Fully 3D-printed carbon nanotube field emission electron sources with in-plane gate electrode

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Abstract
We report the design, fabrication, and experimental characterization of the first fully additively manufactured carbon nanotube (CNT) field emission electron sources. The devices are created via direct ink writing (DIW)—one of the least expensive and most versatile additive manufacturing methods, capable of creating monolithic multi-material objects. The devices are 2.5 cm by 2.5 cm glass substrates coated with two imprints, i.e. a trace made of a CNT ink (the emitting electrode), symmetrically surrounded on both sides by a trace made of Ag microparticle ink (the in-plane extractor gate). The CNT ink is a mixture of (–COOH)-functionalized multiwalled CNTs (MWCNTs), N,N-Dimethylformamide, and ethyl cellulose. Optimization of the formulation of the CNT ink resulted in a MWCNT concentration equal to 0.82 wt% and in imprints with an electrical resistivity equal to 0.78 Ω cm. 3D-printed devices having CNT imprints with active length equal to 25 mm (a single, straight trace with 174.5 μm gap between adjacent Ag microparticle imprints) and 135 mm (a square-loop spiral with 499 μm gap between Ag microparticle adjacent imprints) were characterized in a triode configuration (i.e. using an external anode electrode) at ~2.5 × 10⁻⁷ Torr, yielding emission currents as large as 120 μA (60 μA cm⁻²), start-up voltages as low as 62 V and gate transmission as high as 99%. The low-cost cold cathode technology is compatible with compact applications such as miniaturized mass spectrometry, handheld x-ray generation, and nanosatellite electric propulsion.

Keywords: additive manufacturing of nanosystems, electron sources, field emission, carbon nanotubes, direct ink writing

(Some figures may appear in colour only in the online journal)

1. Introduction

Field emitters quantum tunnel electrons to vacuum due to high electrostatic fields (>3 × 10⁸ V m⁻¹) present on their emitting surfaces [1]; such high electric fields can be generated at moderate voltage (< 100 V) using nanosharp, high-aspect-ratio tips. Compared to thermionic counterparts, field emission cathodes consume less energy, respond faster, and can operate in poorer vacuum [2, 3], making them attractive in compact applications such as pico and nanosatellite electric propulsion, portable mass spectrometry, and handheld x-ray generation [4–7].

A wide variety of materials have been explored as field emitters including Mo [8], Si [9], ZnO [10], and SnO₂ [11]; however, a significant portion of the research in field emission electron sources has focused on carbon nanotubes (CNTs) due to their nanosized tip diameter, high aspect-ratio, high...
electrical conductivity, exceptional mechanical properties, and excellent chemical stability [12–14].

Reported manufacturing methods for CNT field emission electron sources include laser transfer [15], screen printing [16, 17], and plasma-enhanced chemical vapour deposition (PECVD) [18, 19]. However, these manufacturing techniques have associated challenges such as cost, processing time, need of static masks for defining in specific locations the nanostructured emitting material and/or the electrode(s), large gate interception (or the need of advanced assembly methods to attain high transmission [20]), or some combination thereof.

3D printing is maskless, layer-by-layer manufacturing techniques that create solid objects [21]. 3D printing methods are inherently compatible with implementing hierarchical structures with features spanning orders of magnitude in size [22]. Direct ink writing (DIW) is a 3D printing technique in which a paste, i.e. ink, is extruded through a small nozzle, while the nozzle is moved across a platform using numerically controlled stages [23]. DIW offers unique advantages over other 3D printing methods such as compatibility with a very wide range of printable feedstock—including active (e.g. transducing) materials, and feasibility to fabricate monolithic multi-material objects; as a matter of fact, DIW has been used to create a great variety of devices and structures including tissue scaffolds [24, 25], rechargeable batteries [26, 27], microfluidic devices [28], and supercapacitors [29].

