Additive Manufacturing of Conducting Polymers: Recent Advances, Challenges and Opportunities

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ABSTRACT

Conducting polymers (CPs) have been attracting great attention in the development of (bio)electronic devices. Most of current devices are rigid 2D systems and possess uncontrollable geometries and architectures that lead to poor mechanical properties presenting ion/electronic diffusion limitations. The goal of the article is to provide an overview about the additive manufacturing (AM) of conducting polymers, which is of paramount importance for the design of future wearable 3D (bio)electronic devices. Among different 3D printing AM techniques, inkjet, extrusion, electrohydrodynamic and light-based printing have been mainly used. This review article collects examples of 3D printing of conducting polymers such as poly(3,4-ethylene-dioxythiophene) (PEDOT), polypyrrole (PPy) and polyaniline (PANi). It also shows examples of AM of these polymers combined with other polymers and/or conducting fillers such as carbon nanotubes, graphene and silver nanowires. Afterwards, the foremost application of CPs processed by 3D printing techniques in the biomedical and energy fields, *i.e.*, wearable electronics, sensors, soft robotics for human motion, or health monitoring devices, among others, will be discussed.

1. Introduction

Conducting polymers (CPs), including poly(3,4-ethylene-dioxythiophene) (PEDOT), polypyrrole (PPy) and polyaniline (PANi), have been attracting increased interest for the development of several (bio)electronic and energy devices, *i.e.*, electrodes, biosensors, electronic skin, wearable electronics, human motion sensors, health monitoring or soft robotics. Most of current electronic devices are rigid and possess uncontrollable geometries and architectures that lead to poor mechanical properties presenting ion/electronic diffusion limitations.[1] Therefore, the design of disruptive custom (bio)electronic devices is in the process of a transformation from traditional 2D thin films to shape conformable three-dimensional (3D) structures. Traditional manufacturing methods, including solvent casting or spin-coating, are not able to fulfill the third dimension requirement, being necessary the application of emerging additive manufacturing (AM) technologies to yield materials with high spatial resolution.[2] In this regard, different AM and 3D printing technologies have emerged in the last years as promising industrial manufacturing methods.[3] Another important advantage of 3D printing technology is the possibility of fabricating multi-material objects, comprising different materials, *i.e.*, metals, polymers, ceramics, etc., in different sections in only one printing process to fulfill specific requirements, *i.e.*, chemical, mechanical, thermal, electrical features, etc., of a wide application range.[4-5] Regarding electronic field, 3D printing represents a powerful tool for multifunctional electronic materials design and fabrication due to its excellent ability to customize complex, tunable and low-cost three-dimensional structures at the micrometric scale.[6-7]

From the early stages, conducting (semi)conjugated polymers were known for its optoelectronic properties and unique electronic conductivity while having a polymeric nature. However, it is well known that most CPs do not show the typical mechanical properties and easy processing of

thermoplastic polymers such as polyethylene. In fact, most CPs are insoluble and infusible powdery materials difficult to process. For this reason, the extension of additive manufacturing methods to conducting polymers it has been more difficult than to other polymer families. In this review, the adaptation of conducting polymers to the most common used AM and 3D printing techniques will be discussed. In addition to the CPs, 3D printing offers the possibility to use multifunctional inks and 3D structures whose properties can be tailored by incorporating specific polymers, nano-fillers, ionic liquids (IL) and other biological components, which confer to the final structure conductivity, improvement in the mechanical, electrical properties or biocompatibility. For this reason, this review will also cover the 3D printing of CPs reinforced with functional nano-fillers such as carbon nanotubes (CNT), graphene and silver nanowires (Ag-NWs) that have been widely investigated in the last years.[8-10] The synergistic effect between conducting polymers and conducting fillers allows to enlarge its applicability.[9-12]

This review article provides an overview of the recent developments of conducting polymers for additive manufacturing technologies. First, we will shortly explain the different AM technologies used for the 3D printing of conducting polymer materials based on, *i.e.*, inkjet extrusion, electrohydrodynamic and light based printing. In each 3D printing method, we will describe examples of the most common CPs such as PEDOT, PPy or PANi. This description will include examples of the additive manufacturing of different nanocomposites based on CPs and CNTs, graphene or silver nanowires. In the final part of the review, the wide range of applications of 3D printing of conducting polymers mostly in the biomedical field will be discussed. To conclude, the challenges and opportunities for the fully development of additive manufacturing methods of conducting polymers will be highlighted in the conclusion.

2. Main additive manufacturing and 3D printing technologies used for conducting polymers

3D printing is the manufacturing of a structure with a specific design using computer aided design (CAD) and computer aided manufacturing (CAM) software. Depending on the source, 3D printing methods can be classified as follow: (*i*) inkjet printing that uses controlled pulses for material deposition, (*ii*) extrusion-based printing where the source can be considered a mechanic movement, (*iii*) electrohydrodynamic printing which employs a controlled electric field for the deposition process, and (*iv*) light-based printing where lasers or LED are used for the curing/printing process.[6, 11] This section collects the 3D printing processing of the most relevant conducting polymers nowadays.

2.1. Inkjet printing

Inkjet printing operates through the same mechanism as inkjet office printers, which means that material droplets are ejected from a cartridge due to the pressure generated from the formation and collapse of microbubbles inside the nozzle. The bubbles can be generated from thermal, piezoelectric, or electromagnetic stimulus, and the material in form of droplets is deposited on a surface (**Figure 1**).[12] In contrast to extrusion-based printing, inkjet inks should be non-viscous to ensure the properly deposition and minimize the shear forces experienced by the material when it is ejected from the nozzle. Therefore, a viscosity lower than 100 mPa·s is recommended for inkjet inks.[13] This opens the possibility of CPs to be formulated into solvent or water based inks for inkjet printing. However, the low solubility of CPs brings difficulties in the ink formulations.

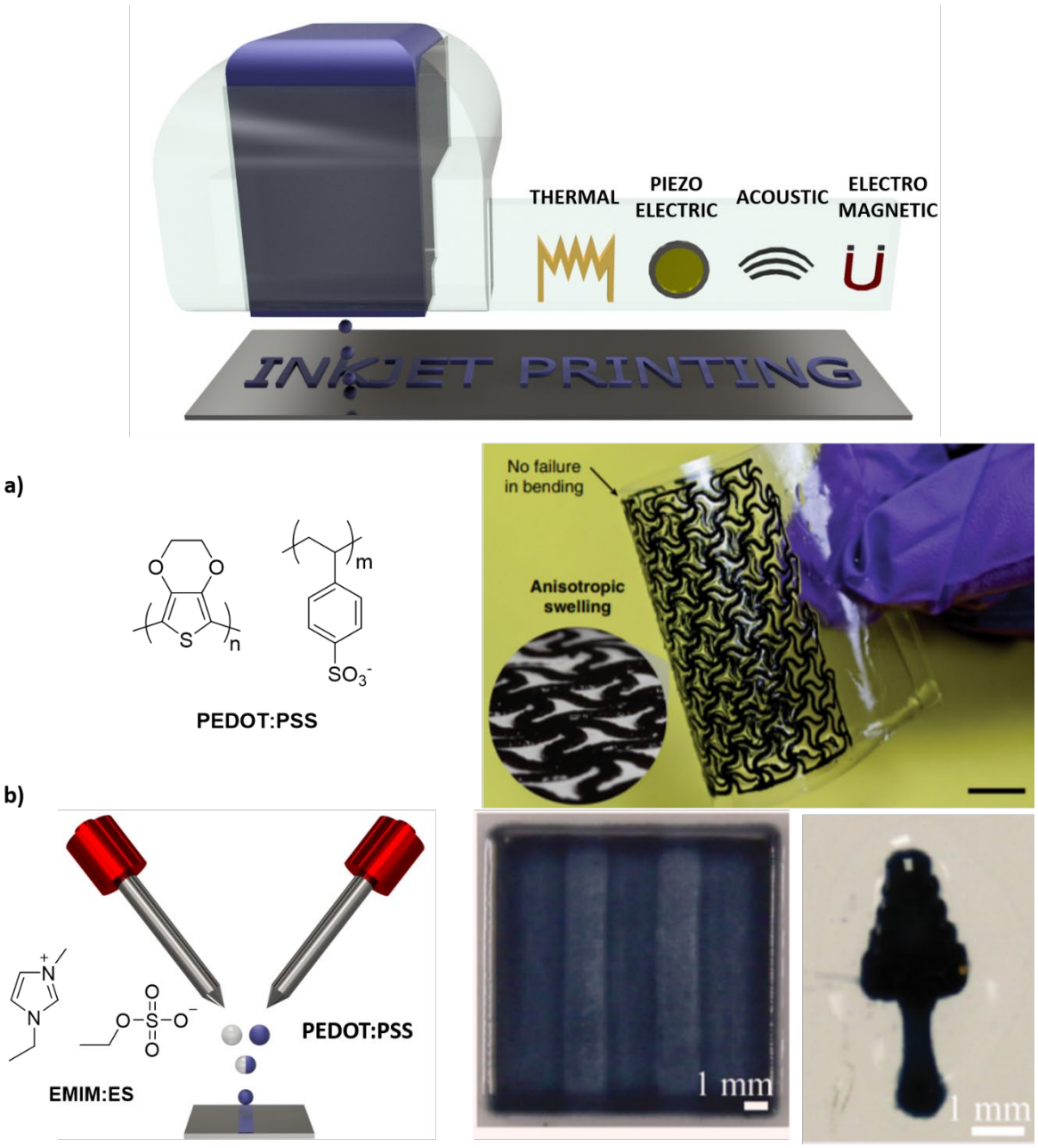

Figure 1. (Top) General scheme of inkjet printing, the material with low viscosity is deposited in drops due to thermal, piezo electric, acoustic or electromagnetic inputs. (Bottom) Two examples of PEDOT:PSS inks: a) PEDOT:PSS/DMSO ink patterned on PET substrates forming complex structures,[14] and b) inkjet printing using coalescing pairs of PEDOT:PSS droplets with ionic liquids (ILs) to manufacture tridimensional structures.[15]

Poly(3,4-ethylenedioxythiophene) (PEDOT)

Nowadays, poly(3,4-ethylenedioxythiophene) (PEDOT) is the most successful commercial CP in the (bio)electronics field due to its inherent properties, such as high conductivity, optical transparency in the form of thin films, thermal and electrochemical stability.[16-17] Moreover, PEDOT properties can be tuned through the use of counterions and secondary dopants, as well as by polymer blending, processing and post-treatment methods.[18-25] The most successful commercial PEDOT material is an aqueous dispersion of poly(3,4-ethylenedioxythiophene) and poly(styrene sulfonate), named as PEDOT:PSS.[16, 26] The different processing methods of this PEDOT:PSS dispersion and the combination with other polymers and conducting fillers allow to tune the electrical, conducting, mechanical and biological properties of the resulting materials.[27-28]

As a first example, the development of three-dimensional electrodes by inkjet printing of PEDOT:PSS based materials will be shown.[29-31] As a representative example, Bihar et al reported the formulation of PEDOT:PSS in inks with a viscosity of 12.2 mPa·s and surface tension of 29 mN m^{-1} that were printed on a commercial stretchable polyamide textile (Dim, knee highs) leading to multilayer electrodes. The printing of PEDOT:PSS layers gave rise to a slight increase of rigidity, but electrodes could be stretched at least up to 200%. The resistance of electrodes formed by 4, 6, 8, and 10 layers increased only by a factor of 6.0, 2.7, 1.4, and 1.5 times respectively, at 100% strain. Furthermore, the resistance of electrodes consisting of 8 printed PEDOT:PSS layers only increased by a factor of 3.5 when taken up to 200% strain.

