Electrospray printing: Unravelling the history of a support free three-dimensional additive manufacturing technology

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In this perspective article the author highlights a revolutionary technology, which makes reality, the ability to print true three-dimensional architectures, containing self-standing and self-supporting overhangs in the nano and micrometer scale, without the need for supports of any kind. There have been many attempts to achieve this feature in the rapid prototyping/additive manufacturing fields but has been met with little or no success. Current approaches to three-dimensional printing of self-standing and overhanging architectures have been achieved with the use of some form of supporting mould, secondary process or structure which could be either in the form of a viscous liquid or a solid structure to the coupling of lasers, temperature etc. Unfortunately, the use of such methodologies brings with them many issues and limitations, while destroying the concept of additive manufacturing. Note the author here defines additive manufacturing as a technology able to add materials when required during the fabrication of a 3D architecture without the need for external assistance or supports. These limitations in classical fabrication processes, restricts the use of advanced materials such as living biological cells to sensitive biomolecules to many others, for the forming of three-dimensional biological and non-biological architectures, whilst also increasing the costs and materials waste, which are required for acting as moulds, supports etc.

Keywords: Electrohydrodynamic jet (e-jet) printing; Support free overhangs; Micro to nano self-supporting architectures; Micro and nano features; Printing fibrous scaffolds

Introduction

Classically, additive manufacturing is defined as the addition of materials during the fabrication stage as opposed to removing materials for fabricating the final architecture [1]. The example that best illustrates this concept, is when pitting of the two technologies well known as stereolithography [2] and milling [3]. The former uses lasers to polymerize a monomer held in a reservoir, which after every passing of the laser, polymerizes (that exposed monomer layer) resulting in a solid layer sitting on a movable platform. Once the laser has completed a layer, the platform holding the previously polymerized layer, within the reservoir accommodating the monomer, moves down a given distance thus exposing an uncured layer of monomer to the repeated laser path. The process is repeated as required to form an architecture layer-by-layer, which has complex features in the nano to micrometre scale. The latter, milling, starts with a block of material which undergoes material removal with the aid of cutters. Thus, making the former economical and significantly reducing waste. Stereolithography has morphed in many ways, yet the concept has remained the same, namely the polymerization/solidification of a light sensitive monomer etc. Recent retrofits of this technology are referred to as continuous liquid interface production (CLIP) and volumetric additive manufacturing (VAM). The reader should note the monomer/resin, acts as the support

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http://dx.doi.org/10.1016/j.mattod.2022.12.006

in which overhangs are formed. Therefore, the final product once fully formed, requires post-processing such as cleaning etc, prior to it being used. The reader should bear in mind that, the remaining liquid in the bath cannot be reused, in particular, in scenarios where the architectures are created for biological and medical applications. In those biological and cellular studies, the cells within these resins are entrapped/gelled (softly held) to hold them in place, prior to them being formed into an architecture, without which, the cells would sedimentate. There are many other pre- and post-processing steps the final cell-bearing architectures need to undergo before seeing exploration in either *in-vitro* or *in-vivo* studies. Although these technologies have contributed a great deal to many areas of research, as have both, soft lithography and dip-pen lithography, the technologies are limited in their ability to process/handle living cells/biomolecules to materials as either multimaterials or graded materials configurations, in a single step. For e.g., the monomers/resins used for suspending cells, have additives which are not cell friendly and will never be used in either short- or long-term biomedical investigations or in clinical medicine, due to their carcinogenicity. The inability for these technologies to directly handle living cells and form architectures requiring minimal intervention has seen the birth of 3D printing.

