Polymer-based smart materials by printing technologies: : Improving application and integration

*J. Oliveira[1,2], V. Correia[1,2] , H. Castro[2], P. Martins[*1] and S. Lanceros-Mendez[3,4,*]*

[1]Centro de Física, Universidade do Minho, Braga, Portugal

[2]Centro Algoritmi, Universidade do Minho, Guimarães, Portugal

[3]BCMaterials, Basque Centre for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.

[4]IKERBASQUE, Basque Foundation for Science, 48013-Bilbao, Spain

KEYWORDS: printing technologies, smart materials, internet of things, additive manufacturing, polymers

Smart and functional materials processed by printing technologies reveal an increasing interest due to small cost assembly, easy integration into devices and the possibility to obtain multifunctional materials over flexible and large areas. After introducing smart materials, printing technologies and inks, this review discusses the materials that are already being printed, mainly piezoelectric, piezoresistive, magnetostrictive, shape memory polymers (SMP), pH sensitive and chromic system materials. Since polymer-based smart materials are particularly attractive for device implementation, this review will focus on printed polymer-based smart materials. Finally, critical challenges and future research directions will be addressed.

1. Introduction

We live in an era of strong advances in science and technology, where industries and science are increasingly interacting in new and exciting ways [1]. This interdisciplinary approach is exemplified in the innovative use of smart materials, which includes knowledge from physics, chemistry, materials science, nanotechnology and biochemistry, as well as electrical and mechanical engineering. This collaborative approach allows the development of an increasing number of smart and functional materials and device applications[1, 2]. Closely connected to the Internet of Things (IoT) concept, smart materials are the key factor for the development of sustainable, wireless and interconnected autonomous smarter devices, systems and even cities [3].

This advanced IoT concept has become a hot-topic in a high number of areas, which include computer networks, virtual and physical objects as well as disruptive devices that are interconnected by using communication technologies, such as mobile and wireless networks, radio-frequency identification, global position system (GPS) and Bluetooth systems [4]**.** The rapid growth in smart materials technologies strongly supports the successful implementation of IoT, allowing a global network where everyone and everything will be interconnected through the Internet[5, 6].

The arising IoT approach is enabling new services, changing production paradigms, making industries more efficient, accelerating fabrication processes, reducing error and promoting complex and more flexible organizational arrangements [7, 8]. The concept of IoT is continually changing and being developed, becoming an important research topic where new and fascinating innovation opportunities will emerge.

Thus, once the world is enhancing its digital dimensionality, every base of society will become "smarter". For that, a new generation of smart materials is required [3].

The smart materials[9-11] research area is a multidisciplinary field that explores the development and implementation of novel and disruptive materials with increased functionality, including self-cleaning and self-healing materials, photomechanical materials, shape-memory materials, and electroactive and magnetoactive materials, among others. Those materials are utilized on smart structures, using their full-potential to improve our health and lifestyle, meeting the nowadays economic, social and environmental challenges[10].

In order to promote sustainability and added value of smart materials it is important to explore and encourage the development and application of more sustainable engineering principles for the production, applications and recycling of materials. It is also important to address how green chemistry and sustainable engineering principles can bring added value to smart materials development and application.[12, 13].

In this context, the printing of smart materials, not only allows a more environmentally friendly production and implementation into devices, but also offers several advantages over other large-scale production methods, namely high speed and low-cost production, patterning ability, compatibility with room temperature process and appropriateness to large areas and flexible substrates[12].

One of the strengths of printing technologies lies in its versatility. An interesting fact that demonstrates the disruptive character of those technologies is that what it is said about smart materials printing today seems very similar to what was said some decades ago with respect to composites: it promises more than simply substitute a former technology, it also encourages scientists and engineers to rethink how the production of a certain material should be done. We all know the importance and implementation that composites have in our days[14], printing technologies should follow the same successful path.

Such printing technologies have attracted particular interest with the use of polymer-based smart materials[15]. Polymers offer several advantages for printable smart-materials technologies[16], namely the low-cost, the higher versatility than inorganic materials and the higher flexibility, as seen in Figure 1. Additionally, their fabrication techniques are simple and can be printed on several types of substrates. There is also the widespread possibility of tailoring its side-chains and molecular structure, introduce neutral or charged fillers, as well as particles with specific properties into the material in bulk or on in polymer composites (its surface region), enabling materials to be fabricated with specific chemical and physical properties[17].

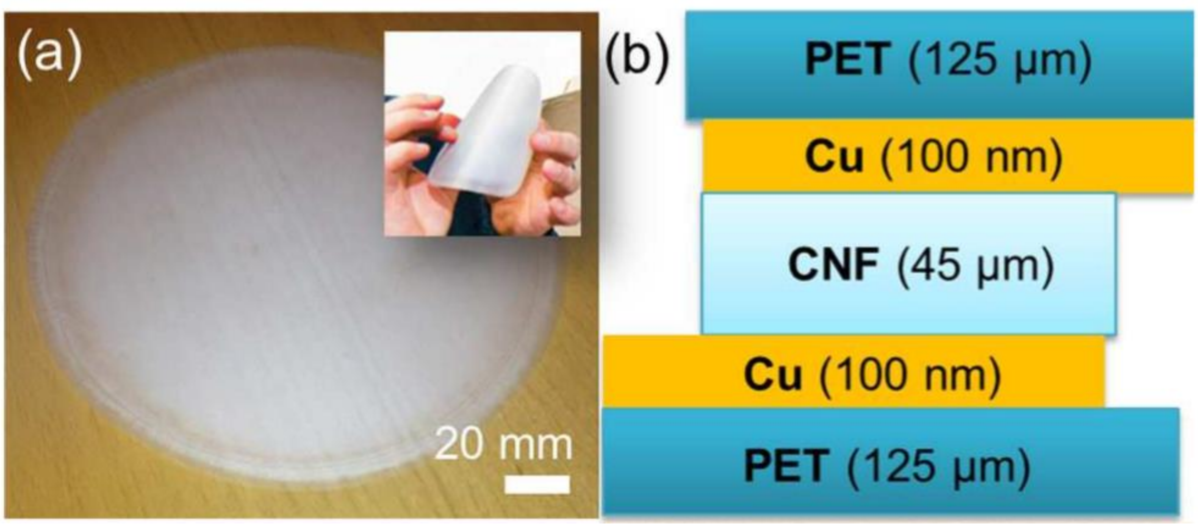

Figure 1. a) Photographs of a fabricated piezoelectric native cellulose nanofibrils and its flexibility (inset). b) Side-view scheme of the polymer-based flexible smart material[18].

This review paper will give particular attention to printed polymer-based materials that are already being incorporated into a high number smart materials device applications.

The key aim of this work is to present the state-of-the-art on the polymer-based smart materials printing as well as to address the main challenges and prospect. Firstly, an introduction to smart materials and materials for printing technologies will be provided, together with a description of the principal printing technologies. Secondly, the state of the art on printed smart materials will be presented. Finally, the future challenges and trends will be outlined, just before the main conclusions.

2. Smart materials – An overview

A high number of new materials with high efficiency/cost ratio and high quality are being used in several fields of engineering and science[19, 20]. With the observed development of materials science, new materials are becoming more (multi)functional, with optimized characteristics and properties[20]. Smart materials are frequently classified as materials that respond to an external stimulation in a specific, predictable and controlled manner[21]. Nevertheless, such definition is way too general, once almost all known materials react or respond to some stimulation. In this way there is a very fine line dividing “smart” and conventional materials[2, 21]. Being better to express the smart materials definition, frequently called “smart behaviour”, in terms of a material that reacts to an external stimulation from its environment in a specific, reliable, dependable, reproducible and useful way [2, 22]. Those useful features have been used for the development of actuators and sensors as well as in a large variety of products, ranging from household goods to innovative automotive components and medical devices[22, 23].

2.1 Smart materials types and applications

Smart materials are adding high value to traditional devices in almost all industries, including medicine, sports, entertainment, security, consumer electronics, banking and food, particularly when used in applications as sensors and actuators[2, 24].

The general definition and interpretation of functional, intelligent and smart structures or materials involves some specific properties such as being clever, sharp, active, fashionable, and sophisticated[12, 25]. Nevertheless, in order to structures or materials achieve reasoning or true intelligence, is necessary the addition of artificial intelligence through microprocessors, computers and control algorithms[25].

Furthermore, the integration of sensors, actuators and high-control is the key factor for the development of smart applications[26].

Smart materials are usually categorized into two different groups; the active ones or the passive ones. Contrary to passive ones, the active ones are materials that show the ability to change their properties or geometry under an external stimulus such as magnetic, thermal or electric, enabling their use as actuators and force transducers. A transducer is a material that transforms one type of energy into another form of energy.

Is possible to find several groups of active smart materials, each of them exhibiting specific characteristics which can be useful in a variety of applications. These materials include shape memory, piezoelectric, piezoresistive, magneto-rheological, magnetostrictive, magnetoelectric, electro-rheological, and chromic materials[27-32].

Piezoelectric materials are key elements in various applications and devices [33, 34] and are characterized by electromechanical transduction [35] in a reversible way. Thus, an electrical signal is generated by applying a mechanical force, while the opposite also can occur, an electrical stimulation induces a mechanical deformation. Such piezoelectric transducers are used as strain and force sensors, for powering wireless sensors (with self-powered capability), in ultrasonic and acoustic dispositives, fuel injection systems and adaptive control systems, among others [32]. Electrostrictive materials are more temperature dependent , making them less used in sensor applications when compared to piezoelectric materials[36]. Additionally and contrary to the piezoelectric materials, where the relation between electric and mechanical variables is linear, electrostrictive materials show a quadratic relation between those properties. Electrostrictive polymers appears as an emerging smart materials tool that allows to develop innovative applications[37] such as artificial tissues and muscles, energy harvesting and actuators, among others [38]. Piezoresistive materials also show a high and increasing interest in both research and industry. The piezoresistive effect explains the electrical resistance variation of a material due to the application of a mechanical stress. This change of the resistance is usually caused by the stretching and/or compression that affects the mobility of the electrons [39]. The most used piezoresistive devices are incorporated in pressure measurement systems [40]**.** Thermo-responsive materials such as shape memory materials (SM), are examples of materials that change their shape with the variation of temperature[41]. Through heating or cooling, these materials can be deformed and returned to their original shape. pH sensitive or chromic systems materials are other examples of smart materials[42]. The first ones, are materials that change one of their intrinsic properties such as colour, electrical or mechanical behaviour among others, as a result of pH alteration whereas the second type of materials modify their colour in reaction to a thermal, electrical or optical stimulus[42, 43]. Finally, magnetostrictive materials undergo mechanical deformation in response to a change in the applied magnetic field [44]. Thus, magnetostrictive materials convert magnetic to mechanical energy or vice versa [25]. Sensors and actuators are obvious applications of those magneto-sensitive materials [25]. Table 1 summarizes the main smart materials already being used, some representative materials and their device applications.

Table 1. Principal smart materials and their device applications.

Smart material	Representative Materials	Applications	References
Piezoelectric and electrostrictive	PZT, PVDF, $BaTiO_3$, Quartz, Parylene-C, ZnO P(VDF-TrFe); $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN-PT)	Touch screen; Led's; Piezofibers; Smart cloths, Actuators and transducers; Tactile sensors; Energy and power harvesting; Energy conversion	45, 46 38 47 48 49
Piezoresistive	Carbon or silver fillers; Microcrystalline silicon; Graphene; PEDOT:PPS	Pressure sensor; Touch screen; MEMS; Biomedical sensors; Strain gauges Tactile sensor; Stress-strain sensors	50, 51 52-54 55-58 59

Magnetostrictive	Terfenol -D; Metglas, $CoFe_2O_4$	Transducers Magnetic sensors; Gas sensor, Magnetoelectric sensor; Energy harvesting; Magnetic field sensing;	25 60, 61 62, 63
pH sensitive and thermo-responsive	Stimuli response polymers (N-isopropylacrylamide (NIPAM), N,N-diethylacrylamide (DEAM), methylvinylether (MVE), N-vinylcaprolactam (NVCl)); Shape memory alloys; Poly(N-isopropylacrylamide) (PNIPAAm)	Biomedical sensors; Tissue engineering; Drug delivery Biosensing	42, 43, 64 65

Smart materials can be used in a large variety of applications due the high number of possible combinations between stimulus and responses. Nevertheless, there is a widely held view that the existing smart materials could find far more uses. The limited commercialization reflects some misconceptions connected to the fabrication and upscaling of smart materials[2, 66]. Thus, the future of smart materials is strongly related to emerging technologies that will make possible to print the entire smart device system using functional inks. As a consequence, printing technologies emerge as an auspicious methodology to produce low cost products, with large area processing and flexibility [67].

Silicon-based smart materials despite being easily tailored and miniaturized, showing high performance (piezoelectricity, conductivity and hysteresis) and advantages such as temperature and chemical stability and the better resistance to aging, are produced through slow, complicated and costly fabrication process, typical of old-style semiconductor materials (**Figure 2**). Further, they do not reach the large variety of effects previously described, unless complex systems are designed and fabricated.

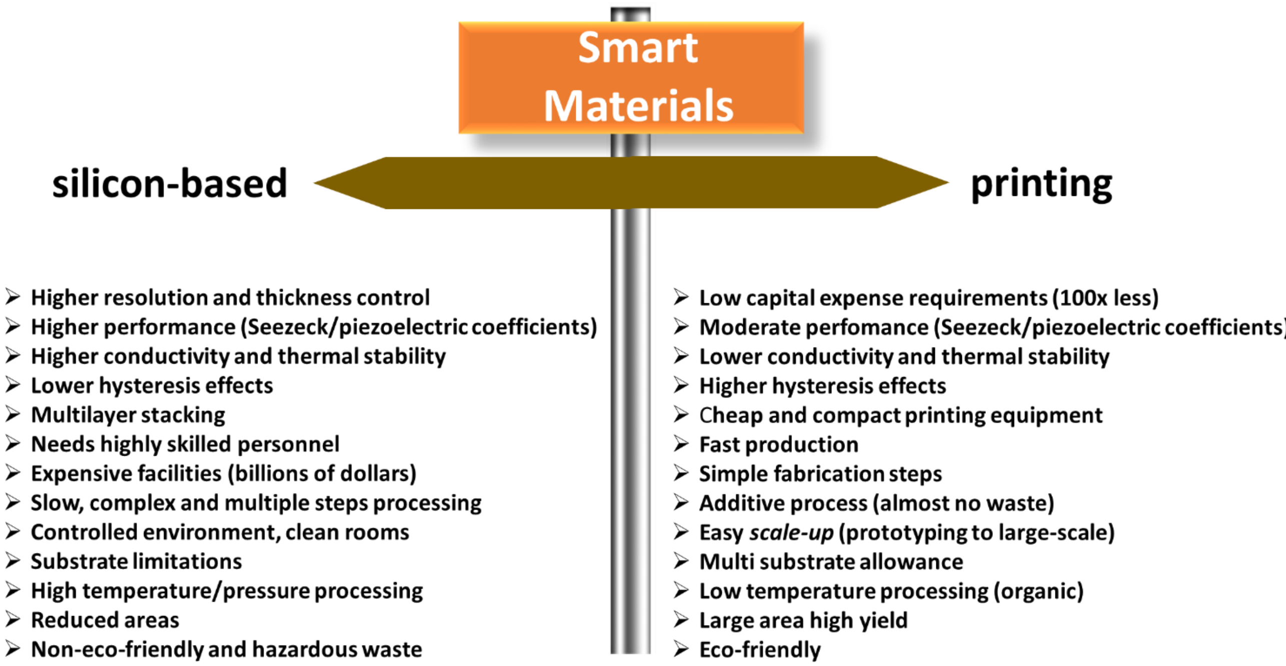

Figure 2. Printing technologies *versus* silicon technologies for the production of smart materials.

