Bioelectronics and Green Electronics for a clean Environment

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Abstract. Some directions of environmental tasks for Romania in collaboration with foreign partners for next decade are: (i) electric and electronic wastes recycling using sustainable future networks suppliers-materials conversion-production, in a chain of countries; (ii) strategies at group of countries till European initiatives about reforestation, deforestation stopping, soils re-invigoration for agriculture including smart irrigation and bio-nano-technologies help, (iii) water depolluting and monitoring in see, rivers, potable water, treatment of the biological contaminated waters; (iv) air contamination with pollutants; (v) human education for the planet conservation. Starting from our achievements in the domain of bioelectronics and green electronics, we propose some directions of action.

Keywords: Environmental biosensors; Green organic semiconductors; Planet care

1. Introduction

Since 2021, in Romania the ecology and clean environment become a priority, after last UE - Romania targets (European Union Council, 2021). We intend to develop multiple connections of different forums of environmental conservations from Romania with foreign mature actors, to encourage challenging reforms, able to ensure the balance between Science & Technology and a cleaner, healthier, more sustainable environment for global population.

We mention some solutions from Bio-Nano-Electronics and Micro-technologies fields: (i) for the reduction of gases and CO- emission, the Si electronics must move to SiC or C electronics, due to a strong minimization of the leakage currents in all CMOS circuits in OFF-state; (ii) different sensors and biosensors for water/air/soil monitoring manufactured by micro-nano-electronics technologies (Ravariu C et al, 2018); (iii) recuperation of rare metals or critical Terra resources from electronic wastes (e.g. Hf, Pt etc); (iv) green organic semiconductor processes of fabrications (Ravariu C. et al, 2020); examples are nano core materials with organic shell instead of materials for electronics with PAH precursors, like usual pentacene (Yang D. et al, 2015); (v) environmental monitoring, clean medicine (Bondarciuc A et al, 2015), environmental education and common practices for people from different countries to enlarge the common initiatives. On the other hand, the co-authors of this paper propose for the next future opportunities in the environment cleaning, launching a Nano-Bio-Engineering and Environment Management (NBEM) master studies program since 2 years ago. The paper presents own contributions and proposes some directions of collaboration.

2. Bioelectronics - contributions in environmental biosensors

During a joint project, our team reported a biosensor fabrication for pesticide detection (Ravariu C. et al, 2015). The background of the technology belongs to microelectronics factories, based on Si-wafer processing, adding an enzymatic layer as bio-receptor. The Si-surface was functionalized by porosification, obtaining a Si-porous layer, as top film able to entrap the Acetyl-cholinesterase (AcHE) enzyme. The biosensors tendencies are defined by the last roadmap traces in integrated electronics, beyond Moore laws that is limited in 2021 (Ahopelto et all, 2019). Recommendations that we deal consist in co-integration of the biological parts with the microelectronics compounds on the same chip (Ravariu C. et al, 2019). Paraoxon belongs to a class of parasympathomimetic substances, like pesticides. Hence, it works together with AcHE inhibitor. In water, it produces a high threat of pollution, being toxic for animals and human. The paraoxon pesticide is usually solved in water and it is applied by spraying to leafs of cotton, rice and trees. After raining, paraoxone is collected in wasted water and finally in earth. This pesticide directly stimulate the muscarinic and nicotinic receptors, or indirectly acts as a potent acetyl-cholinesterase inhibitor for insects. Details of technology were presented elsewhere (Ravariu C. et al, 2015). Now, we indicate some shortcuts for the technological process.

The Si-porous is not purchased from any supplier, and its deposition is not performed from solutions on the Si-wafer, because it can be easily removed and it is not able to bind a *thick* enzymatic layer. Hence, we recommend the Si top-layer conversion from Si-mono-crystalline to Si-porous, by anodic oxidation, under an electrolyzing treatment in 4% HF in Dimethylformamide, at room temperature. In this way, the thin Si-porous layer is grown onto Si-wafer, being strongly anchored to the Si-substrate. Consequently, the porous layer of hundred nanometers thickness is able to capture and bind the next enzymatic layer of hundred microns thickness (Tiffany M. Hoover, 2005, Ravariu C. et al, 2007, Ravariu C. et al, 2009). For paraoxone biosensor we used a capacitive transducer. Finally, the biosensor measured the potential deviation of the capacitive structure between 20mV to 160mV for a paraoxone concentration ranging from 10μM to 1000μM, Figure 1a.

