Envirobot RTD 2013

Inkjet Printing of Carbon Nanotubes Electrodes for Environmental Monitoring

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1. INTRODUCTION

Inkjet printing (IJP) has recently gained a lot of attention, since it enables mask-free deposition of functional inks containing e.g. metallic nanoparticles, biomolecules or polymers that can be treated almost simultaneously by thermal or photochemical post-processing techniques leading to functional devices.[1] Indeed, IJP offers many opportunities to make a relevant impact on environmental monitoring such as by IJP of carbon nanotubes (CNT) electrochemical sensors for the quantification of a wide range of analytes in the environment, since it provides fast, sensitive, non-expensive and highly reliable measurements.[2] Herein we present the use of IJP for the fabrication of CNT sensors and their application to the monitoring of atrazine in aqueous samples in conjunction with a magnetic bead-based immunoassay. Atrazine is a herbicide widely use in the agriculture industry that due to its toxicity has been banned in Europe since 2004, but allowed to be employed till 2010 in order to finish its stock.[3] Despite of it, atrazine can still be found in drinking water samples all over Switzerland and therefore its monitoring became of high importance.

2. MULTILAYER INKJET PRINTING PROCESS AND PACKAGING

Multilayer Inkjet Printing Process

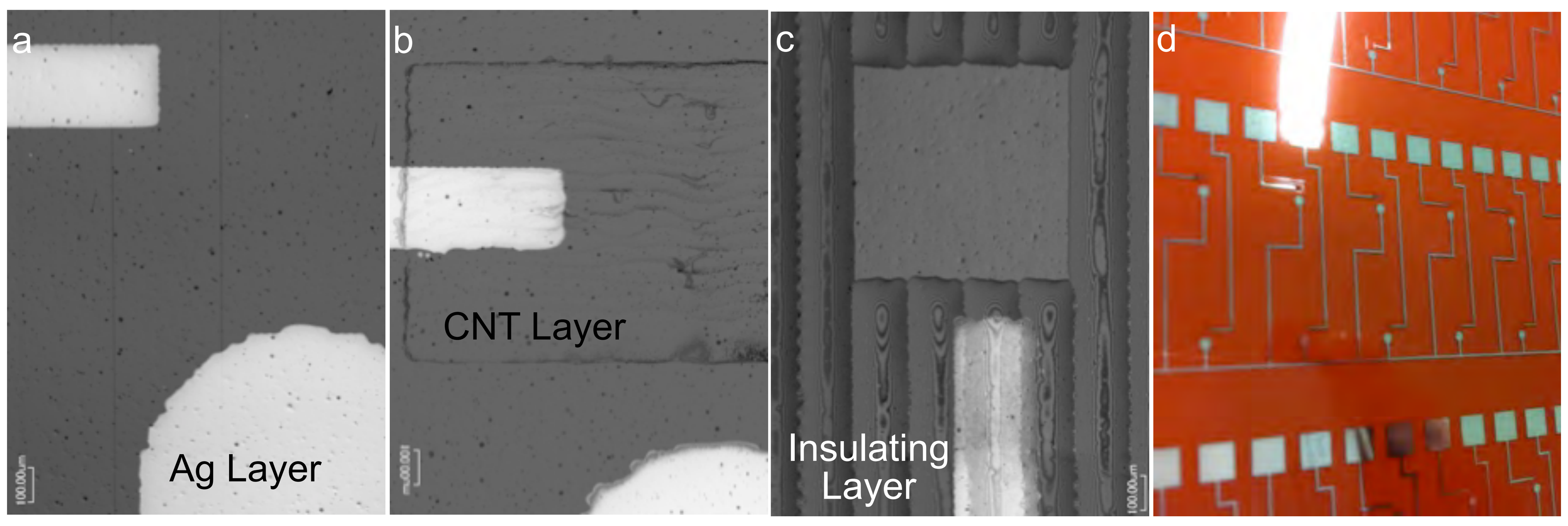


Figure 1. Optical pictures of the multilayer process employed for the microfabrication of two-electrode electrochemical cells based on a) a silver layer for electrical connections and as reference/counter electrode, b) a CNT layer as working electrode and c) an insulating layer for defining precisely the active working electrode area. d) Fabrication of hundreds of stand-alone carbon nanotubes electrodes is also possible.

