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## Perspective

# Nanomaterial-based x-ray sources

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**Abstract**

Following the recent global excitement and investment in the emerging, and rapidly growing, classes of one and two-dimensional nanomaterials, we here present a perspective on one of the viable applications of such materials: field electron emission based x-ray sources. These devices, which have a notable history in medicine, security, industry and research, to date have almost exclusively incorporated thermionic electron sources. Since the middle of the last century, field emission based cathodes were demonstrated, but it is only recently that they have become practicable. We outline some of the technological achievements of the past two decades, and describe a number of the seminal contributions. We explore the foremost market hurdles hindering their roll-out and broader industrial adoption and summarise the recent progress in miniaturised, pulsed and multi-source devices.

Keywords: nanomaterials, electron emission, x-ray sources, field emission, carbon nanotubes

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

Since their discovery in 1895, x-rays have proven central to a myriad of analytical technologies that have allowed for the imaging of otherwise hidden features in complex objects. As a result, x-rays have remained the standard for medical diagnostics and industrial inspection. Despite early excitement and widespread adoption of these new high energy sources, the development and roll-out of innovative emission devices stagnated thereafter. Virtually all modern commercial x-ray sources rely on refractory metal based thermionic sources, as was the case almost a century ago [1]. Though unquestionably functional, such devices necessitate high temperature operation, typically of the order of 1000 °C, making their control and efficiency sub-optimal. Besides this limitation, their lifetime is restricted and the ever more demanding needs of the medical, security and manufacturing communities have stimulated the search for newer, functionally advanced sources with capabilities such as high-speed, pulsed operation and real-time 2D and 3D imaging for *in situ* applications. This is particularly relevant in the pharmaceutical, food security, and heavy industries (figure 1). Indeed, there is considerable global interest in the realisation of low energy, real-time x-ray imaging techniques for advanced computed tomography and tomosynthesis. Replacement of costly and bulky multiple sources and gantries are a central financial driver alongside reduced scanning times. The x-ray field is diverse and has a market value anticipated to reach $10B/year by 2017. Though a significant market, little technological changes have occurred in the underpinning technology this past century. Here we outline some of the key developments in nanomaterial based x-ray sources as well as highlighting the key technological barriers and outstanding functional and manufacturing problems hindering the widespread adoption of these functionally unique systems.