There are numerous reports on printing of CNTs and other carbon-based materials to create freeform objects with high electrical conductivity. One of the most popular methods for printing these structures is the inkjet printing technique, in which droplets of ink, either continuous or on-demand, are deposited on a surface to create layers of material [30]: for example, Robertson et al developed formulations of inkjet-printable feedstock based on CNTs and/or graphene that produce coatings with good electrical conductivity and adhesion to the substrate [31]; also, Kordás et al reported conductive patterns in paper and polymer substrates using inkjet-printable feedstock that contained CNTs [32]. Another technique that has been explored is fusion filament formation (FFF, also known as fused deposition modelling, or FDM [21]), in which molten polymer is extruded from a hot nozzle to form, via rastering, layers of material: for example, Gnanasekaran et al reported that FFF-printed CNT-based polybutylene terephthalate (PBT) composites have better electrical conductivity than graphene-based PBT composites [33]; in addition, Sun and Velásquez-García reported high piezoresistivity (∼23.5) from FFF-printed structures made on a graphite-based composite [34].

In this study, we report the design, fabrication, and experimental characterization of the first fully additively manufactured field emission CNT electron sources. The devices consist of a flat dielectric substrate with two DIW-printed imprints: an imprint made of a CNT ink, i.e. emitting electrode, symmetrically surrounded on both sides by an imprint made of Ag microparticle ink, i.e. extractor gate. The Ag ink is a commercial product, while the formulation of the CNT ink was developed in our lab, resulting in narrow, uniform imprints with high electrical conductivity that quantum tunnel electrons to vacuum when a high enough bias voltage (>62 V) is applied between the CNT ink imprint and the Ag ink imprint. This structure is most efficiently printed using concentric spirals as imprint layouts. Unlike the great majority of field emission cathodes reported in literature that have an out-of-plane gate electrode on top of the field emitters, our design has an in-plane gate placed directly on top of the substrate, side-by-side with the emitting electrode, which significantly reduces the manufacturing complexity of the device and its cost, as well as facilitates high gate transmission. There are reports of field emission sources with in-plane gate [35, 36]; however, they use an interdigitated layout instead of concentric spirals, and are made using conventional manufacturing processes with the disadvantages mentioned above.

2. Methods

2.1. Materials

The Ag ink used in this study is a commercial product made by Voltera (Kitchener ON, Canada). To create the CNT ink used in this work, (–COOH) functionalized multiwalled CNTs (MWCNTs) with purity ≥96%, outer diameter equal to 15–50 nm, and length equal to 10–35 μm were obtained from Nanografì (Jena, Germany), while N,N-Dimethylformamide (DMF) anhydrous (99.8%), and ethyl cellulose (EC), viscosity 10 cP, were purchased from Sigma-Aldrich (St. Louis MO, USA). All the reagents involved in the fabrication of the CNT ink were utilized without further treatment.

2.2. CNT ink fabrication

The CNT ink is composed of a solvent (DMF), a binder (EC, i.e. the material that provides cohesion to the ink), and a filler (MWCNTs, i.e. the material that gives high electrical conductivity to the ink). To manufacture the CNT ink, MWCNT powder is dispersed in DMF using an ultrasonic homogenizer and a stirrer. After that, the EC powder is added to the solution (21% by weight), stirring until all the material is dissolved into the solution. Finally, the resulting ink is poured into an empty cartridge syringe and stored at 5°C–10°C until needed for printing. Two CNT concentrations were explored, i.e. 2 mg of MWCNTs per ml of DMF (0.16 wt%) and 20 mg of MWCNTs per ml of DMF (0.82 wt%); only the ink formulation with the higher concentration of CNTs yielded imprints that can field emit electrons; consequently, the devices that were characterized were made with such ink.

2.3. Device design

The 3D-printed cathode is a flat dielectric substrate with two electrically conductive imprints, i.e. an imprint made of CNT ink, forming the emitting electrode, symmetrically surrounded on both sides by an imprint made of Ag ink, forming the in-plane extractor gate; the use of an in-plane gate greatly facilitates the transmission of the current emitted by the CNT imprint. The gate electrode is printed in a material that is very
conductive to minimize voltage drop due to current interception, while the emitting electrode has a nanostructure that can field emit when a large enough bias voltage is applied.