Silicon-based processing can involve hundreds of steps, in which the different components are deposited, masked and etched. Additionally there's a need to remove unnecessary material [24]. The production of a single batch is a complicated task and can take several weeks in an expensive and highly specialized fabric[24, 67]. These sensors are typically brittle, rigid and are prepared in small areas. Despite innovative attempts to solve these limitations, all introduced further costs and complexity into the final devices, not allowing robust, foldable and reliable devices. Driven by those innovation trends and demands, the related research and development (R&D) of smart materials aims to optimize the production processes with respect to efficiency, high volume production, energy consumption, raw material reduction, and sustainability concerns [24, 26]. Printing is pointed out as one of the possible solutions to these technological challenges, offering several advantages over other large-scale methods, namely patterning low-cost, high speed production, room temperature operation and applicability to flexible substrates (Figure 2). Furthermore, printing technologies provide also direct patterning on a surface without the use of masks, allowing in this way, large autonomy regarding the thickness of the printed material or pattern [68].

2.2 Life-time of smart material devices

The main challenge in today's structural engineering is to better design structures against the damaging effects of natural hazards and related with the life cycle of materials[69].

The environmental impact of smart materials devices comprise the place where the raw building materials came from, their manufacture process, transportation and their disposal at the end of their use. In this way, the key factors to be considered while designing a smart system are the structure design, the used materials, their functionality and life-time[69, 70].

Generally, materials will degrade over time due to fatigue, environmental conditions, or damage incurred during operation. Regarding transistor technologies, circuit design and fabrication procedures become increasingly important, enabling one to implement smart integrated systems—namely, near-field communication (NFC) smart labels , intelligent packaging, and systems on glass, plastic, or bioelectronics [71, 72]. However, the continuous real-time operation of these materials demands robust circuit performance against some parameters such as bias and environmental stress, temperature limit range, among others[72].

In this theme, Martins *et al.* [70] reported bias stress and temperature impact on InGaZnO TFTs and circuits. In the case of bias stress, both gate and drain bias were applied for 60 min. Isolated transistors revealed a variation of the drain current as high as 56% and 172% during bias voltage and temperature stress. It was also reported that the employed circuits were able to counteract it. Inverters and two-TFT current mirrors following simple circuit topologies showed a gain variation below 8%, while the improved robustness of a cascode current mirror design is proven by showing a gain variation less than 5%.

The rapid spread of electrical and electrical mechanical systems in industrial applications has intensely increased the claim for sensors, whose characteristics need to be preserved, enhancing its long-term use. For that, a high number of smart materials are encapsulated to provide insulation and to protect them against moisture, dirt, mechanical injury, among others[69].

Therefore, to improve the reliability and performance of a system, it is essential to path and monitor the conditions of the smart materials as well. Smart materials should be encapsulated or protected with specific materials for defense against operating environments and to provide electrical insulation and thermal dissipation. Many known works have been reported using different known materials in order to ensure the best encapsulation of sensors against chemical, humidity, temperature and environmental degradation factors[1, 73-75].

Following a similar strategy Im *et al.*[74] reported smart materials consisting of ultrathin-film iron (Fe) layers deposited on the PET substrate, Au lines as electrode connection lines, and anion exchange membrane encasing a sensor. In this work, the protection of the sensor from mechanical and chemical stimuli was achieved by encapsulation of the smart materials with an anion exchange membrane which will work not only as a protector, but also as a selector of anions including chloride ions among degradation factors.

Larsson *et al.*[73], reported a encapsulation for smart textile electronics. A combined humidity and temperature sensor was packaged by vacuum casting onto three different types of textiles; cotton, nylon and a waterproof fabric. To the encapsulation, a membrane was made and integrated into the device to protect the sensor from the environment. At the end, the developed sensors showed insignificant performance degradation.

Another good example of efficient smart material encapsulation was reported by Gembaczka *et al.* [75] that described a new kind of encapsulation approach for a capacitive pressure sensor module consisting of two integrated circuits. The authors used a high temperature resistant polyimide–epoxy composite as a die attach material and sealing compound for the bond wire and parts of the chip surface excluding the MEMS pressure membranes. The optimized fabrication process allowed a new kind of hermetic encapsulation for human implants based on MEMS sensors.

In this way, encapsulation and coating of smart materials can improve, maintain and protect the characteristics and performance of the material. The development of smart materials and encapsulation coatings allowed new capabilities.

3. Printed technologies

Smart materials printing is attracting large interest as demonstrated by the increasing research projects number and use of printed smart materials in a high number of application areas [15, 76], as evidenced by the number of published papers and subject areas on Scopus database with the topic "Smart materials printing" from 2000 to 2017 (**Figure 3**).

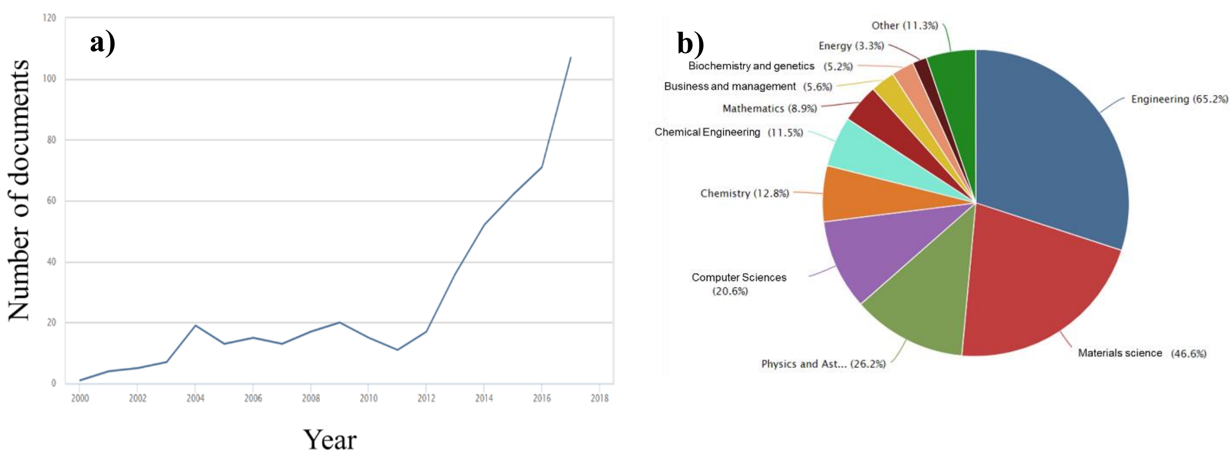

Figure 3. Number (a) and subject areas (b) of the published papers on Scopus database with the topic "Smart materials printing" from 2000 to 2017.

In computer sciences (2004) discussed the introduction of optoelectrical, optical, and electrical functionalities into low-cost products like packages and printed matter that can be used in informatic solutions Kololuoma et al. [77]to increase their information content.

In materials (2006) two-dimensional thin films of carbon nanotubes were tailored by Gruner[78] for for transparent and plastic electronics materials with excellent - and tunable - electrical, optical and mechanical properties.

In Physics and Astronomy (2007) organic and active matrix addressed displays built on electrochemical smart pixels prepared on flexible Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) substrates were reported by Andersson *et al.*[79].

In engineering (2012) Park *et al.* [80]developed highly stretchable electric circuits from a composite material of silver nanoparticles and elastomeric poly (styrene-block-butadiene-block-styrene) fibres.

In Chemistry (2016) and inspired by the chemistry of botanical systems such as tendrils, bracts, leaves and flowers, Gladman *et al.*[81] printed composite hydrogel architectures that are encoded with localized, anisotropic swelling behaviour controlled by the alignment of cellulose fibrils along prescribed four-dimensional printing pathways.

Based throughout this historical evolution and regardless of the area it is verified that an effective printing process relies in two main components: materials and printing technologies.

3.1. Techniques

The two most popular approaches for the development of coating/printing systems are non-contact and contact printing, as schematically represented in **Figure 4**.

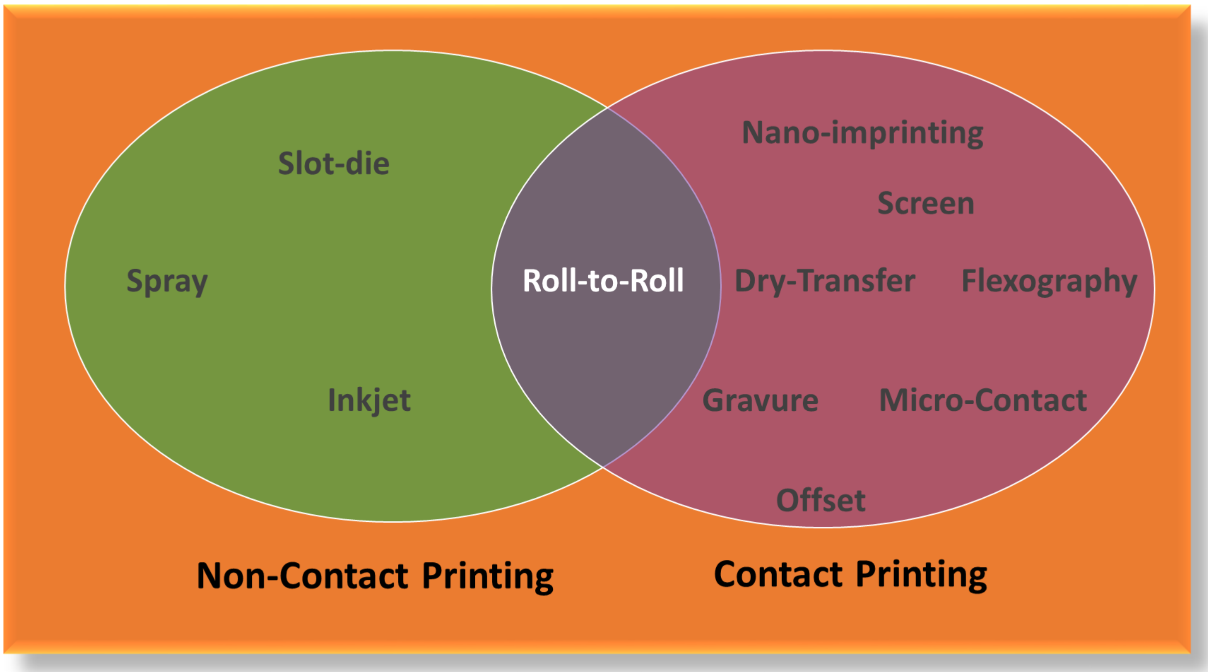

Figure 4. Printing technologies classification diagram (adapted from [82]).

The process involved in the contact printing is characterized by the patterned structures with printed surfaces that are taken into contact with the substrate. In contrast, when a non-contact process is used, the ink is printed through nozzles or holes and the assemblies are developed by moving the substrate holder (or stage) in a pre-designed pattern [82].

Printing technologies by contact process comprise screen, gravure printing, dry-transfer, flexography, micro-contact and offset printing. All of them present some drawbacks (**Table 2)** that difficult their effective use in the production and scale-up of smart materials[82], namely reproducibility limitations, pattern fragility and high cost production. Nano-imprint is just in a take-off stage for large-scale production, so it would be unfair to include it on the drawbacks that difficult its effective use.

Table 2. Summary of the operation mode and limitations of the contact-printing techniques.

Technique	Operation	Limitations	Ref.
Gravure	Uses a metal cylinder with the image engraved or etched on to the surface that rotates through an ink pan, being the ink directly transferred to the substrate. Allows simple scalability.	Short cylinder life span; High cylinder cost; Uneven printing; Ill-defined edges; *Pick out* effect; Low reliability; Unprecise control of shape and sizes.	82-88
Dry-transfer	The mixture of heat and pressure causes the decal (applied without the use of water or other solvent) to stick more strongly to the substrate than to the backing, thus when the backing is removed, the decal remains in the substrate.	Misalignment of the strips; Undercutting of the strips; Inefficient decal transfer; Ill-defined edges; Lack of flexibility in the transfer; Expensive and time-consuming process; Slight bas-relief effect.	89-93
Nano-Imprint	To imprint the pattern, the process utilizes a direct contact between the thermoplastic or UV-curable resist and the template (mould).	Pattern fragility; Defect density control; Time consuming; Expensive process; Low reliability; Collapse of the replica.	94-98
Micro-Contact	The technique utilize the relief patterns on a main stamp to print self-assembled patterns of monolayers of ink on the substrate by conformal contact.	Not suitable for polar inks; Stamp swelling; Stamp deformation decreases the resolution; Surfaces pairing and buckling; Roof collapse; Low reproducibility.	82, 96, 99-101
Flexography	Uses flexible printing plates with backward reading to impart a correct reading impression. The pattern is printed by placing the plate in mechanical contact with the substrate. Allows simple scalability.	Squeezing; Marbling effect; High tensile stresses; Pattern cracks; Non-uniform patterns; High plate and dye cost; Line width limitations.	82-84, 102, 103

Offset	The image is etched by using a depressed or sunken surface to an intermediary surface (blanket), and applied to the final substrate by pressing the blanket against the intermediary surface.	Short blanket life span; Solvent absorption; Undesirable spreading; High rolling resistance; Ill-defined edges; Tedious and expensive process.	66, 83, 84, 86, 104, 105
Screen	The screen is filled with ink and brought into proximity to the substrate. A squeegee is then forced to the screen bringing it into contact with the substrate. The squeegee is then drawn linearly across the screen forcing coating solution through the open areas onto the substrate, reproducing the pattern.	Needs substrates with small roughness; Needs a different frame for each different pattern; The snap-off distance, the speed of the squeegee and the viscosity of the solution have strong influence in the quality of the printed material; Large waste of material, Low maximum resolution.	82, 106, 107

Due to the aforementioned limitations of contact printing technique (**Table 2**), non-contact printing has emerged as an alternative approach for the production of printed smart materials and devices. The most used non-contact printing technologies are ink-jet and spray printing. They require different and optimized characteristics such as viscosity, surface tension, conductivity, maximum particle diameter, type of substrate and optimum temperature (see **Table 3**). The main characteristics of the roll-to-roll systems have been also added to table 3, for comparison.

Table 3. Printing techniques characteristics and ink/substrate requirements for non-contact printing techniques[82, 108-112].

Printing Technology	Characteristics	Ink limitation	Substrate limitations
Inkjet	Allows a large variety of patters; Simple process, widely used in the industry; Ideal for small and medium production volumes; Low time to market; Typical resolution of 0.01 [mm] Limitations include: Coffee-ring effect, bulging, clogging and satellite droplets, which sometimes results in poor reproducibility	Viscosity 8-20 [cps]; Surface Tension 25-36[mN/m]; Max. particle diameter 0.2[µm]; Flash point >45 [ºC].	From very small to large size areas; Flat substrate with small roughness.
Screen	Needs a different frame for each different pattern; Simple process, widely used in the industry; Ideal for small, medium and high production volumes; Low time to market; Typical resolution of 0.2 [mm] Low-cost equipment.	Viscosity 1000-40000 [cps]; Surface Tension 25-36 [mN/m]; Max particle diameter depends on the mesh	From small to medium size areas; Flat and curved substrates with small roughness.
Spray	Low resolution patterns Simple process,	Viscosity 1-1000 [cps]; Surface Tension,	

	Low time to market; Low-cost equipment. Very low resolution typically up to 1 [mm]	Not specified; Max particle diameter 10 [µm]; Flash point >45 [ºC] .	From small to very large size areas ; Any substrate; Any roughness.
Roll-to-Roll	Needs a different roll frame for each different pattern; Time consuming process, widely used in the industry; Ideal from medium to very high production volumes; Typical resolution of 0.05 [mm] Expensive equipment.	Viscosity 5-30 [cps]; Surface Tension 25-36 [mN/m]; Max particle diameter, Not specified ; Flash point >Room Temperature ; Ink curing <100 [ºC].	From very small to medium size areas; Flat and in roll substrate with small roughness.