In a second representative example, Zhao and coworkers prepared an ink based on PEDOT:PSS nanofibrils forming interconnected networks in a very simple method based on mixing volatile additive dimethyl sulfoxide (DMSO) into aqueous PEDOT:PSS solutions followed by controlled

dry-annealing and rehydration, forming hydrogels above 20 S cm^{-1}. The ink was patterned on PET substrates forming complex structures with self-standing ability (**Figure 1a**).[14] Inkjet technique has been also employed for printing coalescing pairs of PEDOT:PSS droplets simultaneously with ionic liquid (IL), 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM:ES), droplets leading to an instantaneous gelation process to form highly conductive structures (**Figure 1b**). In this specific case, micro-reactive inkjet printing (MRIJP) was employed to pattern PEDOT:PSS/IL structures, with viscosities lower than 80 cP, by in-air coalescence of PEDOT:PSS and IL droplets. PEDOT:PSS/IL films prepared by inkjet printing exhibited the same properties than those ones prepared by spin coating, with 89% of optical transmittance and electrical conductivity above 900 S cm^{-1}. Moreover, it was demonstrated the possibility to deposit the 3D-conductive hydrogel through layer-by-layer to finally form patterned structures.[15] Others ILs mixed with PEDOT:PSS were used to build stretchable devices that boosted the electronic conductivity up to 4100 S cm^{-1} under 100% strain. Moreover, these inks were also explored for inkjet printing purposes forming complex structures used as interconnects for field-effect transistor arrays with a device density five times higher than the typical wavy metal interconnects.[32]

The incorporation of different conducting fillers, *i.e.*, carbon nanotubes (CNT), graphene, and silver nanowires (Ag-NWs), into the conductive polymer matrices allows to enhance the final properties of the 3D printed materials as well as extending their applications.[33-38] The employment of inkjet printing methods for the fabrication of conductive composite patterns of PEDOT:PSS incorporating multi-walled carbon nanotubes (MWCNT) led to the orientation of the nanotubes in the printed sample with the subsequent electrical conductivity improvement. Samples with aligned MWCNT showed a 53% enhanced conductivity in comparison with those ones randomly oriented. It was also observed that the orientation of the nanotubes into the ink was also controlled

by their concentration, what means that by increasing the MWCNT from 0.01 wt% to 0.05 wt% percolated networks of well distributed nano-fillers in the printed samples could be obtained.[39] Graphene has been also mixed with PEDOT:PSS to develop hybrid inks able to be processed by inkjet-printing over a polyurethane support improving the thermoelectric properties.[40] Furthermore, it was proven that graphene/PEDOT:PSS printed structures remained stable under static and dynamic bending (for 1000 cycles) conditions.[41] The reinforcement effect of Ag-NWs in PEDOT:PSS based materials has been also explored by inkjet printing. Multilayer films combining PEDOT:PSS and Ag-NWs layers exhibited good electrical properties reaching 10^2 mA cm^{-2} by applying 1.5 V.[42]

Polypyrrole (PPy)

The processing of polypyrrole (PPy) using additive manufacturing and 3D printing has been less explored than PEDOT. Ppy is a conducting polymer with good biocompatibility and high electrical conductivity and seen as an ideal candidate for application in several fields, including chemical sensors and biomedical scaffolds.[37, 43] In an illustrative example, Weng et al.[44] used inkjet printing technology to manufacture conductive polymer scaffolds by interaction of polypyrrole (PPy) with different surfactants, to optimize the surface tension (30.8 mN m^{-1}), viscosity (9.4 mPa s) and conductivity (1.26 S cm^{-1}) of the inks, which were influenced by the oxidant concentration, and make them suitable for inkjet printing. The conductivity of the resulting printed films reached a value of 0.7 S cm^{-1}. In another work, the same authors build up biocompatible scaffolds composed of polypyrrole (PPy) and collagen. For such purpose, the PPy ink, mixed with ethanol as co-solvent to decrease the surface tension and viscosity up to 9.39 cP, was printed over the polyarylate film with a customized waveform for 20 layers with the designed pattern reaching a conductivity of 1.1

S cm^{-1}. Then, the collagen ink was jetted over the PPy lines for 5 layers keeping constant the printing conditions in order to improve the cell adhesion properties of the 3D-printed scaffold.[45]

Polyaniline (PANi)

Polyaniline is a classical conducting polymer well known by its different structures, electronic conductivity and processability. The electroactive behavior of polyaniline (PANi) is enhanced by doping with acids, whereas it is deteriorated by dedoping with bases. This doping/dedoping behavior of PANi, allowing to tune the electrical and electrochemical properties of this material,[46] results in a poor stability.[47] Zhenan Bao et al.[48] fabricated 3D hydrogel patterns by sequential deposition of ammonium persulfate (1.05 cP) and a mixture formed by phytic acid and aniline (0.64-16.0 cP) employing inkjet printing and aerosol printing technologies. It is worthy to point that sequential deposition allowed to control the viscosity making the system suitable for inkjet printing. First, they printed the solution containing the oxidative initiator (ammonium persulfate) followed by printing the second solution containing the aniline monomer. Phytic acid played a double role as it induced the gelation process and acted as doping agent of PANi. The printed materials showed a highly hierarchical structure and a good electrical conductivity with a specific capacitance of ~ 480 F g^{-1} and capacitance retentions of 91% and 83% over 5 000 and 10 000 cycles, respectively. Rajzer and co-workers[49] employed the inkjet printing technique to deposit a conductive PANi layer over a specific surface formed by osteoconductive materials (polycaprolactone, muskoskeletical disorders, gelatin and calcium phosphate nanoparticles (SG5) obtaining 3D networks with a conductivity around 10^{-3} S cm^{-1}. In that case, suitable ink viscosity was obtained by centrifugation at specific conditions (4000 rpm, 30 minutes).

PANi can also act as a stabilizing agent of Ag-NWs to obtain hybrid inks with enhanced electrical properties, as well as specific aspect ratios and viscosity (~ 4.4 cP) that facilitate easy jetting and prevent clogging for optimal inkjet printing manufacturing. Ag-NWs concentration was varied from 10 to 50 mg mL^{-1} in order to produce highly conductive patterns with a resistance lower than 50 Ω sq^{-1} in a minimal number of passes.[50]

2.2. Extrusion-based printing

Extrusion-based printing consists in the layer-by-layer deposition of a material through a movable nozzle which follows a specific shape previously programmed using a software. There are two main extrusion printing methods that differ on the way to low down the polymer. Fused deposition modeling (FDM) uses a polymer in the form of a filament moved throughout a gear mechanism straight to a hot-end where the polymer is melted. On the other hand, direct ink writing (DIW) uses polymers that are semi-melted, in solutions or pastes, which low down by the action of air, pistons or screws (**Figure 2**). Besides this, both FDM and DIW methods require the employment of polymers with specific rheological behavior, viscosity values lower than 10^4 Pa·s for low shear rates (10^{-1} s^{-1}) and 10^1 Pa·s for high shear rates (10^2 s^{-1}), to be printable as well as to retain the desired shape after printing.[13, 51-56] As mentioned before, pristine conducting polymers do not show the typical rheological behavior of polymers, and they need to be combined with other thermoplastic in the form of blends or copolymers to be able to be processed using extrusion based printing methods.

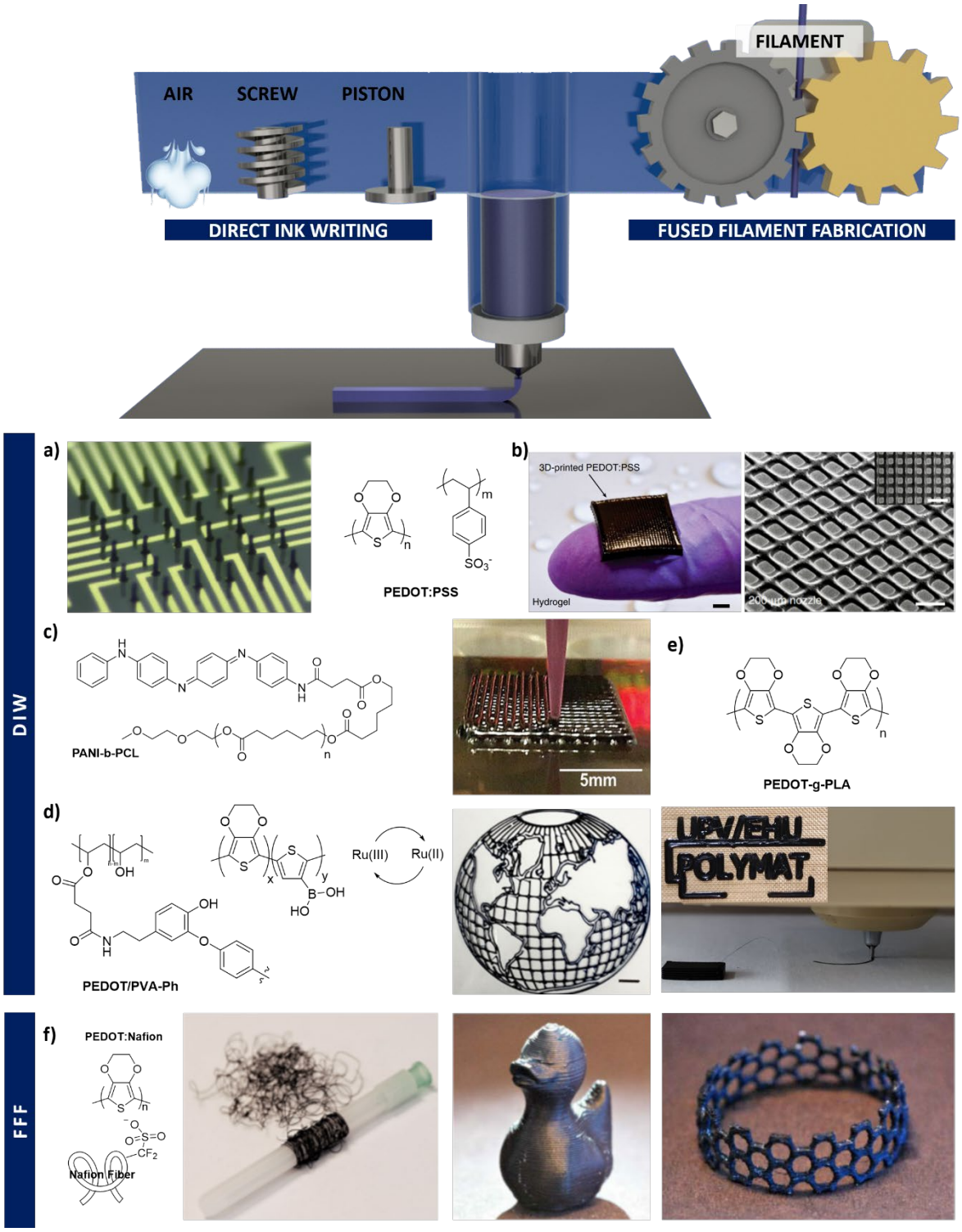

Figure 2. (Top) General scheme of extrusion-based printing method divided in two: direct ink writing (DIW) where the material can be low down through air, screw or piston, and fused filament

fabrication (FFF) where the material is a filament melted by temperature. (Bottom) Different examples of printed materials: Direct ink writing of PEDOT:PSS to form a) 3D pillar electrodes (height: 80 ± 2 μm, and diameter 14 ± 1 μm),[57] b) free-standing 3D layer-by-layer scaffolds with high resolution,[58] c) carboxyl capped tetraaniline graft copolymerized to PCL for DIW method,[59] d) biocompatible 3D scaffolds based on PEDOT-*g*-PLA for tissue engineering,[60] e) printable inks obtained by photopolymerization of PEDOT and coupling reaction of phenols with the catalysis of Ru(II)/APS leading to 3D patterns,[61] and f) PEDOT:Nafion forming filament fused for 3D printing.[62]