Packaging of Multiplexed Microchips

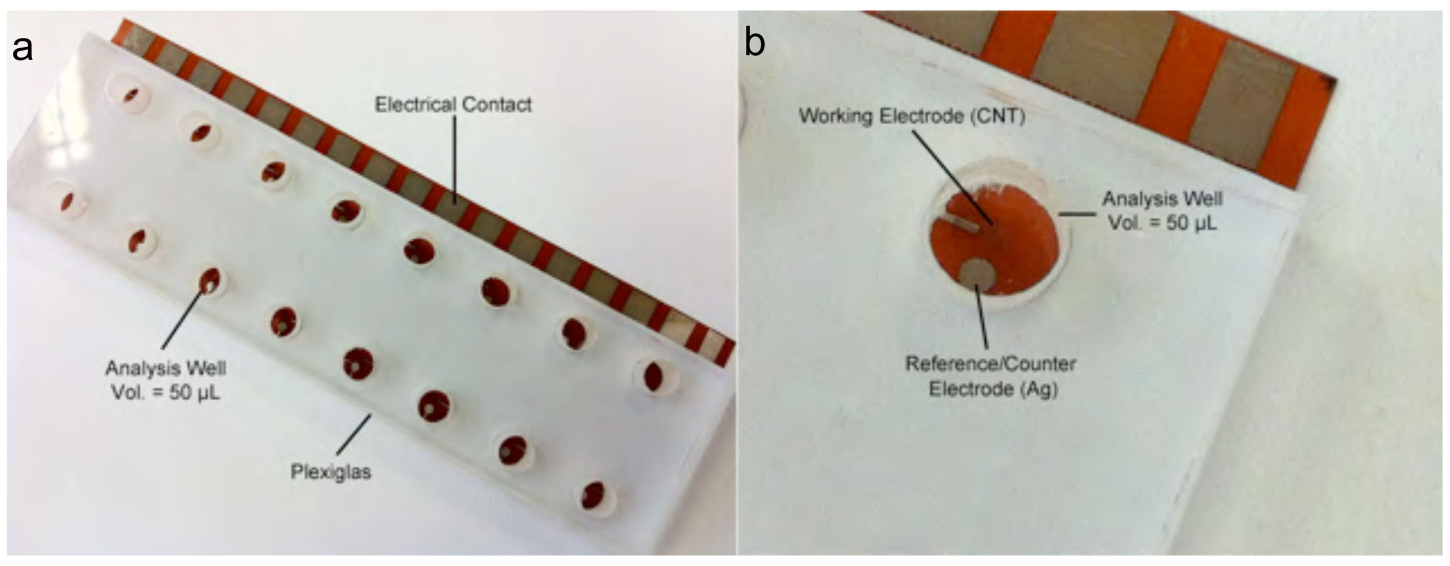
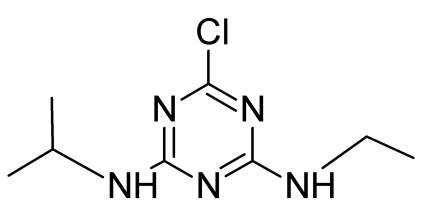


Figure 2. Optical picture of a fully a) multiplexed microchip containing 16 individual two-electrode cells completed with a machined Plexiglass cover for the isolation of each electrochemical cell. b) Optical picture of a single two-electrode cell arrangement with a predefined maximum analysis volume equal to 50 μL. The substrate employed for the fabrication of the inkjet printed chip was polyimide (Kapton).

3. IMMUNOASSAY DETECTION OF ATRAZINE

Relevance:



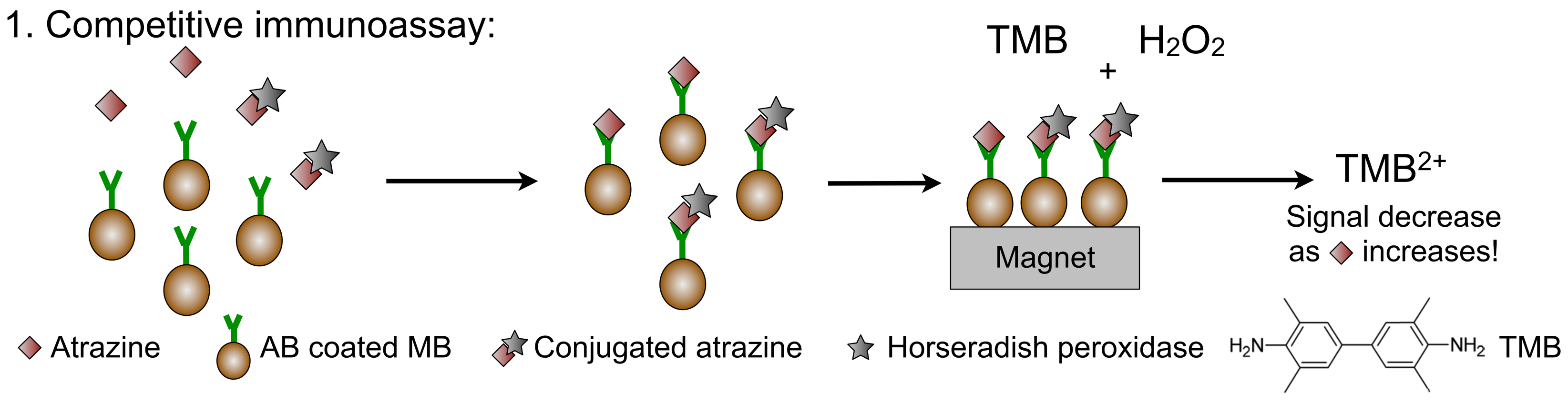
Herbicide banned in Europe in 2004, but allowed to finish stock until 2010, but still widely use in USA.