3D printing has many manifestations, which range from droplet formation to filament drawing techniques, which explore piezoelectricity, solenoid to pressure and screw driven droplet and filament extrusion approaches to name a few [4]. This technology has seen the handling of a wide range of materials including cells. That being said, one common feature all these 3D printing technologies inherit is their inability to handle viscous/-concentrated liquids/suspensions containing concentrated particulate systems, multiple cell types and/or biomolecules. As handling such systems have been known to create needle blockages to other obstacles which cannot be overcome without compromising the deposited resolution. In fact these technologies have negative effects on the handling of living cells/biomolecules as it inflicts and exerts significant pressures on the cells/biomolecules during the extraction to the droplet ejection, where cells/biomolecules undergo shearing, death and denaturing respectively within needles [5]. This limitation has seen the technology temper its hype and promise to print an entire tissue or organ, to forming a small-scale architecture containing limited cell numbers, in the hope to model a tissue or cell-process. The only option for this technology to process both large volumes of either viscous liquids/suspensions and/or mixed cell types, is to either use many large bore printing needles (which significantly compromises printing resolution) to printing repeated times which is time consuming and tedious. In the context of printing 3D architectures, the technology can do so with limited viscosity solutions to those solutions which are shear thinning liquids. Many architectures have been printed using this technology but most importantly in the context of this perspective article, the technology cannot print overhangs which are self-supporting. Overhanging architectures can be printed with the aid of many supports which range from either printing in a viscous liquid bath, the use of supporting architectures (which hold up the overhangs) to the use of either lasers, or temperature etc. These supports (liquids baths in which printing has taken place to those structures used as supports) cannot be reused and therefore are a waste of materials. These many forms of supports as previously stated bring with them many pre- and post-processing steps and limitations (sterility), where the processing of living cells/biomolecules are concerned. These limitations have given birth to the technology referred to here as electrospray printing (EP). Electrospray printing (aka e-jet printing: electrohydrodynamic jet printing) is a manifestation of the technology well-known as either electrohydrodynamic atomization or electrosprays.

Electrosprays

Electrosprays have been in existence since 1628 [6] with subsequent significant contributions from many eminent scientists [7]. The recent most significant contribution came from Professor John Fenn who coupled electrosprays with mass spectrometry to accurately identify biomolecules from their charge to mass ratios, hence giving birth to the widely established technology known as electrospray ionization mass spectrometry (ESI-MS) [8]. These revolutionary findings were recognized by the Nobel Chemistry committee in 2002 [9]. Briefly electrosprays are a class of sprays which are formed by a liquid flowing within a conducting needle held at a higher potential wrt some grounded electrode. The charged liquid on entering the electric field is accelerated towards the grounded electrode thus forming a spray. There are essentially eight parameters governing the process, namely the liquid properties electrical conductivity, viscosity, density, surface tension and relative permittivity, the applied voltage and flow rate of the media to the needle to finally the equipment set-up, respectively. It is noteworthy for the reader to understand at this point that when a balance is struck in all the parameters, the spray forms into the mode referred to as cone-jet mode [10]. Here as the mode's name suggests, a stable cone is formed at the charged needle exit from the apex of which a jet emanates subsequently breaking down into either a three-dimensional conical spray of droplets (Fig. 1a) or a stream of droplets (Fig. 1b). Many needle exit shapes have been investigated, the most common and most explored has been either a straight cut edge or the chamfered edge. Increasingly the latter has become more popular as it reduces the region referred to as the stagnation zone [11].

The investigations into needle configurations does not end there, but extends to the ability to explore needle systems in the coaxial (including side-by-side dual capillary systems), triaxial to multi-axial systems which yield some unique structures [12]. In a materials science standpoint this technology has many unique features which highlight its flexibility and versatility, namely electrosprays use large inner bore needles (>1000um), thus allowing the processing of highly concentrated suspensions containing a wide range of advanced materials (including cells and whole fertilized embryos) [13]. From the processing of both viscous liquids and suspensions (containing either micro and nano molecules/particles), electrosprays are capable of generating droplets and residues in the few nano/micrometres [14]. Much like the needle exit and configurations undergoing investigation, the ground electrode has taken many geometrical variations, primarily seeing it varying from a ring, plate to point. These three ground electrode geometries have been used to either