Poly(3,4-ethylenedioxythiophene) (PEDOT)

Very recently, direct ink writing (DIW) of PEDOT:PSS has been reported.[57, 63] This new, effective and versatile PEDOT:PSS processing technique allows to control the diameter and arrangement of the printed fibers in a precise, localized and highly efficient manner, thus providing great opportunities for the development of microelectronic array devices (**Figure 2a**). PEDOT:PSS pillars with different aspect ratios were fabricated by varying the printing parameters, such as the pulling speed, pulling time, polymer solution concentration, and the tip diameter, leading to high aspect ratio pillars of 7 μm diameter and 5000 μm height. Furthermore, the employment of an organic solvent, ethylene glycol (EG) or dimethyl sulfoxide (DMSO), and a cross-linking agent, (3-glycidyloxypropyl)-trimethoxysilane (GOPS), contribute to enhance the water stability of the printed pillars, which it is of vital importance if the arrays are used in biological applications. The addition of EG or DMSO into the ink decreases the evaporation rate and stabilize the printed structure. Regarding the cross-linker, GOPS locks the PEDOT:PSS chains, through hydrolysis and condensation of silane groups, improving the physical stability of the printed structure upon contact with water. Besides EG and GOPS also induce an electrochemical stability as assessed by

cyclic voltammetry. Furthermore, the printed pillars exhibit high flexibility and robustness. Zhao and co-workers employed the same methodology described before to manufacture controlled shaped three-dimensional layer-by-layer scaffolds using DIW methodology (**Figure 2b**).[58] The resultant scaffold displayed high Young's modulus in dry state (1.5 ± 0.31 GPa), whereas lower values (1.1 ± 0.36 MPa) were achieved in hydrogel state. The 3D-printed structures could achieve high electrical conductivities, 155 S cm^{-1} in dry state and 28 S cm^{-1} in wet state, which could be even increased by shear-induced enhancements in the PEDOT:PSS nanofibril alignment by decreasing the nozzle diameter. In addition to this, the scaffolds showed mechanical and electrical stability, in both dry and hydrogel states, after 10 000 repeated bending cycles. In this line, the addition of triton X to PEDOT:PSS mixed with DMSO provides an excellent viscoelastic behavior with high mechanical stretchability (above 35% strain) and remarkable self-healing properties with a recovery time lower than 1s. This self-healing ability was used to fabricate structures by DIW printing, propelling the mixture by action of a piston, which could be used as thermoelectric generators.[64]

Wearable electronic devices have been also developed by combining PEDOT with the well-known semiconducting polymer poly(3-hexyl thiophene) P3HT. The PEDOT:PSS layer with a thickness of ~300 nm displayed a low sheet resistance of ~70 Ω sq^{-1}. Then, P3HT:PCBM was used to increase the external quantum efficiency (EQE) of the printed scaffolds, so that P3HT:PCBM printed layers with a concentration of 2.7 mg mL^{-1} lead to a thickness of ~50 nm and increased the EQE up to 25.3%.[65]

Interestingly, alternative PEDOT dispersions and copolymers have been specifically designed for extrusion 3D printing methods. In an interesting approach, PEDOT:PSS was included in the copolymerization of 2-acrylamide-2-methylpropanesulfonic acid and N-acryloyl glycinamide

(PNAGA-PAMPS) forming stretchable hydrogels with sol-gel behavior. A flow-like response behavior is observed when the hydrogel is heated up to 90ºC; whereas by cooling down to 60 °C the solution is solidified. During this sol-gel process the material could be extruded from the needles forming tridimensional shapes.[66] Another interesting example by Müller et al. is the polymerization of PEDOT with Nafion, to produce melt-spun PEDOT:Nafion fibers, which were used in fuse filament on 3D printers (**Figure 2f**). This approach shows an interesting case where PEDOT:Nafion printing structures retained the conductivity, ~ 3 S cm^{-1} upon stretching to 100% elongation. Moreover, they demonstrated that 3D printing shapes possessed good performance for organic electrochemical transistors (OECTs).[62] Very recently, our group has built up 3D scaffolds by DIW of a conductive graft copolymer, PEDOT-*g*-PLA, obtained by oxidative chemical polymerization of PEDOT in presence of PLA. Interestingly, these scaffolds not only showed excellent biocompatibility properties in contact with cardiomyocytes and fibroblasts, but also formation of tissue like structures composed of both cell lines (**Figure 2e**).[60] An innovative orthogonal photochemistry-assisted printing (OPAP) technique, combining extrusion printing and light-triggered chemistry, has been developed by Yu and co-workers for fabricating three-dimensional tough conductive hydrogels (TCHs) based on PEDOT and tyramine-modified poly(vinyl alcohol) (PVA-Ph). Ruthenium photochemistry was used to trigger two orthogonal photoreactions, a faster phenol-coupling reaction of PVA-Ph (~27 s) and the polymerization of the conductive polymer precursors including EDOT (~150 s), leading to a porous PVA hydrogel network with shorter PEDOT chains immobilized in the pores. The inherent properties of these hydrogels, such as stretchability, compressibility, toughness and conductivity, make them ideal candidates as pressure sensors and temperature-responsive actuators (**Figure 2d**).[61]

Along the same line, Spencer et al.[67] developed a biocompatible conductive hydrogel, composed of gelatin methacryloyl (GelMA) and PEDOT:PSS, which was bioprinted to form complex 3D cell-laden structures. Firstly, GelMA/PEDOT:PSS was partially cross-linked by mixing the liquid prepolymer with aqueous $CaCl_2$ at 4 °C. Then, the physically cross-linked hydrogel was covalently cross-linked through photopolymerization of the methacryloyl groups present on GelMA. The Young's modulus of these hydrogels varied from 140 to 80 kPa depending on the PEDOT:PSS concentration (0.1 to 0.3 wt% respectively), whereas the electrical properties were improved with the PEDOT:PSS concentration. Moreover, C2C12 cells were mixed with a selected proportion of GelMA/PEDOT:PSS and printed into the $CaCl_2$ bath at 25ºC. In another work, a bioink was obtained by combining methylcellulose and kappa-carrageenan (MC/kCA) hydrogels with PEDOT:PSS conducting polymers. The bioink showed a thixotropic behavior that could be tuned by changing the MC/kCA concentration to obtain easy printable bioinks by DIW with high shape fidelity. In addition, the electrical conductivity increased from ~ 1800 to 3000 μS cm^{-1} by increasing the PEDOT:PSS concentration from 0.1 to 0.3 wt%, whereas the impedance decreased. Besides carbohydrates, PEDOT:PSS has been also combined with carbon methyl cellulose (CMC) for Li-ion batteries. PEDOT-CMC electrodes were printed by DIW forming thick electrodes with high conductivity leading to interconnected tridimensional hierarchical networks, which provide transport paths for Li ions and electrons.[68] Human embryonic kidney 293 (HEK-293) cells were also incorporated to the bioink formulation and the 3D printed structures showed a high cell viability (>96%) over a week, resulting in a promising candidate for biomedical applications.[69]

PEDOT nanocomposite materials have also been designed for extrusion 3D printing methods. As an example, Ou and co-workers[70] incorporated well-dispersed Sb_2Te_3 nanoflakes and MWCNT into PEDOT:PSS polymer matrix to enhance the thermoelectric performance of the printed hybrid

structures. A nominal loading fraction of 85 wt% nano-fillers yielded to a high power factor of 41 $\mu W\ mK^{-2}$ (S of ~ 29 $\mu V\ K^{-1}$ and σ of ~ 496 S cm^{-1}) while maintaining the robustness and mechanical stability of the printed nanocomposites. In another example, Ag-NWs were incorporated within PEDOT:PSS to fabricated transparent and flexible films using roll-to-roll (R2R) and screen printing technologies.[71-72] By applying a potential from 15 to 40 V on the films PEDOT:PSS/Ag-NWs; a stable temperature from 49 to 99 °C was generated in an interval of 30 to 50 s leading to an uniform heating and rapid thermal response, whereas the surface temperature of PEDOT:PSS films remained stable compared to the room temperature.[72] Very recently, Wang and co-workers[73] have developed hybrid multilayer networks made of inorganic (Ag) and organic (PEDOT:PSS) fibers with 1 to 3 µm diameters by using inflight fiber printing (iFP), a one-step process that integrates conducting fiber production and fiber-to-circuit connection. The resulting architecture composed of fiber arrays possessed a high surface area–to–volume ratio, permissiveness, and transparency which made them ideal candidates to be employed as a cell-interfaced impedimetric sensor, a three-dimensional (3D) moisture flow sensor, and non-contact, wearable/portable respiratory sensors.[73] The difference between Ag and Ag-NWs has been tested by printing multilayer architectures based on PEDOT with the slot-die coating technology. [74-75]

Polypyrrole (PPy)

In the case of PPy processed by extrusion methods, the first example corresponds to the grafting of PPy to the double-bond decorated chitosan (DCh) to form a DCh-PPy copolymer. Subsequently, acrylic acid (AA) was polymerized in the presence of DCh-PPy to form a double network hydrogel composed of poly(acrylic acid) (PAA)/DCh-PPy, which was 3D-printed to fabricate electroconductive scaffolds. The healing properties of the PAA/DCh-PPy hydrogel make possible its elastic modulus recovery (2000 Pa) after breaking down while it passes through the needle. But

not only the mechanical properties were recovered, 3D-printed materials showed a 90% electrical recovery in 30 seconds and 96% in 1 minute which make them excellent candidates to be employed in wearable devices.[76] As another example, poly(glycerol sebacate), PPy and nanocellulose were mixed in order to prepare pneumatically impulse inks for DIW printing, building 3D structures used as drug release patches for therapies after myocardial infarction.[77] PPy has were also combined with alginate to build up biocompatible 3D scaffolds by DIW.[78] In this line Distler and co-workers have developed three-dimensional porous scaffolds by DIW of a hydrogel precursor, made of high gelatin-content oxidized alginate-gelatin (ADA-GEL) incorporating PSS and pyrrole (Py), followed by thermal gelation at 22 °C. Subsequently, scaffolds were immersed in a $FeCl_3$ solution to oxide Py leading to the formation of the PPy network inside the ADA-GEL matrix and increasing the conductivity (12 – 16 mS cm^{-1}) and stiffness (G' ~ 1270 Pa) of the hydrogels. These values are in accordance with native cartilage tissues properties, allowing them to be employed as potential 3D scaffolds for electrical assisted cartilage tissue engineering applications.[79]