DIW printers hover the nozzle on top of the substrate and control the flow of ink with the displacement of a piston or a pressure signal and the movement of the nozzle across the substrate; this way of dispensing the ink can cause pooling of the printable material in a general layout, e.g. when the nozzle retracts. Therefore, the layouts of the 3D-printed field emission electron source are designed to minimize variations in the ink flow to facilitate defining arbitrarily long imprints of uniform width, and by extension, with uniform gap between adjacent imprints. For a field emission source with integrated in-plane gate, this can be achieved if the layouts of the electrodes are continuous, long, concentric spirals (figure 1), so that the only points at which the flow of ink significantly varies are at the ends of the imprints. With such layouts, the imprints can easily be pre-screened for electrical conductivity and continuity before field emission characterization in vacuum (this would be challenging to do in the commonly screen-printed, in-plane gate design of interdigitated fingers). The orientation of the spirals can be adjusted to fully cover a given active area, for example, by following the perimeter of the area, spiralling into smaller loops until the full area is covered. The external end of the emitting electrode has a pad covered with Ag ink to minimize contact resistance and facilitate the operation of the device.

The imprint width is limited by the physical properties of the ink and the resolution capability of the DIW printer; the spacing between adjacent imprints should be at least an order of magnitude larger than the alignment capability of the DIW printer to be able to define, to first order, a constant gap between adjacent traces. The imprints are narrow and tightly spaced to reduce the bias voltage required to field emit electrons, to increase the number of emission sites per unit of area, and to be compatible with a wider range of shapes and dimensions of active area.

### 2.4. Device fabrication

The devices were created with a low-cost (~US $3500) printed circuit board (PCB) printer Voltera V-one (Kitchener ON, Canada). The printer is composed of a heated platform, a computer-controlled positioning system, and a piston that squeezes an ink cartridge that is magnetically attached to the body of the printer (figure 2(a)); the displacement of the piston is electrically controlled with a motor. The printer can create multiple layouts using a different ink for each layout, and align the layouts within ~25 μm with respect to previously printed layouts (from the vendor). Each ink requires a calibration process to find a set of parameters (e.g. dispense height, piston feed rate, trim length) that generates traces of uniform width and height for a given layout.

To print a CNT field emission electron source, a 25 mm by 25 mm, clean, flat glass substrate is placed over the platform and fixed with clamps to avoid movement during printing. The printer then scans the surface of the substrate, creating a map that will be used during printing to make sure that the separation between the nozzle and the substrate is kept constant. After that, the emitting electrode is printed at room temperature using as layout a file in Gerber format (figure 2(b)); the substrate is dried in a nitrogen box, and then transferred into a furnace to remove all the organic binder and any remaining solvent (400 °C, 1 h, argon atmosphere). Next, a mechanical treatment is performed on the imprint to release CNT tips from its top surface. Specifically, using pressure, no-residue sticky tape was applied to the top of the CNT imprint; after waiting for a few minutes, the tape is pulled, removing material from the top of the imprint while releasing some CNTs from the bulk. This procedure removes a very small amount of material because (1) inspection of the imprints using confocal microscopy before/after the tape treatment revealed no noticeable difference, (2) no fissures in the CNT imprints after administering the tape treatment were ever observed, and (3) CNT imprints made of the same ink formulation consistently showed the same electrical conductivity. Using sticky tape to release CNTs from the top of imprints is commonly used in screen-printed field emission CNT electron sources [37, 38]. Afterwards, the gate electrode is printed at room temperature using a Gerber file as layout (figure 2(c)), taking care of aligning the new layout to the previously printed emitting electrode layout. Finally, the substrate is baked at 160 °C for 35 min using the built-in heater in the platform of the printer, right after printing, to dry the silver ink imprint and improve its electrical properties. Nozzles with internal diameter equal to 100 μm and 225 μm were used to print the silver ink and CNT ink, respectively.

### 2.5. Ink and device characterization

The electrical resistivity of the CNT and Ag inks was characterized using printed straight lines with constant cross-section on top of custom glass chips that had patterned
Au-sputtered fingers (figure 3) from the company Nanoterra (Cambridge MA, USA). Resistivity measurements were conducted with a multimeter Fluke 8846 A (Everett MA, USA).