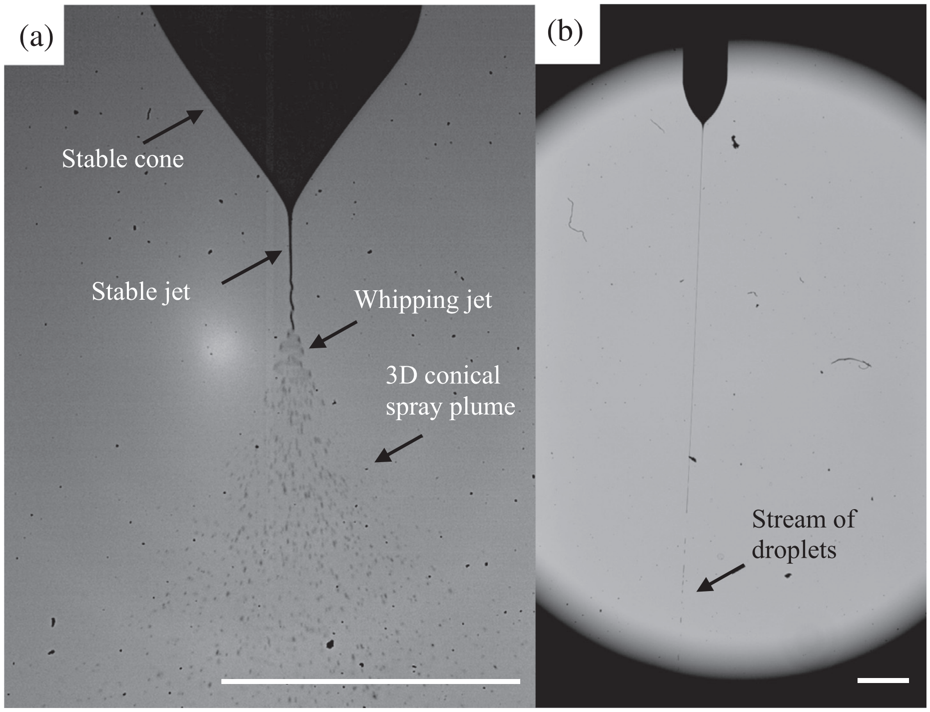

FIGURE 1

Depicts characteristic stable cone jet mode electrospray configurations in (a) spray mode where a 3D conical spray plume evolves as a result of the whipping jet brought about by air drag. Panel (b) illustrates the stable cone-jet mode with the jet undergoing controlled droplet break-up, thus generating a stream of droplets for electrospray printing. Note the liquids subjected to electrosprays in these panels are namely (a) ethanol and (b) polyethylene glycol based respectively. The scale bar in both panels represent ~1800 μm.

form a conical spray or a stream of droplets to their coupling for controlling the external electric field for manipulating the forming spray to droplet flight and their precision deposition. In addition to these features if the technology were to handle a polymeric solution/suspension of a viscosity of approximately 10000 mPa s (this viscosity range varies with the molecular weight of the polymer used etc.) the process will automatically transition to its sister technology known as electrospinning. Succinctly, electrospinning is where the jet unlike in the case of electrosprays, does not undergo break up but elongates into a continuous fibre which on collection over time forms a three-dimensional scaffold [14]. The author will leave electrospinning here, as the focus of this article is on electrosprays. Electrosprays have been explored for the handling of a wide range of materials from structural, functional to biological, for applications spanning the physical to the life sciences [15].

