chemistry proceedings

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Extended Abstract

Customized Screen-Printed Electrodes Based on Ag-Nanoseeds for Enhanced Electroanalytical Response Towards Cd(II), Pb(II) and As(V) in Aqueous Samples [†]

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Abstract: Electrochemical analysis based on screen-printed electrodes (SPEs) represents a great alternative to conventional analytical methods such as ICP-MS or LC-MS due to their portability, sensitivity, selectivity, and cost-effectiveness. In addition, the functionalization of SPEs with nanomaterials has been reported to provide an enhanced analytical performance. In this regard, silver nanoparticles (AgNPs) were synthesized and appropriately characterized, showing spherical silver nanoseeds (Ag-NS) with a diameter of 12.20 ± 0.04 nm. Using drop casting methodology, the synthesized AgNPs were used to modify screen-printed carbon nanofiber electrodes (SPCNFEs). Ag-NS deposition onto the electrode surface was confirmed by scanning electron microscopy (SEM). Furthermore, the analytical response of the modified electrodes (Ag-NS-SPCNFE) was evaluated for the determination of trace Pb(II), Cd(II), and As(V) using differential pulse anodic stripping voltammetry (DPASV), obtaining detection limits of 3.3, 3.7, and 2.6 μg L^{-1}, for Pb(II), Cd(II) and As(V), respectively. Finally, Ag-NS-SPCNFE was tested towards the determination of As(V) in a spiked tap water sample, showing a good agreement with concentrations determined by ICP-MS.

Keywords: screen-printed electrodes; Ag nanoparticles; anodic stripping voltammetry; lead determination; cadmium determination; arsenic determination

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Chem. Proc.* **2021**, 3, x. https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

Water contamination caused by heavy metal ions (HMIs) is a concerning issue due to their high toxicity, non-biodegradability, bioaccumulation, and adverse health effects in humans [1]. In particular, for As, Cd, and Pb, the World Health Organization (WHO) has established the maximum allowed concentration in drinking water as 10 μg L^{-1}, 3 μg L^{-1}, and 10 μg L^{-1}, respectively [2]. The determination of these low concentration levels requires very sensitive analytical techniques such as flameless atomic adsorption spectroscopy (FAAS) [3], inductively coupled plasma mass spectrometry (ICP-MS) [4,5], and hydride generation atomic fluorescence spectrometry (HG-AFS) [6]. However, these analytical techniques require expensive equipment and highly-trained personnel, long analysis time, and high operating costs.

In contrast, electrochemical techniques and anodic stripping voltammetry (ASV) allow the relatively fast determination of trace HMIs with easy-handling and low-cost equipment [7,8]. Stripping techniques present low detection limits and high sensitivity, which can be further improved by modifying the working electrode with nanomaterials [9–11]. In par-ticular, metallic nanoparticles (MNPs) can reduce the electron transfer resistance at the electrode surface, decreasing the electron transfer limited process and consequently catalyzing the electrode's response at low analyte concentrations [12–14]. Indeed, MNPs-modified sensors have been reported to allow the detection of arsenic [15,16], lead [17,18], and cadmium [19,20] at the level of a few μg L^{-1}, fulfilling the WHO guidelines for drinking-water quality [2]. These sensors were based on screen-printing technology, offering significant advantages over conventional voltammetric sensors such as low-cost, disposable character, portability, and commercial availability [1,21]. Thus, in this work, the voltammetric determination of HMIs based on the use of carbon-nanofiber-based screen-printed electrodes (SPCNFEs) modified with silver nanoparticles (Ag-NPs) is proposed. Ag-NPs were synthesized in the shape of silver nanoseeds (Ag-NS), and the resulting modified electrodes were microscopically and analytically characterized for the determination of As(V), Pb(II), and Cd(II) by means of differential pulse anodic stripping voltammetry (DPASV). In addition, the applicability to real sample analysis was demonstrated through the direct determination of As(V) in spiked tap water samples.

2. Materials and Methods

2.1. Apparatus

DPASV measurements were carried out with either a Multi Autolab/M204 Modular Multi Potentiostat/Galvanostat or an Autolab PGSTAT204, attached to a Metrohm 663 VA Stand, as well as a personal computer with NOVA 2.1 software package to control the potentiostat and perform the required data treatment. All the electrochemical instrumentations and software were acquired from Metrohm (Herisau, Switzerland).

