing challenges remain wide, various further research and commercial challenges remain. Many such issues that plague the adoption of some of the techniques reported above are common to those plaguing the broader family of emerging carbon nanotube-based technologies. The initially high cost per unit mass has reduced substantially. CNTs are now routinely synthesised at costs of < \$10/g. Though beneficial, such cost reductions are only important for those applications requiring significant volumes of aligned CNTs. In practice, most applications which require high degrees of alignment do not often fall into this category. Indeed, for many, if not all, electronic and interconnect applications, the cost per unit mass determines little the technologies appeal. Rather the adoption reticence of the wider foundry communities has proven a particularly challenging obstacle to navigate. Nevertheless, just as novel nano- and macro-scale devices based on horizontally aligned CNTs are being rapidly reported, many new markets and commercial entities, floated by larger research embracing conglomerates, are appearing at rate, with these aligned horizontal CNT technologies achieving ever higher technology readiness levels. Yield, single-chirality and reproducibility endure as common barriers to scale-up, as does the need for ever higher packing densities, especially if such nanoscale systems are to compete with current metallic interconnects in integrated circuits. Nonetheless the field continues to gain traction.

V. CONCLUSIONS

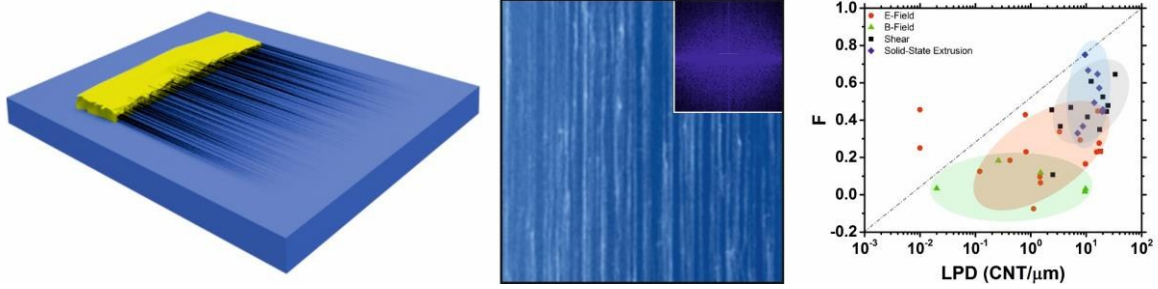
Though significant progress has been made these past two decades, the varied challenges associated with horizontal alignment of carbon nanotubes persist. Both the commercial and fundamental research barriers to wider scale adoption are

significant. Nevertheless, with continued maturity many of the outlined techniques are proving ever more fruitful, with *ex-situ* shearing and solid-state extrusion approaches achieving concurrently high packing densities and high alignment, gaining them traction, particularly for *en masse* production. In contrast, *in-situ* graphoepitaxy currently dominates the fore, with the bottom-up synthesis of nanostructured periodic arrays having much appeal for the realization of nanotube-based computing. Whether carbon nanotubes will achieve future commercial success is unclear, though with further optimization alongside the on-going dominance of the one-dimensional nanostructures and the wider family of nanotechnologies, there remains optimism that one, if not many, of the techniques discussed herein will be employed commercially, at least in one guise or another.