Electrospray printing (EP) 2D/3D layered architectures

Electrospray's ability for handling a wide range of materials as concentrated suspensions yet possessing the capacity of depositing residues much smaller than the diameter of the needle, cued this technology for its utility as a printing approach. The early days of EP saw the three ground electrode configurations namely the ring, plate and point explored for focusing the jet. These preliminary studies demonstrated at the time, the point electrode to be the best for focusing the spray plume to the tip of the pointed electrode [16]. Basic solutions and particulate suspensions were made with coloured ink mixed into the suspensions. Later a piece of A4 paper was placed on the pointed ground electrode and both the flow rate and applied voltage was switched on. It was found that the spray droplets were mostly focused to the tip of the grounded electrode whilst the paper was moved in the x- and y-axes [16]. This set-up was later coupled with a computer-controlled x-y plotting system. In 2002, EP was demonstrated as having the ability to print two dimensional architectures with ceramic suspensions (with particulate loadings of >20 vol%) [16]. The needle system was later upgraded to show the ability to batch print with a three-needle system [17]. Although these first examples showed promise, much progress needed to be made, as on close examination of the residues, it revealed, in both single and multiple needle prints, droplet scatter was highly prevalent. We not only understood at the time that focusing the spray was an issue which required attention but also as a printing technology, the moving of either the printing needle with ground electrode or the movement of the substrate alone would disrupt the electric field between the two electrodes, giving rise to droplet straying. Poon et al. [18], at about the same time showed the coupling of two ground electrode configurations, were found to reduce droplet scattering and further focus the ensuing droplet spray. That being said the two-printing system configurations cannot be directly compared as the liquids and particles used were different. Nonetheless the technology had now entered the materials (as concentrated particulate systems/suspensions) printing arena. Subsequently Wang *et al.* [19], further demonstrated the technology possessing the ability to fabricate structures in the z-axes through layer-by-layer deposition similar to 3D printing. The printed architectures as in 3D printing, required the support of the previously printed structure/layer as a support for the subsequent layer to be deposited on. Interestingly the architectures created using layer-by-layer EP was seen to have similar processing features as those seen with 3D printing, namely ripples on walls etc. Nevertheless, unlike 3D printing, EP has the ability to both process large concentrations of particulate materials as suspensions whilst forming residues at least an order of magnitude smaller than those generated by 3D printers. Hence enabling the printing of finer z-stacked architectures (walls) [20]. While investigations continued for reducing droplet scattering, Jayasinghe noticed on a static substrate, those first droplets deposited, formed a raised hump like structure on the substrate directly under and in contact with the tip of the pointed ground electrode. Continued observation elucidated the growing hump like structure seemed to act as the closest grounded element attracting those charged droplets existing the needle. We also noted as the suspension was wet post-deposition the residue was seen to slowly flow over the raised architecture (hump). Therefore, the raised residue now acted as the closest grounded electrode, hence attracting droplets to its tip, which was seen to subsequently grow in the z-axes. Although we noticed this, we also took note that scatter was still dominant. These observations gave us a clue, to attempt electrospray printing a liquid which had a fast-evaporating solvent-based solution/suspension. The thought here was to follow the workings of electrospinning, namely the solvent-based polymer solution on electrospinning, loses its solvent rapidly to the surrounding atmosphere due to the generated fibres (usually in the diameters of <50 nm) having a large fibre surface area. Therefore, seeing the deposition of either semi-wet or dry fibres at the collection substrate. Similarly in EP, our thoughts were when these fine droplets are generated and in flight the solvent would start evaporating (as the exposed surface area is significant) thus becoming a semi-solid for deposition onto the previous deposit, which is now a residue and solid droplet, which is acting as the closest grounded element. Hence the intention here was to keep spraying, which would give rise to the stacking of droplets (on top of each other) in the z-axes and would possibly extend to the creation of self-supporting overhangs (formed parallel and well above the substrate - base) not requiring any form of support.

Electrospray printing 3D overhanging architectures without supports

In our search for such liquids, we explored a living siloxane sol which had the unique features of continuously evolving as it contained fast-evaporating solvents. The preparation, constituents, and properties of the siloxane sol most important to electrospraying have been previously reported [21]. Initial studies with the sol as prepared demonstrated that the sol properties were not conducive for generating semi-wet droplets on deposition. However as this was a living sol which evolved, at a given time point, when the properties of the sol were measured as reported in our previous works [21] the sol on exposure to electrosprays, were found to form three-dimensional architectures [21]. Our initial observations noted the electrospraying of this class of liquids took place at relative applied voltages (~7kV) to flow rates in the 10^{-9} m^3s^{-1} regimes, during which stable cone-jet mode was achieved. Fig. 2a shows the siloxsane sol undergoing electrospraying in the stable cone-jet mode, with an emanated short and fine jet. Droplet generation was not captured via high-speed photography as the generated droplets at these operational conditions were far too small. Nevertheless, we captured and collected the generated droplets onto TEM grids which on analysis were seen to be near mono-dispersed and in the size range of well below 500 nm (see Fig. 2b).

