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# Low-cost and fast wet-based technique to generate nanostructured organic materials layers and its application to chemiresistive gas-sensing devices

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**Abstract**

Nanostructured materials for sensors and transducers are of great interest to the scientific community due to several advantages that these materials can provide (e.g., integration with large scale manufacturing technologies, enhanced performances, etc.). Nonetheless, large-area, low-cost and fast processing technologies for creating effective sensing nanostructures are still sought for. In this work, a recently described technique called Auxiliary Solvent-Based Sublimation-Aided NanoStructuring (ASB-SANS) has been used to generate poly(3-hexylthiophene) (P3HT, a well known semiconducting polymer) nanofilamentary structures onto interdigitated electrodes. These have been tested as gas sensing layers for volatile organic compounds, delivering promising results.


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*Keywords:* nanostructured materials; gas sensor; P3HT; semiconducting polymer; chemiresistive.

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## 1. Introduction

Conventional organic chemiresistive gas sensors suffer from pronounced sensitivity to humidity, scarce reproducibility, prominent response drift and short device lifetimes [1]. Sensing nanostructures on extended areas have been developed to increase the interacting sensing surface with analytes [2][3], but problems related to the large scale production of these nanostructures are still unsolved. In fact, an ideal method to produce nanostructures should have low cost and short fabrication times, and should be able to produce the needed nanostructures on large areas (at least $cm^2$). Among the existing methods for creating nanostructures (laser ablation, plasma treatments, thermal treatments, sol-gel methods, biological or synthetic templates, nanolithography, surface phenomena, electrospinning, self-assembly, nano-contact printing, properly designed ink-jet printing, ordered assembling of already existing nano-objects), only the sol-gel technique complies with most of these requirements, but it still needs a final step of pyrolysis at high temperatures [4]. This involves high costs and it is not well suited for organic materials (with the exception of the fabrication of mesoporous, disordered structures). However, recently a novel, fast, low-cost and versatile method enabling the fabrication of nanostructures ordered in the meso (micro- to nano-) range, potentially on very large scales, has been reported [5]. The technique, named Auxiliary Solvent-Based Sublimation-Aided Nano Structuring (ASB-SANS), is based on the exploitation of organic crystalline sublimating materials as easily removable templates.

Here, we present the use of the ASB-SANS technique to produce nanofibrillar structures out of a well known semiconducting polymer, poly(3-hexylthiophene) (P3HT), over large areas in standard laboratory conditions. The so-obtained nanofibers have been realized onto interdigitated gold electrodes, and the resulting devices have been tested as gas-sensing layers for acetone, ammonia, and humidity.

### *1.1. ASB-SANS nanostructuring method*

The ASB-SANS technique is carried out dissolving small amounts of the material to be deposited (the Target Material, TM) in a crystalline substance able to sublimate (the Sublimating Substance, SS). To help the dissolution of the TM, an Auxiliary Solvent (AS) is also added to the system. This is chosen to dissolve both the TM and the SS, and to have a boiling point lower than the sublimating temperature of the SS. This approach allows to obtain a ternary solution, that can be easily handled in normal conditions (i.e., at room temperature and ambient atmosphere), and from which organized nanostructures are easily developed. In more detail, ASB-SANS is carried out by at first preparing the liquid ternary solution constituted by the AS, the TM and the SS (Fig. 1a,b). The solution is hence deposited onto a substrate (Fig. 1c), from which the AS starts to evaporate (Fig. 1d). After that, a solid layer constituted by the mixed SS and TM is left, and when the TM concentration within the SS is low enough to allow the latter to crystallize, the SS acts as a template for the TM molecules. Upon SS sublimation (Fig. 1e), the template is self-removed from the layer, leaving at the end of the process a series of organized nanostructures onto the substrate (Fig. 1f). When the SS is able to form needle-like crystals, the resulting TM patterns have fibrillar shapes.