Suggested endocrine disruptor agent.

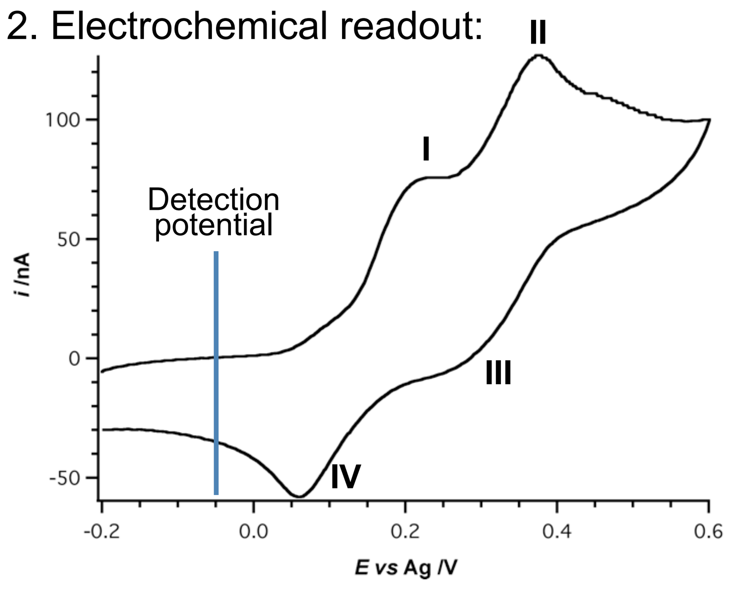
Limit of toxicity in water is 0.1 ppb.

Detection Principle

1. Competitive immunoassay:



2. Electrochemical readout:



Detection principle overview:

1. $TMB + H_2O_2 \xrightarrow{HRP} TMB^{2+} + O_2 + 2H^+$

2. $TMB^{2+} + 2e^- + 2H^+ \longrightarrow TMB$

Figure 3. Cyclic voltammetry of TMB 5 mM in buffer phosphate 50 mM at an inkjet printed CNT electrode. Reference/counter electrode Ag. Scan rate = 50 mV/s. Signals I and II correspond to the oxidation (two-electron transfer) process of TMB to TMB^{2+}, while III and IV represent the reverse process (reduction of TMB^{2+}), thus a potential equal to –0.05 V *vs* Ag was employed for the quantification of the enzymatically produced TMB^{2+}.