From **Table 3** it is possible to conclude that the existing printing technologies despite to intercept each other in certain characteristics, differ in many key issues, such as simplicity and resolution in the equipment setup, scalability and the choice of materials features that are more suitable for printing, among others.[113]. Additionally a high number of materials, comprising biomaterials, polymers, semiconducting materials and carbon nanotubes have been efficaciously printed trough aerosol jet printing once such printing technique can tolerate a much larger viscosity range (1 to 1000 cP)[114]. Advantages of aerosol jet printing such as optimized features, wider range of materials type, broader ink viscosities range and reduced waste, attracted the interest of Smith et al. that used it on the printing of silver nanoparticles lines on polyimide substrates. It was discovered that he choice of parameters is highly dependent on each application type, once some characteristics of the printing procedure (print speed or substrate temperature) may be constrained[114, 115].

Further, a careful selection of the appropriated ink components is also desirable by taking into consideration the main function of the surrounding materials on which a specified pattern will be printed.

3.2. Materials/Inks

Proper printable materials are essential to produce smart products with the required characteristics. A high variety of factors can influence the material selection for printable applications[116, 117]. Thus, printable materials are a key element to be accomplished and engineered to enable further developments in printed smart materials [118].

Inks are at the basis of printed technologies and need to be tailored for a specific printing technology in terms of surface tension and viscosity. Further, substrates are other key element that affects the application of printing systems and the production of printable materials[118].

Common printable materials can be separated into three main categories: conductors, semiconductors and dielectrics. Further, composite materials have been developed for printed devices with photosensitive, piezoelectric, piezoresistive and ferroelectric properties [82], among others. Organic/inorganic hybrid materials were also developed to balance the low speed organic based electronic devices [119].

Most printable materials are reported in the form of solutions with precise properties to consent suitable printing such as nanoparticle dispersion or an good level of physical and chemical stabilities required to preserve an equilibrium between gravitational and Brownian motion of the particles[82].

Many printing technologies also use organic materials that are solution-based, which frequently result in smart materials exhibiting quite modest activity, however suitable for applications such as RFID and displays [82].

3.2.1. Conductors

Conductive inks for printable electronics such as Ag, PEDOT:PSS, ITO, and annealed reduced graphene oxide **-Figure 5-** need to be specially designed in terms of composition and viscosity for the intended application with the desired printing process.

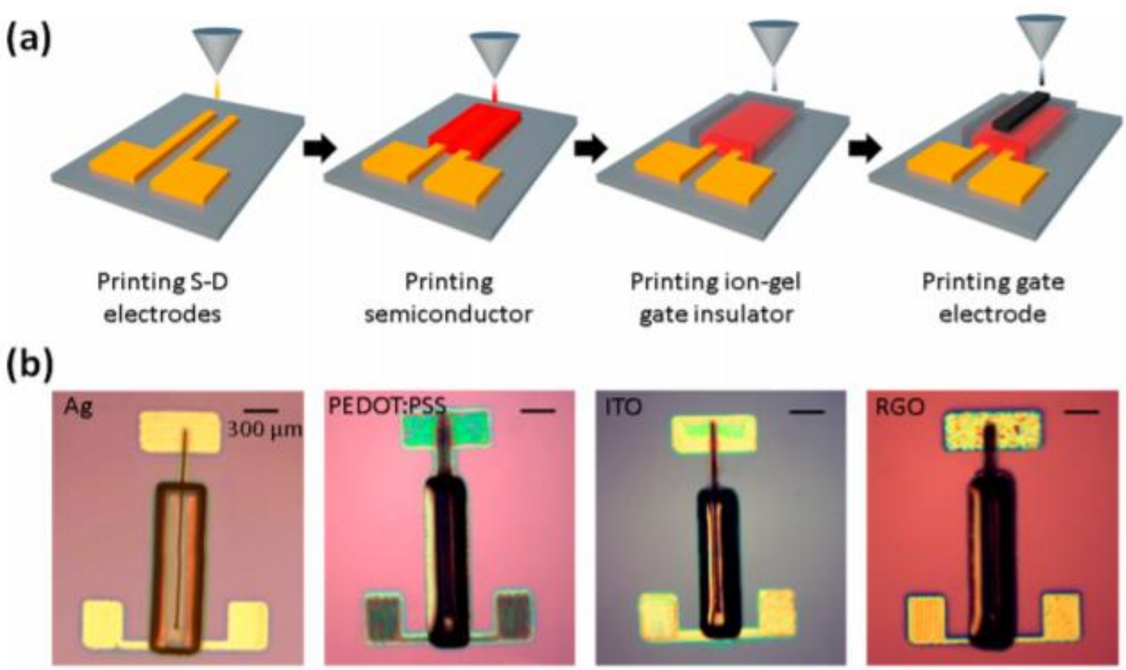

Figure 5. a) Additive fabrication of electrolyte-gated transistors by aerosol jet printing on SiO_2/Si substrates. A top gate (PEDOT:PSS), bottom contact EGT architecture was used in the study with W/L = 1000 µm/50 µm. b) Optical microscope images of printed electrolyte-

gated transistors with different kinds of electrode materials: Ag, PEDOT:PSS, ITO, and annealed RGO[120].

An understanding of the characteristics of the printing technique to be used and the properties of wet ink are both needed in order to identify the suitable characteristics that enable the desired application. Additionally, the surface energy and rheology of the inks will regulate some important features of the final printed image such as the surface properties, cohesion, viscosity, the dry ink structure, the substrate adhesion and the conductivity.

To achieve fully optimized rheology of the inks, research on the printing process, on the specific printing equipment and its production parameters is needed. The ambient conditions is also an important parameter (**Figure 6**).

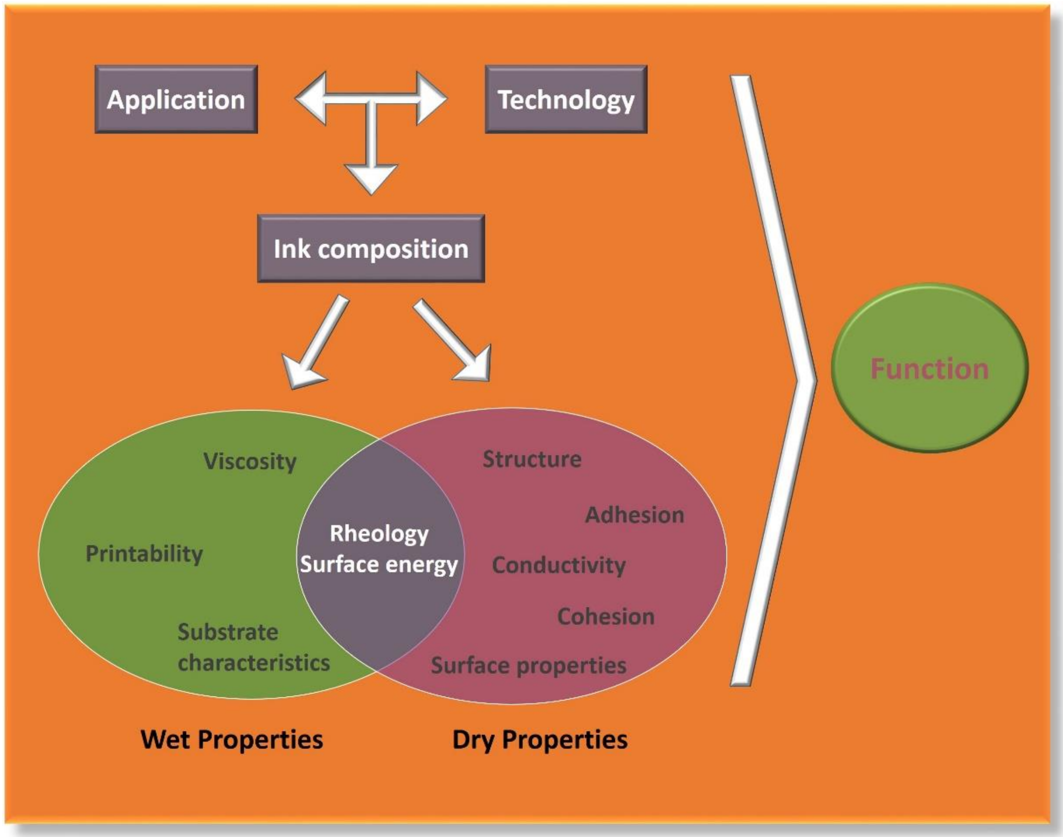

Figure 6. Printing parameters related with the development of a conductive ink.

In this way, a cautious choice of suitable conductive materials is desirable considering the work function of the adjacent materials. Further, according to the chosen printing technology, the properties of the printing inks can be adapted by using surfactants and volatile additives. From the most used conductive metals for printed electronics applications stands out silver (Ag)-based inks due to their good electrical performance and physical properties[82, 121].

Due to its high cost, Ag hardly will be used for up-scalable production of flexible electronic devices. Carbon and copper based inks can be a cheaper option, nevertheless copper-based pastes are not fully functional after printing, once the developed drops immediately spread after deposition leading to larger sizes, when compared to the initial size of the produced droplet [122]. To solve this price/performance problem, highly conductive inks have been fabricated from crystalline organic conducting polymers such as polyphenylene, polyacetylene, polyaniline doped with camphor sulfonic acid, polypyrrol, poly(p-phenylene vinylene), polythiophene polyaniline and 3, 4-polyethylenedioxythiopene-polystyrene sulfonic acid (PEDOT/PSS), in which the chemical structure can be adjusted to get a wide range of electronic and mechanical characteristics [123]. On the other hand, apart from the advantages of easy solution-based fabrication and low-cost processing, organic conductors show much lower electrical conductivity than traditional metals. Ag appears as a good example, once it has an electrical conductivity of 6.30×10^{7} $S.m^{-1}$, whereas the conductivity of a Ag-based ink is 1.0×10^{5} $S.m^{-1}$[82, 124]. Seeking to increase the conductivity of polymer based printable materials, graphene and carbon nanotubes ($\approx1\times10^{8}$ $S.m^{-1}$ conductivity) have been added to polymer matrix such as PDMS[82, 125].

3.2.2. Semiconductors

Semiconducting organic molecules[126, 127] and conjugated polymers [128-130] exhibit suitable characteristics such as solution-based processability and can support the development of inks for sensors, optoelectronic devices or thin-film transistor device structures (Figure 7) taking advantage of their particular rheology, electrical properties, colour or luminescence.

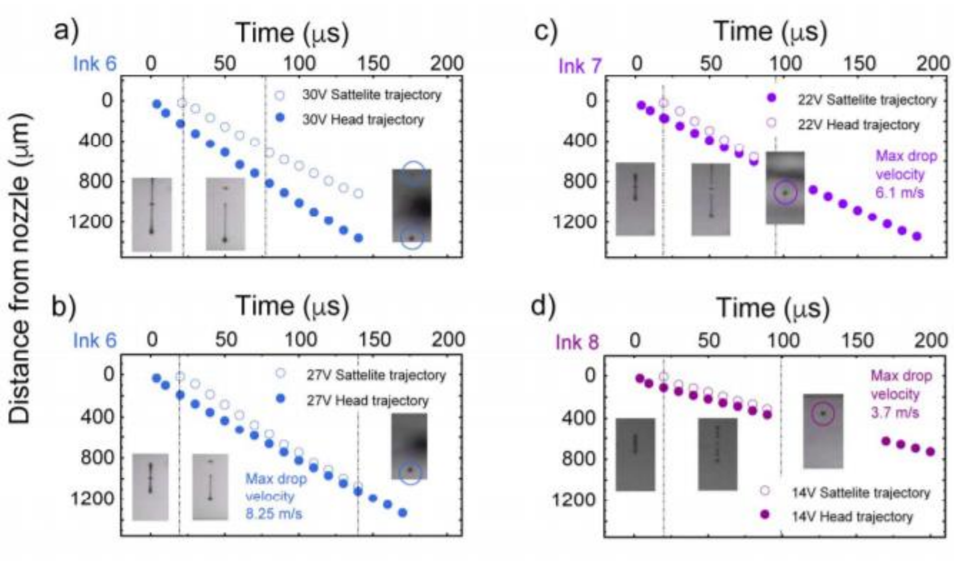

Figure 7. Time dependent drop formation process with satellite and head drop trajectory in respect to the nozzle distance for semiconductor inks containing an indium-based oxo alkoxide precursor to be used in a bottom-contact coplanar thin-film transistor device structures. Images of: (a) ink Tetrahydrofurfuryl alcohol/Tri(ethylene glycol) monoethyl ether at 30 V, (b) Tetrahydrofurfuryl alcohol/Tri(ethylene glycol) monoethyl ether at 27 V, (c) Tetrahydrofurfuryl alcohol/Propylene carbonate at 22 V and (d) Tetrahydrofurfuryl alcohol/Acetonitrile at 14 V firing voltages[131].

Semiconductors represents the most enabling and challenging group material in many functional devices. Performance is usually better with single crystalline materials with high purity. When implemented through inks based on micro- and nanostructures (nanomembranes, nanoribbons, platelets, nanowires or quantum dots), printing techniques provide a simple, yet powerful pathway for the fabrication of device or system configurations that cannot be accomplished over any other method (**Table 5**) [132].

Table 5. Representative ink structure type, transfer protocols, materials, associated surface modifications and corresponding references.

Structure	Materials	Transfer	Surface modifications	Ref.
Nanomembranes, nanoribbons, platelets and bars	Silicon, GaAs, GaN and InP	additive	Heat	[132-135]
Nanowires	Silicon, InAs, and Ge	subtractive	UV, plasma	[132, 136-138]
Quantum dots	CdS, CdSe, ZnS, and ZnSe	deterministic	adhesives	[132, 139-141]

Flexible and low-cost low-pass filters (first and second order) with adjustable cut-off frequency (ranging from 82 Hz to 740 Hz) were printed through inkjet printing [142]. The low-pass filters were optimized and an adaptable cut-off frequency was achieved by an inkjet-printed organic thin-film transistor, allowing signal filtering in applications such as tactile sensing. Further, the influence of the specific chemical, mechanical and thermal treatments, that usually appear in fabrication processes for textiles, on the electrical behaviour of all-inkjet-printed organic thin-film transistors have been addressed[143, 144]. It was shown that the organic thin-film transistors were useful after their application on the fabrics, yet displaying higher degradation in the inkjet printed organic thin-film transistors with shorter channel lengths (L = 10 μm).

Printing technologies have been often used for the fabrication of diodes [145]. Thus, it has been studied the possibility of developing quantum dot light-emitting diodes (QLEDs) with inkjet printing technologies, for the full-colour patterning of QLED displays. Through the control of the quantum dot (QD) ink composition and inkjet printing conditions, QLED pixels were successfully patterned in the 60-in ultrahigh definition TV format, with a resolution of 73 pixels per inch. The inkjet-printed QLEDs revealed a maximum luminance of 2500 cd.m^{-2}, which is still quite low when compared with that of QLEDs produced by spin-coating technique[145].

