New Paradigms on Materials Synthesis and Additive Manufacturing of Flexible Electronics for Energy Applications

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ABSTRACT

Innovations in materials and manufacturing are important enablers of new technologies across multiple engineering fields. Here, we discuss our recent advances in the development of robotic printers for continuous-flow direct writing, an additive manufacturing printing technique; and the synthesis and processing of different conductive and semiconducting material-inks for this method. Also, we address the development and 3D printing of highly mesoporous foam structures and controlling their morphology. Moreover, special considerations for the development of environmentally-friendly inks are discussed, for enhancing the sustainability of manufacturing and reducing the use of harmful solvents. It is believed that novel patterning of functional optoelectronic nanomaterials using continuous-flow direct writing may hold the key for the next generation of low-cost, large-area, flexible optoelectronic devices for energy applications.

Keywords: additive manufacturing, Ag, ZnO, TiO_2, foams, 3D printing.

1 INTRODUCTION

Additive manufacturing comprises a group of revolutionary fabrication techniques, having as principle the addition of materials layer-by-layer to form a desired architecture[1]. Among the printing techniques encompassed by additive manufacturing, continuous-flow direct writing (CDW) represents an important route towards the fabrication of novel optoelectronics[2]–[4]. This versatile, lithography-free method, enables the fabrication of complex 2D and 3D architectures, with virtually no material waste, by the pneumatic deposition of functional inks through a nozzle on digitally pre-defined substrate locations. [5], [6]

Moreover, utilizing CDW to manufacture electronic devices promotes efficient manufacturing and the ability to pattern and post-process various functional materials as required by the device design.

With this in mind, different areas must be addressed, including the features and capabilities of the printing apparatus, the development of the inks for use with this method, and the understanding of the materials transformation under the different energy sources such as heat, ultra-violet (UV) light, and electric potentials.

We discuss our approach for addressing the aforementioned challenges, and the specifics of the development of different materials ink systems to be printed by CDW. Also, we address their processing under different curing/sintering conditions, and investigate the resulting materials' properties, with respect to such conditions.

Highlights of our current projects include the study of the optical, electron transport, mechanical, microstructural, and surface chemistry properties of Ag micro-patterned electrodes[7], TiO_2-based films[8] and printed foams[9], and ZnO-based photosensitive structures[10].

The understanding of the relationships between processing and properties are of paramount importance for the scale-up and industrial adoption of CDW along with the full exploitation of its potential for sustainable manufacturing.

2 CONTINUOUS-FLOW DIRECT WRITING

CDW of electronic components involves the extrusion of a functional inks through a dispensing nozzle on specific locations of a substrate or base structure (in the case of 3D structures). Therefore ink properties such as viscosity, elasticity, and drying are highly important, along with the ink-substrate interactions. The latter, playing a significant role in printing to prevent issues such as delamination, and bulging up of the material after printing. Generally, the better wetting and the higher the viscosity, the better the resolution and adhesion of the inks to the substrates. The relative surface energy between the ink and the substrate can be modified via compositional adjustments to the inks (to modify their polarity and pK_α), and to increase their viscosity[8]. Also, when working with colloidal suspensions and as viscosity of the inks is decreased, the movement of the solvent within the inks (as it is evaporated) and the forces between the colloids may result in aggregation of particles, and particle-concentration gradients in the microstructure[8]. Such colloids' mobility may be associated with Marangoni-flow[11] and/or to the Coffee-ring effect[12]. Another consequence of low viscosity in colloidal suspensions may be poor kinetic stability and sedimentation of the dispersed particles, in turn resulting in clogging of the dispensing nozzles and defects on the prints or no-printing at all. Stabilization of particles in the solution with the aid of polymeric agents is a common solution to these issues [8], [13].

Finally, additional challenges arise from the printer itself, such as available resolution, printing parameters' upper and lower limits, and integration of sensors for feedback control of position, and/or ink flow rate.