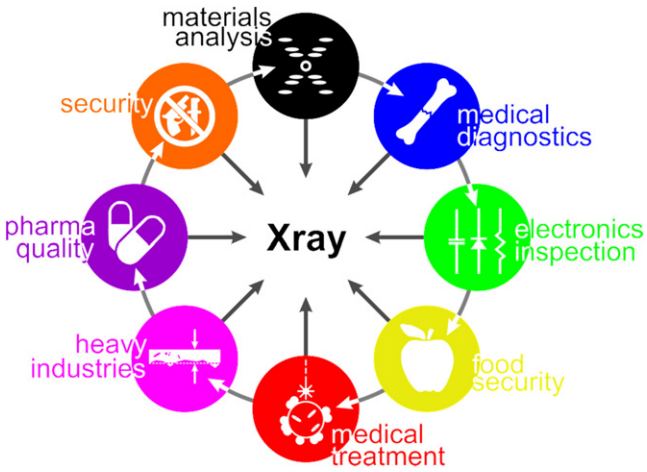


**Figure 1.** The diverse x-ray industry. Adapted from [30].

The cathode assembly provides the source of electrons in conventional x-ray tubes. Although various methods can be employed to form an electron beam, thermionic emission remains the most competitive, primarily due to the maturity of the technology. As an alternative, field emission possesses the ability to stimulate appreciably large currents at room temperature through an emission process that occurs near-instantaneously upon the application of a high extraction voltage. However, the development of field emission-based electron sources has significantly lagged thermionic sources in almost all applications. Figure 2 shows some typical industrial, heated-filament x-ray sources. Whereas thermionic sources can operate for extended periods at reduced vacuum conditions of $10^{-5}$ mbar, in the case of long-lasting true, non-ionising, field emission based x-ray devices, the need for stable high vacuum environments ($10^{-7}$ mbar) and a corresponding reduction in arcing events, alongside the need for reduction in the necessary high drive voltages, has significantly stifled their development to date. The distinct and non-conventional material properties such demanding operating conditions require has proven a major technological barrier, requiring new materials with low sputter cross-sections and high atomic knock-on thresholds. Since 1990, the emergence of a wide range of morphologically and electronically novel nanomaterials has, at least in part, provided one viable means of resolving many of these technological issues. As a result, field emission is returning to the fore as a viable alternative electron emission mechanism in commercial devices. Utsumi *et al* showed that materials with high aspect ratios, such as provided by the many various nanowires, allowed for a significant reduction in the required drive voltages [2]. When considered alongside the long list of other unique physical properties of many such nanomaterials; including but not limited to, in the case of the graphitic nanocarbons, extremely high electrical conductivity, remarkable thermal stability, and robustness towards electromigration, makes x-ray sources, based on field emission from this emerging class of materials, auspicious candidates for next-generation advanced imaging technologies.

The wider research community have embraced this. Meta-analysis of the existing literature clearly highlights that both the one-dimensional and emerging two-dimensional nanomaterials have the potential to mediate dramatic functional improvements. The one-dimensional materials, such as the nanowires and carbon nanotubes (CNTs), permit a substantial reduction in turn-on electric field, whilst two-dimensional materials, such as graphene and the wider transition metal dichalchogenides, have other characteristics that offer great value to developers [3]. Such features rapidly open up the potential for a new class of portable x-ray sources. Laboratory-based research efforts have, to date, strongly evidenced the