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FIGURES



TOC FIGURE

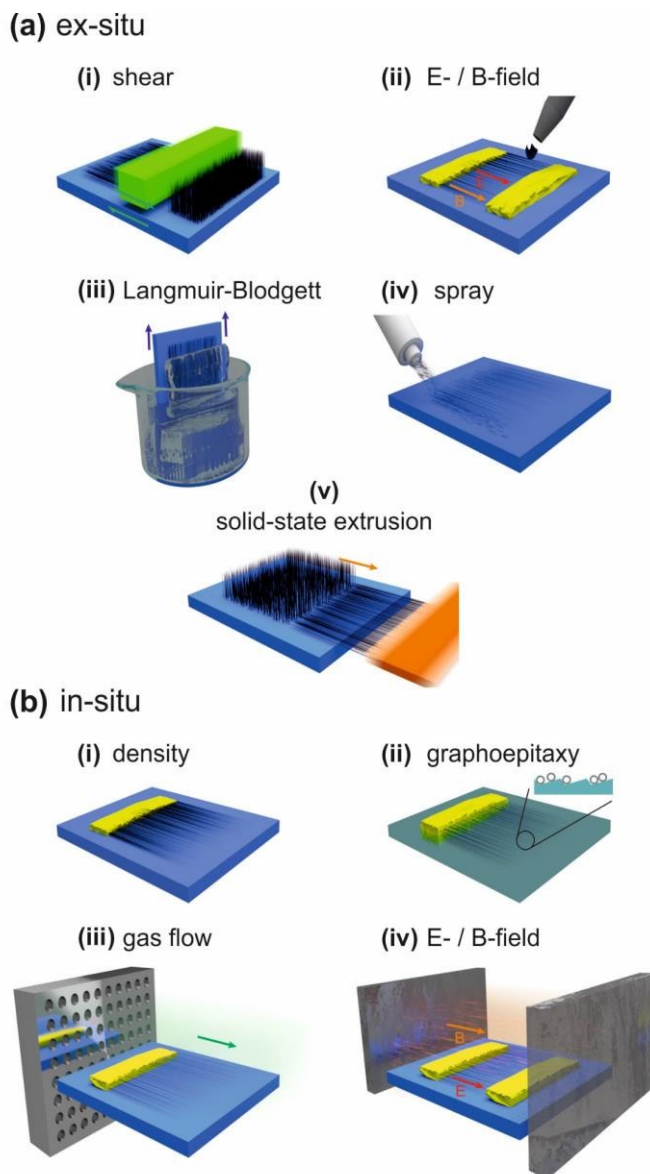


Figure 1: CNT alignment. (a) *ex-situ* techniques including; (i) mechanical shear, (ii) electric (E) and/or magnetic (B) fields, (iii) Langmuir-Blodgett, (iv) spray coating, and (v) solid-state extrusion. (b) *in-situ* alignment techniques including; (i) packing density, (ii) graphoepitaxy, (iii) gas flow, and (iv) electric (E), magnetic (B) and/or plasma.

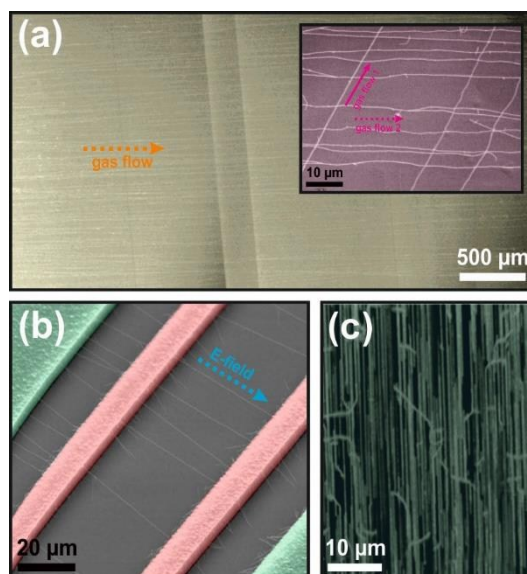


Figure 2: Examples of *in-situ* CNT alignment via; (a) gas flow^{42, 43}, (b) electric-field^{13, 16}, and (c) graphoepitaxy⁴⁴.