Another contribution of our group was in the fabrication of a glucose biosensor with metal meanders, Figure 1b.

For the enzymatic membrane, the glucose-oxidase was immobilized in bovine serum albumin BSA, mixing a glutaraldehyde aq. solution as cross-linker. The technique permits the enzymatic membrane deposition on the Si-wafer surface.

3. Green organic semiconductors

In the domain of Organic Thin Film Transistors (OTFT), the core drawback is that most current organic semiconductors are manufactured with toxic, carcinogenic precursors, like polycyclic aromatic hydrocarbons (PAH) (Das DN et al, 2017). The pentacene is one of the most effective organic semiconductor used in OTFT fabrication (Yang DL et al, 2015), with PAH precursors.

During the technological flow, PAH intermediate compounds are highly toxic for people and waste-water. The carcinogenic properties of PAHs come from their affinity to bind to cellular DNA, causing disruptive effects in living cells. Consequently, a lot of traditional organic semiconductors, like pentacene, tetracene, rubrene or Alq3 suffer from significant toxicity, especially for employees in the organic electronics industry.

Only in the last 2-3 years, the issue raised attention regarding the selection of green, non-polluting manufacturing technologies. In this sense, through academic search on Internet, extremely poor alternatives has been pointed out. In 2019 a solution came from green nanotechnologies (Guru PN et al, 2019). In 2020, another group proposed green technologies for inorganic semiconductors, but closer to our target: nanoparticle-mediated photo-oxidative processes, based on ZnO and TiO_2 semiconductors, represent an efficient technique to remove the PAH precursors from soil or wasted water (Muhammad I et al, 2020).

Ferrite core shell nano-materials with bio-organic external shell belongs to the group of green compounds. Detailed synthesis procedure and dip-coating technological steps for OTFT made by film of ferrite nano-core with PABA outer shell was published elsewhere (Ravariu C et al, 2020). Here, our intention is to better demonstrate the non-toxicity of this compound, based on data from the literature.

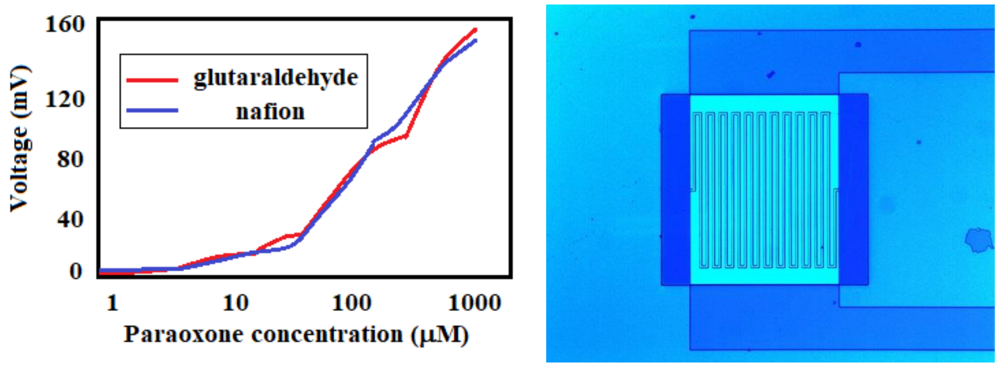
The para-aminobenzoic acid (PABA) is a vitamin, encountered in the human intestinal tract or the plant chloroplasts. PABA respects the molecular conjugation that is the main clause to allow electronic conduction in OTFT. On the other hand, ferrite is again a green compound, because in the human body it can dissociate into Fe+ ions and O- ions, having a distant margin of toxicity. The application of PABA together with polyaniline in bio-transistors was done in 2018, for the realization of a biosensor (Cogal S et al, 2018). A quantitative parameter for the toxicity evaluation is the lethal dose, noted by LD50 that is consistent to a mortality of 50% from an experimental lot of animals, after the substance inoculation of a given dose expressed in mg/kg-body (Parra AL et al, 2001).

Doses of 215.7 mg/kg were administered to rats to observe the effects of PABA on thyroid carcinogenesis. The toxicity probability, including the action of thyroid carcinogenesis was negligible (Hasumura M et al, 2005).