A Crison Basic 20 pH meter (Hach Lange Spain, L'Hospitalet de Llobregat, Spain) was used for pH measurements.

Ag-NS and SPCNFE modified with Ag-NS electrodes were characterized using a JEM-2010 transmission electron microscope (TEM) from JEOL (Tokyo, Japan) and a Gemini scanning electron microscope (SEM) from ZEISS® (Jena, Germany), respectively. Size distribution histograms were calculated using the Image-J version 1.51m software by the National Institute of Health (NIH, Bethesda, MD, USA).

ICP-MS measurements were carried out by means of inductively coupled plasma mass spectrometer model 7800 by Agilent Technologies (Santa Clara, CA, USA).

Commercial SPCNFEs, including working (4 mm disk), counter, and reference electrodes, were purchased from Dropsens (Llanera, Spain).

2.2. Preparation of Working Electrodes

The working electrode (WE) was a SPCNFE modified with silver nanoseeds (Ag-NS-SPCNFE). Ag-NS were first synthesized following a seed-mediated methodology asdescribed elsewhere [11,22]. Then, SPCNFEs were modified by drop casting, dropping 40 μL of Ag-NS onto the working electrode, and evaporating the solvent at 50 °C for 30 min.

2.3. Electrochemical Measurements

DPASV measurements of Pb(II) and Cd(II) were carried out at a deposition potential (E_d) of −1.4 V, applied under stirring conditions during a deposition time (t_d) of 180 s in 0.1 mol L^{-1} acetate buffer (pH 4.5) and scanning the potential from -1.4 to 0.0 V. For As(V) determination, the experimental conditions used were E_d of -1.3 V and t_d of 120 s in 0.01 mol L^{-1} HCl pH 2 with a potential scan from -1.3 to -0.65 V.

A step potential of 5 mV, a pulse time of 50 ms, and a pulse amplitude of 50 mV were employed in all cases. All experiments were performed at room temperature (22 ± 1 °C) and without oxygen removal.

For real sample analysis, tap water samples were collected from the local water distribution network in Barcelona (Spain) and spiked with 20 µg L^{-1} of As(V). Prior to electrochemical analysis, water samples were diluted and acidified with 0.01 mol L^{-1} of HCl (pH 2.0), resulting in a final concentration of 10 µg L^{-1} of As(V). Sample analysis was carried out by means of the standard addition method, performing four successive As(V) additions from a standard solution of 1 mg L^{-1}. DPASV measurements were recorded under the above-mentioned electrochemical conditions.

3. Results

3.1. Microscopic Ccharacterization

Ag-NS synthesis was microscopically confirmed by both SEM (Figure 1a) and TEM (Figure 1b). As it can be deduced from the TEM image, most Ag-NS presented a spherical shape. On the other hand, SEM images were used to calculate the corresponding size distribution histogram (Figure 1c), which was computed from 400 Ag-NSs. The obtained results show that the synthesized Ag-NS presented an average diameter of 12.2 ± 0.4 nm. These structures are in good agreement with the reported shapes of Ag-NPs [23,24].

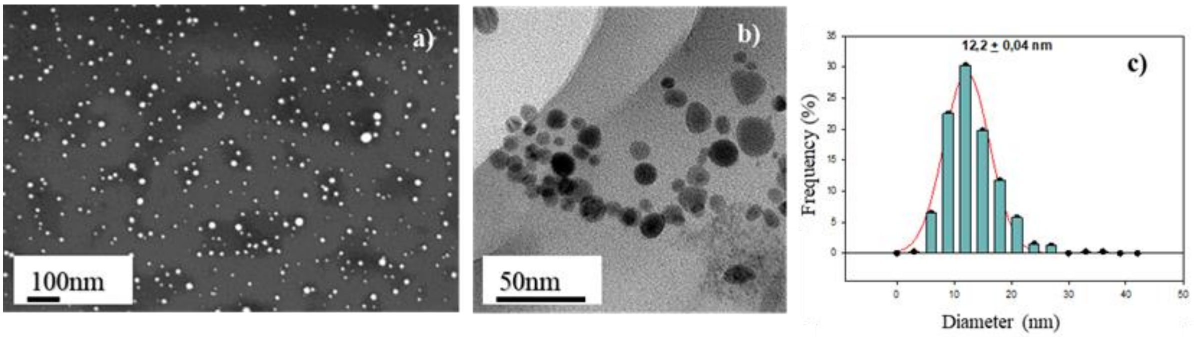

Figure 1. Microscopic characterization of Ag-Nanoseeds (a) SEM micrograph, (b) TEM micrograph and (c) corresponding size distribution histogram [14].

