Field Emission Applications of Graphene

M. T. Cole[1*], C. Li[2], C. M. Collins[1], R. J. Parmee[1], T. Hallam[3], W. Lei[4], S. Ding[4], B. P. Wang[4], G. Duesberg[3], & W. I. Milne[1,5]

[1] Electrical Engineering Division, Cambridge University, 9 JJ Thomson Avenue, Cambridge, UK
[2] National Centre for Nanoscience & Technology, Beijing, 100190, P. R. China
[3] Centre for Research on Adaptive Nanostructures & Nanodevices, Trinity College Dublin, Ireland
[4] Display R&D Center, School of Science and Engineering, Southeast University, Nanjing, P.R. China
[5] Quantum Nanoelectronics Research Center, Tokyo Institute of Technology, Tokyo, Japan
* mtc35@cam.ac.uk

Abstract
Electron emission is a ubiquitous technology. Found in travelling wave tubes, electron beam lithography systems, microwave amplifiers, thin film displays, advanced lighting units, and X-ray sources; the field of nano-vacuum electronics is returning to the fore during the present carbon renaissance. The graphitic nano-carbons out-perform conventional metallic Spindt-like electron emitters across virtually all standardised metrics [1, 2]. Carbon nanotubes (CNT) and, more recently graphene both offer high-aspect ratios, chemical inertness, near instantaneous temporal response and low sputter cross-sections, all of which contribute to their advantageously low turn-on fields, negligible hysteresis and high temporal stability. Nevertheless, the efficient use of these emerging nanomaterials requires the ability to define, with high fidelity and reproducibility, sub-micron-scale periodic features. Here I present an over-view of our recent work on graphene-based field emission devices including the nanoscale graphene fin electron guns, low cost hydrogenated graphene foam emitters, highly electron transparent graphene gated triodes, and the first large-area graphene-based electron emission display.

The efficient use of emerging two-dimensional nanomaterials in various electron emission applications has yet to gain any significant commercial traction, largely due to temporal instabilities and challenges associated with yield and device-to-device reproducibility. Indeed, the devices that have successfully achieved high technology-readiness levels are based on poorly functioning, coarsely deposited, post-growth techniques with little to no spatial registration or controlled material alignment, using techniques often based on simplistic and material-damaging wet chemistry. Enhanced functionality, including resistance toward electromigration and beam shaping, requires the ability to define, with high fidelity and reproducibility, sub-micron-scale periodic features. Herein a printing technique is reported to controllably nanostructure chemical vapor deposited graphene into vertically standing fins (**Figure 1a**). The method allows for the creation of regular arrays of bilayer graphene fi ns, with sharp ridges that, when printed onto gold electrodes, afford a new type of field emission electron source geometry. The approach affords tunable morphologies and excellent long term and cyclic stabilities [3].

Though such graphene films allow for an ultra-high precision means of defining near atomic-scale corrugations, such approaches require skilled manual manipulation in their fabrication and are, as a result, costly. Alternative, low cost approaches are clearly needed. To broach this market challenge we developed a hydrogen plasma treatment of graphene-based foams (GF) to afford an improved field emission performance following transient exposure to hydrogen plasma (**Figure 1b**) [4]. The enhanced field emission mechanism associated with these treated is attributed to an increase in the areal density of lattice defects and the formation of a partially hydrogenated, graphane-like material. The treated GF emitter demonstrated a much reduced macroscopic turn-on field (2.5 V/µm), with an increased maximum current density from 0.21 mA/cm^2 (pristine) to 8.27 mA/cm^2 (treated). The treated GFs vertically orientated protrusions, after plasma etching, effectively increased the local electric field resulting in a 2.2-fold reduction in the turn-on electric field. The observed enhancement is further attributed to hydrogenation and the subsequent formation of a partially hydrogenated structured 2D material, which advantageously shifts the emitter work function, alongside augmentation of the nominal crystallite size of the graphitic superstructure and the constitute macro molecules, are believed to play a key role in the enhanced emission. The hydrogen plasma treatment was also noted to increase the emission spatial uniformity, with an approximately four times reduction in the per unit area variation in emission current density. Our findings suggest that plasma treatments, and particularly those employing hydrogen and hydrogen-containing precursors, may provide an efficient, simple, and low costs means of realizing enhanced nanocarbon-based field emission devices via the engineered degradation of the nascent lattice and adjustment of the surface work function.

