Utilizing Vertically Aligned Carbon Nanotubes Based Working Electrodes for Detection of Heavy Metal Ions and Thiols

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It is a common knowledge that toxic heavy metal ions (lead, cadmium and mercury) are able to enter to organisms and interfere several important metabolic processes. However, essential heavy metals have high affinity to biologically active molecules, and, under specific conditions, can alter key biochemical pathways. The presence of the metal ions induces and/or damages cell homeostasis, transcription, translation, cell dividing etc. Proteins and nucleic acids belong to the main and most important target of both essential and toxic metal ions. Among very sensitive analytical methods for detection of heavy metal ions belong the electrochemical ones. The classic electrochemical instruments are consisted of potentiostat/galvanostat with electrochemical cell including three electrodes (working, reference and auxiliary). However, the trend of analytical techniques is to miniaturize the whole instrument due to many advantages of small devices including portability, low costs and demands on service and operations, sufficient sensitivity and selectivity. Today, the solid electrodes are commonly used as a substitution of formerly used mercury drop electrode due to its toxicity. Moreover, the solid electrodes could be miniaturized easily. The problem is that in comparison to standard electrodes used in laboratories the miniaturized electrodes have much lower response due to their small electrode active area. Therefore it is necessary to preserve the active electrode area though the geometrical size of the electrode is miniaturized. One of the possibilities of preserving the active electrode area is to create nanostructures on the electrode surface.

In the last two decades, nanomaterials in the form of nanotubes and nanowires have begun to be reported as promising materials for wide field of applications. Such materials could be also used for fabrication of miniaturized electrodes. The nanostructured electrodes could be fabricated using several techniques. The easiest fabrication technique is to use a mixture of nanomaterial as a filler with a suitable vehicle, which could be deposited on the electrode substrate using screen-printing, drop-coating, dip-coating, spraying, etc [1-3]. The disadvantage of these nanocomposition-based electrodes is the irreproducible electrode surface with undefined active electrode area. The reproducible nanostructured electrode surface could be fabricated using lithography as a common tool for microelectronics devices implementation, anodization process for nanorods or nanotubes creation [4], etc. One of these techniques is creation of vertically aligned multiwalled carbon nanotubes (MWNTs) grown directly on the electrode surface using CVD.

The aim of this work was to fabricate several types of nanostructured working electrodes of three-electrode electrochemical sensor which is fabricated using standard thick film technology with working electrode made of direct grown MWNTs. These electrodes were compared on various stationary and flow electrochemical instruments for an easy and sensitive determination of heavy metal ions and biologically important thiol called phytochelatin2 (Fig. 1), which belongs to plant peptides playing key role in protection of cell compartments against heavy metals and can be easily detected by electrochemical instruments [5, 6]. The basic shape of the three-electrode electrochemical sensor and its real fabricated sample with gold (ESL 8844-G, Electroscience, UK) working electrode before MWNTs deposition is shown in the figure 1. The MWNTs have been deposited using plasma enhanced CVD direct grown on different electrode underlay on the atmospheric pressure. The deposition was done on the pure Au, Ag and Pt layer without any catalyst and on the 10 nm thick Fe catalyst using the same underlay. The SEM comparison of the electrodes fabricated on the Ag (ESL 9912-K) thick film paste with (up) and without (down) use of catalyst is shown in the figure 2. From the comparison it is clear that both electrodes are covered with vertically aligned MWNTs. Moreover, the electrode with catalyst consists of more clumps. We tested the following working electrodes: i) fabricated direct grown MWNTs based electrodes, ii) hanging mercury drop electrode, iii) carbon tip and connected them to three types of potentiostats: a standard potentiostat (Autolab), a commercially available miniaturized potentiostat (PalmSens) and a home-made potentiostat.

