

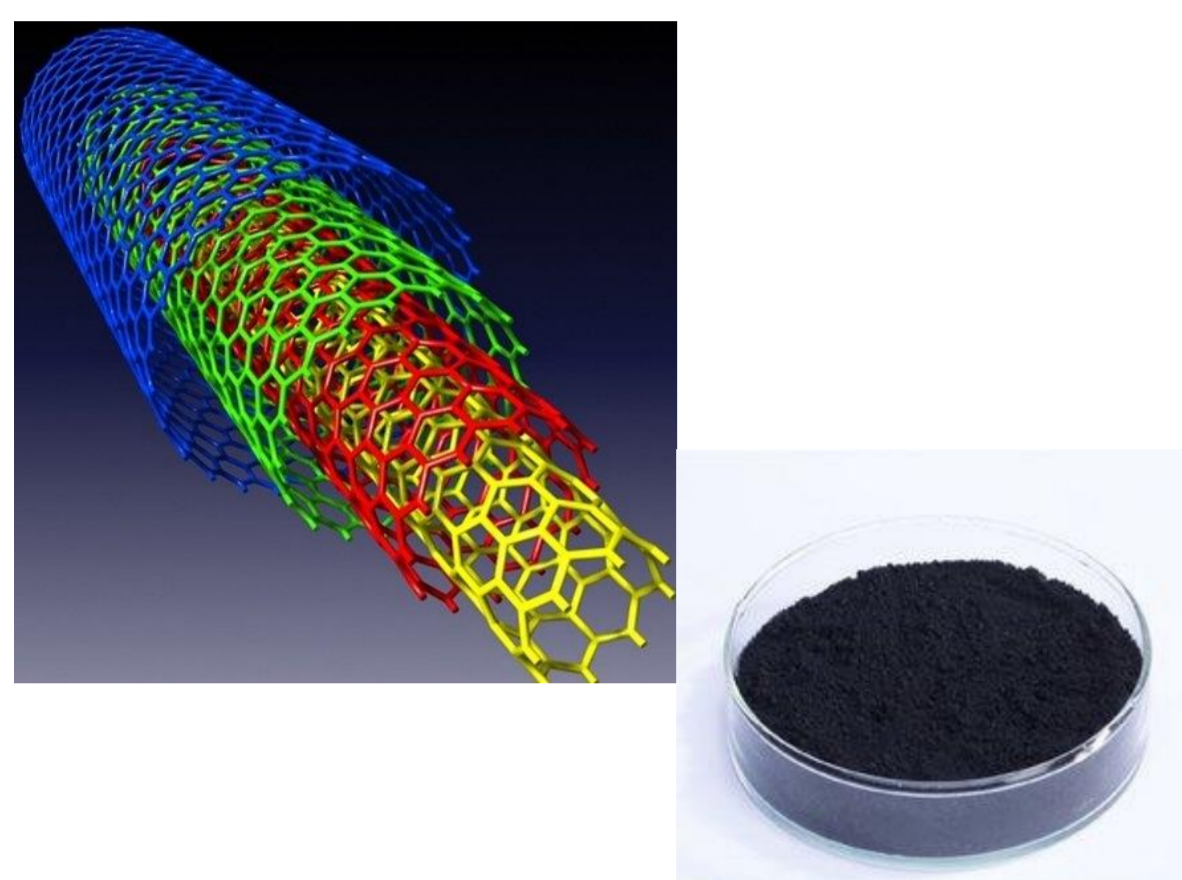
Screen-printed carbon electrode modified with carbon nanotubes as a simple and fast tool for determination of trace concentrations of lead ions