During these initial studies we electrosprayed the sol with straight edge cut needles, and both the ring and plate ground electrode configurations. These studies demonstrated that we were able to form self-supporting and self-standing pillar like architectures having fine overhanging branches [21]. On close examination of the generated architectures via phase contrast microscopy, we found that these structures were fibrous and had a mixture of nano and microstructures. This is unheard of, as electrosprays, are commonly known to generate droplets and not fibres, as in the case of its sister technology, electrospinning. Interestingly on close examination of those recorded high speed digital images, we noted that these fine charged droplets generated were attracted to the growing (as a result of the attraction

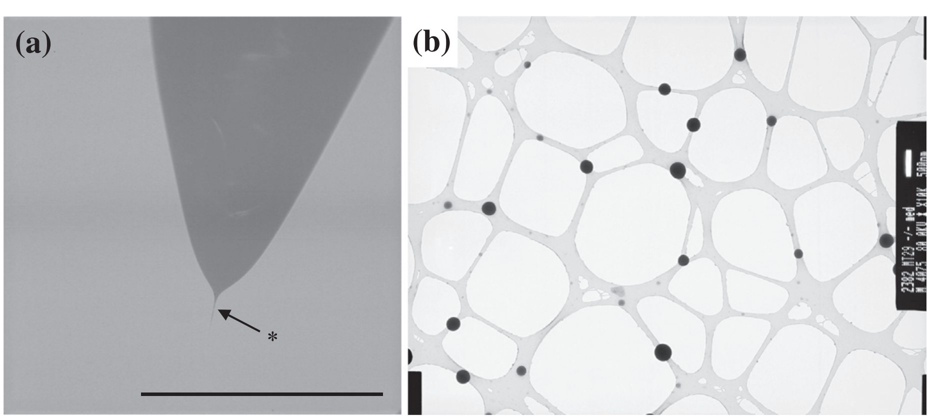

FIGURE 2

Representative (a) a high-speed digital camera image of the electrospraying of the siloxane sol and (b) the generated droplets collected on TEM grids. Note "*" in panel (a) identifies the fine stable jet which emanates from the stable cone. Scale bar in panel (a) represents ~1800 μm.

and attaching) fibrous architecture branches resulting in the formation of fibrous nano and microstructures [21]. Moreover, we noted the formation of self-supporting branches which were overhanging and were seen to maintain their overhanging integrity and nature post-fabrication. Although these results were interesting and exciting, we remained aware that scatter was still taking place significantly.

We continued are inquisitiveness in this system when we investigated the change in ground electrode geometry, to a point, which demonstrate the focusing of a majority of generated electrospray droplets. This was confirmed by the collection of droplets at different positions across and around the ground electrode, which were subsequently analysed via TEM. The initial studies performed electrospraying the sol directly above a pointed electrode placed inline and below, note there was no substrate in this scenario. Fig. 3a-c) demonstrate the rapidly growing multi branched self-supporting architecture which was seen to form on the tip of the pointed ground electrode. Hence, we noted the formation of self-supporting architectures having self-supporting overhangs. Fig. 3c shows when the architecture reaches a height of proximity to the electrospray needle, sparks are found the cross the electrodes (discharging).