Primarily we aimed our attention at the detection of three metal ions, zinc(II), cadmium(II) and copper(II). Electrochemical detection of these ions at a mercury working electrode is routinely used. Redox signals for zinc(II) were observed at –0.9 V, for cadmium(II) at –0.6 V and for copper at–0.2 V versus Ag/AgCl 3M KCl. The calibration curves were strictly linear with detection limits on the order of hundreds of pM. Relative standard deviation did not exceed 2%. Differential pulse anodic stripping voltammetry using HMDE as a working electrode is among the most sensitive analytical techniques used for heavy metal ion detection. However, from a technological point of view, the non-solid electrodes have much lower miniaturization potential than solid electrodes, like silver, gold, carbon or platinum. The MWNTs electrodes nanostructuring is a promising technology for further miniaturization. Fabricated electrodes and carbon tips electrodes were sensitive enough to detect ions down to tens and hundreds nM, respectively. The measured voltammogram is shown in Fig. 4. Various potentiostats were also tested, but the effect of their usage on detection limits was in one order of magnitude. Further, we tested all used potentiostats and working electrodes on analysis of environmental samples. Besides, we analyzed phytochelatin2 by using the instruments and found that the thiol gave well developed response at all electrodes with detection limit app. units or subunits of µM.

Acknowledgement

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References

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Figures

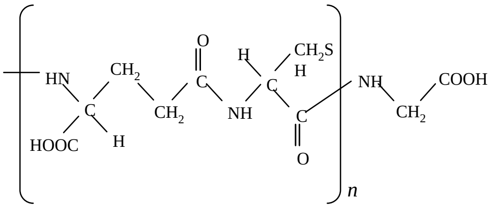

Fig. 1: Structure of phytochelatins.

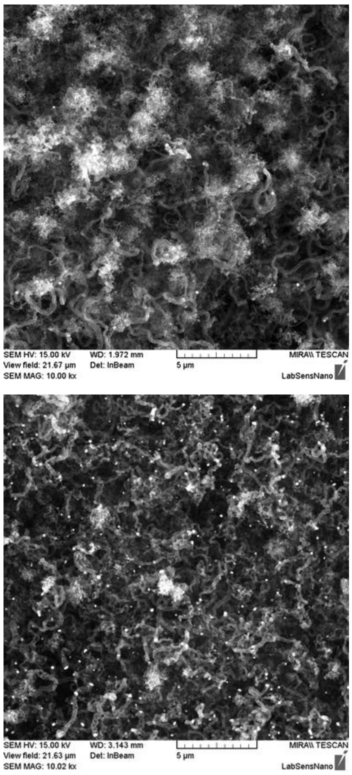

Fig. 2: SEM micrographs of the electrodes fabricated on the Ag based thick film paste with (left) and without (right) use of 10 nm Fe catalyst.

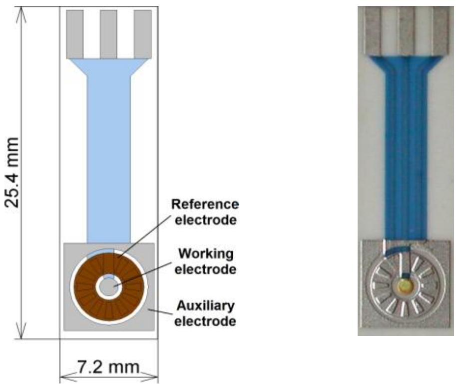

Fig. 3: Three electrode electrochemical sensor design (up) and its fabricated sample before MWNTs deposition (down).

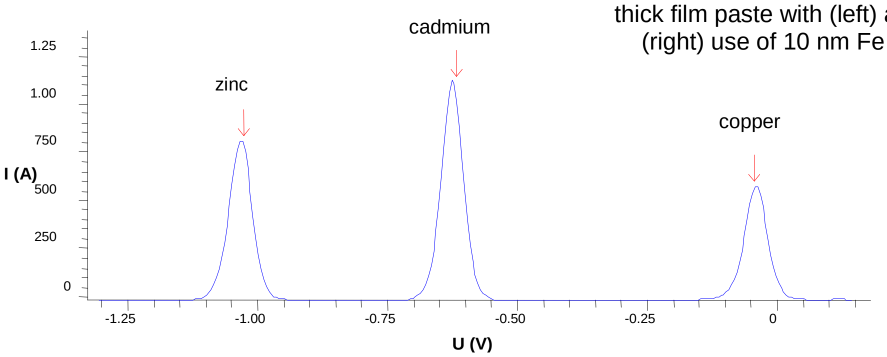

Fig. 4: Typical voltammogram of zinc, cadmium and copper, respectively.