In addition to this, Sun and co-workers[80] found that the morphology of the PPy had an impact on the electrical conductivity of PPy-based scaffolds manufactured by extrusion printing. They employed a printable ink composed of PPy nanostructures (spheres of 50 nm diameter or nanowires of 10 μm length and 100-300 nm diameter) dispersed in a thermosensitive polymer, poly-L-lactide (PLLA) to fabricate scaffolds with ~100 μm size macropores. Interestingly, it was shown that the electrical conductivity of the 3D scaffolds was higher when PPy was disposed in the form of nanowires into the ink and increases with the PPy concentration. In another work, DIW printing was also employed to manufacture wearable electrodes constituted by alternate layers of a PPy-nanotubes ink and a polyvinyl alcohol (PVA) gel ink. It was proven that 3D printed structure

exhibited excellent mechanical stability where dispersed PPy nanotubes provided a stable channel for ion transport with a 93% remained capacitance at the bending angle of 120°.[81]

Among polypyrrole based nanocomposites, it is worth to mention one example of 3D printing PPy with carbon nanotubes. Thus, sensing transducers, emitters, and radio frequency inductors were developed by the uniform dispersion of highly conductive MWCNT into PPy, which allowed to obtain mechanically suitable inks to be processed by meniscus-guided 3D printing.[82]

Polyaniline (PANi)

PANi has been combined with a biodegradable polyester such as poly(ε–caprolactone) (PCL) by melt blending of both polymers leading to PANi:PCL inks, which were processed by screw-assisted extrusion 3D printing to form conducting scaffolds. These scaffolds showed suitable compressive strength (6.45 MPa), conductivity ($2.46 \cdot 10^{-4}$ S cm^{-1}) and human adipose-derived stem cell viability (88%) for bone tissue engineering applications.[83] In another example, Prasopthum et al.[59] followed the same strategy, but in this case the conducting polymer ink was obtained by chemical grafting of PANi and PCL forming a block copolymer, tetraaniline-*b*-PCL-*b*-tetraaniline. 3D scaffolds with centimetre-scale thickness and interconnected pore nanotextures with nanometre-scale nanofibers were also fabricated for bone tissue applications (**Figure 2c**). The average diameter of the PCL/PANi nanofibers decreased as the PANi loading increased, whereas the conductivity significantly increased. This can be explained by the fact that the nanofiber can be split off and separated into thinner nanofibers as the conductivity increases resulting in smaller diameters of the PCL/PANi nanofibers.[84]

As an example of PANi nanocomposite inks, reduced graphene oxide (GO) was mixed with PANi to obtain printable PANi/GO inks with shape fidelity, self-sustainability, and electrical conductivity. 3D printing of this ink gave rise to three-dimensional PANi/GO structures.[85-86]

2.3. Electrohydrodynamic printing

Electrohydrodynamic printing (EHD) is based on the deposition of a material, dissolved in a polarizable liquid, which experiments ion mobility by the action of an electric field that is usually placed between the nozzle and the grounded substrate (**Figure 3**). EHD printing method possesses a high resolution and overcomes the limitation related to the nozzle in the inkjet printing methodology. It can be used in a pulsating or jet mode, creating dots or continues fibers, so the deposition modulates the resolution at the micro or nanoscale domains. The printing quality is affected by the ink properties, such as viscosity, surface tension, electrical conductivity, or dipole moment, besides the process-related factors including the applied voltage, pressure and flow rate. Overall, at low applied voltages and low ink viscosity a dripping mode is observed at the apex of the Taylor cone. By increasing the voltage and keeping a low ink viscosity at low flow rates, the droplet size is much smaller than the nozzle size giving rise to the micro-dripping mode. An increase of the flow rate under these later conditions makes the ink be ejected like a column generating the spindle mode. The employment of high viscosity inks and high voltages generates a thin liquid jet at the apex of the cone known as cone-jet mode. In this line, by increasing the voltage and flow rate up to very high values the unstable and uncontrollable multi-jet mode will be achieved. Among these jetting modes, micro-dripping and cone-jet provide the required printing process controllability for precision manufacturing.[87] Moreover, electrodes can be located around the nozzle, which controls the deposition trajectory, achieving sub-micrometer printing resolution.[88]

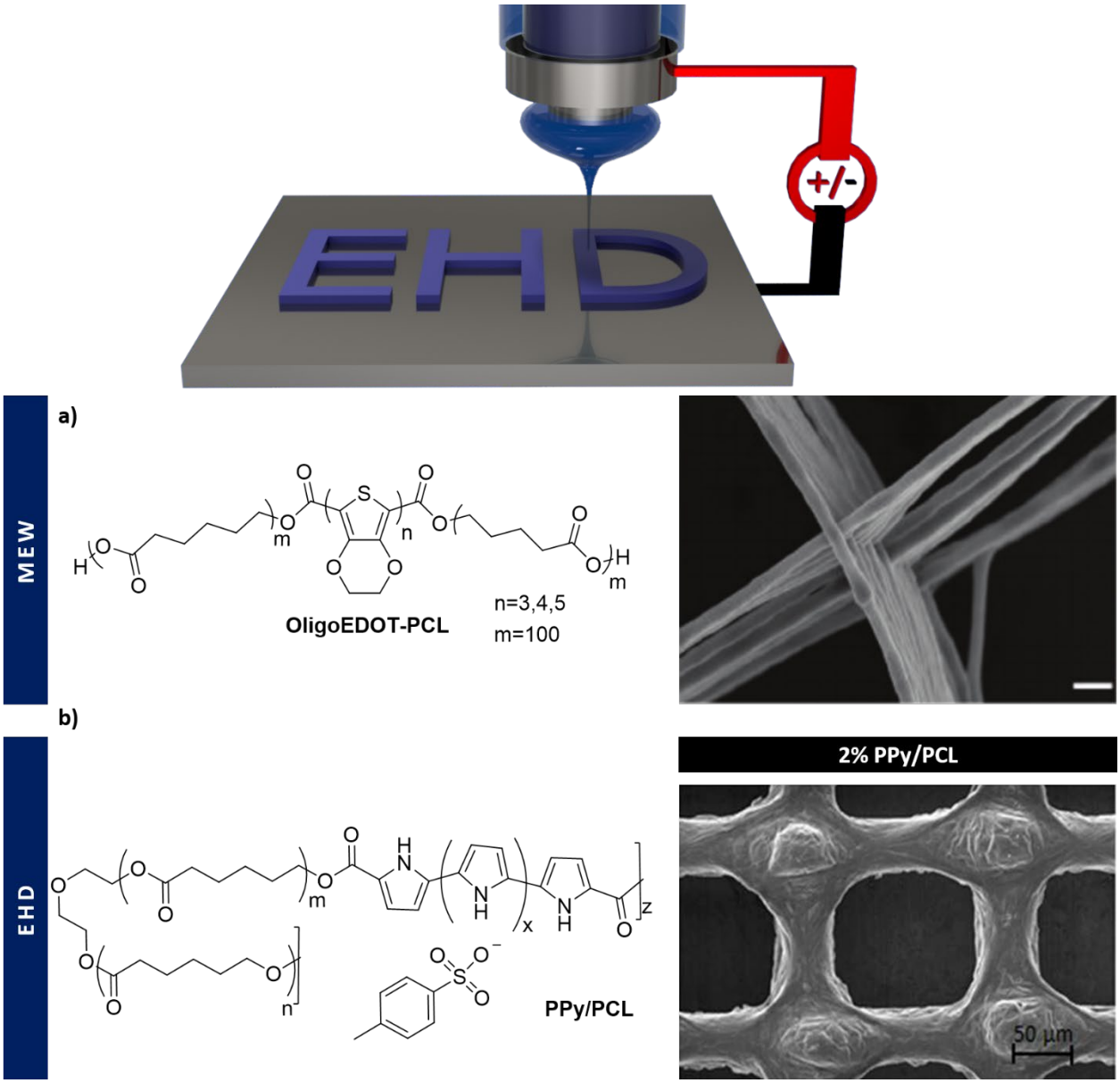

Figure 3. (Top) Electrohydrodynamic printing (EHD) to electrodeposit a polymeric material dissolved in a polarizable liquid through a voltage field. (Bottom) Two examples of printed materials using EHD: a) OligoEDOT-PCL polymer used for melt electro writing forming fibrous scaffolds and b) PPy-g-PCL mixed with PCL leading to an ink that was electrohydrodynamic printed.[89]

Poly(3,4-ethylenedioxythiophene) (PEDOT)

Wearable electronics have been manufactured by EHD of PEDOT based inks. That is the case of PEDOT:PSS which was mixed with poly(ethylene oxide) (PEO) to form a homogeneous EHD printing solution where the addition of PEO raised the viscosity of the inks. PEO/PEDOT:PSS walls with different layer numbers were printed to obtain three-dimensional structures with wall widths in the range of 49.50 to 62.50 μm and wall heights from 0.77 to 57.25 μm. By increasing the number of printed layers from 20 to 100, the resistance was significantly reduced from 2.79 ± 0.37 kΩ cm^{-1} to 0.77 ± 0.05 kΩ cm^{-1}, respectively.[90] In another work, the same authors fabricated multilayer micro/nanofibrous conductive scaffolds through layer-by-layer printing of this PEO/PEDOT:PSS ink, in form of nanofibers (470 nm), with a polycaprolactone (PCL) ink, in form of microfibers (from 2.5 to 9.5 μm). In each layer, eight PCL microfibers were printed and vertically stacked to form parallel microwalls with a wall spacing of 100 μm. Then, PEO/PEDOT:PSS conductive nanofibers were printed on top with a spacing of 50 μm and a similar orientation to the printed PCL microwalls. This procedure was repeated four times to obtain multiscale conductive scaffolds with a Young's modulus of 13.1 ± 0.6 MPa that mimic the micro/nanofibrous architectures of the native cardiac extracellular matrix (ECM). The electrical conductivity of the printed PEO/PEDOT:PSS fibers ($1.72 \cdot 10^3$ S m^{-1}) is much higher than that of the biomaterial blended conductive fibers, at the same time that the impedance of the multiscale conductive scaffolds significantly decreased at physiologically relevant frequencies (<100 Hz) in comparison with pure PCL scaffolds.[91] Moreover, other example showed the use of end-functionalized oligoEDOT constructs as macroinitiators for the polymerization of PCL forming an electroactive block copolymer. They were used to manufacture fibrous structures, via melt electrospinning writing and solution electrospinning, used for neuronal culture (**Figure 3a**).