Thermogravimetal analysis (TGA) of the CNT ink was carried out in a Discovery TGA (TA Instruments, New Castle DE, USA) with a balance precision of 0.1 μg; for this analysis, the samples were heated to 800 °C at a rate of 20 °C min \(^{-1}\) under nitrogen atmosphere. The viscosity of the inks was measured at 1–100 Hz shear rates using an Advance Rheometer AR2000 (TA Instruments, New Castle DE, USA). The morphology of the surface of the Ag and CNT imprints was characterized using a Zeiss Merlin High-resolution SEM (Oberkochen, Germany). Metrology of the 3D-printed field emission devices was conducted using a laser scanning confocal microscope Keyence CX-X200 Series (Keyence, Osaka, Japan).

The 3D-printed field emission cathodes were tested in vacuum inside a grounded chamber in a triode configuration with the emitting electrode grounded, the in-plane gate biased at a voltage between 0 and 850 V, and a suspended anode (a flat, wide cylinder with rounded corners) biased at +1300 V; all three voltages were supplied by calibrated source-measuring units Keithley 2650 (Tektronix, Beaverton OR, USA).

Vacuum was maintained using a dry rough pump and a turbomolecular pump, maintaining the pressure inside the chamber below 2.5 × 10⁻⁷ Torr during the experiments.

### 3. Results and discussion

#### 3.1. Ink characterization

The electrical characterization of the Ag ink and the CNT inks is shown in figure 4. The width and thickness of the imprint made of ink with 0.16 wt% MWCNT concentration are equal to 548.8 μm ± 90.9 μm and 702.3 nm ± 90.0 nm, respectively, while the width and thickness of the imprint made of ink with 0.82 wt% MWCNT concentration are equal to 297.5 μm ± 18.3 μm and 4.6 μm ± 0.1 μm, respectively; therefore, a five fold increase in the concentration of CNTs while keeping the binder concentration constant resulted in a two fold decrease of the imprint width and a seven fold increase in the thickness of the imprint. The width and thickness of the imprint made of Ag ink are equal to 154.3 μm ± 11.4 μm and 10.4 μm ± 0.3 μm, respectively. The least-squares fittings of the data in figure 4 demonstrate linearity between the length of the imprint and its electrical resistance, as expected from an ohmic material. The resistivity was calculated using the equation

$$ R = 2R_o + \frac{\rho}{A} x, $$

where \( R \) is the electrical resistance of the imprint, \( R_o \) is the contact resistance, \( \rho \) is the electrical resistivity of the imprint, and \( A \) and \( x \) are the cross-sectional area of the imprint and the length of the imprint, respectively. Given that the electrical resistivity of Au and Ag are very high, the data from the silver imprints was corrected for the voltage drop taking place across the interdigitated fingers. The contact resistance of the ink with 0.16 wt% MWCNT concentration (i.e. 36.6 kΩ) is an order of magnitude larger than the corresponding value for the ink with 0.82 wt% MWCNT concentration (i.e. 2.9 kΩ); however, the electrical resistivity is only two times larger (1.53 Ω cm versus 0.78 Ω cm). The resistivity values of the CNT inks are comparable to values from single-crystal doped Si. As expected, the electrical resistivity of the silver ink is orders of magnitude smaller than the resistivity values of the CNT inks (i.e. 90.4 μΩ cm), close to the typical value provided by the vendor, and almost two orders of magnitude
larger than the bulk value of Ag (i.e. 1.59 $\mu$Ω cm). The contact resistance of the imprint made of Ag ink (i.e. 7.0 Ω) is also orders of magnitude smaller than the values obtained from imprints made of CNT ink.