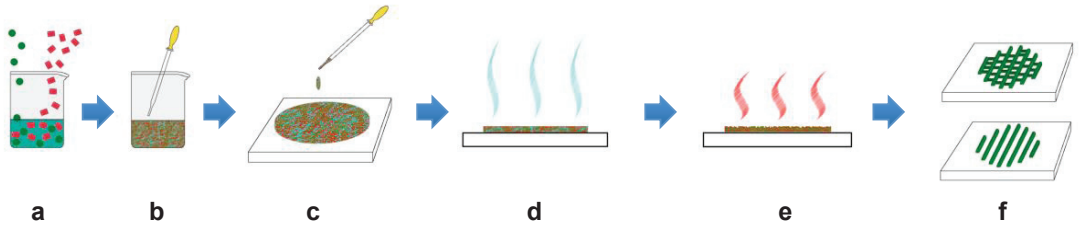


Fig. 1. Sketch of the ASB-SANS process to fabricate nanostructures on a substrate: a) the TM (green spheres) is mixed with the SS (red diamonds); b) the AS (cyan liquid in the beaker) is added to the binary solution; c) the ternary mixture is deposed on the substrate by drop casting; d) the AS starts to evaporate (cyan vapours) before the sublimating matrix; e) after the AS is gone, the organic crystal progressively sublimate (red vapours) through vanishing crystallites domains containing the polymer; f) arrays of TM nanofibers, connected or isolated depending on the sublimate-to-polymer ratio used, have formed on the substrate.

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### *1.2. Gas sensors fabrication*

Para-dichlorobenzene (PDCB) was used as the SS, since in its liquid (melted) phase, it may dissolve many organic materials, either molecular or polymeric, and it forms needle-like crystals. It is also fully miscible with a number of organic solvents, including chloroform (CHCl3), which was hence used as the AS. Moreover, CHCl3 has a boiling point much lower than the PDCB sublimation temperature. Thanks to this, it is possible to prepare in normal conditions homogeneous liquid ternary solutions constituted by PDCB/CHCl3/P3HT, which can be deposed on substrates to obtain, after CHCl3 evaporation, the sublimation of the PDCB followed by the formation of P3HT nanostructured layers. To obtain the sensing devices, Si/SiOx substrates were used to fabricate interdigitated electrodes by standard lithography techniques and ease the subsequent scanning electron microscopy (SEM) examination.

Figure 2 shows P3HT nano-micro fibers deposited on gold interdigitated electrodes on Si/SiOx substrates. These nanostructures were obtained by deposing a ternary solution P3HT:$CHCl_3$:PDCB in ratio 5 mg: 1 mL: 200 mg. The solution was deposited by drop casting and was allowed to evolve as described above, delivering well defined P3HT nanostructures. Notably, SEM imaging shows that developed fibers have uniform widths down to a few tens of nm, though conserving lengths well over several tens of microns (Fig. 2c).

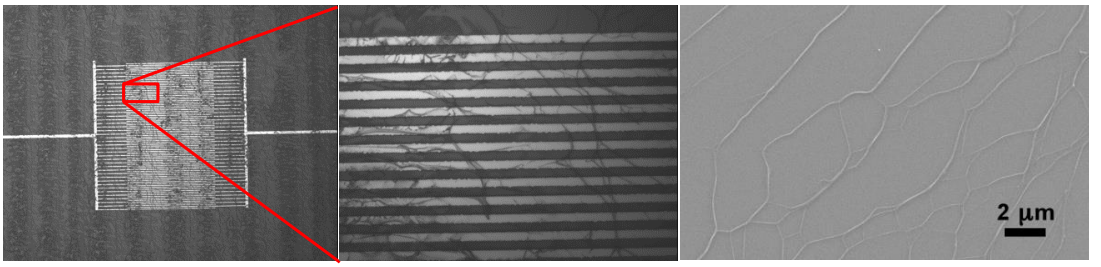


Fig. 2. Interdigitated gold electrodes with P3HT nano/microfibers deposited by ASB-SANS. a) wide view of the device b) magnification of a selected area (red rectangle in Fig. 2a); (c) SEM image of P3HT nanofibers on Si/SiOx.

