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**Effect of electrochemical decoration of silver nanoparticles on arsenic detection performance**

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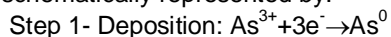
**Abstract**

Silver functionalized-synthetic zeolite-carbon nanotubes-epoxy composite (AgSZ-CNT) electrode was obtained by two-roll mill procedure and tested for arsenic (III) detection in water using anodic stripping voltammetry (ASV) technique. In order to improve the electroanalytical parameters for arsenic (III) detection, silver nanoparticles were electrodeposited under potentiostatic conditions on AgSZ-CNT electrode surface, resulting a new electrode named (Ag)AgSZ-CNT. Both electrodes were tested for arsenic (III) detection and better results were reached using (Ag)AgSZ-CNT electrode.

AgSZ-CNT was obtained by two roll mill procedure using multi-wall carbon nanotubes (MWCNTs) with average diameter of 9.5 nm and average length of 1.5  $\mu\text{m}$ , purchased from Nanocyl, Belgium. Synthetic A-type zeolite (SZ) was prepared using natural zeolite from Mirsid, Romania, with 68% wt. clinoptilolite as a silicon source and sodium aluminate as aluminium source, as we previous described [1]. The detailed description of carbon nanotubes based composite electrode preparation was also, previously reported by our group [2]. The electrodeposition of silver nanoparticles on electrode surface was achieved by maintaining the electrode potential at value of -0.4 V/SCE in 0.1 M  $\text{AgNO}_3$  solution for three seconds, which represents the optimum electrodeposition conditions. This optimum electrodeposition conditions was established in direct relation with the best useful signal for the detection of 1 mM arsenic (III). Electrochemical measurements were carried out using an Autolab PGSTAT 302N (Metrohm Autolab, The Netherlands) controlled with GPES 9.4 software and a three-electrode cell, with a saturated calomel reference electrode (SCE), a platinum counter electrode and the composite working electrode. The electrode surfaces were characterized morphologically by scanning electron microscopy (SEM) and SEM images are presented in Figure 1a and b.

These silver-based electrodes were tested for arsenic (III) detection taking into account the demand for the development of fast and sensitive detection method. Arsenic (As) is a common trace element present in water from natural and anthropogenic sources, which is characterized by high toxic properties and as consequence, it exhibits a very negative impact on the human health.

Most electrochemical methods involve anodic stripping voltammetry (ASV), which suppose two steps: first corresponding to reduction of arsenic (III) at the electrode surface for a certain time followed by the second step of electrochemically stripping from the electrode surface resulting a faradic response that is direct proportionally with arsenic concentration. The processes corresponding to these steps can be schematically represented by:



Carbon nanotubes-based electrodes have been reported for anodic stripping voltammetric detection method for various heavy metals determination [3]. Functionalized-zeolite-modified electrodes represent an alternative to the carbon-based electrodes that do not exhibit electrocatalytic effect towards target analyte or to improve its performance. [4]. In this context, to combine the properties of carbon nanotubes and silver effect towards arsenic detection, AgSZ-CNT and (Ag) AgSZ-CNT electrodes were prepared.

Cyclic voltammetry (CV), differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) techniques were used to elaborate the ASV-based detection schemes of arsenic (III) from aqueous solution. In Figure 2a and b are presented series of CVs recorded at both electrodes. The deposition potential of -0.4 V/SCE for the deposition time of 120 seconds represent the optimum operating conditions for the arsenic deposition step prior to the all anodic stripping voltammetric experiments. SWV technique operated at 0.2V modulation amplitude, 0.02 V step potential and 10 Hz frequency allowing the best sensitivity and the presence of the silver nanoparticles on the electrode enhanced the electroanalytical performance in relation with the sensitivity and the detection potential value (Table 1).