The viscosity is an important parameter for a DIW-printable ink: on the one hand, if the viscosity of the ink is too small, the ink will spill over the substrate instead of defining a continuous, constant imprint with width similar to the width of the nozzle; on the other hand, if the viscosity of the ink is too large, stable flow through the nozzle might not be achievable and the piston mechanism might even jam due to large hydraulic resistance opposing its movement. The viscosity of the CNT ink can be modulated by varying the concentration of the polymeric binder (i.e. EC) or the filler (i.e. MWCNTs). Figure 5 shows the viscosity of the inks as a function of the shear rate; the data were collected at room temperature. In all cases, the data demonstrate shear thinning behaviour; however, only the CNT inks are satisfactorily described as pseudoplastic fluids, i.e. show a simple power-law dependence between viscosity and shear rate. The viscosity of the ink with 0.16 wt% MWCNT concentration varies between 108 Pa s and 2 Pa s, while the viscosity of the ink with 0.82 wt% MWCNT concentration varies between 112 Pa s and 3 Pa s. For shear rates above 5 Hz, the viscosity of the ink with 0.82 wt% MWCNT concentration is about twice the viscosity of the ink with 0.16 wt% MWCNT. The viscosity of the Ag ink has the same order of magnitude of the viscosity of the CNT inks, varying between 49 Pa s and 1.5 Pa s, but is significantly larger than the viscosity of the CNT inks for shear rates between 10 and 70 Hz.

In a non-Newtonian, power-law fluid, the shear stress $\tau$ is proportional to the $n$-power of the shear rate

$$\tau = K \left( \frac{du}{dr} \right)^n$$

(2)

where $K$ is the flow consistency index (in Pa s$^n$), $n$ is the flow behaviour index (dimensionless), $u$ is the velocity of the fluid, $r$ is the spatial coordinate across which the flow field changes (i.e. the radial coordinate in the case of a long, circular pipe like the printer’s nozzle); the expression within square brackets is the effective viscosity [39]. Therefore, for both CNT inks the flow behaviour index is about 0.1 (see least-square fittings of figure 5). A rough estimate of the average shear rate is given by

$$\left( \frac{du}{dr} \right) \sim \frac{U}{R}.$$  

(3)

where $U$ is the average speed of the fluid (also the rastering speed of the nozzle) and $R$ is the inner radius of the nozzle. The typical speed of the nozzle during printing is $\sim 4$ mm s$^{-1}$; therefore, the average shear stress of the Ag ink during printing is 80 Hz (50 μm inner nozzle radius), while the average shear stress of the CNT inks during printing is 36 Hz (112.5 μm inner nozzle radius). Consequently, the average effective viscosity during printing is equal to $\sim 4.6$ Pa s for the Ag ink, $\sim 4.1$ Pa s for the 0.16 wt% CNT ink, and 6.5 Pa s for the 0.82 wt% CNT ink.

The binder and solvent in the CNT ink serve as a transport medium in which the CNTs travel while the ink is extruded over the substrate. However, the binder and solvent are poor electrical conductors, contrary to the CNTs that exhibit high electrical conductivity; consequently, the binder and solvent must be removed from the imprint after printing. In order to find the decomposition temperature of the polymeric binder and solvent, a TGA analysis was performed (figure 6). The data show that the polymeric binder decomposition temperature is about 400 °C, while the MWCNTs start to degrade at around 500 °C. The removal of
DMF solvent starts at 153 °C, as shown for the CNT ink characteristic. According to these results, the annealing temperature of the CNT imprints can be set between 400 °C and 500 °C, which ensures that the binder and solvent are removed without damaging the MWCNTs.

3.2. Device characterization

3.2.1. Device metrology. Two device designs were implemented and characterized, i.e. a single-trace of CNT ink symmetrically surrounded by two traces of silver ink (figure 7(a); this device emulates a typical portion of spiral in a general layout design) and concentric square-loop spirals (figure 7(d)). The 3D metrology of the devices is shown in figures 7(b) and (e), respectively, while line scans of the cross-section of the devices are provided in figures 7(c) and (f), respectively; a summary of the key parameters from the metrology is shown in table 1. The traces made with the CNT ink are about as wide as the traces made with the Ag ink, but they are significantly thinner. Some difference in height and width profile can be observed between the single-trace device and the square-loop device (figures 7(c) and (f)), which is due to the specific parameters used to print each set of layouts, e.g. flow rate, trim length. The spacing between traces is indirectly defined by the pitch between adjacent traces and the trace width, which is mainly affected by flow rate, ink viscosity, and nozzle diameter.