4. QUANTIFICATION OF ATRAZINE IN WATER

Verification of TMB Monitoring

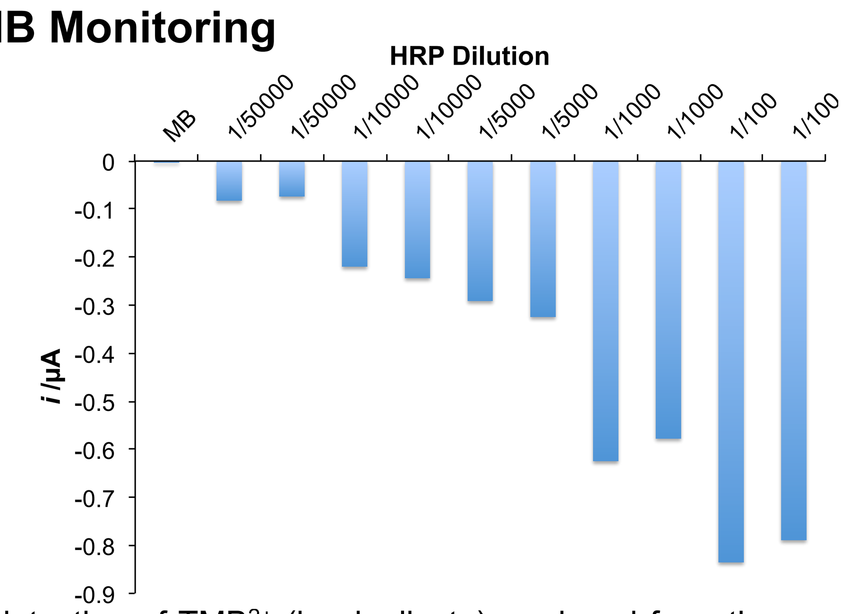


Figure 4. Amperometric detection of TMB^{2+} (by duplicate) produced from the enzymatic reaction between TMB, H_2O_2 and different dilutions of Horseradish peroxidase (HRP) by using the inkjet printed carbon nanotubes electrodes.

Atrazine Calibration Curve

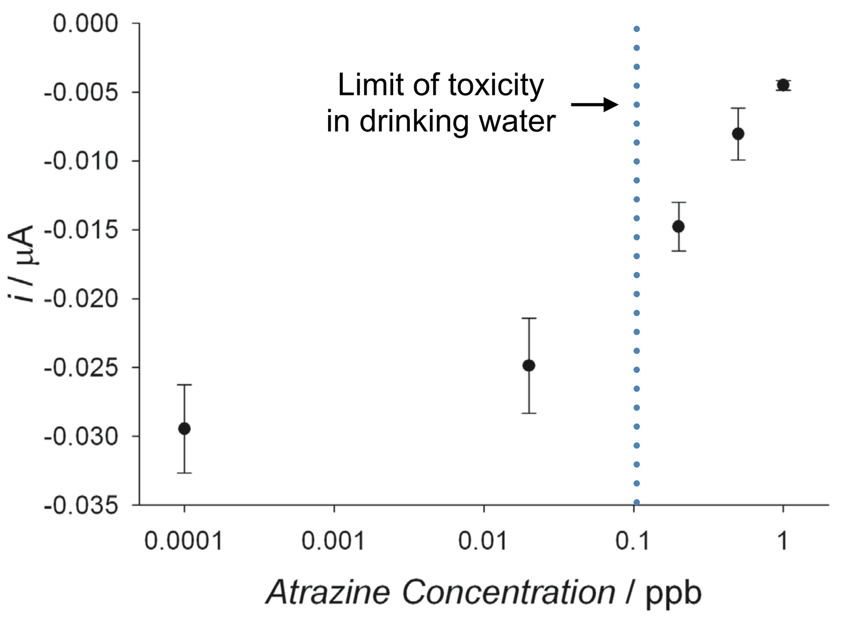


Figure 5. Calibration curve for atrazine by using a magnetic bead immunoassay with electrochemical readout by using the inkjet printed carbon nanotubes sensors. The error bars represent the standard deviation of a triplicate. A very good sensitivity in the low ppb atrazine concentration range was achieved by the present methodology. Please note that the atrazine concentration axis is in a logarithmic scale.

5. CONCLUSIONS AND PERSPECTIVES

A multilayer inkjet printing process has been developed for the microfabrication of carbon nanotubes sensors applied to the environmental monitoring of atrazine in water. With this aim, a competitive magnetic bead-based immunoassay was employed for the specific recognition of atrazine. The electrochemical read-out of the employed competitive immunoassay demonstrate the possibility to detect atrazine with a high sensitivity (i.e. in the low ppb range) that allows for the unequivocal differentiation of atrazine toxic levels in water. Moreover, thanks to the fact that electrochemical strategies coupled to IJP are easy to miniaturize and multiplex, high throughput analysis can be carried out with the individually addressable 16 two-electrode electrochemical cells. Future experiments will be focused on the quantification of atrazine in real samples and the implementation of the present methodology into the envirobot system.

References

1. M. Singh, H.M. Haverinen, P. Dhagat, G.R. Jabbour, Inkjet printing-process and its applications, Adv. Mater. 22 (2010) 673.

2. A. Lesch, F. Cortés-Salazar, M. Prudent, J. Delobel, S. Rastgar, N. Lion, J-D. Tissot, P. Tacchini, H.H. Girault, Large scale inkjet-printing of carbon nanotubes electrodes for antioxidant assays in blood bags, Electroanal. Chem. 61 (2014) 717.

3. EDEXIM Chemical Information for Atrazine". Retrieved 2014-02-10 from European Commision, Institute for Health and Costumer Protection.

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