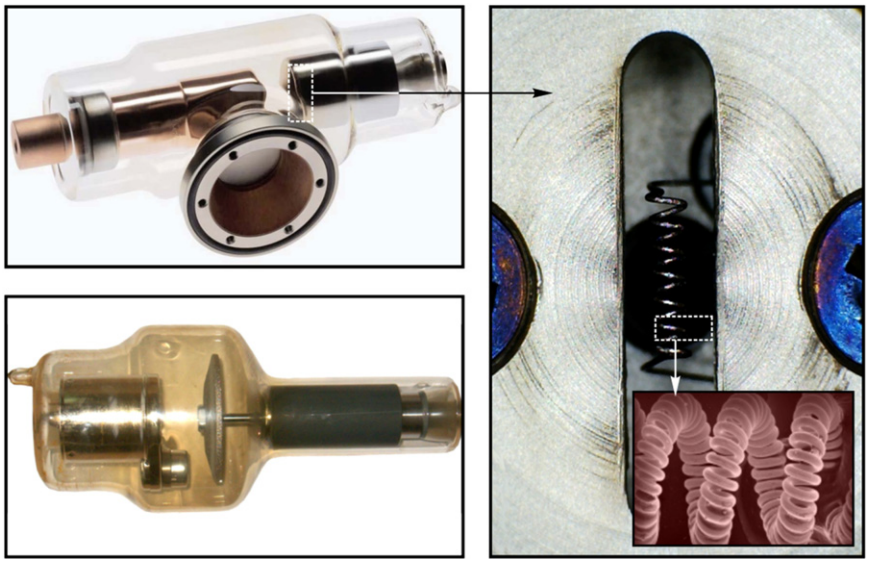

**Figure 2.** Example conventional thermionic-based x-ray sources. Adapted from [30].

potential of nanomaterials as efficient field electron emission sources. Nearly 6000 manuscripts were published on nanomaterial-based field electron emission between 2000 and 2015, however, and rather paradoxically, there were a relatively small number of published manuscripts on x-ray sources incorporating nanomaterial cathodes for the same time frame. In contrast, the commercial landscape for nanomaterial-based x-ray sources has grown at a similar rate; around 1000 patents were lodged between 2010 and 2015. There is clear commercial interest. Nevertheless, there is an evident disparity between the underpinning materials research community and the exploitation of such materials in commercial x-ray devices. Whilst a not-insignificant number of patents have been lodged, very few devices have made it to market. The present commercial landscape is dominated by small to medium-sized enterprises, each with its niche device. There has been on-going interest from some larger international conglomerates, such as Thales Electron Devices [4], Philips and Siemens. Siemens showed substantial commitment this past decade, particularly towards fast-scan airport inspection systems. Working with Xintek Inc., from 2007 via a joint venture called XinRay Systems (North Carolina USA), significant inroads were made towards a demonstrable multi-pixel device, however this collaboration was terminated in 2011. A collaboration between NASA and Oxford Instruments (CA, USA) in 2004, lead to published work on a MWCNT-based miniature source [5–7]. Oxford Instruments publically stated their on-going commitment towards the development of micro focal CNT sources. Their Eclipse II, battery operated miniature tubes (160 $\times$ 38 mm), capable of 3 W operation used CNT field emitters with a mass of 300 g. Few other compact commercial nano-based systems have yet become available. Significant functional advances in temporal stability, high beam currents, reduced turn-on fields, functional enhancements, and inexpensive mass fabrication remain strong market barriers. It is the challenging interface between emerging nano materials science and electrical engineering that make the commercialisation terrain elusive. Worldwide there is but a hand full of registered companies involved in developing nano-based x-ray sources, with very few devices available in the market.

Of those that have made it to high technology readiness levels almost all are based on disordered mats of nanomaterials, which only partly exploit the underpinning benefits of these high aspect ratio materials. More can be done to optimise their engineering and nanoscale morphologies. Xintek Inc. are a leader in the field, having demonstrated a range of screen-printed devices and multi-source systems

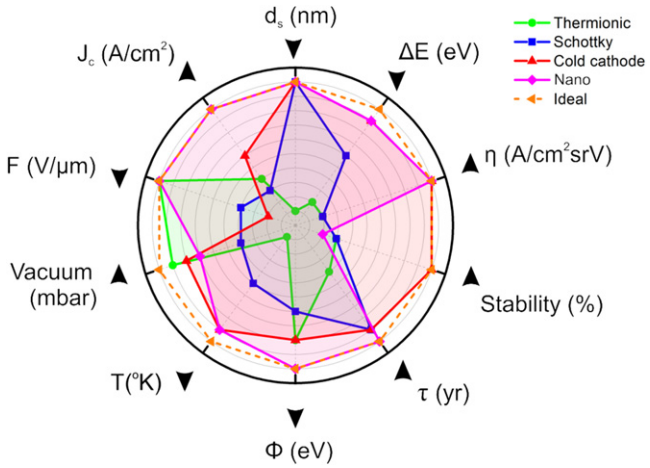


**Figure 3.** Polar plot of the performance figure of Merits for Thermionic, Schottky, Cold Cathode, Nano and ideal electron sources which underpin almost all commercial x-ray source technologies to date. Here $J_c$ is the current density, $F$ is the turn-on electric field, 'Vacuum' denotes the operating vacuum, $T$ the typical operating temperature, $\Phi$ the emitter work function, $\tau$ the lifetime, 'Stability' is the temporal stability, $\eta$ the electron-optical brightness, $\Delta E$ the energy spread of the emitted electrons, ds the virtual source size.

[8]. More recently, Cambridge X-ray Systems have demonstrated highly aligned, sub-micron patterned emitters. Certainly it is likely that this proof-of-concept multi-source technology will likely lead to nanoscale multi-source devices. Major outstanding challenges nonetheless remain. These include achieving high current densities, in excess of 1 A cm$^{-2}$ with multi-beam emission, in addition to further reductions in turn-on electric fields. In the case of nano-ink based emitters, this when combined with the need for aggressive and lengthy seasoning/conditioning has slowed development. Even with recent advances in nanomaterials synthesis and chemistry, this remains difficult. Progress continues.