Neurons presented elongated neurite length under electrical stimulation demonstrating the promising use of these scaffolds for further tissue engineering applications.[92] As another example, high-performance organic field-effect transistors (OFETs) and complementary logic circuits were manufactured by EHD. For that purpose, two different polymers were synthesized by polymerization of PEDOT with PSS-fluoromethyl derivated PEDOT:[P(SS-*co*-TFPMA)] or PEDOT:PSS with polyethylene glycol methyl ether (PEGME). The printed electrode presented different work function (WF) values, according to the Schottky−Mott rule, to be considered as the next generation of integrated circuits and other multifunctional electronic devices.[93]

Polypyrrole (PPy)

In a recent study, a tailored made biodegradable and conductive block copolymer, PPy-*b*-PCL, was used as a printable ink to fabricate 3D porous scaffolds by EHD (**Figure 3b**). Different PPy-*b*-PCL concentrations (0.5, 1, and 2% v/v) were used to obtain scaffolds with average fiber diameters ranging from 33 μm (0.5%) to 44 μm (2%) and an average pore size of 125 μm. PPy-*b*-PCL had a positive effect on the conductivity, which was significantly enhanced from 0.28 mS cm^{-1} (0.5%) to 1.15 mS cm^{-1} (2%); whereas the Young's modulus slightly decreased from 51 MPa (0.5%) to 35 MPa (2%).[89]

Polyaniline (PANi)

PANi doped with hydrochloric acid (HCl), camphorsulfonic acid (CSA), or a mixture of both led to formation of conducting polymer inks able to be processed by EHD. The printing of these inks over polymer substrates gave rise to the fabrication of flexible gas sensors.[94]

2.4. Light-based 3D printing

Light-based 3D printing is based on the photopolymerization of a prepolymer or monomer in liquid state placed inside a vat through a spatially controlled solidification in a specific shape, forming the 3D structure.[95] Two main methods are employed, stereolithography (SLA) and digital light processing (DLP) (**Figure 4**). SLA photocures the resin by a laser beam controlled under a deflection mirror and the liquid is solidified on the surface where the light spot is scanned. Regarding DLP, a digital micro-mirror device (DMD) formed by millions of mirrors is used to directly project a 2D image onto the photosensitive material. Moreover, SLA occurs in the top part of the vat, photocuring the resin point-by-point through the laser beam, whereas in the case of DLP the light source projects the entire slice in the bottom part of the vat where the photopolymerization takes place.[51] Besides these two methods, selective laser sintering (SLS) can be consider a light-based printing technique, where a photo-crosslinkable prepolymer in powder is mixed with other polymers, metals, or ceramics to form composites that can be sintered by the action of a high power laser.[96] However, CPs are rarely obtained by photopolymerization which limits the applicability of light-based printing to inks where the CP is dispersed with a light-sensitive curable material.

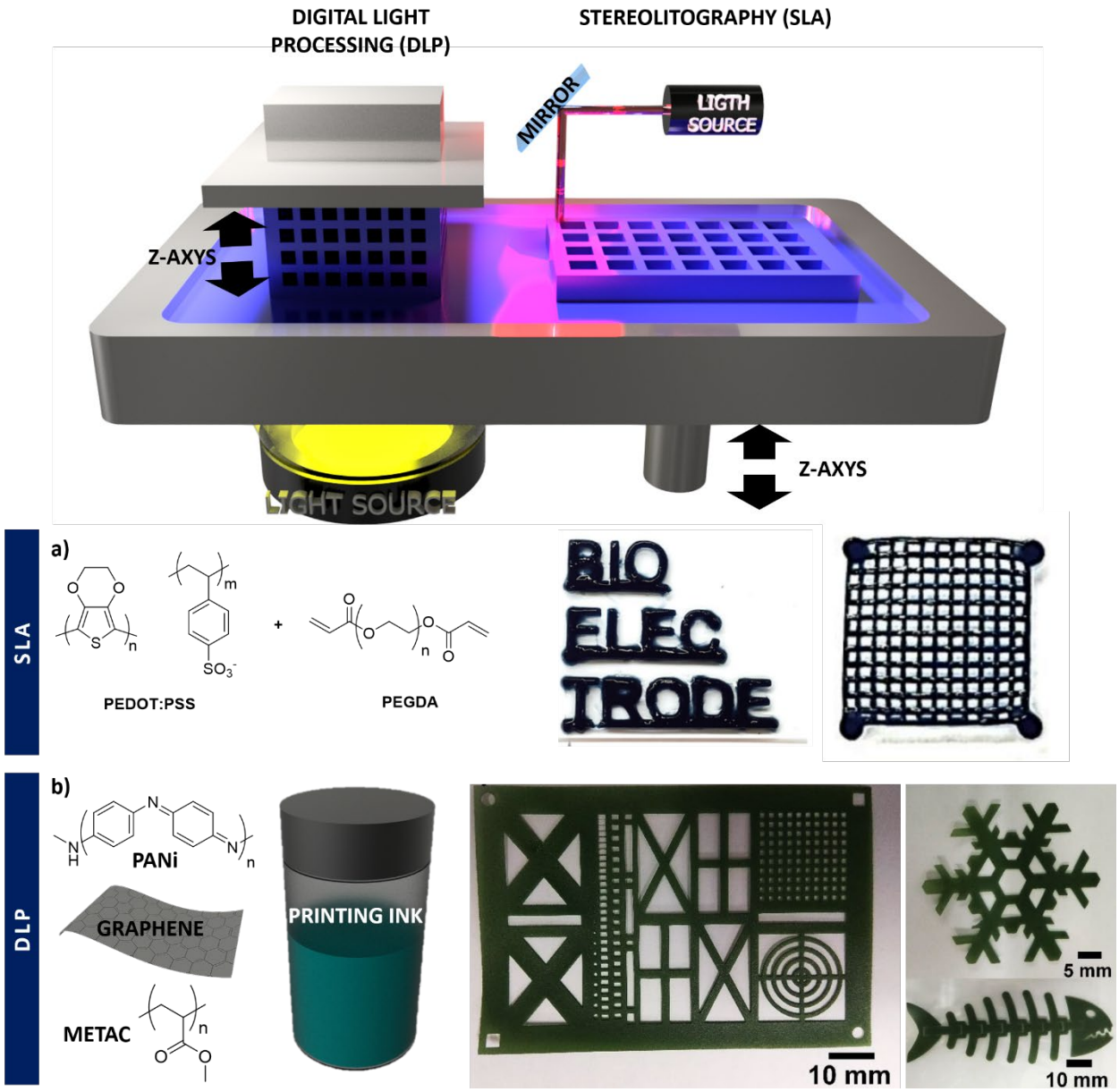

Figure 4. (Top) Light-based printing methods divided in two: digital light processing (DLP), where the photopolymerization occurs in the bottom of the vat, and stereolitography (SLA), which uses a laser pulse to polymerize the resin placed in the top. (Bottom) Two different examples of light based printing: a) PEDOT:PSS mixed with ethylene glycol and PEGDA to form cross-linked structures by SLA printing method,[97] and b) composite ink based on PANi, graphene and METAC to be processed by DLP forming customizable structures with different shapes.[98]

Poly(3,4-ethylenedioxythiophene) (PEDOT)

PEDOT:PSS aqueous dispersion has been printed *in-situ* by SLA into a hydrogel matrix, formed by photopolymerization of poly(ethylene glycol) diacrylate (PEGDA) (**Figure 4a**). For that purpose, PEDOT:PSS is formulated in a solution of ethylene glycol and water (1:8). Then, PEGDA containing 0.5 wt% photo-initiator (bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide) was added to the previous solution to obtain the conducting polymer ink to be printable by SLA. Computer-aided design based architectural models with square pores and different fiber spacing, 500, 600 and 800 μm, were selected to print the 3D structure by UV laser exposure leading to well-integrated scaffolds with predesigned geometries. The presence of PEGDA allowed to decrease the sheet resistance of the 3D printed materials from 968.0 ± 245.1 Ω sq^{-1} to 662.0 ± 100.6 Ω sq^{-1}. The enhanced electrical properties are attributed to the realignment of densely packed and highly ordered PEDOT:PSS structure.[97] Three-dimensional PEGDA:PEDOT structures printed by SLA were also studied by other authors for long-term monitoring of adsorbed volatile organic compounds. They proposed a proof of concept where variations in the structure and conductivity could be used for monitoring hazardous compounds associated to cumulative adsorption effects.[99]

Regarding PEDOT nanocomposites, as a first example PEDOT:PSS was interpenetrated *in-situ* into nanostructured electrically conductive hydrogels (NECHs) that contained multi MWCNT doped with a hydrophilic photoresist, which were ultrafast laser processed as an absorbent 3D scaffold. Two photon hydrogelation boosted the manufacturing of 3D scaffolds in the nanoscale domain at very high resolution, where the inclusion of PEDOT enhanced the mechanical and electrical properties of 10^{-2} S cm^{-1}.[100] The same methodology was used by Cho and coworkers[101] to fabricate stretchable transistors operating at (< 1V). Three-dimensional graphene/PEDOT:PSS structures have been also manufactured by light based printing of this hybrid ink over a substrate,

making use of a shadow mask with the desired geometry, leading to materials with significant areal capacitances of 23 mF cm^{-2}, higher than those ones obtained by spray-coating (5.4 mF cm^{-2}).[102-103]

Polyaniline (PANI)

Graphene sheets mixed with PANi can be embedded in a polyacrylate resin solution to obtain an ink able to be processed by light based printing. The printed sculptures of the graphene/PANi components, showed a low electrical conductivity of $4 \cdot 10^{-9}$ S cm^{-1}, as it was assessed using a 4-point probe measurement system (**Figure 4b**).[104] As well as polyacrylates, PANi nanofibers can be mixed with polyurethanes and graphene in different compositions to form inks that can be printed using DLP-type method.[98]

3. Trending applications in (bio-opto) electronics and energy devices

Most developments related to 3D printing of conducting polymers are related to applications in the (bio)electronic field as electrodes, sensors, supercapacitors, wearable electronics, electronic skin, human motion sensors, health monitoring or soft robotics.

3.1. Bioelectronic applications

3D printing represents a powerful tool for building up electronic tissue engineering devices due to the possibility of using polymers, which confer to the final structure conductivity, improvement of the mechanical properties, biocompatibility, at the same time that it is able to customize complex architectures to mimic the extracellular matrix and other body tissues or organs to restore damaged body functions.[58]

PEDOT, PPy and PANi printed structured have shown excellent biocompatibility in contact with cells.[49, 80, 91] PEDOT:PSS/PEO conducting fibers incorporated within PCL matrix guided H9C2 myoblasts and primary cardiomyocytes cell alignments with enhanced cell proliferation capability.[91] PPy/ PLLA scaffolds showed a cell viability higher than 80% in contact with L929 fibroblasts[80] and PPy/PCL scaffolds exhibited an increase of human embryonic stem cells (hESC-NCSCs) proliferation comparing with pure PCL matrix.[89] The same behaviour was observed in the case of PANi/PCL macrostructures in contact with C2C12 mouse myoblasts[84] and osteoblast cells.[49] Besides this, CPs are attractive because of the electrochemical stimulus that can supply to cells in contact with them, which are the primary means of intercellular communication between electroactive cells.[105-106] In this regard, stimulation of the substrate is presented as a promising tool for tissue engineering. Micro-structured PPy:PVA/collagen scaffolds allowed the electrical stimulation of PC12 cells culture on them inducing their differentiation, as monitored via type III ß-tubulin expression, with extending neurites forming neural networks. The electrical stimulation at precise current values (~ 1 mA) induced significant outgrowth and orientation of neurites compared to unstimulated cells, as it was assessed by measuring the median neurite length with values of 23.34 and 32.71 μm for unstimulated and stimulated cells, respectively.[45, 107]