Other studies have looked at the effect on embryonic development of different doses of PABA (5, 15, 50mg/Kg) injected into pregnant rats. Para-aminobenzoic acid at all doses tested has no harmful effect and does not affect organogenesis. At doses of 5 and 15 mg / kg, PABA does not affect growth, but reduces the value of parieto-coccygeal diameter and body mass. At a dose of 50 mg / kg, the increase of the fetal body weight is reduced by 0.05%, but it is usually normalized during postnatal development (Stroeva OG et al, 1998).

These values indicate much lower toxicity of PABA than PAH, like benzo[k]fluoranthene with LD50 = 14 μg/kg or other PAHs with LD50 sub-90 μg/kg, (Brunström B et al, 1991). For safety considerations, the median LD50 dose of PABA goes up to 2g/kg in dogs (Maki, T et al, 2000).

Besides to these observations, PABA or Bx vitamin, is an intermediate compound in the synthesis of folic acid in bacteria and it is found in food as a cofactor of B vitamin (Solar S et al, 2011), presenting low toxicity for human operators in a factory.



(a) (b)

Figure 1. (a) Biosensor voltage curve versus concentration of paraoxone. (b) Electrodes design with metallic meanders.

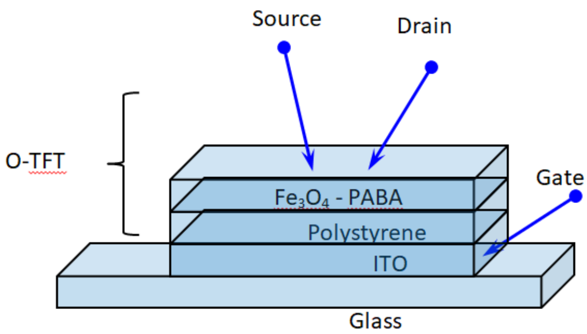
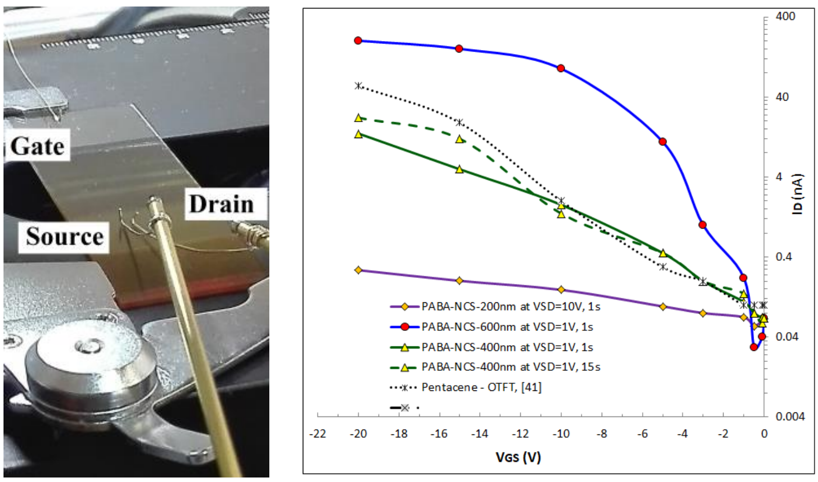


Figure 2. Conceptual O-TFT: layers and electrodes position.



(a) (b)

Figure 3. (a) Experimental O-TFT with Fe_3O_4-PABA active layer as organic semiconductor; (b) Measured I_D-V_{GS} characteristics of the O-TFT with p-type film and green technologies of fabrication, besides to I_D-V_{GS} characteristics of the Pentacene O-TFT from literature.

4. Conclusions

The papers presented two main directions of the microelectronic technologies. Enzyme immobilization on direct grown nano-porous material on a Si-wafer allowed pesticide biosensor fabrication. Green precursors were associated for friendly technologies for development of organic semiconductor. Technologies were based on non-toxic nano-core shell of ferrite with para-aminobenzoic acid outer shell.

Acknowledgement

The article is financed by the Polytechnic University of Bucharest, through the project "Engineer in Europe" in online system, registered at the Ministry of Education under no. 140 / GP / 19.04.2021, by using the fund for financing special situations that cannot be integrated in the form of financing state higher education institutions.

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