Arrays of microwells equipped with a recessed ring nanoelectrode and a disk microelectrode for nanoelectrochemistry investigations

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The increasing interest in miniaturized analytical systems involving small-volume samples induces to the development of "Nanoelectrochemistry", which combines the advantages of nanotechnology and electroanalysis. As a result, several research works attempted to miniaturize complete electrochemical cells. This is an important challenge because of the necessity to minimize the sample volume when dealing with toxic waste, or precious body fluids, expensive reagents, or to precisely trap single cells. Microwells with recessed ring nanoelectrodes are a novel kind of electrochemical devices that attract big attention. Similar to ultra-microelectrodes, they exhibit high current density, fast response time, reduced charging current and high signal to noise ratio. In addition, their small volumes make them well suited for the detection of low concentrations or for the analysis of individual cells. In the current study, recessed platinum ring nanoelectrodes (RNE) and disk ultramicroelectrodes (DME) (surface: $21 \mu m^2$ and $64 \mu m^2$, respectively) into microwells (diameter: 9 µm, depth: 5.2 µm) were realized using silicon-based technology (Figure 1). These electrochemical devices were characterized by cyclic voltammetry with different redox probes (ex. ferrocene methanol: Fc(MeOH)) using a single well or arrayed configurations, and optimised compared to COMSOLTM simulations. Steady-state sigmoïdal responses were evidenced for the DME devices in agreement with theoretical studies. Similar results were obtained for the RNE ones and validated by our theoretical model (Figure 2). To check the confinement effects within microwells, devices were used in generator-collector mode. Chronoamperometry (Figure 3) was used to quantify the amplification and collection factors: around 1.3 and 0.67, respectively. All these results demonstrate that such microsystems could be effectively used for the electrochemical analysis of single cells.



Figure 1: SEM image of $9 \,\mu\text{m}$ diameter SiO₂ microwell showing the bottom layer recessed microdisk, the middle layer ring nanoelectrode



Figure 3: Chronoamperograms for recessed disk/ring electrodes in 1 mM Fc(MeOH) solution (respective electrical bias: 0.4 and 0V).



Figure 2: Comparison between simulated (solid line) and experimental (dotted line) cyclic voltammograms detected in 1 mM Fc(MeOH) solutions with the platinum ring nanoelectrodes in microwells