The morphology of the surface of the Ag imprints is shown in figure 8(a); the Ag ink is composed of faceted particles with size on the order of micrometres. The morphology of a CNT imprint after receiving the mechanical treatment is shown in figure 8(b); the micrograph evidences that the CNTs are protruding over the surface, which is essential to achieve field emission. In contrast, SEMs of imprints made of CNT ink with 0.16 wt% MWCNT concentration that received the mechanical treatment showed very few CNTs protruding, which led us to refrain from using such ink in devices. The histogram of the diameter distribution of the CNT powder used to manufacture the inks is shown in figure 8(c). Diameter sizes in the range of 16–50 nm were counted, with an average diameter equal to 26 nm.

3.2.2. Current–voltage (I–V) characteristics. Figure 9(a) shows typical I–V characteristics of the single-trace field emission electron sources. The start-up voltage of these devices is equal to 90 V (emission current of 5 nA). The maximum current collected by the anode is 12.0 μA (6 μA cm⁻²) when the bias voltage between the emitting electrode and the gate is equal to 850 V. There is linearity between the emitted current and the anode current, as evidenced by figure 9(b), with over 99% of the emitted current transmitted by the gate; given that the anode is effectively hovering on top of the device, the linearity shows that the anode current is emitted by the device.

Figure 10(a) shows typical I–V characteristics of the square-loop field emission electron sources. The start-up voltage of these devices is equal to 62 V (emission current of 5 nA), while the maximum current collected by the anode is 120 μA (60 μA cm⁻²) when the bias voltage between the emitting electrode and the gate is equal to 850 V. There is linearity between the emitted current and the anode current, as evidenced by figure 10(b), with over 97% gate transmission; given that the anode is effectively hovering on top of the device, the linearity shows that the anode current is emitted by the device.

3.2.3. Fowler–Nordheim (FN) analysis. Field emitted current follow the FN equation [1], i.e.

\[ I \propto V^2 \exp \left( \frac{-6.49 \times 10^6 e^1.5}{\beta V} \right) \]  

(4)

where \( I \) is the electron current produced by a field emitter biased at a voltage \( V \) with respect to the gate electrode, and \( \beta \), in cm⁻¹, and \( \phi \), in eV, are the field enhancement factor of the field emitter and the work function of the emitting surface, respectively. Therefore, a plot of \( \ln(I/V^2) \) versus \( 1/V \) should map a straight line if the current is field emitted. Figure 11 shows the FN plot of the transmitted current (anode current) for the data plotted in figures 9 and 10. The goodness of fit of the least-squares fittings in figures 11(a) and (b) indicate that the anode current, and by extension most of the emitted current, are the result of barrier tunnelling of electrons into vacuum due to the high electric field on the emitter tips. The slopes of the two plots are fairly similar—this is expected because both emitting electrodes were made with the same ink formulation and source materials. For a CNT forest with a proximal gate the field factor is, to first order, equal to the inverse of the tip radius of the tips [19, 40]. From the slope of the least-squares fitting of figure 11(a), a field factor equal to 1.25 × 10⁶ cm⁻¹ is estimated, which corresponds to a MWCNT tip diameter equal to 16.1 nm assuming a workfunction of 4.81 eV for CNTs; similarly, from the slope of the least-squares fitting of figure 11(b), a field factor equal to 9.60 × 10⁵ cm⁻¹ is estimated, which corresponds to a tip diameter equal to 20.8 nm. These values fall within the distribution of tip diameters previously estimated (figure 8(c)), and are towards the lower end of the
distribution; this is expected because sharper tips are more likely to emit than duller tips for a given bias voltage.