Leading from these observations and studies, we wanted to test whether we are able to build an overhanging bridge like architecture without supports. Hence, we setup the equipment with the pointed grounded electrode and initiated the electrospraying of the sol [22]. We noted as previously observed we generated a pillar like architecture after which we switch the applied voltage and flow rate off and moved the electrospray needle and ground electrode to another position on the substrate and reinitiated spraying. As before we saw the fabrication of another pillar. From the second pillar we then started to move the needle very slowly towards the first pillar, at which time we saw the second pillar growing a branch which was attached to the second pillar and extended beyond (growing towards the first pillar) [22]. As we continued the spraying and the very small movements towards the first pillar, we noticed the overhanging branch from the second pillar was growing with it attracting a majority of charged droplets to it. We say majority as we noticed the stray droplets on the substrate. The fine movement towards the first pillar was later seen to grow the branch extending from the second to the first pillar. The droplets on reaching the first pillar seem to fuse the overhanging branch from the second pillar seamlessly to the first pillar. Fig. 4 depicts the architecture

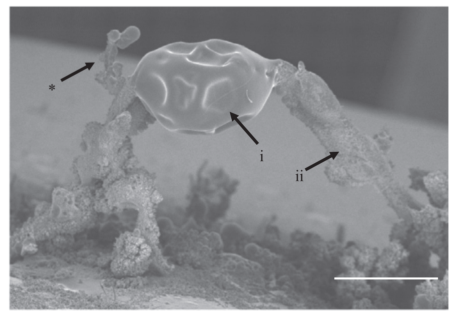

FIGURE 4

Characteristic scanning electron micrograph of the architecture generated using electrospray printing in three-dimensions. Note the small grown branch identified by "*". The reader should also note in this image the textural differences indicated by (i) and (ii). Scale bar represents ~50 μm.

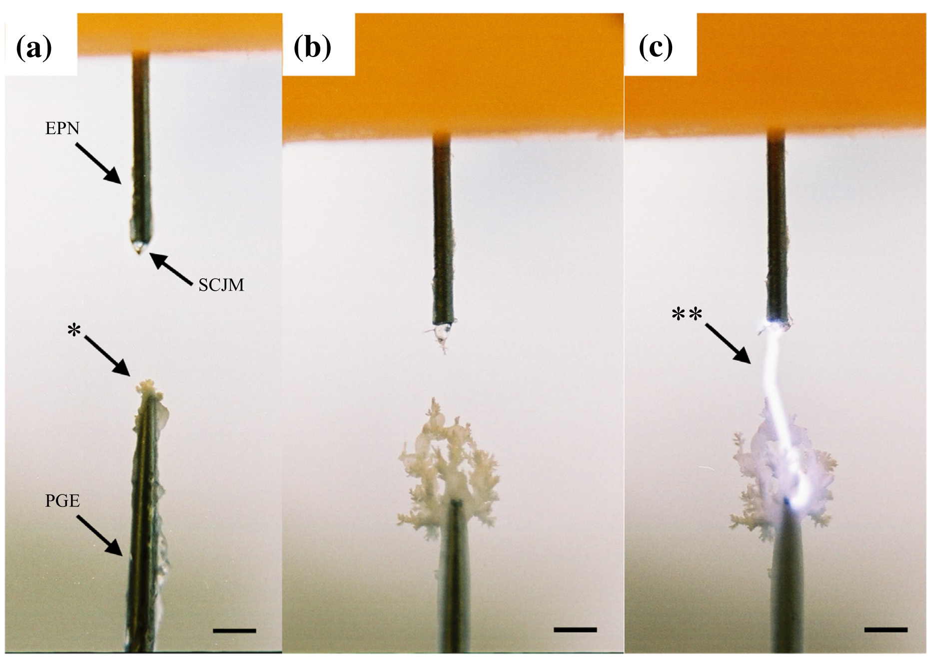

FIGURE 3

Characteristic digital images of the (a) electrospray initiated in the stable cone-jet mode with the pointed ground electrode, (b) depicts the fast grown self-supporting architecture having self-supporting overhangs. Panel (c) shows a spark crossing the electrodes as a result of discharging, taking place as the growing architecture reaching proximity to the electrospraying needle. The abbreviations: EPN: electrospray needle, SCJM: stable cone-jet mode, PGE: pointed ground electrode. Note "*"in panel (a) indicates the growing architecture on the tip of the pointed grounded electrode, and "**"in panel (c) identifies the spark crossing the two electrodes during discharge. The scale bar in all three panels represent ~3 mm.

generated. We noted that in the architecture depicted in Fig. 4 the overhanging branch had a large structure which was almost centrally placed on the extending branch. This was a direct result of the over exposure of that position to the electrospray process. Nevertheless, we noted the structures that were surrounding the main architecture, which were created by stray droplets.