Although nanomaterial based electron sources have impressively proven themselves in their lab-based operation, commercial devices remain in their infancy despite the significant wider research efforts, a consequence of the non-standard fabrication processes required and the variation therein. Broadly speaking, all nanomaterials fall within two manufacturing categories; those fabricated through conventional top-down lithographic processes [9, 10], and those fabricated through bottom-up self-assembly. The first being cheap and readily accessible for proof-of-principle devices, whilst the more infrastructurally expensive latter has been shown to be initially costly yet extremely fruitful in defining ultra-high aspect ratio emitters, with both CNTs and nanowires [11, 12]. Most efforts to date have focussed on the nanocarbon allotropes, with CNTs and diamond [13, 14] dominating. Indeed, across almost every standardised industrial metric, the nanocarbons have consistently offered superior performance relative to more conventional technologies (figure 3). Research in x-ray sources based on the nanocarbons is on-going, particularly from groups in Beijing (China), North Carolina (USA) and Cambridge (UK) [15–26]. Nevertheless, a number of fundamental challenges remain, the majority of which intimately relate to the fabrication procedures employed. Figure 4 outlines some of the most common fabrication techniques. More exotic approaches are continuing to come on-line, although most employ printing techniques using nanomaterial-based inks. This severely limits the degree of alignment attainable in these aggregated systems. Moreover, aggregation of nanomaterials is common and ink formulations as a result often employ vacuum unstable surfactants and media to form homogenous and printable inks. Such processes, though simple, inexpensive and rapid, almost invariably reduce the ultimate temporal stability of the fabricated devices, as well

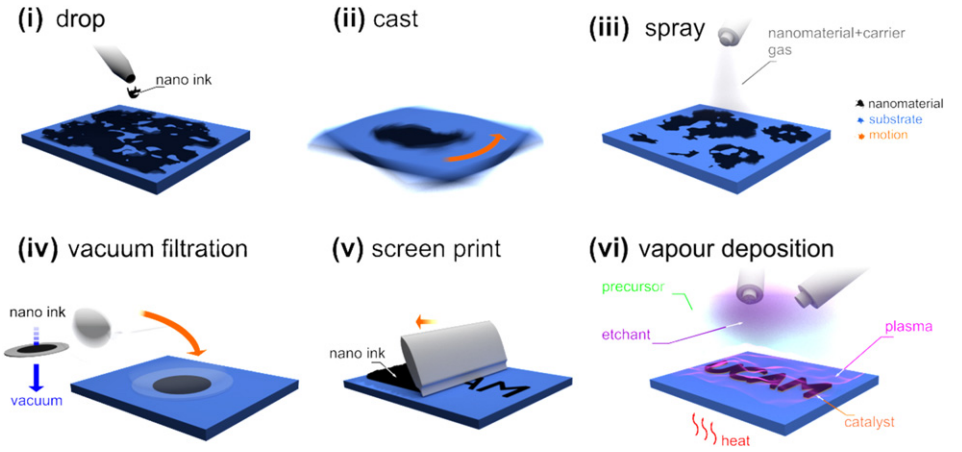


**Figure 4.** Nano-material electron emitter fabrication. Nanomaterial deposition techniques used for the realisation of nanomaterial based x-ray sources.