Despite those proofs of concepts with these printed semi-conductors structures, new strategies are needed to achieve films with very good macromorphology (high-fidelity footprint and uniform cross-section) and nanomorphology on unstructured substrates using conventional printing technologies[146].

3.2.3. Dielectrics

Dielectric layers are vital for the production of many printed electronic devices and are usually distributed into two main groups, taking into account their printed thicknesses: thick (>1 µm) and thin (≤1 µm) dielectrics [112]. Thin films are important for printed low-profile components namely organic transistor gates and metal-insulator-metal capacitors. In the other hand, thick dielectric films are typically used to develop dielectric substrates with patterned selectivity[112, 147]. When inks-based conductive nano-particles are combined with dielectric inks, ink-jet printing can be used to produce complex bottom-up electronic structures in a purely additive process[112, 148].

Optimized layers of dielectric materials are essential for applications that require high capacitance printed structures. That requirement allows proper insulation needed to obtain low voltage operation for field effect devices and to prevent leakage currents [82]. In order to stimulate the activation of the medium caused by electric field (or other transduction phenomena) a uniform layer of dielectric material is needed. Generally, the organic dielectric material, with low-cost price, large quantities availability and high solubility in numerous solvents, are more easily printable than the inorganic counterparts [149].

The printing of dielectric materials is of particular significance in printed electronics, once the dielectric/semiconductor interface is of main importance for the stability and optimized performance of the devices[150].

The intense research for low-cost dielectric films patterning procedures usually focus on photodefinable gate dielectrics namely acryl-based polymer, polyvinylphenol (PVP), sol-gel-derived siloxane-based hybrid polymers and polyimides. Nevertheless it is possible to find reports on organic dielectric materials for printed electronics such as poly (methyl methacrylate), polyvinyl alcohol, polyethylene terephthalate and polystyrene[82, 151].

Finally, besides the use of dielectric coatings in technological electronic devices, solution treated organic dielectric materials are also utilized, likewise for the concluding encapsulation of printed materials and devices[82, 150].

4. Printed smart materials: From inorganic materials to polymer-based materials

Since the key innovations on smart materials for printing technologies have been achieved in piezoelectric, electrostrictive, piezoresistive, shape memory, pH sensitive, chromic and magnetostrictive materials, the following sub-sections will mainly focus on them.

4.1. Piezoelectric

Piezoelectric actuators and sensors are a well-known and established technology, used into a wide range of industrial fields including aeronautics, automotive, and non-destructive testing[152, 153]. With the global requirements for increased efficiency, safety, low-cost, scalability, diminished materials waste, simple patterning and low production costs, printing technologies are very appealing for piezoelectric devices development [82, 152, 154].

Kuscer *et al.* developed a piezoelectric ink composed of Pb(Zr0.53Ti0.47)O3(PZT) particles with an average size of 170 nm and stabilized with polyacrilic acid. The ink was jetted onto a platinized alumina substrate and well dispersed in a mixture of water and glycerol [155] and then used for the fabrication of thick films (~6 μm) by piezoelectric ink-jet printing. The printing technique was successfully executed at room temperature with a 21 μm nozzle, a 20 μm drop spacing and a 15 V jetting amplitude at 2Hz of maximum operating frequency. The ink had 3.2 mPas viscosity at a shear rate of 100 s^{-1}, 1.6 $g.cm^{-3}$ density and 10.4 zeta-potential (Z) value. After thermal treatments (heating at 500°C and sintering at 1100°C) a PZT structure with a local piezoelectric d_{33} coefficient of 15 $pm.V^{-1}$ was obtained, suitable for technological applications.

By combining PZT, polyvinylidene-trifluoroethylene (PVDF-TrFE) copolymer and N,N-dimethylformamide (DMF) as a solvent, Dietze *et al.* [156] reported a 10 $pm.V^{-1}$ piezoelectric coefficient and a 80 $\mu Cm^{-2}K^{-1}$ pyroelectric coefficient on a 5 μm thick screen-printed PZT/ PVDF-TrFE composite films. Such printed films were obtained from a ink with 20 volume percentage (vol.%) of PZT and with dynamic viscosities of 39 Pa.s and 9 Pa.s at a shear rate of 20 s^{-1} and 100 s^{-1}, respectively. DMF has been selected as solvent due to its low vapour pressure at room temperature (3.7 hPa) when compared to other PVDF solvents such as methyl-ethylketone (105 hPa), which avoids the evaporation from the paste to be printed. Such results, together with the low-temperature processing and corona poling enable these composites for up-scalable production of low-cost materials and devices. Another piezoelectric ink based on PZT was presented by Ferrari *et a*l [157] with potential application in the fields of MEMS, sensors, actuators and power harvesting. Such ink was constituted by PZT milled powder and a polymeric low-temperature binder in weight ratio of 2:1 and with a 1 g/cm^3 ink density.

After screen-printing using a 325 mesh screen on alumina substrate, a dielectric constant of $\varepsilon = 100$ was obtained a value of 0.8 $\mu C.cm^{-2}$ remanent polarization with a maximum applied electric field of $\approx$ 13 $MV.m^{-1}$. The ink viscosity was later optimized for values lower than 40 cP, allowing printing by a drop-on-demand technology. In order to achieve such viscosity value, the piezoelectric ink was dispersed (in a1/3 weight ratio) on ethylene glycol diacetate. The printing procedure was performed with a driving pulse of 60 V amplitude, 3 μs time (rise and fall), 20 μs duration and a driving frequency of 80 Hz.

Taking advantage of another piezoelectric material, barium titanate ($BaTiO_3$), Sakai *et al.* [158] prepared a ≈30 μm thick film patterns on ethyl cellulose substrates through an ink-jet method. The ink was prepared by mixing $BaTiO_3$ powder (20 wt.%) with water, polyethylene glycol and a polycarboxyl ammonium-based dispersant using an ultrasonic homogenizer, and later with methyl alcohol, being obtained a 10 mPas dynamic viscosity at a shear rate of 24.5s^{-1} [158]. The printing process was carried out with a 2 mm distance between the head and the substrate, 75 mm intervals between dots and a driving frequency of 4 kHz. The printed ink was then heated at 130 ^{o}C for 30 min and annealed at 600 ^{o}C. The measured dielectric constant at 1kHz, remnant polarization and coercive field of the water-based ink containing $BaTiO_3$ powder were 2200, 3.1 $\mu C.cm^{-2}$ and 1.1 $kV.cm^{-1}$, respectively. Thick films of $BaTiO_3$ with 15µm were fabricated using Pt substrate and by screen-printing technique[159]. Saturation polarization, coercive field and piezoelectric coefficient of the textured thick film were 7.5 $\mu C.cm^{-2}$, 2.9 $kV.cm^{-1}$ and 136 $pm.V^{-1}$, respectively.

Almusallam *et al.* [154] also presented a low temperature type PZT/PVDF with 0-3 connectivity composite produced using screen-printed process and flexible textiles. The optimal composition had a weight ratio of 12/1 (PZT/polymer), exhibiting a relative dielectric constant of 146 (at 1 kHz) and a maximum d_{33} of: 70 $pC.N^{-1}$ for polyester–cotton, 40 $pC.N^{-1}$ to Kapton and 36 $pC.N^{-1}$ to alumina substrates.

Such development on printed flexible piezoelectric materials is of particular and significant interest once it will enable suitable sensitive electronic systems, specially electronic skins that can be involved around a robot’s body, prosthetic hands or even fabrication of piezoelectrics on large areas wafers cheaper than the standard commercially available. The research in this field is slowly moving towards those approaches.

4.2 Shape memory polymers, pH sensitive and chromic system materials

Shape memory polymers are attracting increasing interest as they are able to return from a temporary deformed state to their primary state, by the application of external stimulation, such as temperature alteration [160, 161].

In the area of shape memory materials, can be found reports on the fabrication of strain gauges with the use of a thermally contracting shape memory polymer (SMP) made by inkjet printing. The simple fabrication process allowed the obtention for the first time of strain gauges pre-compressed through a substrate size contraction of 2.5x[162]. Davies *et al.*[160], reported the construction by inkjet printing of an optical and non-reversible temperature sensor by using a shape memory polymer. This sensor has shown a highly attractive response for time temperature devices with rigid demands on confining the use to a precise temperature for its entire lifetime. This approach can also be followed in areas such as medical industry and food packaging control. The control of pH values of liquids for applications on and biological, industrial and environmental areas requires some characteristics such as being stable, compact, sensitive and of simple use. Meeting those requirements, Yiheng Qin *et al* [163] reported the development of functionalized SWCNTs for pH sensing by inkjet printing. The electrodes, printed on glass substrates, have shown a reproducible pH sensitivity of 48.1 mV.pH^{-1}. Such sensitivity value increased to 61 ± 0.1 mV pH^{-1} and 57 ± 0.6 mV pH^{-1} with the successful use of a highly loaded palladium (Pd) based ink [163].

Thus, the deposition of Pd thin films, from a highly concentrated ink (>14 wt.%), was reported using an inkjet printing procedure[163]. The surface tension and viscosity of the solution were adapted by the use of toluene. For that, a thermolysis process was applied trying to adjust the continuous and uniform Pd films to the stable printed ink. With the utilization of just one printing layer, a very low resistivity of 2.6 $\mu\Omega.m^{-1}$ of the Pd film was presented. Aiming to prove the electrochemical pH sensing capability, the printed Pd films surfaces were oxidized for ion-to-electron transduction and the underlying layer was left for electron conduction.

Both developed inkjet printing processes reported by Qin *et al.* and pH electrodes with sensing properties offer a cost-effective alternative for electrochemical control systems and devices. Later, Wang *et al.*[164] presented a formulation of pH-sensitive Pd catalyst ink for deposition of selective electrodeless of copper on a PET substrate based on styrene (St)-co-N, N-dimethyl-dimethylaminoethyl methacrylate (DMAEMA) nanocomposite catalyst ink.

It is believed that using inkjet printing of thermochromic conjugated polymers, will bring an innovative prospective application for temperature sensors. Bora Yoon *et al*[165] discussed such issue with the development of thermochromic conjugated polymers based on a single component ink system for inkjet printing to be used on QR code images (Figure 8).

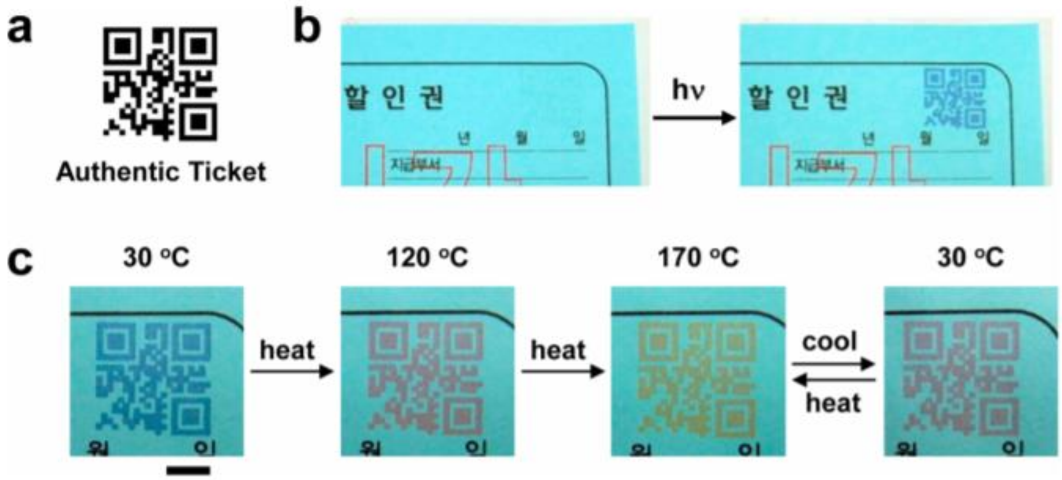

Figure 8. QR code image encoded with the word “Authentic Ticket”. (b, c) Images of printed QR codes used on a parking ticket utilizing: (b) ink from DA 3 as printed (left), after 254 nm UV irradiation (1 mW cm^{-2} , 5 min) (right), and (c) thermal treatment [165].

Due to its suitable stability characteristics and size distribution, the single diacetylene (DA) component ink can be successfully applied to substrates such as papers by using a simple inkjet printer from office. When the diacetylene printed paper was irradiated with UV radiation it was observed the formation polydiacetylene (PDA) images with blue colour that revealed reversible thermochromic transitions in precise temperature intervals, very appropriate for QR codes.

Lee *et al* [166] also developed a chromatic sensing nanocomposite material based on ZnO/10,12-pentacosadiynoic acid (PCDA) composites through the inkjet printing technique. The composites of ZnO/poly-PCDA have shown stable and reversible chromatic properties at typical thermochromic transition temperatures which increased the application potential on bio-, thermal- and stress-sensor devices.

4.3. Piezoresistive

Being piezoresistive transductors the most popular materials group for deformation and pressure sensing, the fast development of piezoresistive technologies led to a high market demand for such devices[167, 168]. Piezoresistive sensors embrace a wide range of applications such as automobile industry, biomedical, oceanography, and aerospace, among others[167].

Printing technologies offer large manufacturing flexibility over traditional manufacturing processes to fabricate more complex and advanced piezoresistive structures [168].

In this way, piezoresistive sensors based on the conductive polymerpoly (3,4- ethylen dioxythiophene) oxidized with polystyrene sulfonated acid (PEDOT/PSS) were obtained by Al-Chami *et al.* [169] through a low-cost ink-jet printing technology. To ensure a maximum conductivity, DMF solvent was introduced to the PEDOT/PSS solution and the mixture was then printed on a paper substrate.

It was shown that PEDOT/PSS can maintain its piezoresistive properties. The resulting gauge factor (GF) was initially ≈-80 and then increased in modulus to ≈-280, for values of strains up to 0.015%. Possible successful applications for such sensors made by inkjet printing are those that can benefit of a good mechanical coupling (when deposited on flexible substrates) such as in smart textiles.

In an approach closer to the needs of the industry Agrawal *el al.* [170] produced a soft structured polymer strain sensors composed of PEDOT/PSS, inkjet printed on mercerized cotton fabrics. The printed sensors revealed GF ranging from -10 to -5. Such GF value was strongly dependent on the type of the fabric but independent in the fabric orientation.

Keeping the focus on smart textiles, Calvert *et al.* [68] used ink-jet printing to deposit silver conductive lines and PEDOT sensors onto fabrics. It was observed that PEDOT sensors responded to a tensile strain by decreasing the resistance with a varying GF from -5 to -20. It should be noted that this compares positively with conventional strain gauges (GF≈+2). It was also proven that these kind of sensors were suitable for monitoring human knee motion and are very useful for medical applications once they cycle to strains above 10%.

Strain sensors such as single sensors, sensor arrays and a sensor matrix have been also developed through inkjet-printing and screen-printing technologies by Correia *et al* [171]. Sensors with dimensions of 1.5 mm×1.8 mm, gauge factors up to 2.48 and interdigitated structures with a 30 µm distance lines have been accomplished based on PEDOT and conductive silver inks, printed by inkjet technique.

The screen-printed SEBS/CNT piezoresistive composite with 4wt% of CNT was achieved with inks with an optimized viscosity of ≈1100 cp and using a polyester screen with an opening of ≈60 µm and a surface tension of 17 N.