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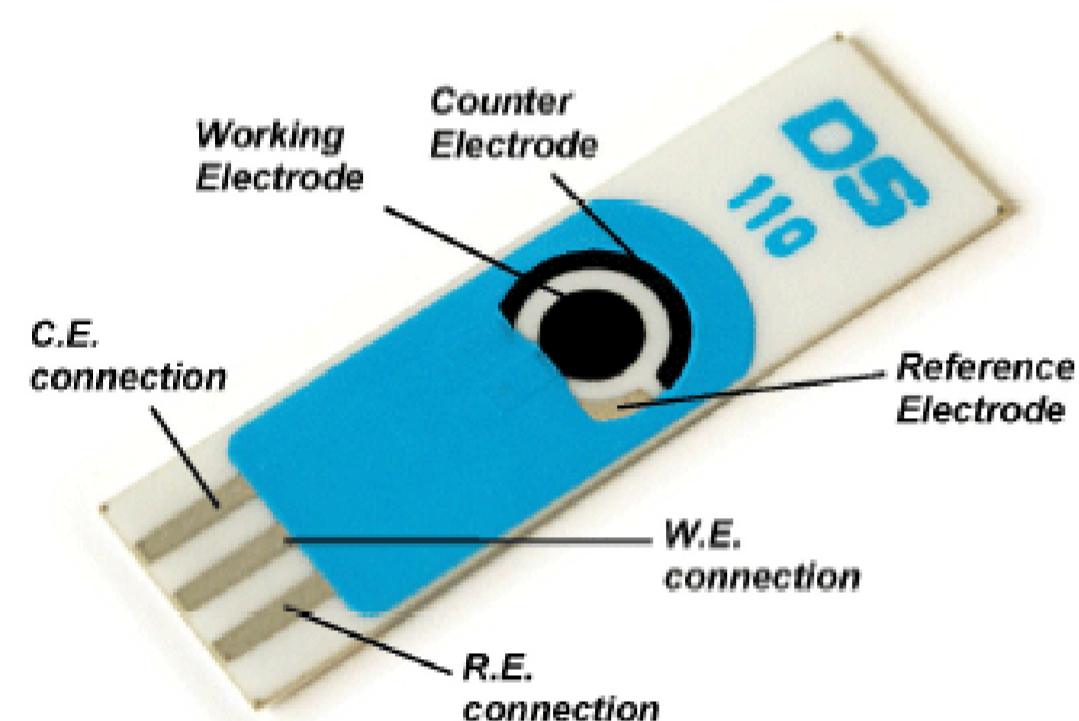
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[<https://www.indiamart.com/proddetail/multi-walled-carbon-nanotubes-21117659412.html>]

Electrochemical sensors are attractive analytical devices because they combine high sensitivity and simplicity with low instrumentation cost. Currently, a major challenge in electroanalysis is the development of miniaturized and portable electrochemical sensors made of alternative and inexpensive materials. These devices require only small volumes of samples and reagents, which is highly desirable from an economic and environmental point of view. A good solution to address this challenge is screen-printing technology as an established method for the preparation of portable chemical sensors. Screen-printed electrodes (SPEs) are widely used and the range of materials from which they are made continues to expand. One of these materials are carbon nanotubes (CNTs). They improve electrode properties important in voltammetric measurements, for example, increase the surface of the working electrode. Also they exhibit good chemical stability and excellent electrical conductivity. In our work, we proposed use of screen-printed carbon electrode modified with carbon nanotubes (SPE-CNTs) as a simple and fast tool for determination of trace concentrations of lead ions.



Screen-printed electrode (SPE)

[<https://nlab.pl/en/products/eurochemia/electrodes/screen-printed-electrodes.html>]

Composition of the solution in voltammetric cell:

- ✓ analysed sample
- ✓ 0.1 M HCl
- ✓ $1 \cdot 10^{-4}$ M Cu(II)

Anodic voltammetric procedure for Pb(II) determination

- copper film was plated and lead was accumulated on the SPE-CNTs simultaneously at the potential -1.5 V for 120 s
- differential pulse stripping voltammogram was recorded, after 5 s equilibration time, while the potential was scanned from -1.0 V to -0.3 V at a scan rate of 90 mV s^{-1} and pulse height of 100 mV
- electrochemical cleaning of the SPE-CNTs was performed at the potential -1.4 V for 10 s and next +0.2 V for 10 s. In this step the remains from the previous measurement were reduced to the metallic state and then were stripped from the electrode.

Preliminary measurements showed that there is no possibility of direct lead accumulation on the SPE-CNTs. Therefore, it was necessary to form a copper film on the SPE-CNTs by introducing Cu(II) ions into the measured solution. Figure 1 presents images of the morphology of SPE-CNTs surface unmodified (A) and after copper film modification (B).

The influence of the concentration of Cu(II) in the solution used to create the copper film on the surface of the SPE-CNTs on the lead signal was examined. As shown, the stripping signal of lead sharply increased with the Cu(II) concentration increase in the range between $5 \cdot 10^{-6}$ and $5 \cdot 10^{-5}$ M, at a higher concentration of Cu(II) the lead signal continued to increase, but slightly, to a concentration of $1 \cdot 10^{-4}$ M, and then remained constant.