as necessitating time-consuming seasoning periods, often as high as several hundreds of hours, in order to remove these deleterious surface species. Chemical vapour deposition (CVD) offers intrinsic advantages to align and selectively deposit nanomaterials in a clean approach on a wide range of substrates, which greatly benefits the aspect ratio and uniformity of the emitters. CVD, *in situ* synthesised nanomaterials can also be used without additional purification, though improvements in emission temporal stability have been reported with the removal of the seeding catalyst particles in the case of carbon nanotube electron emitters. Nonetheless, in both the screen printing and CVD approaches, weak adhesion between the electron emitters and the substrate continue to plague such devices. Emitter delamination has proven a major technological problem. Joule heating at high emission current densities, coupled to the necessarily high electric fields, allows for substantial torque induction and subsequent emitter removal. This poses severe reliability and life time issues for all nano-ensemble based x-ray sources. Other manufacturing challenges are outstanding, including; low device-to-device functional consistency, device yields, robustness towards ion bombardment, lifetime enhancement, temporal emission stability, high voltage stability, focal spot size reduction and consistency, and x-ray flux and dose improvement. Underpinning almost all of these issues is the need for fabrication reproducibility at commercially viable costs. Nevertheless, substantive commercial progress will not be made until the underlying nanomaterials growth and manufacturing processes are made compatible, and familiar, to those incumbent systems employed in existing CMOS foundries. New nanomaterial growth techniques based on established foundry deposition systems must be identified, alongside new catalysts that are known stable in such foundry environments. The use of gold colloidal catalysts in the growth of silicon nanowires by CVD, for example, will certainly be a key factor in preventing their adoption in standard CMOS devices, for fear of contamination of existing chip lines. The same is true for many reported nanomaterials and the catalysts used in their production.

Functional issues have also prevented the roll-out of many developed devices. One such example, which has constrained portable device development is in achieving the ultra-low turn-on devices necessary for operation far from the inter-electrode breakdown regime. This remains a difficult task. Such low voltage operation is critical in producing usefully high current densities and technologically relevant lifetimes. There are, however; some promising strategies to further optimise existing nanomaterial scaffolds to fulfil the demanding functional requirements. Of these, one of the most interesting is the coating of materials, or adlayers, on the nano-scaffolds. The use of low work function adlayers promotes

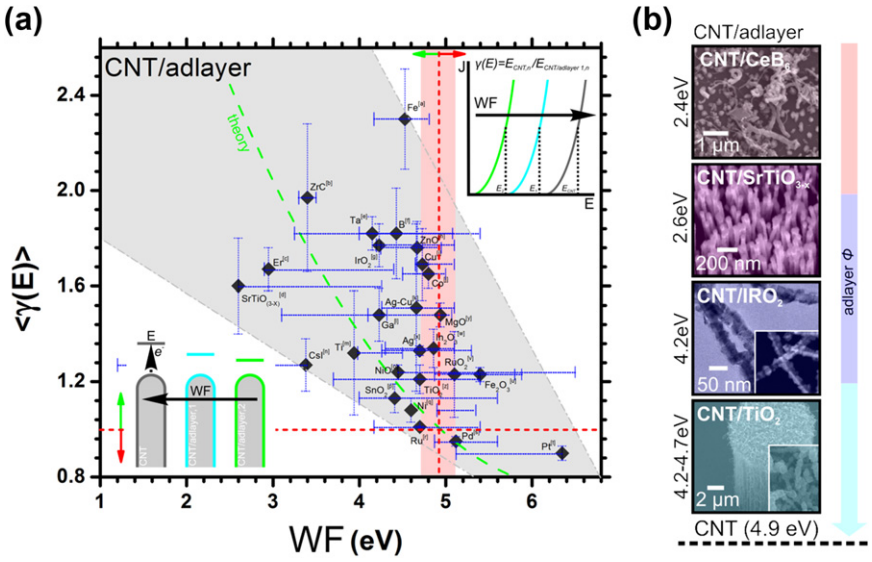


**Figure 5.** (a) Enhancement of carbon nano-based electron sources as a function of adlayer work function (WF). (b) Scanning electron microgrpahs of various adlayers on carbon nanotube scaffolds.

emission at much reduced electric fields. Figure 5 summarises some of the more common adlayers considered to date. Such approaches benefit from the morphological advantages of the nanomaterial, whilst also exploiting the electronic characteristics of the otherwise planar adlayer. The composite material functions better than either of the individual components. Indeed, the exploitation of the novel properties of various nanomaterials allow for new device geometries capable of enhanced function, such as the use of graphene as a highly transparent gate electrode [23]. This general approach of combining nanomaterials has also lead to the development of hermetically sealed emitters with structured adlayers that have been shown to both reduce the turn-on field and also to enhance emission stability [27, 28]. Though certainly for the functional betterment of these devices, such multi-nanomaterial systems further compounds issues relating to challenging manufacturing.