The cross-section of the square-loop field emission electron source was simulated using Maxwell SV to assess the field enhancing effect of the electrode arrangement; the simulation predicts that surface electric fields as high as $6.7 \times 10^6$ V m$^{-1}$ would be generated on the edges of the emitting electrode when a gate bias voltage equal to 1100 V is applied between the gate and the emitting electrode (figure 12). Therefore, the simulation results indicate that the electrodes alone are not able to trigger field emission at bias voltages below $\sim$500 kV. Consequently, having released MWCNT tips from the bulk of the imprint is essential to cause field emission of electrons at much smaller bias voltage. These results compare well with the literature. For example, Youh et al reported a screen-printed flat panel light

Table 1. Summary of metrology of the 3D-printed field emission electron sources shown in figure 7. Each value is the average of over 300 measurements.

| Device type     | Gap between traces (μm) | Trace width Ag ink (μm) | Trace width CNT ink (μm) | Trace height Ag ink (μm) | Trace height CNT ink (μm) | Total active length CNT trace (mm) |
|-----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------------------|
| Single-trace    | 174.5                   | 281                     | 280                     | 22.5                    | 5                       | 25                                |
| Square-loop     | 499                     | 187                     | 204                     | 19                      | 5.5                     | 135                               |
source with SiC nanowires as field emitters and in-plane gate structure [35]; at 1 kV anode bias voltage their devices produced up to ∼38 μA cm⁻² (gate bias voltage equal to 500 V) with 90% gate transmission. Also, Ulisse et al reported a photolithography-defined, semiconductor clean-room-made, triode with extractor finger structure and CNT electron source for GHz applications [41]; their device generated about 40 μA (40 μA cm⁻²) of electron current (2.6 kV anode bias voltage; current increases to 120 μA for 3.4 kV anode bias voltage). In addition, Zhang et al reported a photolithography-defined, semiconductor cleanroom-made field emission electron source with hydrothermally grown ZnO nanostructures as field emitters and in-plane gate electrode [42]; the devices produced ∼100 μA (4 μA cm⁻²) with 26% gate interception with 2 kV anode bias voltage and 300 V gate bias voltage. Moreover, Yang and Velásquez-García reported the fabrication of a 3D-printed electron impact gas ionizer with CNT field emission electron source.

Figure 9. Emitted current, gate current, and collected (anode) current versus gate electrode-to-emitting electrode bias voltage (a) and currents intercepted by the gate and collected by the anode versus emitted current (b) for a single-trace electron source.

Figure 10. Emitted current, gate current, and collected (anode) current versus gate electrode-to-emitting electrode bias voltage (a) and currents intercepted by the gate and collected by the anode versus emitted current (b) for the square-loop electron source.

Figure 11. FN plot of the anode current for a single-trace device (a) and a square-loop device (b).
that had a substrate with PECVD-grown CNTs as electron source and a suspended grid as gate electrode [40]; although their field emission cathode emitted 1.4 mA at a 700 V gate bias voltage, their device had a gate transmission equal to only 31.5%.

One of the strengths of 3D printing is its capability to create low-to-mid volume batches, complex parts, and customized parts at a fraction of the cost of traditional manufacturing, with significant waste reduction [43, 44]. The cost in materials of the CNT ink is estimated at US $1.47/ml, while the cost of the commercial Ag ink is US $55/ml, and the cost of each glass substrate is US $0.14; therefore, for the square-loop device reported in this study, the amount of CNT ink used costs ~US $0.12, while the amount of Ag ink used costs ~US $2.20, resulting in a total cost in materials below US $2.50 per device. This cost compares favourably to the cost associated with screen printing and semiconductor cleanroom manufacturing.

Given the performance and dimensions of the fully-printed field emission electron sources, three tentative applications are suggested: compact mass spectrometry, pico and nanosatellite electric propulsion, and compact x-ray generation. First, the devices could be used in a miniaturized mass spectrometer [45, 46]; a summary of key specifications of selected reported systems is shown in table 2 [47–50]. Mass spectrometers generate mass spectra by sorting out ions in vacuum using electrical and/or magnetic fields; the ions can be created in various ways at external (ambient pressure) or internal (vacuum) conditions. For internal ion generation, a preferred method is electron impact ionization, in which neutral gas molecules are ionized via fragmentation using a stream of energetic electrons [51]. The devices reported in this study could be used as electron source in an electron impact gas ionizer; benefits of using CNT electron sources includes compatibility with low-vacuum (10 mTorr level [19]) operation, which lines up well with the general trend of relaxing the vacuum requirements in this kind of compact instruments. The electron current required in a mass spectrometer with an electron impact ionizer is related to the noise floor of the detector, the transmission efficiency of the mass filter, and the ionization efficiency of the ionizer (i.e. how many ions generates per electron emitted). The noise floor of a typical mass spectrometer detector is on the order of 1 pA. In a typical mass filter (e.g. a quadrupole), a few percent of the ions created by the ionizer get transmitted. The ionization efficiency is linear with pressure, and at 20 mTorr is about 19% [19]. Therefore, for a typical lower bound of electron impact ionization pressure (~1 μTorr), the electron current required is on the order of 10 μA.