Cell-laden scaffolds

3D printing also offers the possibility to use functional bioinks with cells encapsulated, commonly known as bioprinting technology, to obtain cell-laden structures.[13, 108] As a first example, human embryonic kidney 293 (HEK-293) cells were encapsulated within MC/kCA/PEDOT:PSS hydrogels leading to a bioink with controlled electrical conductivity. Bioprinted structures maintained high HEK-293 cell viability (>96%) over a week, confirming the *in vitro* biocompatibility.[69] The same approach has been employed by other authors. Spencer et

al.[67] mixed C2C12 cells with prepolymer printable solutions composed of GelMA/PEDOT:PSS. Quantification of live/dead and actin/DAPI assays showed a high viability and spreading of C2C12 cells in the printed structure, which could be used as electroactive tissue structures on demand from medical scans (**Figure 5**). As previously, cell-laden conducting polymer scaffolds can be also stimulated electrically to induce cell differentiation. For that purpose, immortalized dorsal root ganglion (DRG) neuronal cells were firstly encapsulated within a GelMA hydrogel precursor. Further, the cell-laden hydrogel was carefully dispensed in the conductive hydrogel PEDOT:PSS to be light-based printed. The cell-laden conductive hydrogel structure was brought in contact with neurogenic differentiation medium and subjected to electrical stimulation, 1000 mV per sample of the steady state direct current (DC) electric field for 2 days. Results showed the neural differentiation of encapsulated DRG cells using various neuronal gene markers, such as brain-derived neurotrophic factor (BDNF), Neurotrophin-3 (NT-3), and erbB2.[97] Another example was shown by Travas-Sejdic et al.[57] who encapsulated human neural stem cells (NSCs) within a conductive polysaccharide-based biogel to be printed onto conductive PEDOT:PSS pillars. Gel-laden cells differentiated into neurons and glia with or without stimulation; however, stimulated constructs comprised large numbers of densely packed cells abutting the underlying substrate, with polarized neuronal cells exhibiting axons and dendritic arborizations, respect to unstimulated ones. These results allow to anticipate the potential utility of this platform for electroceuticals, drug screening, and regenerative medicine.

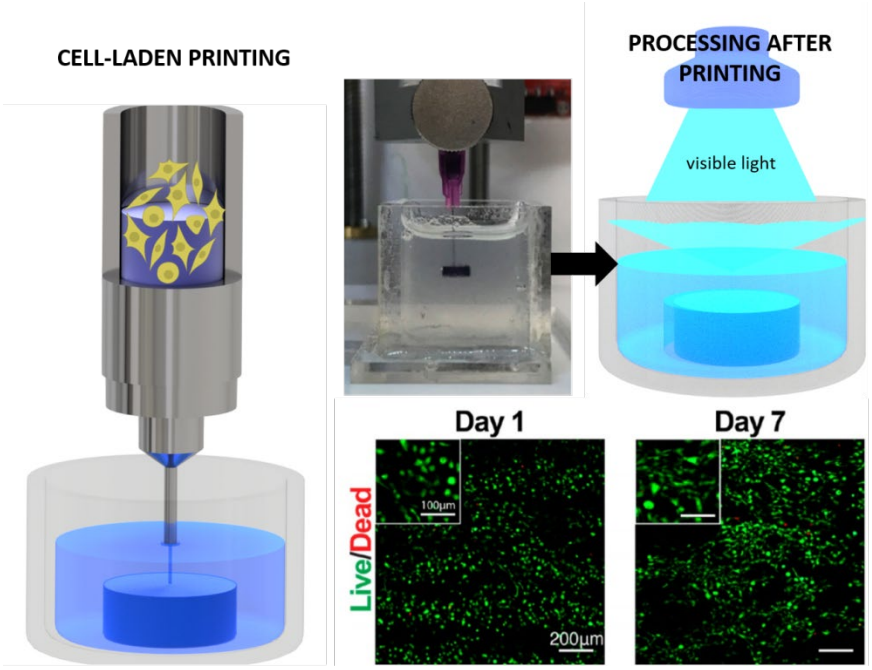

Figure 5. Cell-laden printing of PEDOT:PSS, GelMA and C2C12 cells within a calcium chloride solution that induce the first physical crosslinking. After bioprinting, the structure is chemically crosslinked across the vinyl group throughout visible light exposure showing excellent cell viability (Adapted from ref[67]).

Biosensors and electrophysiology

As a representative example, PEDOT:PSS based electrode was manufacured by inkjet printing to record physiological data.[29] This wearable device was tested by recording electrocardiograms (ECG) from a volunteer. Measurements were conducted between the two forearms, over a period of 40 days at different time intervals (t = 0, 4 h, 8 h, 24 h and 40 days). The mean signal-to-noise ratio (SNR), calculated at t = 0 was 12.93 ± 0.80 dB and remained constant during the first 24 h of recording. After 40 days, the printed electrode exhibited signs of slight degradation with a decrease in SNR to 7.28 ± 5.28 dB. Furthermore, a cholinium lactate-based ionic liquid gel ink was chosen to be printed on top of PEDOT:PSS layers to improve the contact between the conducting polymer

and skin, as such gels lead to high quality contacts with long term stability. These gel-assisted electrodes made low impedance contacts to the skin and yielded recordings with a quality comparable to commercial wet Ag/AgCl electrodes, but with the advantage that there were not dried and using a more compatible format with wearable diagnostics. These results allow to validate the use of the designed textile electrodes as customizable health monitoring devices for electrophysiology recordings. 3D printing PEDOT:PSS microstructures can be also employed as soft neural probes for *in vivo* single-unit recording.[58] In that case, *in vivo* electrophysiology was performed in young adult mice after probe implantation in the mice cranium by surgery. Electrophysiological recording was carried out by coupling the 3D-printed soft neural probe with Neuro Nano Strip Connectors and results showed that the 3D-printed soft neural probe could record continuous neural activities in a freely moving mouse over two weeks (**Figure 6a**).

Very recently, Wang et al.[73] designed non-contact, wearable/portable respiratory moisture sensors based on 3D printing of Ag and PEDOT:PSS fibers. In the first configuration, a single-layer PEDOT:PSS fiber array is printed on a plastic frame to be subsequently attached to the exterior of a disposable mask for respiration rate monitoring. This sensor showed good responsive resistance of the fiber array returned to the baseline level in less than 3 s after a normal breathing, which is very important for fast breathing detection. In the second configuration, a trilayer 3D sensor was fabricated by sandwiching a poly (vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] midlayer, able to detect sound by acoustically driven piezoelectricity, within the PEDOT:PSS fiber arrays. This sensor can be attached to a phone camera for simultaneous collection of image, sound, and breath humid content variations, to detect the respiratory moisture flow that permeates from a mask. An additional advantage of this sensor is that allows to identify the signature of breath leakage distinguishing between breathing and coughing. These findings are

particularly important in the global outbreak of acute respiratory diseases, *i.e.*, coronaviruses, rhinovirus, etc., to mitigate transmission risk.[73]

Electronic skin (e-skin) and robotics for tissue engineering

Further applications of 3D printing technology in tissue engineering field, comprise the fabrication of electronic skin (e-skin) materials, which are able to mimic the properties of some human organs to be employed in regenerative medicine.[109] Wearable human-interactive devices able to enhance the comfort, convenience, and security of humans, are attractive to be used in this field covering a wide range of applications, from robotics to clinical monitoring.[110] It is worth to note that in order to develop e-skin materials enabling seamless integration with the human body, a combination of different properties, such as stretchability, self-healing ability, high mechanical toughness, tactile sensing capability and stimuli responsiveness, is required.[111-113]

As a first example, a super tough electro-tendon robotic finger able to transmit actuation force in robotic hands have been manufactured by printing of a hybrid ink composed of spider silk, PEDOT:PSS and SWCNT. Spider silk provides toughness to the tendon driven transmission system, whereas mechanical flexibility and electrical conductivity are given by PEDOT:PSS. Furthermore, the incorporation of SWCNT into the silk contributes to an overall reinforcement of all these properties. The electron-tendon had a toughness of 420 MJ m^{-3} and a conductivity of 1.077 S cm^{-1}, which was maintained after 40,000 bending stretching cycles due to the fact that the wrinkled structure flattened upon stretching preventing any changes in the conductive path. In addition to this, it was able to transmit signals and force from the sensing and actuating systems simultaneously, to be used to replace the single functional tendon in humanoid robotic hand to perform grasping functions.[114] As another example, stretchable micro-supercapacitors (MSC)

were developed by laser induced printing of polyurethane, graphene and PEDOT:PSS. This MSC could be attached to a human finger or other body parts, demonstrating an excellent flexibility and compatibility with artificial intelligent devices that undergo bending and stretching. It was mechanically stable after 1000 bending cycles showing high capacitance retention (~ 98%) and only a 1% capacitance loss, compared with the flat state, when subjected to random twisting and folding mimicking the conditions of wearing the device on a human finger (**Figure 6b**).[103] Apart from that works, PANi based sensors with high stretchability (~500%) and electrical conductivity (0.12 S cm^{-1}) were fabricated by screen printing of this conducting polymer in combination with polyacrylic acid (PAA) and phytic acid. While stiffness is given by PANi, the presence of PAA as a soft counterpart allowed to form intermolecular hydrogen bonds with PANI chains along with electrostatic interactions leading to self-healing materials able to mimic the dynamic network structure of dermis. Moreover, the presence of phytic acid as dopant allowed to create additional physical crosslinking points giving rise to a 600-fold increase of the electrical conductivity and a 4-fold strength increase.[115]

Temperature sensing is another important parameter needed to be measured during the physical interaction of robots with real-world objects for e-skin applications. For that purpose, Vuorinen et al.[40] fabricated skin-conformable temperature sensors by inkjet-printing of a graphene/PEDOT:PSS ink on top of a skin-conformable polyurethane plaster (adhesive bandage).[40] The initial resistance of the material before cycling measurements was ~ 9 kΩ. Then, samples were heated from 35 °C to 45 °C to be subsequently cooled back down to 35 °C, mimicking the human skin temperature and possible temperature deviations on top of human epidermis. It was pointed that the resistance decreased when temperature increased, thus graphene/PEDOT:PSS behaves as a negative temperature coefficient (NTC) material. The average

Temperature Coefficient of Resistance (TCR or α) of the sensor was 0.047% per degree Celsius. In this regards, another skin conformable printed temperature sensor was fabricated with PEDOT:PSS incorporating graphene oxide (GO) as a temperature sensitive layer and silver (Ag) as contact electrodes with a sensitivity of 1% per degree Celsius. By increasing the temperature from 25 °C to 100°C, a 80% decrease in resistance across the GO/PEDOT:PSS layer is measured. The sensor's response is stable and repeatable under static and dynamic bending (for 1000 cycles) conditions. This sensor was even attached to a robotic hand to allow the robot to act by using temperature stimuli (**Figure 6c**).[41]