Other interesting works from Ferreira *et. al* [172] and Costa *el al.* [173] reported the development of polymer based piezoresistive materials with GF from 2 to 18. The characteristics of such materials can be easily tailored to be printed. This fact was demonstrated in composites developed through spray and screen printing, using a combination between a polymer matrix biocompatible thermoplastic elastomer, styrene-ethylene/butylene-styrene (SEBS) and multi-walled carbon nanotubes (MWCNT), as nanofillers. These composites have been also integrated with an electronic data acquisition system with RF communication (Figure 9)[51].

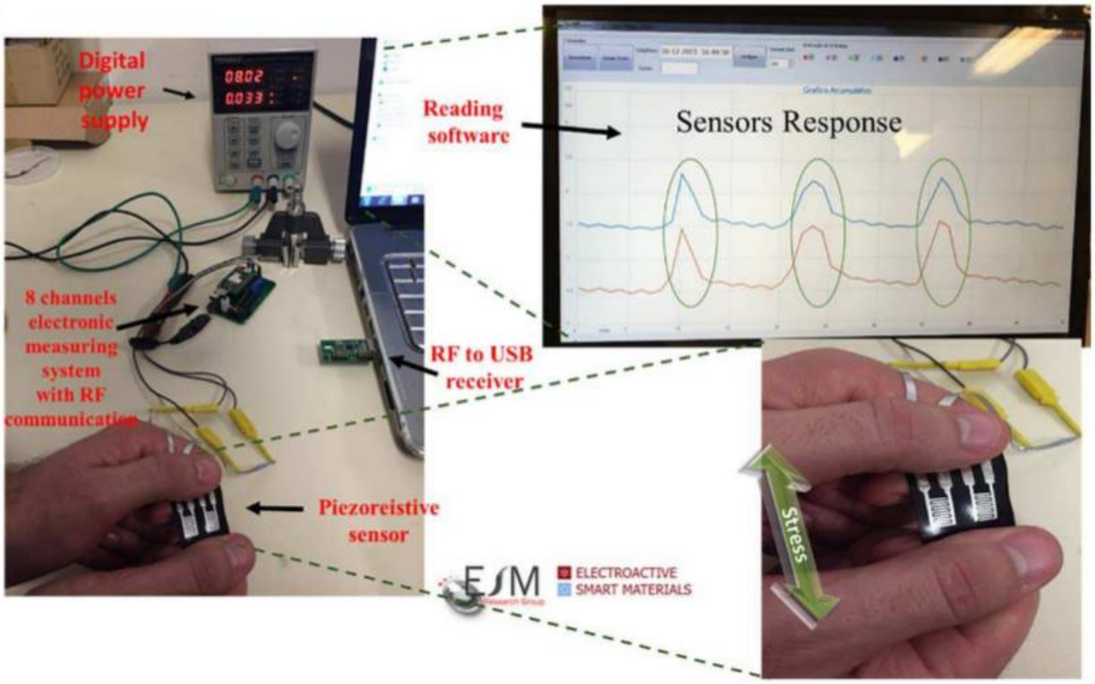

Figure 9. Real image of the piezoresistive sensor developed with the 5 wt % content of MWCNT[51].

The reported deformations (larger than 700%) revealed the excellent mechanical properties of the developed composites. It was observed a small mechanical hysteresis that increased with the strain and filler content. Composites with 5 wt % of MWCNT revealed suitable piezoresistive properties up to strains of 80%, with a suitable linearity between electrical response and mechanical deformation. The electrical percolation threshold was found at around ≈ 1 wt % MWCNT content. Piezoresistive sensors were then produced by spray and screen printing, demonstrating good sensing capabilities also when incorporated into the optimized readout electronic system and RF communication system.

4.4. Magnetostrictive

Another relevant type of transducing materials are the magnetostrictive materials[174]. They find application in sensing element in structures, actuation and supersonic generator, among others[175, 176]. Magnetostrictive films have been common used as micropumps with the onset of MEMS, micro-electro mechanical systems.[177]. Printing technologies provide a comparatively inexpensive and robust tool for producing magnetostrictive sensors and actuators [178].

The process used to fabricate a magnetostrictive thick-film , using Terfenol-D as active material, is similar to the one reported in the piezoelectric thick-films discussed in Section 3.1 [179].

The first studies on an innovative thick-film magnetostrictive material developed by screen-printing were presented by Ghabham *et al* [178, 180]. The thick-film based on the giant magnetostrictive material Terfenol-D and was printed onto 0.25 mm thick, 96% alumina substrates.

Although the levels of magnetostriction (50 ppm) were lower than the bulk material (250 ppm), they are superior than to some magnetostrictive composite materials[174, 178]. Additional work is needed with respect to ink optimization formulation in order to tune them to applications in micro-actuators and MEMS. Additionally, the effects of humidity and temperature during the fabrication need to be further studied to identify and minimize any degradation of the magnetostrictive response[180]. Through the removal of the voids within the film, a meaningful improvement in the magnetostrictive thick film may be obtained. The inclusion of a suitable filler material to eliminate the voids within the thick film, appears as an good option to solve this problem[180].

Nonetheless, the fabrication of printable magnetostrictive materials endures as a difficult and challenging task. Karnaushenko *et al.*[181], has innovatively developed an ink with magnetic properties that presented giant magnetoresistance (GMR) flakes which can be easily printed on numerous substrates, such as polymer, ceramic or even paper. GMR sensors were initially deposited on silicon wafers with a buffer layer based on photosensitive polymer AR-P 3510. The resulting GMR sensors revealed rolled-up or flake-like structures emerging from the inherent strain of the deposited GMR films[182].

A different approach given by Onuta *et al*.[183], is related with the production of an electromagnetic energy harvester composed of a magnetostrictive $Fe_{0.7}Ga_{0.3}$ film and a piezoelectric thin film based on $Pb(Zr_{0.52}Ti_{0.4}8)O_3$ and a 3.8-μm-thick Si cantilever. The harvested peak power of 0.7 $mW.cm^{-3}$ at 1 Oe was around six times higher than the value reported in the Terfenol-D/PZT/Terfenol-D laminate structures which stimulated the development of novel flexible energy harvesting materials[182].

By combining magnetic and the piezoelectric behaviour, it is possible to obtain multiferroic (MF) and magnetoelectric (ME) materials, which promote increased application flexibility as smart materials that can be activated both magnetically and electrically [184]. Starting from the pioneers studies on the magnetoelectric response of P(VDF-TrFE)$CoFe_2O_4$ composite [63, 185], it is possible to change the viscosity of the composite allowing its fabrication by spray-printing.

With the traditional doctor blade technique, the ME composite with 7 weight percentage (wt.%) of $CoFe_2O_4$ nanoparticles and 80 wt% of DMF solvent has a 2 $g.cm^{-3}$ density and a 2000 cp viscosity, values that are incompatible with the spray-printing technique (**Table 3**). Increasing the solvent content will have has as a consequence the decrease in the ME ink viscosity to 900 cp, allowing its spray-printing.

The advantages of spray printing such as its simplicity, industry compatibility, high production volumes and low time to market are major advantages when compared to the minor drawback of a lower ME response [28, 184].

It should be also noted that polymer-based printing can be also highly relevant to energy storage materials, thermoelectrics and photovoltaics as well.

5. Summary, conclusions and future trends

As a summary, the main printed smart materials found in the literature are shown in Table 6, together with their corresponding printing techniques and applications.

Table 6. Printed smart materials: Type, technique, device application and reference.

Smart material	Type	Technique	Device	Ref.
PZT/ polyacrilic acid	piezoelectric	ink-jet	Mechanical transducers	155
PZT/ PVDF-TrFE		screen	Mechanical sensors/transducers	156
PZT/polymer			Sensors and energy harvesters	157
$BaTiO_3$/PEG			Capacitors and thermistors	158
$BaTiO_3$/ethyl cellulose			Actuators, MEMs, transducers, sensors	159
PZT/PVDF			Electronic skins	154

PEDOT/PSS	piezoresistive	ink-jet	Smart textiles	169
				170
PEDOT/Ag			Smart textiles, biomedical monitoring	68
		ink-jet and screen	Strain sensors	171
PVA/ MWCNT		spray and screen		186
Terfenol-D/ ESL type 400	magnetostrictive	screen	Micro-actuators, MEMS	178, 180
GMR flakes/polymer AR-P3510		roll-to-roll, flexography, spray and screen	Magnetic sensors	181
Fe0.7Ga0.3/PZT		sputtering	Energy harvesters	183
Polystyrene Cholesteric liquid crystalline polymer	SMP	ink-jet	Microfluidic food and pharma-ceutical products	162 160
SWCNTs Pd/PET	pH sensitive	ink-jet	Environmental, industrial, and biological monitoring	163 164
Diacetylene		ink-jet	Temperature sensors, devices based on paper,	165

PCDA)/ZnO	chromic		and barcodes applied to anti-counterfeiting areas Thermal sensors, biosensors and stress sensors	166

Together with the materials in **Table 6**, other applications such as fully Roll-to-Roll Printable Wireless Sensor-Signage operating at 13.56 MHz tags for smart packaging; the reported novel ways of producing piezoelectric freestanding microstructures directly on fabrics which have potential use in sensing, actuation, and energy harvesting devices; or the 3D printer which "prints" such blood vessel structure, utilizing a bioresorbable polymer, are good examples that demonstrate the potential of printed smart materials[187-189].

It can be concluded that smart materials have already found uses in a large variety of products and industries but the technology is still in its infancy. As it matures, it will be part of our everyday life. While smart materials science has typically focused on the development of functional materials based on inorganic components, it is important to take into account that there are an increasing number of polymeric materials that have also shown functional smart behaviour, namely piezoelectricity. With advances in polymer electronics, polymer smart materials and printing technologies, have large potential to be applied on sensors and actuators [82, 184]. Those kind of materials can be printable trough similar printing technologies used in the printing of metallic or ceramic films, but without the problems related with fragility, clogging, sintering and control of particle size [82, 156, 184]. Though, there are some matters such as lower functional response, thermal and mechanical stability that need to be addressed before a widespread use [184].

Together with the advances in new functional materials and sensor/actuator designs, there is also interest in the development of novel and flexible processing guides to directly print smart materials. Once the screen printing technique proven to be the easiest way to produce printed films (specifically active inorganic materials), innovative tools employing more accurate and flexible fabrication methods will be developed. With high and specific interest appear other techniques such as transfer printing, inkjet droplet deposition, molding/embossing and laser sintering [184].

For each printing technology the ink’s physical–chemical properties should be tailored without disregarding the printing technology. Solvent´s characteristics, such as density, boiling point, solubility, viscosity, specific gravity and surface tension, are particularly significant for the successful printing of fully-functional smart materials [190]. Further, a larger variety or UV curable inks should be developed to improve the production process and pattern definition.

It should also be noted that most of the new products from printing technologies should be based on products from renewable or sustainable resources that are more environmentally friendly and do not harm human health. Such *green* concepts are increasingly important for the development of sustainable printing technologies.

In socioeconomic terms, the cost/efficiency ratio optimization of printing technologies and their use on smart materials production will allow the emergence of new device applications, and revolutionize the industry scenario. As a consequence, sensing, actuation and printed electronics will also present a key socioeconomic impact leading to innovative printed electronics solutions[82].

This fusion of printing technologies and smart materials will impact innovative services and products, which cover a larger group of needs presented by customers, allowing alternatives to the operation configurations on personal and server computer devices. This new approach will not only deliver new market services and competences, but will also lead to lower operating costs Such disruptive (and necessary) move in smart materials technologies promotes a similar shift in printing. Nowadays leading smart materials services need to include mobility, cloud technology, and to allow standards in the Internet of Things[191]. The IoT promises to optimise and improve our daily life quality based on intelligent devices and smart objects working connectively and jointly[192].

Despite the advantages of mixing the Internet of Things, the smart materials and printing processing concepts, most of the current commercially available smart materials devices are not based on printing technologies. This multidisciplinary concept has a strong scientific and economic potential in this increasingly interesting field.

It is also certain that technologies based on printing processes form a set of powerful strategies that promote the printing of a variety of materials, ranging from energetic nano-applications to biomedical applications. Successful printing at such lower scales, as micro and nanometre scales, is a milestone for science and engineering research. Therefore, the next decade will witness further advances in existing printing methods and will see the emergence of new ones[113, 193].

In short, this work suggests that by combining the production of smart materials with printing technologies such as ink-jet, screen, spray and roll-to-roll, some of the problems regarding the large-scale production of smart materials are solved.

Material solutions with adjusted rheological properties, with optimized smart behaviour and optimum *green processing* parameters are the major missions of this research area. Despite all the innovative approaches mentioned in this work, the optimization in the fabrication of smart materials for printing technologies is still an issue that requires further and intense research.

The predictable IoT (re)evolution demands for smarter systems and devices that are more efficient generically, completely autonomous, recyclable and *green*-obtained (if possible), biodegradable (or at least biocompatible), with extreme low-cost fabrication and the flexibility to be implanted in the highest number of objects as possible. Aiming to achieve these demanding and challenging prospects, several printing technologies and smart materials have to be merged or conciliated.

AUTHOR INFORMATION

Corresponding Author

*pmartins@fisica.uminho.pt

Author Contributions

All authors have given contributions for the written manuscript. The final version of the manuscript was approval for all authors.

Funding Sources

Portuguese Foundation for Science and Technology (FCT)

Basque Government Industry Department

Spanish Ministry of Economy and Competitiveness

ACKNOWLEDGMENTS

This work was supported by the Portuguese Foundation for Science and Technology (FCT) in the framework of the Strategic Funding UID/FIS/04650/2013 and projects PTDC/EEI-SII/5582/2014 and PTDC/CTM-ENE/5387/2014. P. Martins, V. Correia and J. Oliveira thanks the FCT for the FCT-SFRH/BPD/96227/2013, SFRH/BPD/97739/2013 and SFRH/BD/98219/2013 grants respectively. The authors thank financial support from the Basque Government Industry Department under the ELKARTEK Program and funding by the Spanish Ministry of Economy and Competitiveness (MINECO) through the project MAT2016-76039-C4-3-R.

ABBREVIATIONS

CCR2, CC chemokine receptor 2; CCL2, CC chemokine ligand 2; CCR5, CC chemokine receptor 5; TLC, thin layer chromatography.