Second, the electron sources could be used as part of a handheld x-ray source for applications such as materials analysis via fluorescent spectroscopy [52] and radiography [5, 9, 53–56]; a summary of key parameters of selected reported compact x-ray sources is shown in table 3. The bias voltages required to activate our field emission electron source are over an order of magnitude smaller than the bias voltage required to produce x-rays via bremsstrahlung, and the currents are of the right order of magnitude. For creating x-ray images, what is important is the number of photons created per exposure; the number of photons is proportional to the electrons supplied during the exposure, that is, the electron current times the exposure time. Therefore, a cathode with significantly less current could generate the same images by increasing the exposure time. However, if needed, possible approaches for increasing the current emitted by our devices include (i) making the emitting area larger, (ii) making the imprint patterns finer and spaced tighter, and (iii) using thinner CNTs.

Third, the CNT fully-printed electron sources could be used as neutralizers in pico and nanosatellite electric propulsion [57]; a summary of key parameters of selected reported pico and nanosatellite electric thrusters is shown in table 4 [58–61]. For in-orbit manoeuvres, electric propulsion is preferred over chemical propulsion because it uses more efficiently the propellant (the speed of the jet in a chemical rocket is limited by the amount of energy generated by the chemical reaction, while the speed of the beam in an electric rocket can be arbitrarily increased using a suitable bias voltage [62]). Most electric thrusters emit a positive beam to provide thrust to the spacecraft, hence requiring a source of electrons to keep overall charge neutrality; however, in a nanosatellite, the standard hollow cathode technology is not attractive because it consumes propellant at a flow rate comparable (or even larger) than the propellant used to produce thrust. Unlike metal-based field emission sources [63], CNT cathodes can withstand the oxygen traces found at Low-Earth Orbit (LEO), hence becoming practical in many potential nanosatellite applications including Earth surveillance, communications, and weather monitoring. The devices reported in this study would be adequate to neutralize the beam in certain missions, e.g. LISA [60]; in other cases, a device with an order of magnitude larger area that produces an order or magnitude more current is required, which is compatible with the capabilities of DIW and with the dimensions of a picosatellite (1–3 cubic liters, 600 cm²–1400 cm² surface area [64]). Other means for increasing the current emitted by our
devices are making finer and tighter imprint patterns and using thinner CNTs.

### 4. Conclusions

We reported the design, fabrication, and characterization of the first fully additively manufactured CNT field emission electron sources. The devices were made via DIW printing and consist of a flat dielectric substrate with a trace made of a CNT ink as emitting electrode, symmetrically surrounded on both sides by a trace made of Ag microparticle ink as in-plane extractor gate. The CNT ink with 0.16 wt% MWCNT concentration has an electrical resistivity equal to 1.53 $\Omega$ cm, but showed a very small number of nanotubes protruding on the surface, which resulted in no field emission. In contrast, the CNT ink with 0.82 wt% MWCNT concentration has an electrical resistivity equal to 0.77 $\Omega$ cm and showed a great profusion of released nanotubes on the surface, which resulted in electron field emission. Electrical characterization of printed devices resulted in start-up voltages as small as 62 V and in emission currents as high as 120 $\mu$A ($60 \mu$A cm$^{-2}$) with high (>97%) gate transmission. The 3D-printed cathode technology is of interest in applications such as portable mass spectrometry, handheld x-ray sources, and neutralizers for pico and nanosatellite electric propulsion.

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