Field emission x-ray sources, based on nanomaterials, have experienced continued development, spear-headed largely by the family of graphitic nano-carbon allotropes. Xintek Inc. (USA) were one of the first to demonstrate a multi-source system capable of near real-time three-dimensional reconstruction (figure 6(a)). Though bulky, their devices consisted of more than 30 individual addressable macro-scale sources formed from DC-conditioned, electrophoretically deposited CNTs (Insert, figure 6(b)). Systems consisting of up to 52 sources have also been constructed, with more recently micro-integrated multi-source devices for electrotherapy applications, having been reported (figure 6(b)). Various compact and miniature sealed sources have also been developed (figure 6(c)), with the Electronics and Telecommunications Research Institute, Korea having demonstrated one of the smallest tubes, to date (figure 6(d)); the size and form make it well-suited for brachytherapy and *in vivo* applications. Nevertheless, such developments have yet to gain any market traction due to various limitations associated with the nanomaterial deposition techniques and underlying manufacturability. Cambridge X-ray Systems have developed a number of unique emission geometries based on the use of low-cost CVD of patterned and vertically aligned CNTs (figure 6(e)). There has also been great interest shown in pulsed-mode devices. The ability to rapidly switch an x-ray source opens up many interesting possibilities particularly when allied with advanced image processing techniques. Field emission sources have a unique potential for ultra-fast, pulsed operation as the maximum operation frequency is principally dictated by the drive