In the structure shown in Fig. 4, we also noticed the surface texture of the architecture having a difference, namely varying from a rough to a smooth one. We are in the process of understanding this variation whether it may be a direct result of the sol explored or the spraying process (precipitating due to spraying etc). We continued our fabrication studies but repeating the process giving rise to the structure depicted in Fig. 4, however on this occasion we wanted to build a third pillar at the centre of the bridge, thus investigating whether the fabricated bridge was able to handle, the weight of another structure [22]. Hence after repeating and building the bridge as previously showed (Fig. 4), we held the electrospray needle at the centre of the bridge, at a higher distance, which was seen to generate a pillar. Further exposure saw the pillar grow branches from random and staggered points along the third pillar which gave rise to further extending, self-supporting overhanging branches, which maintained their stability and were seen to give rise to the forming of subbranches [22]. All of which were stable on the first formed architecture which did not give way (Fig. 5a). As previously stated, the surface textures are an aspect we are currently investigating, and we saw a similar textural variation on some of the generated branches as seen in Fig. 5b.

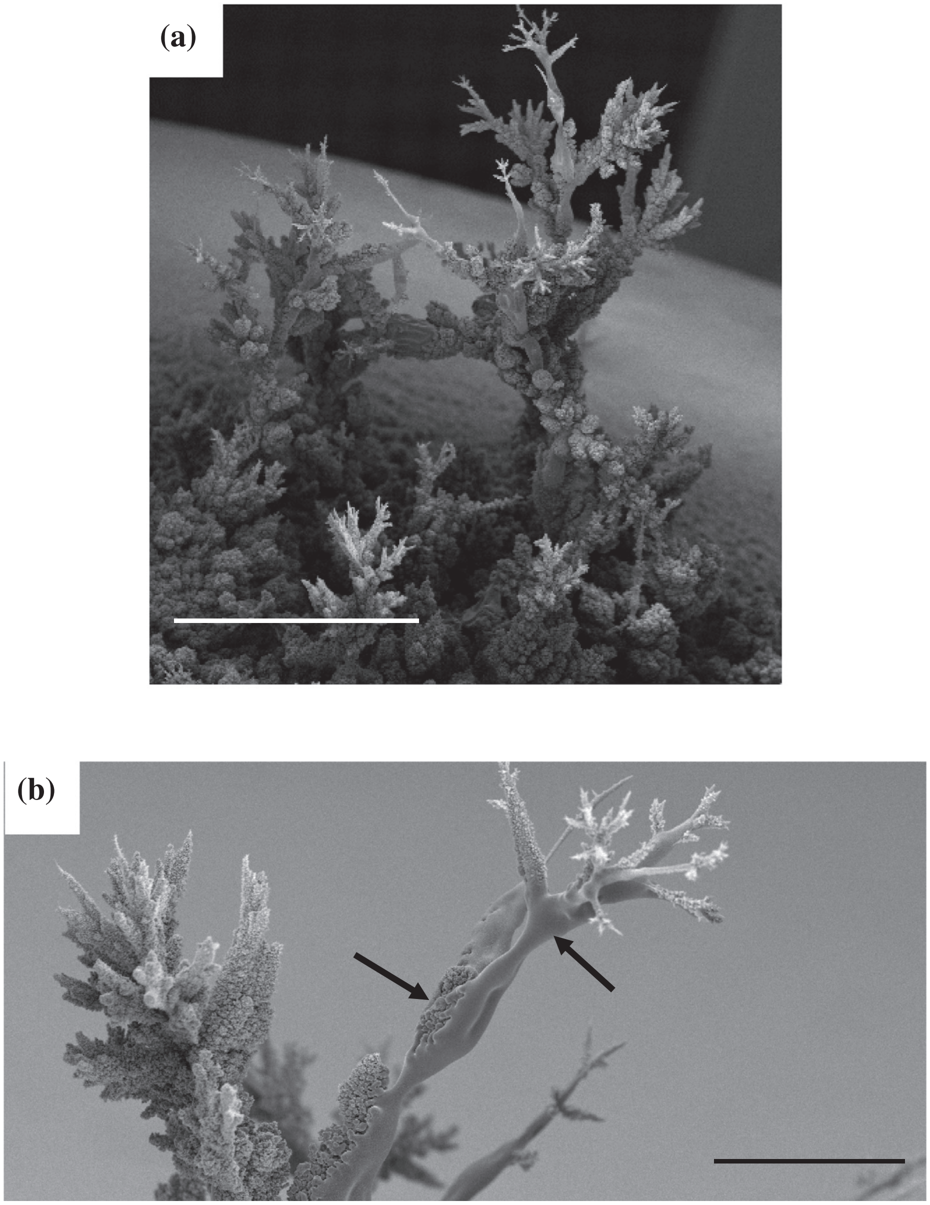

FIGURE 5

Representative scanning electron micrographs of (a) the three-dimensional architecture generated by electrospray printing. Notably the structure formed on the bridge as generated and shown in Fig. 4, is here shown having the capability of supporting the weight of the printed structure. Panel (b) depicts the branches which have features in both the micro and nanoscale. As previously mentioned, we are in the process of trying to understand why there are two surface textures (indicated by arrows). Scale bars in panel (a) and (b) represent ~200 μm and ~50 μm respectively.

These studies demonstrate the power electrospray printing have to the 3D fabrication enterprise, as it possesses the ability to build self-supporting architectures with self-supporting overhangs without the need for any form of mould or supporting structure. Thus is the only technology to date able to do so. Since this discovery many other research groups have explored these findings for many applications and the technology has undergone further development which has seen the significant reduction in scattering/straying droplets [23–25]. Subsequent developmental studies have combined these efforts to seen the emergence of a technology exploring aerosolised materials and molecules which have been printed as 3D self-supporting architectures having self-supporting overhangs and many other complex features [26]. Here the authors not only have advanced electrospray printing but have most notably got rid of all the scattering/straying droplets, which is a remarkable advancement. Furthermore, the technology has been developed to print in both continuous and drop-on-demand modes [27].