Table 1. The comparative electroanalytical performance for arsenic (III) detection for both electrodes

Electrode type	Technique	Potential value V / SCE	Sensitivity mA / mMcm <sup>-2</sup>	Correlation coefficient, R <sup>2</sup>
AgSZ-CNT	DPV	0.10	0.191	0.974
	SWV	0.14	2.558	0.981
(Ag)AgSZ-CNT	DPV	0.05	22.455	0.981
	SWV	0.09	23.254	0.996

### Acknowledgments

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### References

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### Figures

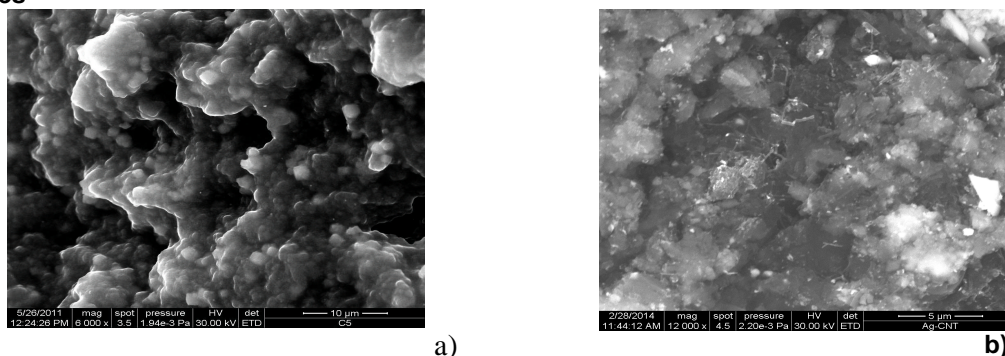


Fig. 1. SEM images of the surfaces of: a) AgSZ-CNT, b) (Ag)AgSZ-CNT electrodes

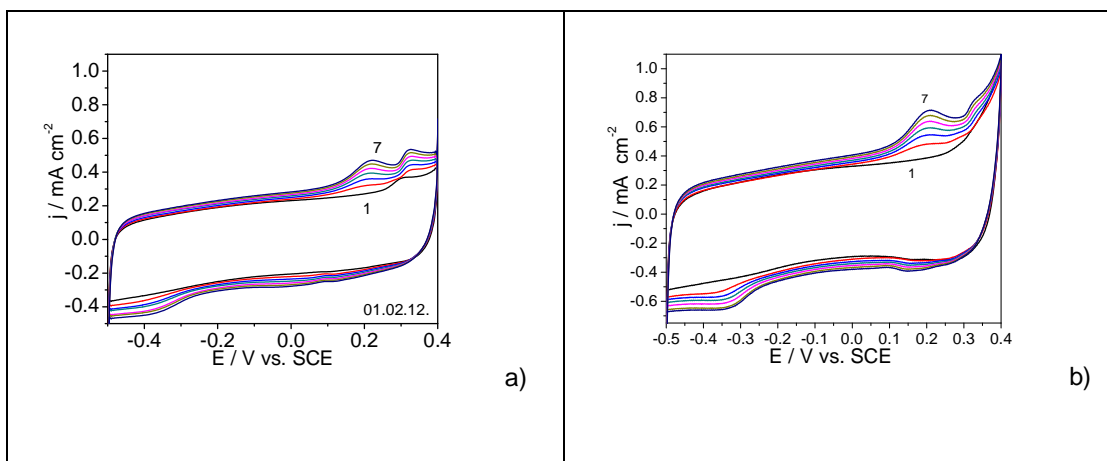


Fig. 2. CVs recorded composite electrode in 0.09 M Na<sub>2</sub>SO<sub>4</sub>+ 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte (curve 1) and in the presence of 0.2- 1.2 mM As concentration range (curves 2- 11) with a preconditioning of electrode at -0.4 V/SCE at deposition time of 120 s, potential scan rate: 0.05 Vs<sup>-1</sup>, potential range: -0.5 to +0.4 V/SCE, at: a) AgSZ-CNT, b) (Ag)AgSZ-CNT electrodes