REFERENCES

1. Murphy, E. B.; Wudl, F. "The world of smart healable materials", Progress in Polymer Science **2010**, 35, 223-251.
2. Bogue, R. "Smart materials: A review of capabilities and applications", Assembly Automation **2014**, 34, 16-22.
3. Hinchet, R.; Seung, W.; Kim, S. W. "Recent Progress on Flexible Triboelectric Nanogenerators for SelfPowered Electronics", ChemSusChem **2015**, 8, 2327-2344.
4. Elkhodr, M.; Shahrestani, S.; Cheung, H. "The Internet of Things: Vision & challenges", In IEEE 2013 Tencon - Spring, TENCONSpring 2013 - Conference Proceedings, 2013 pp. 218-222.
5. Gubbi, J.; Buyya, R.; Marusic, S.; Palaniswami, M. "Internet of Things (IoT): A vision, architectural elements, and future directions", Future Generation Computer Systems **2013**, 29, 1645-1660.
6. Atzori, L.; Iera, A.; Morabito, G. "The Internet of Things: A survey", Computer Networks **2010**, 54, 2787-2805.
7. Granjal, J.; Monteiro, E.; Sa Silva, J. "Security for the internet of things: A survey of existing protocols and open research issues", IEEE Communications Surveys and Tutorials **2015**, 17, 1294-1312.
8. Bandyopadhyay, D.; Sen, J. "Internet of things: Applications and challenges in technology and standardization", Wireless Personal Communications **2011**, 58, 49-69.
9. Urban, M. W. "Intelligent polymeric coatings; Current and future advances", Polymer Reviews **2006**, 46, 329-339.
10. Hossain, M. S.; Gonzalez, J. A.; Hernandez, R. M.; Shuvo, M. A. I.; Mireles, J.; Choudhuri, A.; Lin, Y.; Wicker, R. B. "Fabrication of smart parts using powder bed fusion additive manufacturing technology", Additive Manufacturing **2016**, 10, 58-66.
11. Wang, T.; Farajollahi, M.; Choi, Y. S.; Lin, I. T.; Marshall, J. E.; Thompson, N. M.; Kar-Narayan, S.; Madden, J. D. W.; Smoukov, S. K. "Electroactive polymers for sensing", Interface Focus **2016**, 6.
12. Sofyan, N.; Yuwono, A. H.; Harjanto, S. "Green and smart materials properties design and production for sustainable future", International Journal of Technology **2016**, 7, 362-365.
13. Sanchez-Vazquez, S. A.; Hailes, H. C.; Evans, J. R. G. "Hydrophobic polymers from food waste: Resources and synthesis", Polymer Reviews **2013**, 53, 627-694.
14. Winkless, L. "Is additive manufacturing truly the future?", Metal Powder Report **2015**.
15. Khoo, Z. X.; Teoh, J. E. M.; Liu, Y.; Kai Chua, C.; Yang, S.; An, J.; Leong, K. F.; Yeong, W. Y. "3D printing of smart materials: A review on recent progresses in 4D printing", Virtual and Physical Prototyping **2015**.
16. Kardel, K.; Ghaednia, H.; Carrano, A. L.; Marghitu, D. B. "Experimental and theoretical modeling of behavior of 3D-printed polymers under collision with a rigid rod", Additive Manufacturing **2017**, 14, 87-94.
17. Harsányi, G. "Polymer films in sensor applications: A review of present uses and future possibilities", Sensor Review **2000**, 20, 98-105.

18. Rajala, S.; Siponkoski, T.; Sarlin, E.; Mettänen, M.; Vuoriluoto, M.; Pammo, A.; Juuti, J.; Rojas, O. J.; Franssila, S.; Tuukkanen, S. "Cellulose Nanofibril Film as a Piezoelectric Sensor Material", ACS Applied Materials and Interfaces **2016**, 8, 15607-15614.
19. Döring, A.; Birnbaum, W.; Kuckling, D. "Responsive hydrogels-structurally and dimensionally optimized smart frameworks for applications in catalysis, micro-system technology and material science", Chemical Society Reviews **2013**, 42, 7391-7420.
20. Liu, J.; Xie, C.; Dai, X.; Jin, L.; Zhou, W.; Lieber, C. M. "Multifunctional three-dimensional macroporous nanoelectronic networks for smart materials", Proceedings of the National Academy of Sciences of the United States of America **2013**, 110, 6694-6699.
21. Bogue, R. "Smart materials: A review of recent developments", Assembly Automation **2012**, 32, 3-7.
22. Qiu, X.; Hu, S. ""Smart" materials based on cellulose: A review of the preparations, properties, and applications", Materials **2013**, 6, 738-781.
23. Martins, P.; Lopes, A. C.; Lanceros-Mendez, S. "Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications", Progress in Polymer Science **2014**, 39, 683-706.
24. Schroeter, K. "Printed sensors: Enabling new applications", Sensor Review **2008**, 28, 6-11.
25. Tzou, H. S.; Lee, H. J.; Arnold, S. M. "Smart materials, precision sensors/actuators, smart structures, and structronic systems", Mechanics of Advanced Materials and Structures **2004**, 11, 367-393.
26. Seifert, T.; Sowade, E.; Roscher, F.; Wiemer, M.; Gessner, T.; Baumann, R. R. "Additive manufacturing technologies compared: Morphology of deposits of silver ink using inkjet and aerosol jet printing", Industrial and Engineering Chemistry Research **2015**, 54, 769-779.
27. Jain, A.; Prashanth, K. J.; Sharma, A. K.; Jain, A.; P.n, R. "Dielectric and piezoelectric properties of PVDF/PZT composites: A review", Polymer Engineering and Science **2015**, 55, 1589-1616.
28. Silva, M.; Reis, S.; Lehmann, C. S.; Martins, P.; Lanceros-Mendez, S.; Lasheras, A.; Gutiérrez, J.; Barandiarán, J. M. "Optimization of the magnetoelectric response of poly(vinylidene fluoride)/epoxy/vitrovac laminates", ACS Applied Materials and Interfaces **2013**, 5, 10912-10919.
29. Phan, H.; Dao, D. V.; Nakamura, K.; Dimitrijev, S.; Nguyen, N. "The Piezoresistive Effect of SiC for MEMS Sensors at High Temperatures: A Review", Journal of Microelectromechanical Systems **2015**.
30. Song, I. S.; Kim, W. Y.; Kim, C. Y.; Kim, B. H.; Kim, H. K.; Ahn, T. J. "Sensitivity enhancement of a UV photo-sensor based on a fiber Bragg grating coated by a photomechanical functional polymer", Sensors and Actuators, A: Physical **2015**, 232, 223-228.
31. Romero Gómez, J.; Ferreiro Garcia, R.; De Miguel Catoira, A.; Romero Gómez, M. "Magnetocaloric effect: A review of the thermodynamic cycles in magnetic refrigeration", Renewable and Sustainable Energy Reviews **2013**, 17, 74-82.
32. Khan, A.; Abas, Z.; Soo Kim, H.; Oh, I. K. "Piezoelectric thin films: An integrated review of transducers and energy harvesting", Smart Materials and Structures **2016**, 25.

33. Newns, D. M.; Elmegreen, B. G.; Liu, X. H.; Martyna, G. J. "High response piezoelectric and piezoresistive materials for fast, low voltage switching: Simulation and theory of transduction physics at the nanometer-scale", Advanced Materials **2012**, 24, 3672-3677.
34. Liu, W.; He, D.; Ruan, Y.; Ruan, X.; Fu, X.; Stefanini, C. "Preliminary study on piezoresistive and piezoelectric properties of a double-layer soft material for tactile sensing", Medziagotyra **2015**, 21, 238-243.
35. Pintér, Á.; Huba, A. "Study of pressure-sensitive materials for floor sensor networks", Periodica Polytechnica, Mechanical Engineering **2016**, 60, 32-40.
36. Yang, G.; Liu, S. F.; Ren, W.; Mukherjee, B. K. "Temperature dependence of electrostrictive properties of PMN-PT-LA ceramics", Ferroelectrics **2001**, 262, 201-206.
37. Liu, Y.; Ren, K. L.; Hofmann, H. F.; Zhang, Q. "Investigation of electrostrictive polymers for energy harvesting", IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control **2005**, 52, 2411-2417.
38. Le, M. Q.; Capsal, J. F.; Galineau, J.; Ganet, F.; Yin, X.; Yang, M. D.; Chateaux, J. F.; Renaud, L.; Malhaire, C.; Cottinet, P. J.; Liang, R. "All-organic electrostrictive polymer composites with low driving electrical voltages for micro-fluidic pump applications", Scientific Reports **2015**, 5.
39. Bao, M.-H. "Chapter 8 - Capacitive pressure transducers and accelerometers", In Handbook of Sensors and Actuators; Min-Hang, B. Ed.; Elsevier Science B.V., 2000 pp. 319-352.
40. Eaton, W. P.; Smith, J. H. "Micromachined pressure sensors: Review and recent developments", Smart Materials and Structures **1997**, 6, 530-539.
41. Zhang, Q.; Kratz, K.; Lendlein, A. "Shape-memory properties of degradable electrospun scaffolds based on hollow microfibers", Polymers for Advanced Technologies **2015**, 26, 1468-1475.
42. Suarato, G.; Li, W.; Meng, Y. "Role of pH-responsiveness in the design of chitosan-based cancer nanotherapeutics: A review", Biointerphases **2016**, 11.
43. Hackney, S. "Colour measurement of acid-detector strips for the quantification of volatile organic acids in storage conditions", Studies in Conservation **2016**, 1-15.
44. Valadkhan, S.; Morris, K.; Khajepour, A. "Review and comparison of hysteresis models for magnetostrictive materials", Journal of Intelligent Material Systems and Structures **2009**, 20, 131-142.
45. Anton, S. R.; Sodano, H. A. "A review of power harvesting using piezoelectric materials (2003-2006)", Smart Materials and Structures **2007**, 16.
46. Mohammadi, F.; Khan, A.; Cass, R. B. "Power generation from piezoelectric lead zirconate titanate fiber composites", In Materials Research Society Symposium - Proceedings, 2002 pp. 263-268.
47. Cheng, Z. Y.; Bharti, V.; Xu, T. B.; Xu, H.; Mai, T.; Zhang, Q. M. "Electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymers", Sensors and Actuators, A: Physical **2001**, 90, 138-147.
48. Damjanovic, D.; Newnham, R. E. "Electrostrictive and piezoelectric materials for actuator applications", Journal of Intelligent Material Systems and Structures **1992**, 3, 190-208.
49. Ur; #353; #269; , H.; Santo Zarnik, M.; Kosec, M. "Pb(Mg1/3Nb2/3)O3–PbTiO3 (PMN-PT) Material for Actuator Applications", Smart Materials Research **2011**, 2011, 6.

50. Liang, J.; Tong, K.; Pei, Q. "A Water-Based Silver-Nanowire Screen-Print Ink for the Fabrication of Stretchable Conductors and Wearable Thin-Film Transistors", Advanced Materials **2016**, 5986-5996.
51. Gonçalves, R.; Larrea, A.; Zheng, T.; Higgins, M. J.; Sebastian, V.; Lanceros-Mendez, S.; Martins, P. "Synthesis of highly magnetostrictive nanostructures and their application in a polymer-based magnetoelectric sensing device", European Polymer Journal **2016**, 84, 685-692.
52. Yu, X.; Thaysen, J.; Hansen, O.; Boisen, A. "Optimization of sensitivity and noise in piezoresistive cantilevers", Journal of Applied Physics **2002**, 92, 6296-6301.
53. Alpuim, P.; Chu, V.; Conde, J. P. "Piezoresistive sensors on plastic substrates using doped microcrystalline silicon", IEEE Sensors Journal **2002**, 2, 336-340.
54. Germer, W. "Microcrystalline silicon thin films for sensor applications", Sensors and Actuators **1985**, 7, 135-142.
55. Bae, S. H.; Lee, Y.; Sharma, B. K.; Lee, H. J.; Kim, J. H.; Ahn, J. H. "Graphene-based transparent strain sensor", Carbon **2013**, 51, 236-242.
56. Yan, C.; Wang, J.; Kang, W.; Cui, M.; Wang, X.; Foo, C. Y.; Chee, K. J.; Lee, P. S. "Highly stretchable piezoresistive graphene-nanocellulose nanopaper for strain sensors", Advanced Materials **2014**, 26, 2022-2027.
57. Zhao, J.; He, C.; Yang, R.; Shi, Z.; Cheng, M.; Yang, W.; Xie, G.; Wang, D.; Shi, D.; Zhang, G. "Ultra-sensitive strain sensors based on piezoresistive nanographene films", Applied Physics Letters **2012**, 101.
58. Zhu, S. E.; Krishna Ghatkesar, M.; Zhang, C.; Janssen, G. C. A. M. "Graphene based piezoresistive pressure sensor", Applied Physics Letters **2013**, 102.
59. Savagatrup, S.; Chan, E.; Renteria-Garcia, S. M.; Printz, A. D.; Zaretski, A. V.; O'Connor, T. F.; Rodriquez, D.; Valle, E.; Lipomi, D. J. "Plasticization of PEDOT:PSS by common additives for mechanically robust organic solar cells and wearable sensors", Advanced Functional Materials **2015**, 25, 427-436.
60. Davino, D.; Visone, C.; Giustiniani, A. "Vibration energy harvesting devices based on magnetostrictive materials", In Bridge Maintenance, Safety, Management, Resilience and Sustainability - Proceedings of the Sixth International Conference on Bridge Maintenance, Safety and Management, 2012 pp. 1511-1518.
61. Lenz, J.; Edelstein, A. S. "Magnetic sensors and their applications", IEEE Sensors Journal **2006**, 6, 631-649.
62. Xiangfeng, C.; Dongli, J.; Yu, G.; Chenmou, Z. "Ethanol gas sensor based on CoFe2O4 nano-crystallines prepared by hydrothermal method", Sensors and Actuators, B: Chemical **2006**, 120, 177-181.
63. Martins, P.; Lasheras, A.; Gutierrez, J.; Barandiaran, J. M.; Orue, I.; Lanceros-Mendez, S. "Optimizing piezoelectric and magnetoelectric responses on CoFe 2O4/P(VDF-TrFE) nanocomposites", Journal of Physics D: Applied Physics **2011**, 44.
64. Schmaljohann, D. "Thermo- and pH-responsive polymers in drug delivery", Advanced Drug Delivery Reviews **2006**, 58, 1655-1670.
65. Reyes-Ortega, F. "pH-responsive polymers: Properties, synthesis and applications", In Smart Polymers and their Applications, 2014 pp. 45-92.

66. Grau, G.; Kitsomboonloha, R.; Swisher, S. L.; Kang, H.; Subramanian, V. "Printed transistors on paper: Towards smart consumer product packaging", Advanced Functional Materials **2014**, 24, 5067-5074.
67. Street, R. A.; Ng, T. N.; Schwartz, D. E.; Whiting, G. L.; Lu, J. P.; Bringans, R. D.; Veres, J. "From printed transistors to printed smart systems", Proceedings of the IEEE **2015**, 103, 607-618.
68. Calvert, P.; Patra, P.; Lo, T. C.; Chen, C. H.; Sawhney, A.; Agrawal, A. "Piezoresistive sensors for smart textiles", In Proceedings of SPIE - The International Society for Optical Engineering, 2007.
69. Wang, W.; Srinivasan, V.; Chua, K. C. "Extending the lifetime of wireless sensor networks through mobile relays", IEEE/ACM Transactions on Networking **2008**, 16, 1108-1120.
70. Martins, J.; Bahubalindruni, P.; Rovisco, A.; Kiazadeh, A.; Martins, R.; Fortunato, E.; Barquinha, P. "Bias stress and temperature impact on InGaZnO TFTs and circuits", Materials **2017**, 10.
71. Myny, K.; Steudel, S. "Flexible thin-film NFC transponder chip exhibiting data rates compatible to ISO NFC standards using self-aligned metal-oxide TFTs", In Digest of Technical Papers - IEEE International Solid-State Circuits Conference, 2016 pp. 298-299.
72. Rogers, J. A.; Ghaffari, R.; Kim, D. H. Stretchable Bioelectronics for Medical Devices and Systems; Springer International Publishing, 2016.
73. Larsson, A.; Tran, T. N.; Aasmundtveit, K. E.; Seeberg, T. M. "Encapsulation for smart textile electronics - Humidity and temperature sensor", In Studies in Health Technology and Informatics, 2015 pp. 207-212.
74. Im, H.; Lee, Y.; Kim, D. H.; Inturu, O.; Liu, N.; Lee, S.; Kwon, S. J.; Lee, H. S.; Kim, S. "A highly sensitive ultrathin-film iron corrosion sensor encapsulated by an anion exchange membrane embedded in mortar", Construction and Building Materials **2017**, 156, 506-514.
75. Gembaczka, P.; Görtz, M.; Kraft, M. "Development of an implantable integrated MEMS pressure sensor using polyimide epoxy composite and atomic layer deposition for encapsulation", Biomedical Engineering **2014**, 59, s1053-s1054.
76. Ahmed, M. U.; Hossain, M. M.; Safavieh, M.; Wong, Y. L.; Rahman, I. A.; Zourob, M.; Tamiya, E. "Toward the development of smart and low cost point-of-care biosensors based on screen printed electrodes", Critical Reviews in Biotechnology **2016**, 36, 495-505.
77. Kololuoma, T.; Tuomikoski, M.; Mäkelä, T.; Heilmann, J.; Haring, T.; Kallioinen, J.; Hagberg, J.; Kettunen, I.; Kopola, H. "Towards roll-to-roll fabrication of electronics, optics and optoelectronics for smart and intelligent packaging", In Proceedings of SPIE - The International Society for Optical Engineering, 2004 pp. 77-85.
78. Gruner, G. "Carbon nanotube films for transparent and plastic electronics", Journal of Materials Chemistry **2006**, 16, 3533-3539.
79. Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. "Printable all-organic electrochromic active-matrix displays", Advanced Functional Materials **2007**, 17, 3074-3082.