2.1 Development of Continuous-Flow Direct Writing Robotic Printer

The main printing parameters asociated to this technique are: extrusion pressure, writing speed and dispensing height (i.e. nozzle distance to substrate), see Figure 1.a. The ink is loaded in syringe-type cartridges. Then, as the pressure is applied, it flows out of the nozzle and is deposited over the substrates in any desired pattern. The designs, and therefore resulting prints, can be rapidly modified by changing the printing codes, consisting in *x-y-z* coordinate sets describing the desired printing trajectory. The pneumatic pressure and printing speeds can be changed as well to render different printed geometries (i.e. thinner/thicker prints), with concomitant effects on the printed microstructures[8], [10], as will be discussed more in detail in the ZnO and TiO_2 sections.

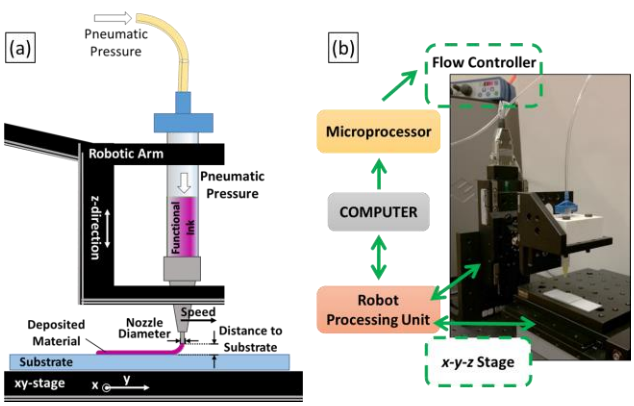

Figure 1: (a) Continuous-flow direct writing schematic, and (b) lab-built robotic printer image and configuration (arrows in green indicate the communication directions).

Commercially available robotic arms for CDW, though robust and reliable, often limit the capabilities of this method when customization becomes important; e.g. when large patterns are to be printed exceeding the available dimensions of the printing stage, or when the desired printing resolution is out of the range of the printer.

Lab-built robotic printers, such as the one shown in Figure 1.b. (designed and built in the FEST Lab), address this issues by having the flexibility to implement a different *x-y-z* stage with fine-tunable servo controllers that give position control down to 100 nm in the *x* and *y* directions and 50 nm in the *z* direction. Additional advantages of lab-built printers include having the versatility of expanding the available tools for printing (such as programming tools to design the printing patterns, generate mapping-parameter programs to investigate the printing conditions more efficiently, low-cost and interchangeability of parts/controlling units, and the possibility to implement and improve different feedback controlling systems that include sensors to correct issues such as clogging of the nozzles, and to adapt to changes in the substrate geometry; as well as multiple ink cartridges and energy sources like UV-light heating elements, etc. to transform the inks as they are deposited.

As indicated in Figure 1.b., the FEST-Lab robotic printer implements two control systems to adjust movement in the 3 axes and dispensing materials at specific locations.

3 INK SYNTHESIS AND PRINTING OF CONDUCTIVE / SEMICONDUCTING STRUCTURES

The development of inks for additive manufacturing of functional materials, is a critical step for the successful printing of device components. This stage encompasses the understanding of the chemical and physical reactions occurring within the inks from their formulation, through their deposition, to their transformation into stable materials able to resist different chemical, mechanical, or thermal stresses. Highlights of the developments for different conducting and semiconducting ink materials, using CDW, are further described in the next subsections.

3.1 Ag Inks as Conducting Structures and Contact Materials

Conducting structures are axial elements of electronic devices, as electrodes or contact materials, to ensure electron transport. Ag inks for electrodes and contacts are widely used in additive manufacturing of energy devices due to the high electrical conductivity, stability and robustness of Ag. Despite these advantages, due to the high cost of Ag, advances in the synthesis of Ag inks that yield nearly 100% metallic Ag solids are still a need; here, the advantages of precise material deposition offered by CDW become apparent.

The Ag ink patterns, shown in Figure 2, are patterned using CDW on PEN substrates and cured at 150°C. For the synthesis of the precursor inks, a Ag salt in solution is reduced with the aid of weak bases such as n-ethanolamines, and growth of the metallic particles is controlled by the capping role of stabilizing polymers such as polyacrylic acid (PAA). It is found that the choice of reducing agent greatly affects the yield of the Ag nanoparticles synthesized as described above[7]. The Ag yield is also found to be strongly influenced by the nucleation conditions (temperature and time), where temperature exhibits more significant effects[7]. Difference in the post-processing of the printed structures, result in different electrical performance; electrical resistivity values in the order of 10^{-6} Ω·cm are obtained for 150°C treated patterns (compatible with the polymeric substrates).