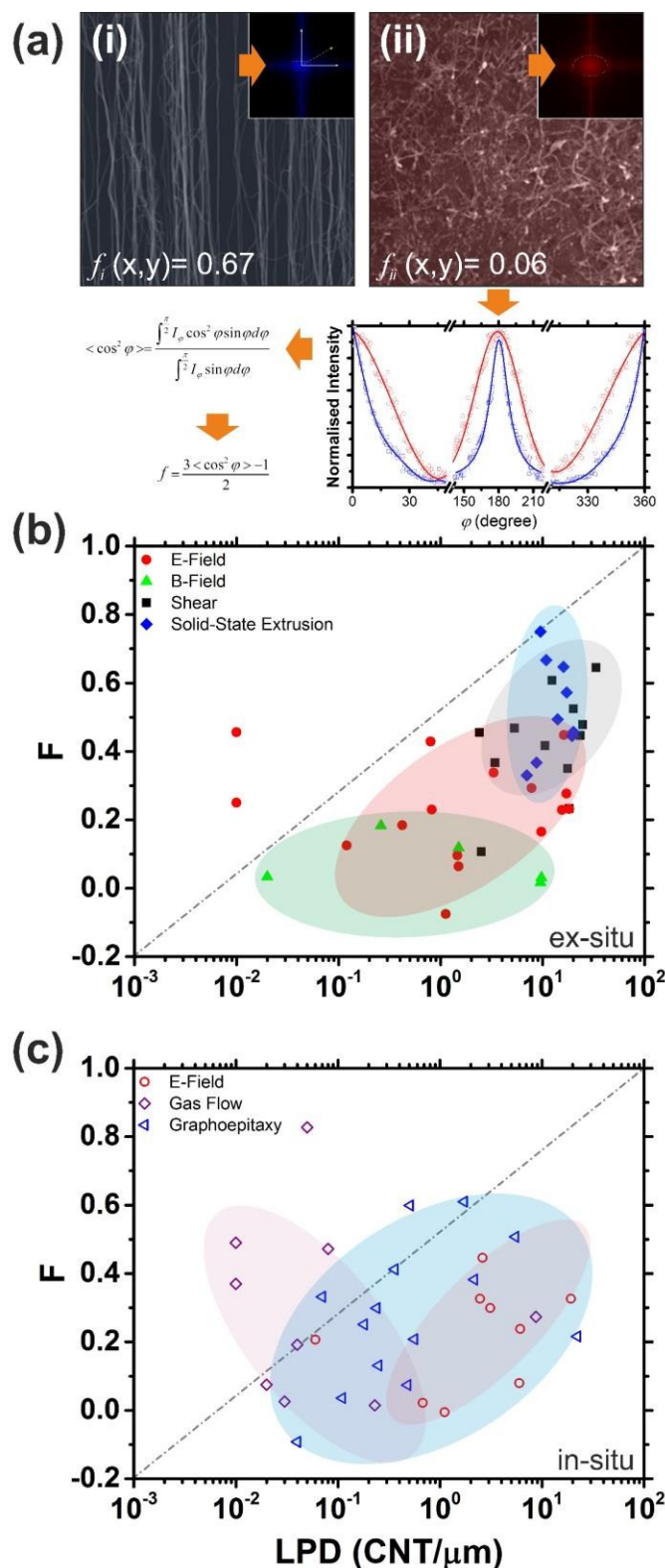


Figure 3: (a) Degree of Alignment quantification. Example scanning electron micrographs of (i) well-aligned⁴⁵ and (ii) largely misaligned⁴⁶ films with (inset) associated FFT generation and Herman's Orientation Factor (f) fitting. Herman's Orientation Factor as a function of Linear Packing Density (LPD) for various published horizontal alignment techniques; (b) *ex-situ* (E-Field⁴⁶⁻⁶⁷, B-Field⁶⁸⁻⁷⁶, Shear^{1, 77-87}, and Solid-State Extrusion^{45, 88-100}) and (c) *in-situ* (E-Field¹⁰¹⁻¹⁰⁸, Flow Directed¹⁰⁹⁻¹¹⁷, and graphoepitaxy¹¹⁸⁻¹³⁵).

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