80. Park, M.; Im, J.; Shin, M.; Min, Y.; Park, J.; Cho, H.; Park, S.; Shim, M. B.; Jeon, S.; Chung, D. Y.; Bae, J.; Park, J.; Jeong, U.; Kim, K. "Highly stretchable electric circuits from a composite material of silver nanoparticles and elastomeric fibres", Nature Nanotechnology **2012**, 7, 803-809.
81. Sydney Gladman, A.; Matsumoto, E. A.; Nuzzo, R. G.; Mahadevan, L.; Lewis, J. A. "Biomimetic 4D printing", Nature Materials **2016**, 15, 413-418.
82. Khan, S.; Lorenzelli, L.; Dahiya, R. S. "Technologies for printing sensors and electronics over large flexible substrates: A review", IEEE Sensors Journal **2015**, 15, 3164-3185.
83. Søndergaard, R. R.; Hösel, M.; Krebs, F. C. "Roll-to-Roll fabrication of large area functional organic materials", Journal of Polymer Science, Part B: Polymer Physics **2013**, 51, 16-34.
84. Moonen, P. F.; Yakimets, I.; Huskens, J. "Fabrication of transistors on flexible substrates: From mass-printing to high-resolution alternative lithography strategies", Advanced Materials **2012**, 24, 5526-5541.
85. Park, H.; Kang, H.; Lee, Y.; Park, Y.; Noh, J.; Cho, G. "Fully roll-to-roll gravure printed rectenna on plastic foils for wireless power transmission at 13.56MHz", Nanotechnology **2012**, 23.
86. Kang, H. W.; Sung, H. J.; Lee, T. M.; Kim, D. S.; Kim, C. J. "Liquid transfer between two separating plates for micro-gravure-offset printing", Journal of Micromechanics and Microengineering **2009**, 19.
87. Secor, E. B.; Lim, S.; Zhang, H.; Frisbie, C. D.; Francis, L. F.; Hersam, M. C. "Gravure printing of graphene for large-area flexible electronics", Advanced Materials **2014**, 26, 4533-4538.
88. Xiao, Y.; Huang, L.; Zhang, Q.; Xu, S.; Chen, Q.; Shi, W. "Gravure printing of hybrid MoS<inf>2</inf>@S-rGO interdigitated electrodes for flexible microsupercapacitors", Applied Physics Letters **2015**, 107.
89. Dahiya, R. S.; Adami, A.; Collini, C.; Lorenzelli, L. "Fabrication of single crystal silicon micro-/nanostructures and transferring them to flexible substrates", Microelectronic Engineering **2012**, 98, 502-507.
90. Qin, G.; Seo, J. H.; Zhang, Y.; Zhou, H.; Zhou, W.; Wang, Y.; Ma, J.; Ma, Z. "RF characterization of gigahertz flexible silicon thin-film transistor on plastic substrates under bending conditions", IEEE Electron Device Letters **2013**, 34, 262-264.
91. Oh, T. Y.; Woo Jeong, S.; Chang, S.; Choi, K.; Jun Ha, H.; Kwon Ju, B. "The silicon Schottky diode on flexible substrates by transfer method", Applied Physics Letters **2013**, 102.
92. Ma, Z.; Zhang, K.; Seo, J. H.; Zhou, H.; Sun, L.; Yuan, H. C.; Qin, G.; Pang, H.; Zhou, W. "Fast flexible electronics based on printable thin mono-crystalline silicon", In ECS Transactions, 1 Edition, 2011 pp. 137-142.
93. Lock, E. H.; Delongchamp, D. M.; Schmucker, S. W.; Simpkins, B.; Laskoski, M.; Mulvaney, S. P.; Hines, D. R.; Baraket, M.; Hernandez, S. C.; Robinson, J. T.; Sheehan, P. E.; Jaye, C.; Fisher, D. A.; Walton, S. G. "Dry graphene transfer print to polystyrene and ultra-high molecular weight polyethylene - Detailed chemical, structural, morphological and electrical characterization", Carbon **2015**, 86, 288-300.
94. Alom Ruiz, S.; Chen, C. S. "Microcontact printing: A tool to pattern", Soft Matter **2007**, 3, 168-177.

95. Auner, C.; Palfinger, U.; Gold, H.; Kraxner, J.; Haase, A.; Haber, T.; Sezen, M.; Grogger, W.; Jakopic, G.; Krenn, J. R.; Leising, G.; Stadlober, B. "High-performing submicron organic thin-film transistors fabricated by residue-free embossing", Organic Electronics: physics, materials, applications **2010**, 11, 552-557.
96. Li, B.; Zhang, J.; Ge, H. "A sandwiched flexible polymer mold for control of particle-induced defects in nanoimprint lithography", Applied Physics A: Materials Science and Processing **2013**, 110, 123-128.
97. Choi, N. J.; Lee, J.; Bang, G. S.; Lee, H. K.; Moon, S. E.; Yang, W. S.; Lee, H. "Fabrication of nano scale electrode for sensor using nanoimprint lithography", Journal of Nanoelectronics and Optoelectronics **2015**, 10, 480-484.
98. Kettle, J.; Whitelegg, S.; Song, A. M.; Wedge, D. C.; Kotacka, L.; Kolarik, V.; Madec, M. B.; Yeates, S. G.; Turner, M. L. "Fabrication of planar organic nanotransistors using low temperature thermal nanoimprint lithography for chemical sensor applications", Nanotechnology **2010**, 21.
99. Perl, A.; Reinhoudt, D. N.; Huskens, J. "Microcontact printing: Limitations and achievements", Advanced Materials **2009**, 21, 2257-2268.
100. Nagato, K. "Injection compression molding of replica molds for nanoimprint lithography", Polymers **2014**, 6, 604-612.
101. Molina-Lopez, F.; Briand, D.; De Rooij, N. F. "Inkjet and microcontact printing of functional materials on foil for the fabrication of pixel-like capacitive vapor microsensors", Organic Electronics: physics, materials, applications **2015**, 16, 139-147.
102. Sidén, J.; Nilsson, H. E. "Line width limitations of flexographic- screen- and inkjet printed RFID antennas", In IEEE Antennas and Propagation Society, AP-S International Symposium (Digest), 2007 pp. 1745-1748.
103. Faddoul, R.; Reverdy-Bruas, N.; Blayo, A.; Haas, T.; Zeilmann, C. "Optimisation of silver paste for flexography printing on LTCC substrate", Microelectronics Reliability **2012**, 52, 1483-1491.
104. Lundström, J.; Verikas, A.; Tullander, E.; Larsson, B. "Assessing, exploring, and monitoring quality of offset colour prints", Measurement: Journal of the International Measurement Confederation **2013**, 46, 1427-1441.
105. Sheats, J. R.; Biesty, D.; Noel, J.; Taylor, G. N. "Printing technology for ubiquitous electronics", Circuit World **2010**, 36, 40-47.
106. Krebs, F. C. "Fabrication and processing of polymer solar cells: A review of printing and coating techniques", Solar Energy Materials and Solar Cells **2009**, 93, 394-412.
107. Blayo, A.; Pineaux, B. "Printing processes and their potential for RFID printing", In ACM International Conference Proceeding Series, 2005 pp. 27-30.
108. Choi, H. W.; Zhou, T.; Singh, M.; Jabbour, G. E. "Recent developments and directions in printed nanomaterials", Nanoscale **2015**, 7, 3338-3355.
109. Ando, B.; Baglio, S. "All-inkjet printed strain sensors", IEEE Sensors Journal **2013**, 13, 4874-4879.
110. Sung, D.; De La Fuente Vornbrock, A.; Subramanian, V. "Scaling and optimization of gravure-printed silver nanoparticle lines for printed electronics", IEEE Transactions on Components and Packaging Technologies **2010**, 33, 105-114.

111. Optomec "Aerosol Jet Technology"; Optomec Ed., 2014 pp. http://www.optomec.com/additive-manufacturing/printed-electronics/aerosol-jet-technology.
112. Tehrani, B. K.; Mariotti, C.; Cook, B. S.; Roselli, L.; Tentzeris, M. M. "Development, characterization, and processing of thin and thick inkjet-printed dielectric films", Organic Electronics: physics, materials, applications **2016**, 29, 135-141.
113. Ru, C.; Luo, J.; Xie, S.; Sun, Y. "A review of non-contact micro- and nano-printing technologies", Journal of Micromechanics and Microengineering **2014**, 24.
114. Tan, E.; Jing, Q.; Smith, M.; Kar-Narayan, S.; Occhipinti, L. "Needs and Enabling Technologies for Stretchable Electronics Commercialization", MRS Advances **2017**, 2, 1721-1729.
115. Michael, S.; Yeon Sik, C.; Chess, B.; Sohini, K.-N. "Controlling and assessing the quality of aerosol jet printed features for large area and flexible electronics", Flexible and Printed Electronics **2017**, 2, 015004.
116. Saleh, E.; Woolliams, P.; Clarke, B.; Gregory, A.; Greedy, S.; Smartt, C.; Wildman, R.; Ashcroft, I.; Hague, R.; Dickens, P.; Tuck, C. "3D inkjet-printed UV-curable inks for multi-functional electromagnetic applications", Additive Manufacturing **2017**, 13, 143-148.
117. Vafaei, S.; Tuck, C.; Wildman, R.; Ashcroft, I. "Spreading of the nanofluid triple line in ink jet printed electronics tracks", Additive Manufacturing **2016**, 11, 77-84.
118. Hoffman, J.; Hwang, S.; Ortega, A.; Kim, N. S.; Moon, K. S. "The standardization of printable materials and direct writing systems", Journal of Electronic Packaging, Transactions of the ASME **2013**, 135.
119. Sun, Y.; Rogers, J. A. "Inorganic semiconductors for flexible electronics", Advanced Materials **2007**, 19, 1897-1916.
120. Gift, S. J. G. "New precision rectifier circuits with high accuracy and wide bandwidth", International Journal of Electronics **2005**, 92, 601-617.
121. Tobjörk, D.; Österbacka, R. "Paper electronics", Advanced Materials **2011**, 23, 1935-1961.
122. Kim, D. S.; Khan, A.; Rahman, K.; Khan, S.; Kim, H. C.; Choi, K. H. "Drop-on-demand direct printing of colloidal copper nanoparticles by electrohydrodynamic atomization", Materials and Manufacturing Processes **2011**, 26, 1196-1201.
123. Nambiar, S.; Yeow, J. T. W. "Conductive polymer-based sensors for biomedical applications", Biosensors and Bioelectronics **2011**, 26, 1825-1832.
124. Rajan, K.; Roppolo, I.; Chiappone, A.; Bocchini, S.; Perrone, D.; Chiolerio, A. "Silver nanoparticle ink technology: State of the art", Nanotechnology, Science and Applications **2016**, 9.
125. Novoselov, K. S.; Fal'Ko, V. I.; Colombo, L.; Gellert, P. R.; Schwab, M. G.; Kim, K. "A roadmap for graphene", Nature **2012**, 490, 192-200.
126. McCall, K. L.; Rutter, S. R.; Bone, E. L.; Forrest, N. D.; Bissett, J. S.; Jones, J. D. E.; Simms, M. J.; Page, A. J.; Fisher, R.; Brown, B. A.; Ogier, S. D. "High performance organic transistors using small molecule semiconductors and high permittivity semiconducting polymers", Advanced Functional Materials **2014**, 24, 3067-3074.

127. Zhong, H.; Smith, J.; Rossbauer, S.; White, A. J. P.; Anthopoulos, T. D.; Heeney, M. "Air-stable and high-mobility n-channel organic transistors based on small-molecule/polymer semiconducting blends", Advanced Materials **2012**, 24, 3205-3211.
128. Kang, M.; Yeo, J. S.; Park, W. T.; Kim, N. K.; Lim, D. H.; Hwang, H.; Baeg, K. J.; Noh, Y. Y.; Kim, D. Y. "Favorable Molecular Orientation Enhancement in Semiconducting Polymer Assisted by Conjugated Organic Small Molecules", Advanced Functional Materials **2016**.
129. Cheung, G. Z.; Yu, B.; Liu, M.; Gong, Z.; Kohl, J.; Petoukhoff, C. E.; Piotrowiak, P.; O'Carroll, D. M. "Effects of conjugated polymer incorporation on the morphology and energy harvesting of solution-processed, phthalocyanine-based thin films", Synthetic Metals **2016**, 220, 469-476.
130. Mayer, A. C.; Toney, M. F.; Scully, S. R.; Rivnay, J.; Brabec, C. J.; Scharber, M.; Koppe, M.; Heeney, M.; McCulloch, I.; McGehee, M. D. "Bimolecular crystals of fullerenes in conjugated polymers and the implications of molecular mixing for solar cells", Advanced Functional Materials **2009**, 19, 1173-1179.
131. Meyer, S.; Pham, D. V.; Merkulov, S.; Weber, D.; Merkulov, A.; Benson, N.; Schmechel, R. "Soluble metal oxo alkoxide inks with advanced rheological properties for inkjet-printed thin-film transistors", ACS Applied Materials and Interfaces **2017**, 9, 2625-2633.
132. Carlson, A.; Bowen, A. M.; Huang, Y.; Nuzzo, R. G.; Rogers, J. A. "Transfer printing techniques for materials assembly and micro/nanodevice fabrication", Advanced Materials **2012**, 24, 5284-5318.
133. Menard, E.; Lee, K. J.; Khang, D. Y.; Nuzzo, R. G.; Rogers, J. A. "A printable form of silicon for high performance thin film transistors on plastic substrates", Applied Physics Letters **2004**, 84, 5398-5400.
134. MacK, S.; Meitl, M. A.; Baca, A. J.; Zhu, Z. T.; Rogers, J. A. "Mechanically flexible thin-film transistors that use ultrathin ribbons of silicon derived from bulk wafers", Applied Physics Letters **2006**, 88.
135. Baca, A. J.; Meitl, M. A.; Ko, H. C.; Mack, S.; Kim, H. S.; Dong, J.; Ferreira, P. M.; Rogers, J. A. "Printable single-crystal silicon micro/nanoscale ribbons, platelets and bars generated from bulk wafers", Advanced Functional Materials **2007**, 17, 3051-3062.
136. Ford, A. C.; Chuang, S.; Ho, J. C.; Chueh, Y. L.; Fan, Z.; Javey, A. "Patterned p-doping of InAs nanowires by gas-phase surface diffusion of Zn", Nano Letters **2010**, 10, 509-513.
137. Fan, Z.; Ho, J. C.; Takahashi, T.; Yerushalmi, R.; Takei, K.; Ford, A. C.; Chueh, Y. L.; Javey, A. "Toward the Development of Printable Nanowire Electronics and Sensors", Advanced Materials **2009**, 21, 3730-3743.
138. Fan, Z.; Ho, J. C.; Jacobson, Z. A.; Razavi, H.; Javey, A. "Large-scale, heterogeneous integration of nanowire arrays for image sensor circuitry", Proceedings of the National Academy of Sciences of the United States of America **2008**, 105, 11066-11070.
139. Kim, T. H.; Cho, K. S.; Lee, E. K.; Lee, S. J.; Chae, J.; Kim, J. W.; Kim, D. H.; Kwon, J. Y.; Amaratunga, G.; Lee, S. Y.; Choi, B. L.; Kuk, Y.; Kim, J. M.; Kim, K. "Full-colour quantum dot displays fabricated by transfer printing", Nature Photonics **2011**, 5, 176-182.
140. Kim, L.; Anikeeva, P. O.; Coe-Sullivan, S. A.; Steckel, J. S.; Bawendi, M. G.; Bulović, V. "Contact printing of quantum dot light-emitting devices", Nano Letters **2008**, 8, 4513-4517.