Electro-mechanical characterization of the printed structures[7] also reveals recovery behavior upon release of the mechanical stress (Figure 2.c.) making these inks/printed structures useful for sensing applications (see Figure 2.b.)

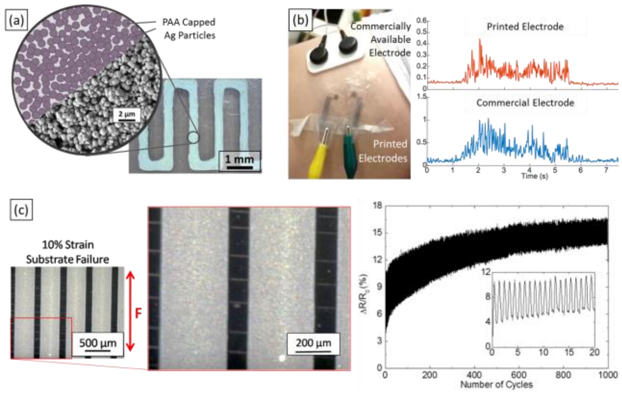

Figure 2: (a) Printed electrode (photograph) and SEM image and schematic of Ag-pattern microstructure. (b) Comparison of commercial and printed electrodes electromyogram (EMG) response. (c) Optical microscope images of the Ag patterns' surface showing substrate failure while Ag lines remain intact, and change in electrical resistance ΔR/R in % of the printed line pattern as a function of cyclic tensile stress loading.

3.2 ZnO Inks: Tuning Orientation through Printing.

ZnO structures are used in various devices due to their piezoelectric and photosensing properties. The synthesis of Al doped ZnO from sol-gel inks, was used to investigate the crystallization mechanism of the precursor inks into ZnO tunable textured films. The results suggest that the viscosity and printing parameters of the inks, can be used to control the crystalline structure preferential orientation. As shown in Figure 3, crystallization starts at the surface of the printed film and the volumetric contraction (from the inks' organics removal during heat treatments), causes wrinkling of the ZnO surfaces and crystalline growth in directions other that (002) [10], with important implications for the performance of devices fabricated using these materials.

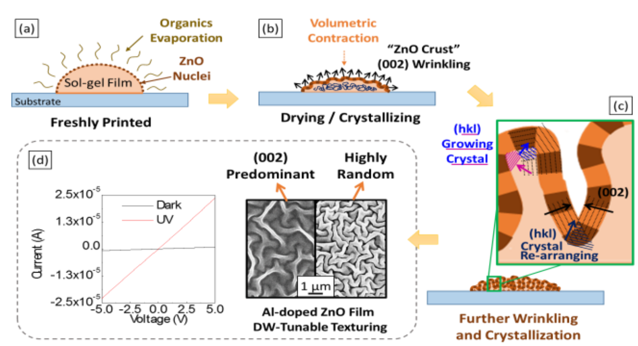

Figure 3: (a-c) Drying and crystallization mechanism; and (d) microstructure (SEM of surface), and photo-response of ZnO printed structures.

3.3 Mesoporous TiO_2 Structures from Aqueous Hybrid Inks: Inducing Crystallization at Mild Temperatures

The formulation, printing and crystallization of TiO_2-based inks, from environment-friendly aqueous inks, at low-temperatures (up to 150°C) or using UV-light, have been investigated, to understand the role and interactions of the different ink constituents and the obtained microstructures' properties, including their surface chemistry, roughness and photocatalytic performance[8]. It is found that the photocatalytic properties of the inks precursor TiO_2 particles greatly influence the crystallization, mechanical stability and photocatalytic activity of the synthesized films. In particular, the use PAA is found to enhance the printability and adhesion properties, as well as the formation of bridging structures from the organic complex transformation into TiO_2[8] (Figure 4.b.), indicating that polymers with strong polarities favor such crystallization. Again, relationships between the printing parameters and the resulting microstructural properties are established (Figure 4.c) and underline the importance of tuning the viscosity of the inks to improve printing fidelity.