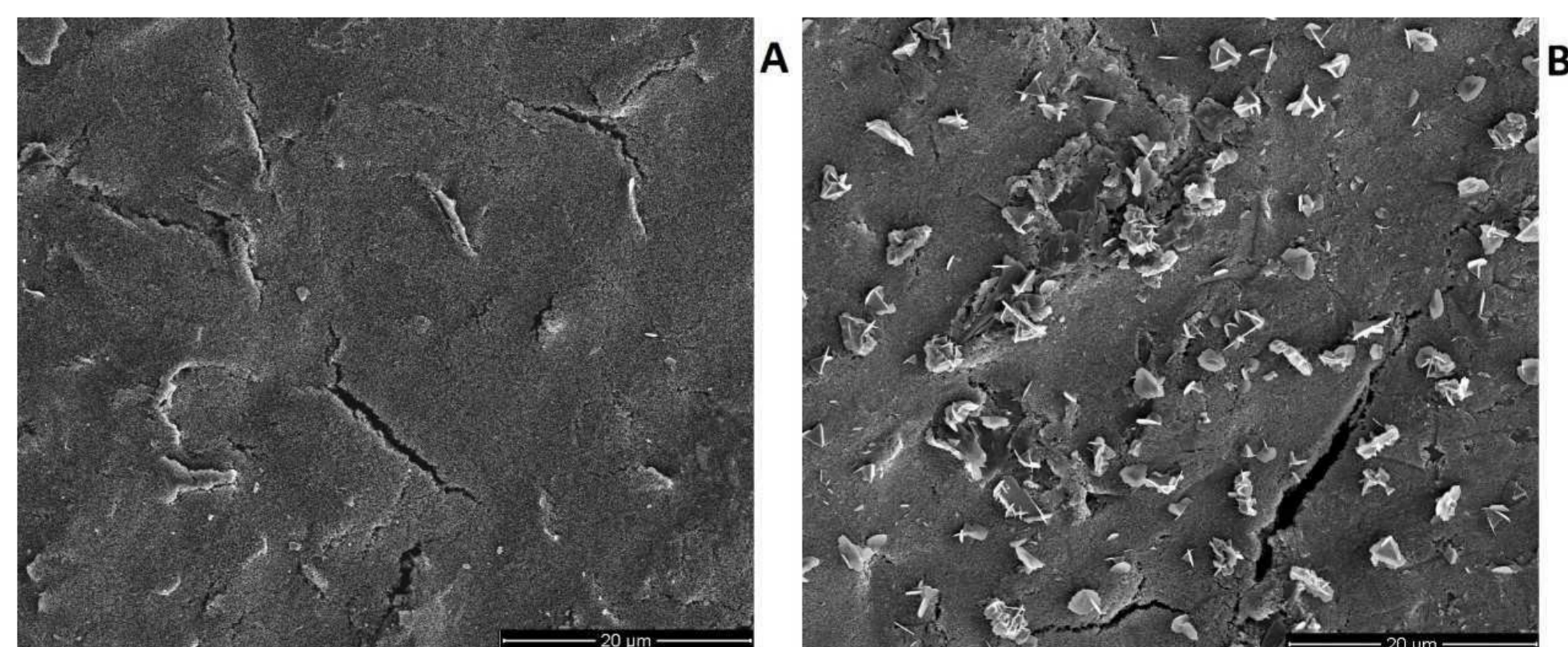


Figure 1. Images obtained through scanning electron microscope for the bare (A) and modified with copper film (B) SPE-CNTs working electrode.

Table. Analytical results of Pb(II) determination in natural water samples. The samples were examined after 10-fold dilutions using the standard addition method.

Sample	Pb(II) added [nM]	Pb(II) found [nM]	Recovery (%)
Tap water	20.00	19.68	98.4
Rain water	20.00	20.30	101.5
Bystrzyca river	20.00	19.06	95.3

Analytical performance of the Pb(II) determination

- ✓ limit of detection $2.4 \cdot 10^{-10}$ M
- ✓ linear range from $8 \cdot 10^{-10}$ M to $1 \cdot 10^{-7}$ M