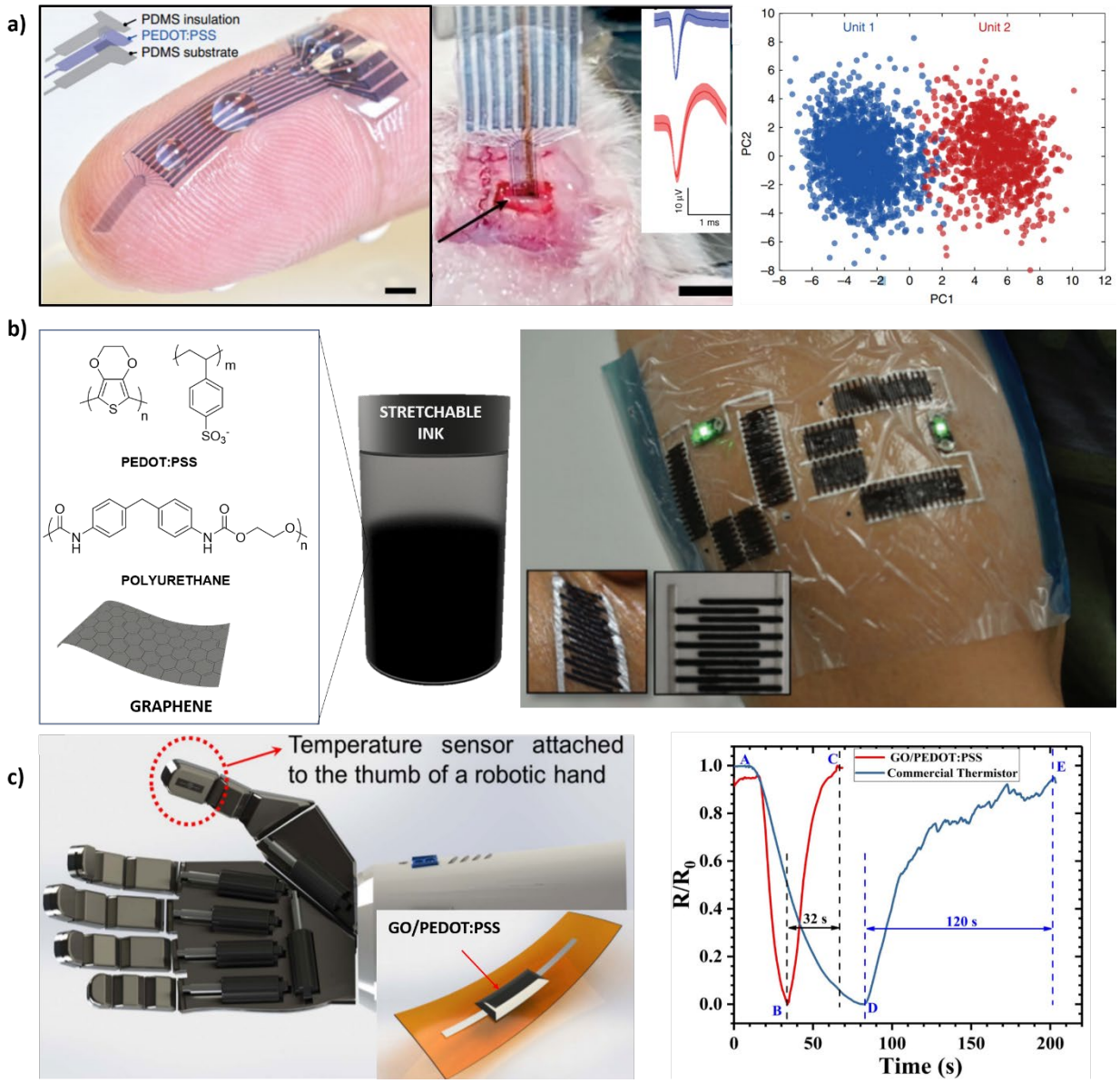

Figure 6. Different set-ups manufactured by 3D printing of CPs to be employed as sensors. a) PEDOT:PSS electrodes printed with high resolution by extrusion based printing and implanted in the mice cranium for electrophysiological recordings and average two units spike waveforms recorded from individual channel of the probe over time (ref[58]). b) Polyurethane/graphene/PEDOT:PSS ink used for manufacturing ultrathin devices on a flexible substrate to be attached on body parts without losing capacitance (Adapted from ref[103]). c)

Temperature sensor based on PEDOT:PSS and graphene oxide inserted in a robot interface allowing the detection of physical interactions with real-world objects, improving commercially available thermistor (ref[41]).

3.2. Energy devices

CPs processed by 3D printing have been also employed in another fields to act as wearable storage devices, supercapacitors, transistors and photodetectors, among others.

Wearable energy storage devices

Organic electrochemical transistors (OECTs) have been manufactured by 3D printing of PEDOT:Nafion fibers and being able to retain their conductivity (3 S cm^{-1}) upon stretching to 100% elongation.[62] In another case, OFETs were fabricated by EHD of PEDOT:PSS showing excellent electrical properties, including the on/off switching ratio higher than 10^7 and the highest carrier mobility greater than 1 cm^2 V^{-1} s^{-1}.[93] Another example is based on the manufactured of stretchable transistors by inkjet printing of PVDF and PEDOT:PSS together with SWCNT, which displayed mobilities of 30 cm^2 V^{-1} s^{-1} and currents per channel width of 0.2 mA cm^{-1} at 1 V operation voltage.[116]

Besides this, stretchable and self-healing wearable thermoelectric generators (TEGs) were fabricated by 3D printing of a ternary composite of PEDOT:PSS blended with a polymeric surfactant, Triton X-100 as a healing agent, and DMSO as a thermoelectric performance booster. TEGs exhibited a power output of 12.2 nW, which was retained more than 85% after damage induced by repetitive cutting.[64]

Graphene doped PEDOT:PSS 3D printed structures can be also employed as micro-supercapacitors (MSCs) with a significant areal capacitance of 5.4 mF cm^{-2} and good capacitance retention ~75% (from 10 to 1000 mV s^{-1}).[102] Another example is the DIW of PPy leading to high-performance supercapacitors with high areal capacitance (200 mF cm^{-2}) able to be 93% retained after bending.[81] Flexible MSCs based on PANi have been also fabricated by DIW of this conducting polymer together with graphene oxide reaching areal capacitances in the rage of 153.6 – 1329 mF cm^{-2}. [85-86, 117]

Electrodes of PEDOT:PSS combined with carboxymethyl cellulose (CMC) were printed by DIW and used for Li-ion batteries. PEDOT:PSS/$LiFePO_4$ electrode exhibits high areal capacity (5.63 mAh cm^{-2}) and high stability after 100 cycles, maintaining 92% of its capacitance. Xiaoling Cui and co-workers indicated that tortuosity or square pores geometry in the micrometer-sized provided effective transport paths for Li^+ and electrons, which is beneficial for the electrolyte penetration and charge transfer. However, extra-thick electrode (up to 1.43 mm) hindered the transmission dynamics and decreased the rate capability.[68]

Sensors, photodetectors, light emitting cells and solar cells

Regarding sensors, PEDOT has been the main conducting polymer processed for this application. Temperature sensors based on PEDOT:PSS and incorporating CNT or carbon were able to reach TCR as high as 0.25% per degree Celsius and 0.61% per degree Celsius, respectively.[110, 118] Humidity sensors based on PEDOT:PSS doped with graphene oxide (GO) were also developed. Results showed that the sensor exhibited excellent humidity sensing properties in a wide response range (0.13 – 68.46%), short response and recovery time (39 and 57 s, respectively), as well as high repeatability and flexibility with no significant variation of the sensor

resistance after folding 200 times.[119] Based on the same principle, film heaters were manufactured by screen printing of PEDOT:PSS and Ag-NWs. The composite film with 74.1% transmittance could be heated from 41 to 99 °C at the driven voltages from 15 to 40 V, showing an uniform heating and rapid thermal response.[72]

Organic photodetectors were also developed by multilayer inkjet printing of PEDOT:PSS in combination with P3HT:PCBM. The printed photodetector exhibited a photoresponse when photoexcited at 405, 465, 525, and 635 nm, showing the highest responsivity at 405 nm and a strong frequency dependence from 25 to 1000 Hz.[120] Another trending application of PEDOT:PSS based printed materials is focused on the fabrication of the highly demanded light emitting cells (LECs). Inkjet printing of PEDOT:PSS together with a polymer electrolyte based on a PCL-co-TMC:TBABOB allowed to manufacture LECs with a luminance over 10^4 cd m^{-2} and efficiencies of 2 cd A^{-1}.[30] Furthermore, the printing of these materials over ultraflexible parylene C substrates, usable for conformable electronics, allowed to obtained wearable devices with a maximum brightness of 918 cd m^{-2} and stable operation at a luminance higher than 100 cd m^{-2} for 8.8 h, with a turn-on time of 40 s to reach 100 cd m^{-2}.[31]

Electrodes manufactured by 3D printing of conducting polymers have found applications in the fabrication of solar cells. That is the case of fully inkjet printed multilayer Ag-NWs and PEDOT:PSS electrodes, where Ag-NWs are placed at the bottom and top, leading to semitransparent organic solar cells with a power conversion efficiency of 4.3% per cm^2.[42] As another example, organic solar cells with a total area of 186 cm^2 were manufactured by multilayer printing of PEDOT:PSS and P3HT:PCBM with Ag placed at the bottom and top, as previously. These cells showed an active-area power conversion efficiency of 1.6% with good operational stability both under low light and 1 sun conditions.[74]

Table 1. Main conducting polymers processed employing different 3D printing technologies and relation of the printed materials with the electrical properties and final applications.

Conducting Polymer	Secondary polymer	Conducting filler	3D printing technique	Electrical properties	Final structure dimension/Applications	Ref.
PEDOT:PSS	-	-	Inkjet	0.8 kΩ cm^{-2}	2D-3D/Electrophysiology	29
				0.2 – 1.8 cd A^{-1}, 20 mA cm^{-2}	LECs, wearable electronics	31
	-	-	DIW	15 – 50 S cm^{-1}	3D/Sensors and soft electrochemical probes	63
				28 - 155 S cm^{-1}	2D-3D/Soft neural probes, wearable electronics	14, 58
				137 S cm^{-1}	3D/Thermoelectric generators	64
	PCL-*co*-TMC: TBABOB		Inkjet	1.2 cd A^{-1}, 0.3 lm W^{-1}	3D/LECs	30
	EMIM:ES	-	Inkjet	900 S cm^{-1}	3D/Biolectronics devices	15
	P3HT:PCBM	-	Inkjet	0.0019 A W^{-1}	2D/Photodetector	120
	P3HT:PCBM	Ag-NWs and ZnO	R2R		2D/solar cells	75
	PEGDA	-	SLA	662 – 968 Ω sq^{-1}	3D/Neural tissue engineering	97
				0.055 S cm^{-1}	3D/Volatile organic compounds' adsorbents (VOCs)	99
	PEO	-	EHD	0.8 – 2.8 kΩ cm^{-1}	3D/Wearable electronics	90
	PCL	-	EHD	$1.72 \cdot 10^3$ S m^{-1}	3D/Cardiac tissue engineering	91
	PEGME P(SS-*co*-TFPMA)	-	EHD	425 – 450 S cm^{-1}	2D-3D/Organic field-effect transistors (OFETs)	93
	PNAGA:PAMPS	-	DIW	0.2 – 2.2 S m^{-1}	3D/Biosensors and electroactive scaffolds	66
	GelMA		DIW	-	3D/Cell-laden structures	67
	MC/kCA	-	DIW	1800 – 3000 µS cm^{-1}	3D/Cell-laden structures	69
	Cellulose:Alginate	-	DIW	5.7 S m^{-1}	3D/Energy storage	121
	Carboxymethyl cellulose	-	DIW	10.3 S cm^{-1} - 0.9 S cm^{-1}	3D/Energy storage	68