Applications

Electrospray printing to date has handled a wide range of advanced materials (in many configurations, namely as graded materials and/or as multimaterials), ranging from structural, functional to biological materials, for a plethora of applications. These span the controlled deposition of micro and nano (molecular) materials as residues sized in the micro and nanoscale at controlled proximities, respectively [28]. To the handling of highly conducting materials such as metals powders in suspension for printing conducting tracks (electrical circuits) [29]. The technology has also been used for the direct handling and precision deposition of a wide range of biomolecules and living cells [30]. This has exposed this bioplatform for developing tissues, biological models (both as single and multi-compartmentalised spheroids and organoids) to a wide range of biomedical and clinical applications. In coda electrospray printing has only just begun its journey as a printing methodology, and already has elucidated its significant implications to many fields of research and development. The future and longevity for this technology and its consequences to the real world, are truly promising.

Conclusions

This perspective article establishes the developmental studies and journey, electrospray printing has undergone. The technology is unique in the way that its capable of handling a wide range of materials with large bore needles yet capable of generating droplets and residues in the few micro and nanometres. Combing these features with its ability to deposit these generated droplets with precision have seen the birth of a printing technology capable of printing true three-dimensional architectures, which are both self-supporting and having self-supporting overhanging structures. It is notable that the generated self-supporting overhangs are longer than the pillars from which they extend. These features are impossible to achieve without supports or other external processes, as shown by classical 3D printing technologies. Thus, highlights this technology as a front running 3D support free printing technology. In the eyes of the author, those developments that are currently underway and those that have been achieved, see the future for electrospray printing with little or no limits.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The author gratefully acknowledges the Royal Society of the United Kingdom for funding these advanced investigations at the BioPhysics group.

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