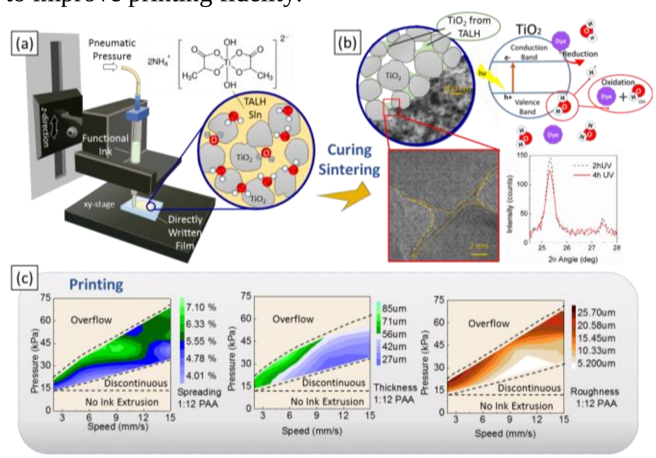

Figure 4: (a) Low-temperature direct writing of TiO_2-based mesoporous films, (b) bridging role of crystallizing TiO_2 from Ti(IV) bis (ammonium lactato) dihydroxide (TALH) and photocatalysis mechanism, and (c) printing space and microstructural relationships for 1:12 TALH:TiO_2 PAA ink system (mol:mol).

3.4 TiO_2 Foams: Enabling 3D printing and Tuning Foam Morphology

As pointed out earlier, the viscous properties of the inks are critical for enabling the fabrication of 3D structures. In the case of the TiO_2 aqueous inks, the obtained viscosity regimes (~1 Pa·s) allowed only for the fabrication of films. To achieve further controlling of the viscosity and realizing free-standing and spanning 3D structures, the previously studied TiO_2 inks were formulated as foams resembling oil in water emulsion systems (see Figure 5).

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These foams also exploit the advantages of hierarchically ordered mesoporous systems, with applications across multiple fields, due to the improved electron transport and high surface area associated to such structures[14]. By controlling their composition (liquid-solid-oil phase ratio) and the processing conditions, their viscosity and foam morphology (i.e. open- or closed-cell configuration) are tuned; in turn, affecting their photocatalytic performance, and indicating higher photocatalytic activity for open-cell structures[9].

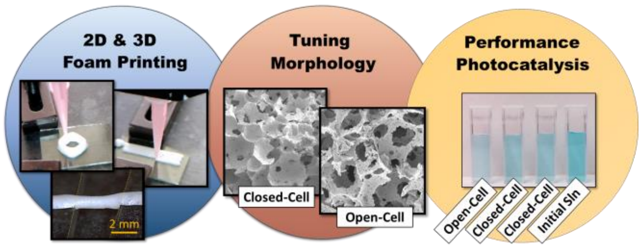

Figure 5: Tuning the printing of TiO_2-based foams, their morphology and photocatalytic performance.

These foams' synthesis process makes use of abundant, innocuous, and biocompatible materials; which promotes their use beyond energy applications, including biomedical scaffolds. Furthermore, the use of aqueous stable ink systems, enables their fabrication at open-air conditions, and signifies important steps towards sustainable and scalable manufacturing of semiconducting devices.

4 SUMMARY AND OUTLOOK

In this article we discuss the advantages and current challenges associated with additive manufacturing of flexible electronic devices, including the development of equipment, and functional inks to print the active material layers in the devices using CDW. Furthermore, we show examples of alternative routes to tune the printing, adhesion, and inks transformation into stable materials with specific functionalities, controlling their microstructure, morphology, crystalline orientation and performance. Moreover, we consider manufacturability constrains such as low-temperature conditions, aiming for synthesis of materials that are compatible with polymeric substrates further enabling their manufacturability. Finally, we underline the importance of using innocuous and water-stable materials, as pivotal precursors for sustainable manufacturing.

Additive manufacturing represents a vast field of fabrication techniques focusing on the efficient use of functional materials and the adoption of the most efficient designs; consequently, engineering of materials and equipment for additive manufacturing of flexible energy devices are the major enablers of such a concept.

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