141. Steckel, J. S.; Snee, P.; Coe-Sullivan, S.; Zimmer, J. P.; Halpert, J. E.; Anikeeva, P.; Kim, L. A.; Bulovic, V.; Bawendi, M. G. "Color-saturated green-emitting QD-LEDs", Angewandte Chemie - International Edition **2006**, 45, 5796-5799.
142. Castro, H. F.; Correia, V.; Sowade, E.; Mitra, K. Y.; Rocha, J. G.; Baumann, R. R.; Lanceros-Méndez, S. "All-inkjet-printed low-pass filters with adjustable cutoff frequency consisting of resistors, inductors and transistors for sensor applications", Organic Electronics: physics, materials, applications **2016**, 38, 205-212.
143. Castro, H. F.; Sowade, E.; Rocha, J. G.; Alpuim, P.; Machado, A. V.; Baumann, R. R.; Lanceros-Méndez, S. "Degradation of all-inkjet-printed organic thin-film transistors with TIPS-pentacene under processes applied in textile manufacturing", Organic Electronics: physics, materials, applications **2015**, 22, 12-19.
144. Castro, H. F.; Sowade, E.; Rocha, J. G.; Alpuim, P.; Lanceros-Méndez, S.; Baumann, R. R. "All-inkjet-printed bottom-gate thin-film transistors using UV curable dielectric for well-defined source-drain electrodes", Journal of Electronic Materials **2014**, 43, 2631-2636.
145. Han, J.; Ko, D.; Park, M.; Roh, J.; Jung, H.; Lee, Y.; Kwon, Y.; Sohn, J.; Bae, W. K.; Chin, B. D.; Lee, C. "Toward high-resolution, inkjet-printed, quantum dot light-emitting diodes for next-generation displays", Journal of the Society for Information Display **2016**, 24, 545-551.
146. Lim, G. H.; Zhuo, J. M.; Wong, L. Y.; Chua, S. J.; Chua, L. L.; Ho, P. K. H. "A transition solvent strategy to print polymer:fullerene films using halogen-free solvents for solar cell applications", Organic Electronics: physics, materials, applications **2014**, 15, 449-460.
147. Cook, B. S.; Tehrani, B.; Cooper, J. R.; Tentzeris, M. M. "Multilayer inkjet printing of millimeter-wave proximity-fed patch arrays on flexible substrates", IEEE Antennas and Wireless Propagation Letters **2013**, 12, 1351-1354.
148. Cook, B. S.; Mariotti, C.; Cooper, J. R.; Revier, D.; Tehrani, B. K.; Aluigi, L.; Roselli, L.; Tentzeris, M. M. "Inkjet-printed, vertically-integrated, high-performance inductors and transformers on flexible LCP substrate", In IEEE MTT-S International Microwave Symposium Digest, 2014.
149. Ellinger, C. R.; Nelson, S. F. "Design freedom in multilayer thin-film devices", ACS Applied Materials and Interfaces **2015**, 7, 4675-4684.
150. Mathews, N.; Lam, Y. M.; Mhaisalkar, S. G.; Grimsdale, A. C. "Printing materials for electronic devices", International Journal of Materials Research **2010**, 101, 236-250.
151. Jeong, S.; Kim, D.; Moon, J. "Ink-jet-printed organic-inorganic hybrid dielectrics for organic thin-film transistors", Journal of Physical Chemistry C **2008**, 112, 5245-5249.
152. Stevenson, T.; Martin, D. G.; Cowin, P. I.; Blumfield, A.; Bell, A. J.; Comyn, T. P.; Weaver, P. M. "Piezoelectric materials for high temperature transducers and actuators", Journal of Materials Science: Materials in Electronics **2015**, 26, 9256-9267.
153. Lee, C.; Mahamud, R.; Farouk, T.; Tarbutton, J. A. "Preliminary study of corona-assisted additive manufacturing process of piezoelectric thermopolymer", In Proceedings - ASPE 2015 Spring Topical Meeting: Achieving Precision Tolerances in Additive Manufacturing, 2015 pp. 155-158.
154. Almusallam, A.; Yang, K.; Zhu, D.; Torah, R. N.; Komolafe, A.; Tudor, J.; Beeby, S. P. "Clamping effect on the piezoelectric responses of screen-printed low temperature PZT/Polymer films on flexible substrates", Smart Materials and Structures **2015**, 24.

155. Kuscer, D.; Noshchenko, O.; Uršič, H.; Malič, B. "Piezoelectric properties of ink-jet-printed lead zirconate titanate thick films confirmed by piezoresponse force microscopy", Journal of the American Ceramic Society **2013**, 96, 2714-2717.
156. Dietze, M.; Es-Souni, M. "Structural and functional properties of screen-printed PZT–PVDF-TrFE composites", Sensors and Actuators A: Physical **2008**, 143, 329-334.
157. Ferrari, M.; Ferrari, V.; Guizzetti, M.; Marioli, D. "Piezoelectric low-curing-temperature ink for sensors and power harvesting", In Lecture Notes in Electrical Engineering, 2010 pp. 77-81.
158. Sakai, Y.; Futakuchi, T.; Adachi, M. "Preparation of BaTiO3 thick films by inkjet printing on oxygen-plasma-modified substrates", Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers **2006**, 45, 7247-7251.
159. Fu, F.; Shen, B.; Xu, Z.; Zhai, J. "Electric properties of BaTiO3 lead-free textured piezoelectric thick film by screen printing method", Journal of Electroceramics **2014**.
160. Davies, D. J. D.; Vaccaro, A. R.; Morris, S. M.; Herzer, N.; Schenning, A. P. H. J.; Bastiaansen, C. W. M. "A printable optical time-temperature integrator based on shape memory in a chiral nematic polymer network", Advanced Functional Materials **2013**, 23, 2723-2727.
161. Raasch, J.; Ivey, M.; Aldrich, D.; Nobes, D. S.; Ayranci, C. "Characterization of polyurethane shape memory polymer processed by material extrusion additive manufacturing", Additive Manufacturing **2015**, 8, 132-141.
162. Roberts, R. C.; Zeng, S.; Tien, N. C. "Design and fabrication of buckled metal strain gauges using shape memory polymer and inkjet additive microfabrication", In 2015 IEEE SENSORS - Proceedings, 2015.
163. Qin, Y.; Alam, A. U.; Howlader, M. M. R.; Hu, N. X.; Deen, M. J. "Inkjet Printing of a Highly Loaded Palladium Ink for Integrated, Low-Cost pH Sensors", Advanced Functional Materials **2016**, 26, 4923-4933.
164. Wang, P. C.; Chang, C. P.; Youh, M. J.; Liu, Y. M.; Chu, C. M.; Ger, M. D. "The preparation of pH-sensitive Pd catalyst ink for selective electroless deposition of copper on a flexible PET substrate", Journal of the Taiwan Institute of Chemical Engineers **2016**, 60, 555-563.
165. Yoon, B.; Shin, H.; Kang, E. M.; Cho, D. W.; Shin, K.; Chung, H.; Lee, C. W.; Kim, J. M. "Inkjet-compatible single-component polydiacetylene precursors for thermochromic paper sensors", ACS Applied Materials and Interfaces **2013**, 5, 4527-4535.
166. Lee, J.; Yarimaga, O.; Lee, C. H.; Choi, Y. K.; Kim, J. M. "Network polydiacetylene films: Preparation, patterning, and sensor applications", Advanced Functional Materials **2011**, 21, 1032-1039.
167. Kumar, S. S.; Ojha, A. K.; Pant, B. D. "Experimental evaluation of sensitivity and non-linearity in polysilicon piezoresistive pressure sensors with different diaphragm sizes", Microsystem Technologies **2016**, 22, 83-91.
168. Vatani, M.; Engeberg, E. D.; Choi, J. W. "Conformal direct-print of piezoresistive polymer/nanocomposites for compliant multi-layer tactile sensors", Additive Manufacturing **2015**, 7, 73-82.
169. Al-Chami, H.; Cretu, E. "Inkjet printing of microsensors", In 2009 IEEE 15th International Mixed-Signals, Sensors, and Systems Test Workshop, IMS3TW '09, 2009.

170. Agrawal, A.; Patra, P. K.; Calvert, P. D. "Printed soft structured piezoresistive strain sensor", In 2007 NSTI Nanotechnology Conference and Trade Show - NSTI Nanotech 2007, Technical Proceedings, 2007 pp. 32-35.
171. Correia, V.; Caparros, C.; Casellas, C.; Francesch, L.; Rocha, J. G.; Lanceros-Mendez, S. "Development of inkjet printed strain sensors", Smart Materials and Structures **2013**, 22.
172. Ferrreira, A.; Rocha, J. G.; Ansón-Casaos, A.; Martínez, M. T.; Vaz, F.; Lanceros-Mendez, S. "Electromechanical performance of poly(vinylidene fluoride)/carbon nanotube composites for strain sensor applications", Sensors and Actuators, A: Physical **2012**, 178, 10-16.
173. Costa, P.; Silva, J.; Sencadas, V.; Simoes, R.; Viana, J. C.; Lanceros-Méndez, S. "Mechanical, electrical and electro-mechanical properties of thermoplastic elastomer styrene-butadiene-styrene/multiwall carbon nanotubes composites", Journal of Materials Science **2013**, 48, 1172-1179.
174. Martins, P.; Silva, M.; Lanceros-Mendez, S. "Determination of the magnetostrictive response of nanoparticles via magnetoelectric measurements", Nanoscale **2015**, 7, 9457-9461.
175. Martins, P.; Kolen'Ko, Y. V.; Rivas, J.; Lanceros-Mendez, S. "Tailored Magnetic and Magnetoelectric Responses of Polymer-Based Composites", ACS Applied Materials and Interfaces **2015**, 7, 15017-15022.
176. Gonçalves, R.; Martins, P.; Correia, D. M.; Sencadas, V.; Vilas, J. L.; León, L. M.; Botelho, G.; Lanceros-Méndez, S. "Development of magnetoelectric CoFe<inf>2</inf>O<inf>4</inf> /poly(vinylidene fluoride) microspheres", RSC Advances **2015**, 5, 35852-35857.
177. Zhang, W.; Zhang, W.; Jiang, H.; Peng, B.; Yang, S. "Preparation and characterization of thick magnetostrictive films", Journal of Magnetism and Magnetic Materials **2003**, 261, 118-121.
178. Grabham, N. J.; White, N. M.; Beeby, S. P. "Thick-film magnetostrictive material for MEMS", Electronics Letters **2000**, 36, 332-334.
179. Setter, N. Electroceramic-Based MEMS: Fabrication-Technology and Applications; Springer US, 2005.
180. Grabham, N. J.; Beeby, S. P.; White, N. M. "The formulation and processing of a thick-film magnetostrictive material", Measurement Science and Technology **2002**, 13, 59-64.
181. Karnaushenko, D.; Makarov, D.; Yan, C.; Streubel, R.; Schmidt, O. G. "Printable giant magnetoresistive devices", Advanced Materials **2012**, 24, 4518-4522.
182. Liu, Y. W.; Zhan, Q. F.; Li, R. W. "Fabrication, properties, and applications of flexible magnetic films", Chinese Physics B **2013**, 22.
183. Onuta, T. D.; Wang, Y.; Long, C. J.; Takeuchi, I. "Energy harvesting properties of all-thin-film multiferroic cantilevers", Applied Physics Letters **2011**, 99.
184. Dorey RA, L. G. "Printed Films", In Printed actuators; J Hormadaly, M. P. Ed.; Elsevier Science, 2012.
185. Martins, P.; Gonçalves, R.; Lanceros-Mendez, S.; Lasheras, A.; Gutiérrez, J.; Barandiarán, J. M. "Effect of filler dispersion and dispersion method on the piezoelectric and magnetoelectric response of CoFe2O4/P(VDF-TrFE) nanocomposites", Applied Surface Science **2014**, 313, 215-219.

186. Gonçalves, B. F.; Oliveira, J.; Costa, P.; Correia, V.; Martins, P.; Botelho, G.; Lanceros-Mendez, S. "Development of water-based printable piezoresistive sensors for large strain applications", Composites Part B: Engineering **2017**, 112, 344-352.
187. Schurr, M. O. "Microtechnology in surgical devices", In Emerging Technologies in Surgery, 2007 pp. 89-97.
188. Kang, H.; Park, H.; Park, Y.; Jung, M.; Kim, B. C.; Wallace, G.; Cho, G. "Fully roll-to-roll gravure printable wireless (13.56 MHz) sensor-signage tags for smart packaging", Scientific Reports **2014**, 4.
189. Wei, Y.; Torah, R.; Yang, K.; Beeby, S.; Tudor, J. "A screen printable sacrificial fabrication process to realise a cantilever on fabric using a piezoelectric layer to detect motion for wearable applications", Sensors and Actuators, A: Physical **2013**, 203, 241-248.
190. Sousa, R. E.; Costa, C. M.; Lanceros-Méndez, S. "Advances and Future Challenges in Printed Batteries", ChemSusChem **2015**, 8, 3539-3555.
191. Kim, H.; Hwang, K. "The Shifting Printing Paradigm: A goodbye to traditional printing technology", IEEE Consumer Electronics Magazine **2015**, 4, 42-49.
192. Keoh, S. L.; Kumar, S. S.; Tschofenig, H. "Securing the internet of things: A standardization perspective", IEEE Internet of Things Journal **2014**, 1, 265-275.
193. Roselli, L.; Borges Carvalho, N.; Alimenti, F.; Mezzanotte, P.; Orecchini, G.; Virili, M.; Mariotti, C.; Goncalves, R.; Pinho, P. "Smart surfaces: Large area electronics systems for internet of things enabled by energy harvesting", Proceedings of the IEEE **2014**, 102, 1723-1746.

SYNOPSIS (Word Style “SN_Synopsis_TOC”).

Printed polymer-based smart materials is an area of increasing interest due to the increasing scientific and technological interest.

This paper presents a review of various printing technologies as well as the smart materials that are already being printed. Critical challenges, future requirements and research directions have been indicated, addressing how printing technologies can meet smart materials requirements and vice-versa.