Aside from graphene's various advantageous mechanical and electrical properties, it possesses a number of potentially technologically exploitable broadband optical properties that are of particular interest for electron beam devices. As illustrated in **Figure 1c**, highly electron transparent gate

electrodes have been fabricated from chemical vapor deposited bilayer graphene transferred to Mo grids with experimental and simulated data, showing that liberated electrons efficiently traverse multi-layer graphene membranes with transparencies in excess of 50–68% [5]. The graphene hybrid gates are shown to reduce the gate driving voltage by 1.1 kV, whilst increasing the electron transmission efficiency of the gate electrode significantly. Integrated intensity maps show that the electron beam angular dispersion is dramatically improved (87.9 °) coupled with a 63% reduction in beam diameter. Impressive temporal stability is noted (<1.0%) with surprising negligible long-term damage to the graphene. A 34% increase in triode perveance and an amplification factor 7.6 times that of conventional refractory metal grid gate electrode-based triodes are noted, thus demonstrating the excellent stability and suitability of graphene gates in micro-triode electron sources.

Finally, here we also report on the fabrication and functionality of the first graphene-based field emission-based display [6]. A shown in **Figure 1d**, a 21 cm graphene-based transverse electron emission display panel has been realised, fabricated using a screen-printed triode edge electron emission geometry employing chemical vapor deposited (CVD) graphene supported on vertically aligned carbon nanotubes (CNT) which allows for the quenching of electrostatic shielding induced by the proximal bulk substrate. Integrated ZnO tetrapod electron scatterers have been shown to increase the emission efficiency by more than 90%. Simulated electron trajectories validate the observed emission characteristics with driving voltages less than 60 V. Fabricated display panels have shown real-time video capabilities that are hysteresis free (<0.2%), have extremely stable lifetimes (<3% variation over 10 h continuous operation) in addition to rapid temporal responses (<1 ms).

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Figures

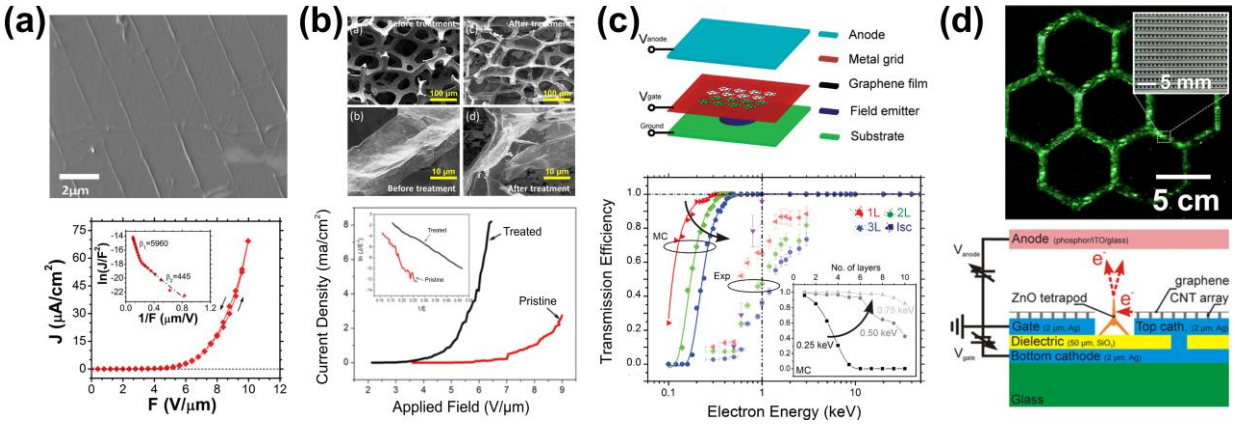

Figure 1 (a) Example scanning electron micrograph of a graphene-fin based electron emitter, and the corresponding emission performance. **(b)** Typical scanning electron micrographs and field emission profiles of partially hydrogenated graphene foam field emitters before and after treatment. **(c)** Scheme depicting a highly electron transparent graphene gate electrode in a nanocarbon triode electron source. Variation in beam transmission as a function of electron energy. **(d)** An Optical micrograph and scheme cross-section of the first video-rate, monochromatic graphene-based field emission display.