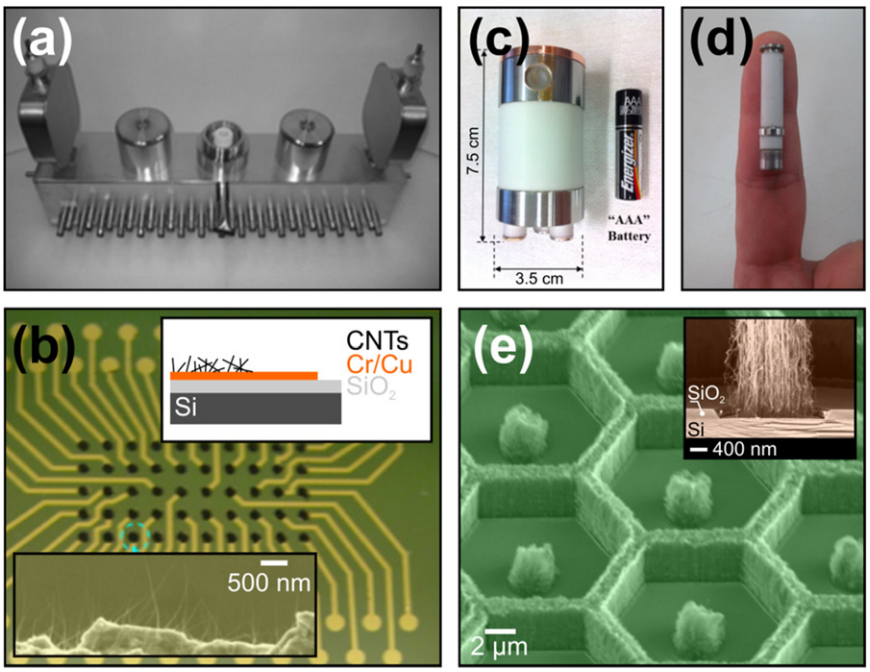


**Figure 6.** Progress in carbon nanotube-based x-ray sources. (a) Xintek Inc. distributed CNT tomosynthesis unit consisting of 31 individually addressable x-ray sources enclosed in a single vacuum chamber, and below a schematic the corresponding drive circuitry. Adapted from [8]. (b) An on-chip multi-source electrophoretically deposited CNT electron sources. Insert depicts a cross-sectional electron micrograph of the as-deposited disordered CNTs (scale bar: 500 nm) and a schematic cross-section of the device structure. (c) A 7.5 cm long sealed CNT-based x-ray source operating at 30 kV [31]. (d) A disordered miniature CNT, brazed triode x-ray source fabricated by ball milling, and firing of a CNT paste on the apex of a 0.6 mm Kovar rod, and operated at 12 kV [32]. (e) Scanning electron micrographs of patterned, aligned CNT electron sources by Cambridge X-ray Systems. Adapted from [30].

electronics and the transit time associated with the electron tunnelling at the emitter–vacuum interface. Most systems demonstrated have been capable of DC or low frequency operation, with only a small subset of devices operating at frequencies of more than a few tens of kHz.

To date nanomaterial synthesis costs have hindered the adoption of nanomaterials in bulk, composite-applications. Conversely, however, as each x-ray source requires only an extremely small quantity of nanomaterial, the majority of the cost is not, paradoxically, associated with the nanomaterial growth per se, but rather with the wider fabrication processes, and the manufacturing nuances therein. $\$10/g^{*}$ of nanomaterial ($^{*}$CNTs, at the time of publication) is entirely commercially feasible. The central manufacturing challenge lies in identifying suitable, scalable, and parallel means of fabricating devices in their entirety via inexpensive, high-yield, automated processes. Advanced manufacturing lies at the heart of significantly reducing the cost per unit. The need for advanced manufacturability remains, perhaps the most critical technological barrier. Progress is nonetheless evident [29]. Vapour deposition approaches may soon represent a viable means of manufacturing. Notwithstanding, even in the absence of such general technological barriers, to overcome the dominant market force; namely adoption inertia associated with existing technologies, significant added functionality is critical. Although retrofitting of such systems may be costly, previous inaccessible or difficult market sectors are being identified. The outlook is certainly challenging, though not prohibitive. Whilst the above goes some way to explain the lack of commercially available products, research efforts continue, and it is likely that the formation of further commercial entities will follow. The lab-to-fab road map remains nonetheless treacherous. Though slow, the prospects of field

emission based x-ray sources will undoubtedly gain traction. There is much scope for rapid growth following the introduction of industry-accepted growth processes. Indeed, it is the highly parallel fabrication, coupled to emerging added on-chip functionality and increasingly accessible advanced manufacturing processes based on community accepted catalytic systems, which will play pivotal roles in establishing the broader adoption of nanomaterial based x-ray sources.