	PVA-Ph	-	DIW, light based	0.5 – 3.5 S m^{-1}	3D/Sensors, actuators	61
	-	CNT	Screen / shadow mask printing	63 mΩ sq^{-1}	3D/Wearable sensors	115
	Spider silk	SWCNT	-	1077 S cm^{-1}	3D/Electron-tendon	114
	PVDF		Inkjet	0.2 mA cm^{-2}, 30 cm^2 $V^{-1}s^{-1}$	2D/Stretchable transistors	116
	-	MWCNT	Inkjet	6.7 S cm^{-1}	2D/-	39
			Aerosol-jet	41 μW/mK^2, 29 μV K^{-1}, 496 S cm^{-1}	2D/Energy storage wearable devices	70
			Light based	0,4 S cm-^{1}	3D/Nanorobotics	100
	-	Graphene	Inkjet	9 kΩ	2D/Electrophysiology	40
					2D/Electronic skin (eSkin)	41
	-	Graphene	Aerosol-jet	1080 μF cm^{-2}	2D/Wearable power supplies	102
			Light based	5.4 – 23 mF cm^{-2}	2D/Wearable electronics	103
	-	Ag-NWs	Inkjet	10^2 mA cm^{-2}	3D/Organic solar cells	42
	-	Ag-NWs	R2R	0.5 – 1.3 Ω sq^{-1}	2D/Electrodes	71-72
	-	Ag	iFP	70 S cm^{-1}	3D/Cell-interfaced impedimetric sensor, moisture flow sensor, and non-contact, wearable/portable respiratory sensors	73
	-	Ag and ZnO	R2R	1000 W m^{-2}	2D/Solar cells	74
PEDOT	Nafion	-	DIW	3 S cm^{-1}	3D/Electrochemical transistors	62
	PLA	-	DIW	1.8 – 300 μS cm^{-1}	3D scaffolds/Tissue engineering	60
PPy	~~Gemini surfactants~~	-	Inkjet	0.7 S cm^{-1}	2D/Electronic devices, tissue engineering scaffolds	44
	Collagen	-	Inkjet	1.1 S cm^{-1}	2D/Neural tissue engineering	45, 107
	PCL	-	EDH	0.28 - 1.15 mS cm^{-1}	3D/Peripheral neuronal regeneration	89
	DCh, PAA		DIW	25 – 70 S cm^{-1}	3D/Human motion detection	76

	PLLA	-	DIW	0.48 S cm^{-1}	3D/Electroactive tissue engineering scaffolds	[80]
	PVA	-	DIW	200 mF cm^{-2}	3D/Supercapacitors, wearable storage devices	[81]
	Poly (glycerol sebacate):cellulose	-	DIW	34 mS cm^{-1}	3D/Cardiac patches	[77]
	Alginate	-	DIW	4.07 – 6.33 mS cm^{-1}	3D/Tissue engineering	[78]
	Alginate-gelatin	-	DIW	12 – 16 mS cm^{-1}	3D/Cartilage tissue engineering	[79]
	-	MWCNT	meniscus-guided 3D printing	25 S cm^{-1}	3D/Sensing transducers, emitters, and radio frequency inductors	[82]
PANi	~~Phitic acid~~	-	Inkjet Aerosol	480 F g^{-1}	3D/Supercapacitors, batteries, biosensors, bioelectrodes	[48]
		-	EHD	76 – 755 kΩ	3D/Sensors	[94]
	PCL, gelatin, SG5	-	Inkjet	10^{-3} S cm^{-1}	3D/Bone tissue engineering	[49]
	PCL	-	DIW	$0.25 \cdot 10^{-4}$ S cm^{-1}	3D/Bone tissue engineering	[83]
				$6.2 \cdot 10^{-6}$ S cm^{-1}	3D/Cartilage tissue regeneration	[59]
				-	3D/Tissue engineering	[84]
	-	Graphene	DIW	150 – 1300 mF cm^{-2}	3D/Flexible microsupercapacitors	[85-86]
				238 F g^{-1}	3D/Electrodes	[117]
	polyacrylate	Graphene	Light based, spray	$4 \cdot 10^{-9}$ S cm^{-1}	3D/Bioelectronics devices	[104]
	polyurethane	Graphene	DLP	$1.37 \cdot 10^{-6}$ S cm^{-1}	3D/Biomedical devices	[98]
	-	Ag-NWs	Inkjet	50 Ω sq^{-1}	2D/Electrodes	[50]

4. Conclusions and future perspectives

This article aims at presenting a comprehensive overview concerning to additive manufacturing of most common conducting polymers, such as PEDOT, PPy and PANI, employing 3D printing techniques. Additive manufacturing of CPs presents great opportunities in the design of new

devices and applications in the (bio)electronic field. However, CPs show important limitations in terms of processability. Therefore, their combination with other polymers and nanoadditives that improve their processability at the same time that keep the high conductivity is needed for their processing by additive manufacturing methods. In this regard, 3D printing of CPs has started to be explored very recently and portrays a field with a huge number of possibilities and applications in the future. A summary of all works referenced in this review article is collected in **Table 1**, where conducting polymers mixed with other polymers and/or conducting fillers are listed and related with the 3D printing technique employed, the electrical properties and final applications.

Among different CPs used for 3D printing, PEDOT is the most studied, and specially the commercial dispersion PEDOT:PSS, which has resulted the preferred material for different authors. Furthermore, PEDOT based inks have been processed employing several 3D printing techniques, *i.e.,* inkjet, extrusion, electrohydrodynamic and light-based printing. But not only that, PEDOT:PSS has been also processed in combination with other polymers, solvents, hydrogels and conducting fillers leading to tailor-made inks with tunable conducting properties to be employed in a wide range of applications. Other conducting polymers, such as PPy and PANi, have introduced high degree of novelty and used for the synthesis of tailored made conducting copolymers. In fact, very elegant tetramers or block copolymers based on PPy and PANi have been used for direct ink writing, electrohydrodynamic and inkjet printing leading to three-dimensional conducting scaffolds.

On the other hand, P3HT, which is one of the most popular semiconducting polymers used for solar cell applications, has been scarcely investigated using additive manufacturing. There are only few examples concerning to additive manufacturing of P3HT:PCBM inks, employing SLA,[122] slot –die coating[123] and aerosol-jet printing,[101, 124] leading to artificial human eyes, medical sensors,

generators and transistors, respectively. In our opinion the AM of this polymer should find many opportunities in the near future. Similarly, it is worth to mention that other (semi)conducting polymers such as poly(*p*-phenylene-vinylene) (PPV), polyfuran (PF) and others polythiophenes (PTh), have not been explored yet which shows many future opportunities.

Moreover, in our opinion nanocomposites formed by conducting fillers and CPs and processed by 3D printing methods have been under investigated. Besides works referenced previously in this review, there is only an example where PPy is mixed with black phosphorous to be printed by the extrusion-based method leading to electrodes for energy storage.[125] However, other bidimensional materials, *i.e.*, inorganic MXenes, MOFs, graphenes among other emerging 2D nanomaterials, represent a big challenge to be mixed with CPs and processed by 3D printing to form hybrid conducting materials with several possibilities and new applications. In addition to this, there are emerging printing methodologies such as selective laser sintering (SLS), two photon polymerization printing (2PP), volumetric printing, and fused filament fabrication, which still remain mostly unexplored for conducting polymers opening a new door of possibilities and applications in the future. Finally, it is worth to note that ionically conductive matrices, such as iongels, could be also processed employing all these 3D printing techniques and employed for the applications previously described.[126]

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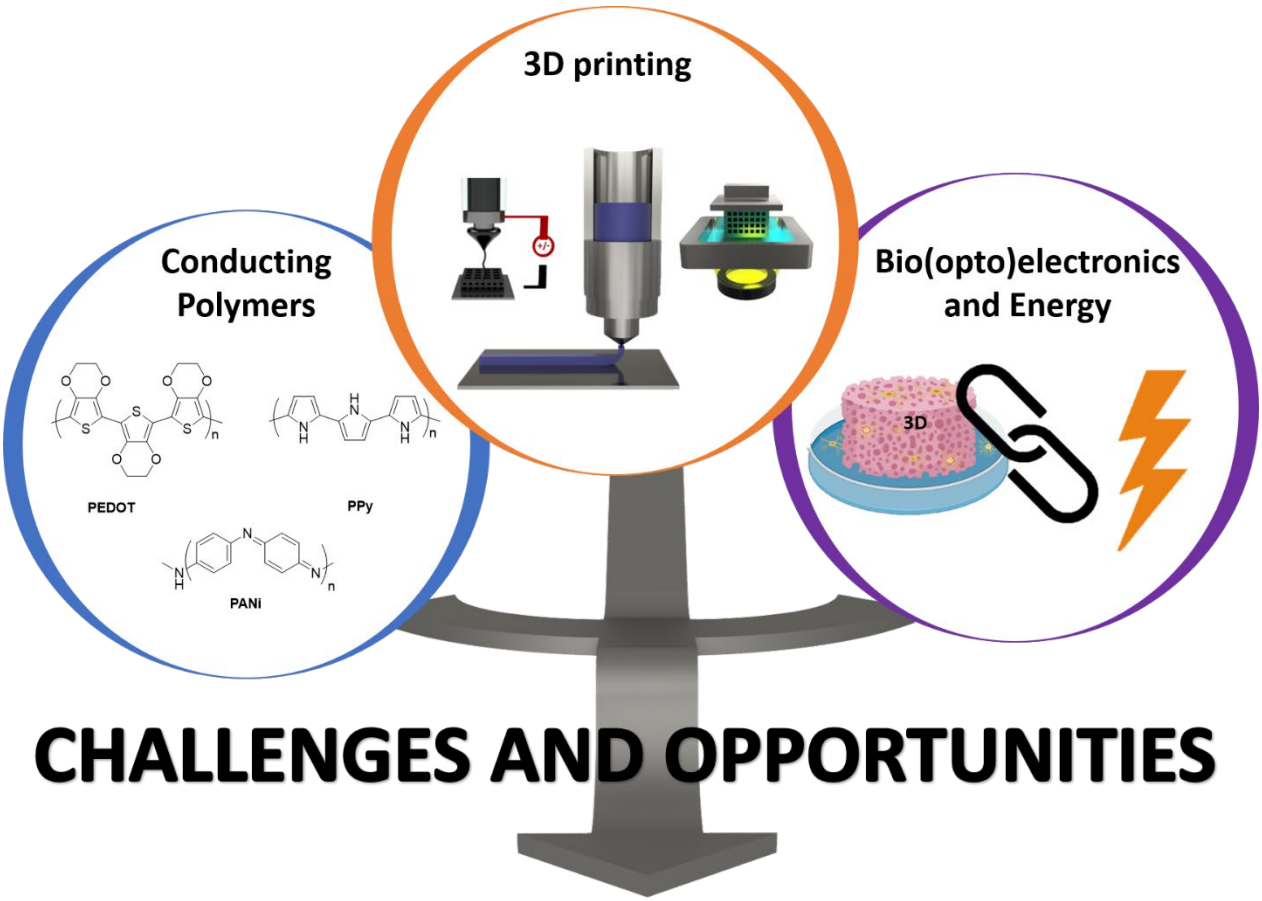
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3D
CHALLENGES AND OPPORTUNITIES