## 2. Experimental results and discussion

This paper presents preliminary tests carried on ASB-SANS P3HT nanostructured layers as gas sensors with respect to plain P3HT devices fabricated by spin coating a $CHCl_3$/P3HT binary solution.

Electrical measurements have been carried out by using a Keithley 2400 connected to a computer and managed by a LabView interface. Devices have been characterized in air at room temperature by applying low voltage biases.

In order to excite sensors, a fixed volume of the analyte saturated vapors were sprayed over the sensing surface by means of a glass syringe.

In Figure 3a normalized current plots for acetone, ammonia, and humidity for both ASB-SANS P3HT and plain P3HT devices are reported. As it can be noticed, ASB-SANS P3HTdevices evidenced no analyte permeation within the polymer layer as conductivity always increased with the analyte. On the contrary, plain-P3HT devices exhibited a conductivity decrease vs acetone and ammonia, which is has already been reported in literature [6]. This clearly points towards a response dictated by surface effects in ASB-SANS nanostructured layers. Moreover, ASB-SANS P3HT nanostructure showed much shorter recovery times (below 1 second) with respect to plain films. This can be seen in figure 3b where sensors responses have been interpolated to derive approximate baseline recovery times.

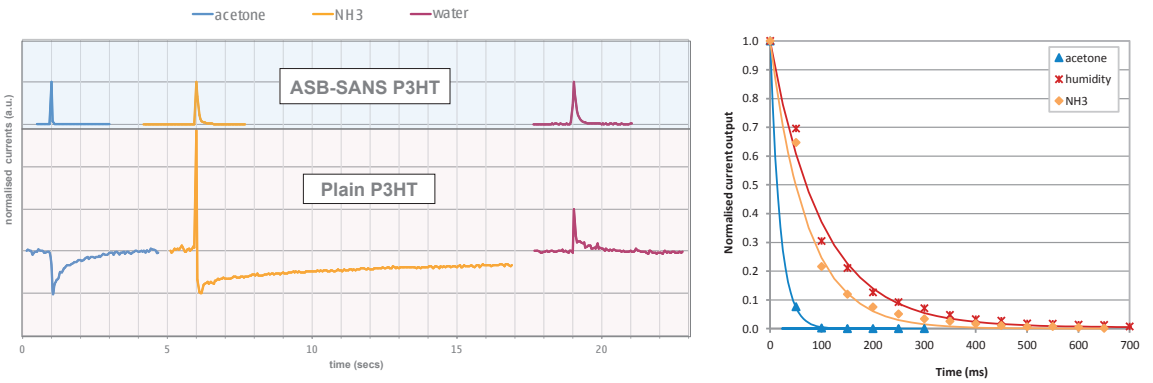


Fig. 3. (a)Normalized current responses of ASB-SANS P3HT and plain-P3HT with respect to acetone (blue plots), ammonia (green plots) and water (red plots). (b) Comparison between ASB-SANS P3HT time responses.

## 3. Conclusion

In this work, ASB-SANS-generated P3HT nanofibers have been deposited onto patterned electrodes and tested as gas-sensing layers for volatile organic compounds (VOCs). Performances of the ASB-SANS nanostructured layers have been compared to those of P3HT layers obtained with standard wet-processing techniques. Results indicate that ASB-SANS P3HT nanostructured layers respond faster and recover to the initial state very quickly compared to standard P3HT layers.

In summary, it has been shown that ASB-SANS is a novel wet-based technique which may offer an easy and low-cost approach to the fast deposition of nanostructures over large areas. The technique is applicable to a range of polymeric materials and the work carried here demonstrates that ASB-SANS nanostructures can provide enhanced performances. In fact, response traces associated to ASB-SANS P3HT show that physical phenomena underlying the absorption/desorption processes are different and favour faster desorption responses with respect to a plain, P3HT spin-coated layer.

Further work is in progress in order to fully characterise properties and behaviour of ASB-SANS nanostructure polymeric films as sensing layers to gas and vapours.

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