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## References

[1] Coolidge W D 1913 *Phys. Rev.* **2** 409–30
[2] Utsumi T 1991 *IEEE Trans. Electron Devices* **38** 2276–83
[3] Li C *et al* 2014 *Adv. Funct. Mater.* **24** 1218–27
[4] Mazellier J 2012 Carbon nanotubes based photocathodes for multisource x-Ray generators *Nanotechnology: Advanced Materials, CNTs, Particles, Films and Composites* vol 1 (Austin, TX: NSTI) ch3
[5] Sarrazin P, Blake D, Delzeit L, Meyyappan M, Boyer B, Snyder S and Espinosa B 2004 *Adv. X-ray Anal.* **47** 8
[6] Killian J L, Zuckerman N B, Niemann D L, Ribaya B P, Rahman M, Espinosa R, Meyyappan M and Nguyen C V 2008 *J. Appl. Phys.* **103** 064312
[7] Silan J L, Niemann D L, Ribaya B P, Rahman M, Meyyappan M and Nguyen C V 2009 *Appl. Phys. Lett.* **95** 133111
[8] Qian X *et al* 2012 *Med. Phys.* **39** 2090–9
[9] Anirban B, Michael E S, Arash A F and Fernando V-G L 2015 *J. Phys. D: Appl. Phys.* **48** 225501
[10] Shuo C, Hill F A, Heubel E V and Velasquez-Garcia L F 2015 *J. Microelectromech. Syst.* **24** 373–83
[11] Zhou J 2003 *Adv. Mater.* **15** 1835–40
[12] Satoshi O, Shigeo O, Junichi N, Yoshiaki O, Haruhiko I and Hidetoshi S 2008 *Japan. J. Appl. Phys.* **47** 7303
[13] Fukumoto S, Honma A, Kaneko J H, Nishibayashi Y, Ueda A, Yamamoto Y, Imai T, Fujita F, Kawamura S and Furusaka M 2008 *Diam. Relat. Mater.* **17** 764–7
[14] Rangsten P, Ribbing C, Strandman C, Hök B and Smith L 2000 *Sensors Actuators* A **82** 24–9
[15] Chang S X and Zhou O Carbon Nanotubes Field Emission X-ray for Research and Clinical Applications in Radiation Oncology http://amos3.aapm.org/abstracts/pdf/77-22629-310436-91429.pdf. (Accessed: 19 August 2014)
[16] Zhang J, Cheng Y, Lee Y Z, Gao B, Qiu Q, Lin W L, Lalush D, Lu J P and Zhou O 2005 *Rev. Sci. Instrum.* **76** 094301
[17] Zhang J, Yang G, Cheng Y, Gao B, Qiu Q, Lee Y Z, Lu J P and Zhou O 2005 *Appl. Phys. Lett.* **86** 1–3
[18] Zhang J, Yang G, Lee Y Z, Chang S, Lu J P and Zhou O 2006 *Appl. Phys. Lett.* **89** 064106
[19] Zhang J, Yang G, Lee Y Z, Cheng Y, Gao B, Qiu Q, Lu J P and Zhou O 2006 A multi-beam x-ray imaging system based on carbon nanotube field emitters *Proc. SPIE* **6142** 614204
[20] Zhu W, Bower C, Zhou O, Kochanski G and Jin S 1999 *Appl. Phys. Lett.* **75** 873–5
[21] Cole M T, Collins C, Parmee R, Li C and Milne W I 2015 Nano carbon electron emitters: advances & applications *Chemical Functionalisation of Carbon Nanomaterials: Chemistry & Applications—Structure & Synthesis* (London: Taylor and Francis)
[22] Cole M T, Hallam T, Milne W I and Duesberg G S 2013 *Small* **10** 95–9
[23] Cole M T *et al* 2013 *Adv. Funct. Mater.* **24** 1218–27
[24] Cole M T, Li C, Zhang Y, Shivareddy S G, Barnard J S, Lei W, Wang B, Pribat D, Amaratunga G A J and Milne W I 2012 *ACS Nano* **6** 3236–42
[25] Cole M T *et al* 2011 Novel nanostructured carbon nanotube electron sources *Int. Conf. on Materials for Advanced Technologies (Singapore)* (Pan Stanford Publishing)
[26] Cole M T, Teo K B K, Groening O, Gangloff L, Legagneux P and Milne W I 2014 *Sci. Rep.* **4** 4840
[27] Ding S, Li C, Lei W, Zhang Y, Qasim K, Cui H, Zhang X and Wang B 2012 *Thin Solid Films* **524** 245–8

[28] Li C *et al* 2010 *Appl. Phys. Lett.* **96** 143114–7
[29] Teo K B K *et al* 2003 *Nanotechnology* **14** 204–11
[30] Parmee R, Milne W I and Cole M T 2014 *Nano Convergence* **2**
[31] Kim J-W, Jeong J-W, Kang J-T, Choi S, Choi J, Aha S and Song Y-H 2013 A digital compact x-ray tube with carbon nanotube field emitters for advanced imaging systems *Proc. SPIE: Medical Imaging 2013—Physics of Medical Imaging* p 6
[32] Kang J-T, Kim J-W, Jeong J W, Choi S, Choi J, Ahn S and Song Y-H 2013 *ETRI J.* **35** 1164–7