SEM micrographs were also obtained for a bare SPCNFE (Figure 2a) and an Ag-NS-SPCNFE (Figure 2b) to assess the modification of SPCNFEs by drop casting. Compared to the non-modified carbon nanofiber surface of the bare electrode, Ag-NS can be spotted as white dots deposited onto the carbon nanofibers in the modified electrode (Ag-NS-SPCNFE), thus confirming the successful modification of the working electrode.

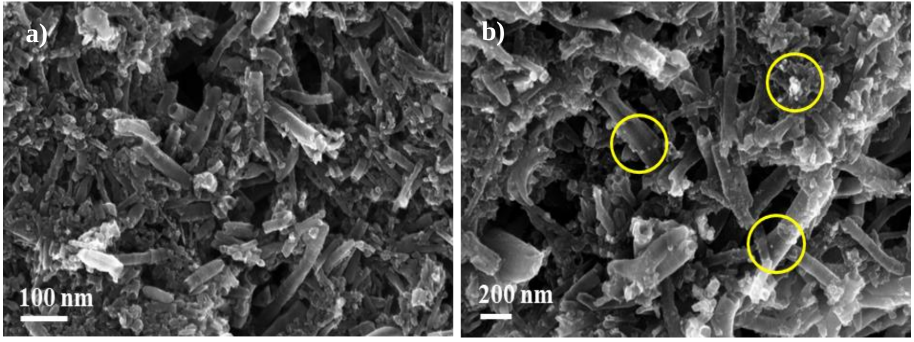

Figure 2. SEM micrographs for (a) Bare SPCNFE, and (b) Ag-NS-SPCNFE modified using the drop casting methodology [11,14].

3.2. Electrochemical Characterization

DPASV measurements were carried out in solutions containing either Pb(II), Cd(II), or As(V). Well-defined voltammetric peaks were obtained in all cases, with peak potentials of ca. -0.65 V, -0.75 V, and -1.0 V for Pb(II), Cd(II), and As(V), respectively (see figure 3a).

Individual calibration curves of Pb(II), Cd(II), and As(V) were obtained by DPASV by increasing metal ion concentration in the ranges 1.9 to 150.0 μg L^{-1}, 0.6 to 120.6 μg L^{-1}, and 1.0 to 50.1 μg L^{-1}, respectively. The obtained data were used to calculate the corresponding analytical parameters (i.e., sensitivity, limit of detection (LOD), limit of quantifycation (LOQ), and linear range), which are displayed in Table 1.

From this data, LODs and LOQs were calculated by using the Miller and Miller procedure [25,26].

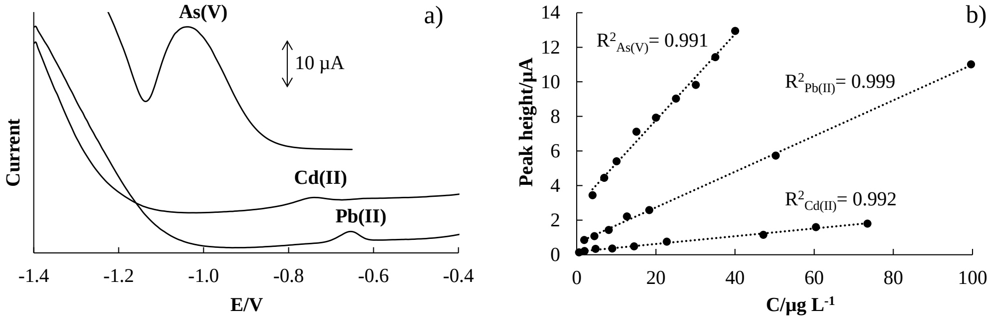

Figure 3. (a) DPASV voltammograms of Pb(II), Cd(II), and As(V) at 25 μg L^{-1} and (b) their calibration plots at the previously mentioned conditions using Ag-NS-SPCNFE.

Table 1. Calibration data for the individual determination of Pb(II), Cd(II), and As(V) using Ag-NS-SPCNFE and the corresponding buffer and DPASV parameters (see the experimental section for more details).

Analyte	LOD (μg L^{-1})	Linear range (μg L^{-1})[a]	R^2	Sensitivity (nA μg^{-1} L)[b]
Pb(II)	3.3	11.00-99.6	0.999	103 (1)
Cd(II)	3.7	12.2-73.4	0.992	22 (1)
As(V)	2.6	8.9-40.0	0.991	260 (10)

[a] The lowest value of the linear range corresponds to the LOQ. [b] The standard deviations are expressed in parentheses

As shown in Table 1, good linear response between the peak heights and the concentration of the different analytes was achieved using the Ag-NS-SPCNFE. LODs were at μg L^{-1} levels in all cases, and similar or even lower to other LODs reported in the literature. For example, LODs of 3.30 and 4.43 μg L^{-1} for Pb(II) and Cd(II), respectively, were reported using a graphene/polyaniline/polystyrene (G/PANI/PS) nanoporous fiber modfied screen-printed carbon electrode [27]. Also, the obtained LOD for As(V) is considerably lower than that reported using boron-doped diamond electrodes and ASV (12 μg L^{-1}) [28]. However, it is important to mention that Ag-NS-SPCNFE for the determination of As(V) presented a more restricted linear range in which the highest value is limited to a lower concentration value (until 40.0 μg L^{-1}) compared to the one reached by Nagaoka *et al.* (until 100 μg L^{-1}) [28].

In terms of sensitivities (nA μg^{-1} L), which were calculated as the slope of the calibration curves, Ag-NS-SPCNFE exhibited higher sensitivity toward As(V) (260 nA μg^{-1} L). In the case of Pb(II) and Cd(II), the sensitivities were significantly lower (103 and 22 nA μg^{-1} L, respectively).

3.3. Application to The Analysis of Spiked Tap Water

The applicability of Ag-NS-SPCNFE for real sample determination was evaluated through the determination of As(V) in a spiked tap water sample. The determination of As(V) was performed in triplicate by the standard addition calibration method. Representative voltammograms are shown in Figure 4. As it can be observed, a well-shaped As(V) peak and a good correlation between peak area and concentration were acquired. Sample concentration calculated by extrapolation was 10.04 µg L^{-1} (SD:0.37 µg L^{-1}), which is in good agreement with values obtained by ICP-MS (10.7 µg L^{-1}, SD:0.20 µg $µL^{-1}$), as an analytical reference technique. These results confirm the suitability of Ag-NS-SPCNFE for the analysis of real samples.

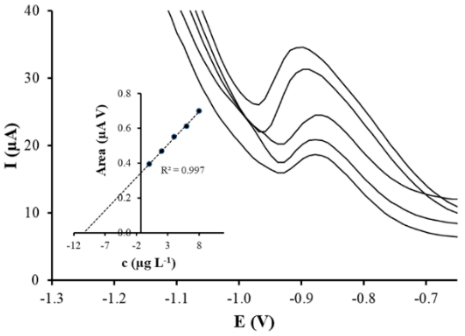

Figure 4. DPASV measurements of As(V) in a spiked tap water sample on Ag-NS-SPCNFE at pH 2.0 applying an E_d of -1.30 V and a t_d of 120 s. Inset: As(V) standard addition plot [11].

4. Conclusions

In this work, a DPASV method for the determination of trace Pb(II), Cd(II), and As(V) based on the modification of SPCNFE with Ag-NS has been proposed. The Ag-NSs were synthesized, microscopically characterized, and used for the modification of SPCNFEs.

The analytical performance of the modified electrode was evaluated for the three studied analytes. It was demonstrated that Ag-NS-SPCNFE is suitable for determining Pb(II), Cd(II), and As(V) at low µg L^{-1} levels, showing wider linear ranges for Pb(II) and Cd(II) but lower sensitivities as compared to As(V). Regarding previous studies of Pb(II), Cd(II), and As(V) determination, the LODs achieved in this investigation are equal or lower than other LODs previously reported.

The suitability of Ag-NS-SPCNFE for real sample analysis was demonstrated for the determination of As(V) in spiked water samples, achieving comparable results to those obtained by ICP-MS measurements with good reproducibility.

Funding: This research has been funded by Ministerio de Ciencia, Innovación y Universidades, and European Union Funds for Regional Development (FEDER), projects CTM2015-68859-C2-2-R and CGL2017-87216-C4-3-R, as well as by the Generalitat de Catalunya (Project 2017SGR312 and 2017SGR-311).

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