

# Antimonene-Modified Screen-Printed Carbon Nanofibers Electrode for Enhanced Electroanalytical Response of Metal Ions

Maria A. Tapia <sup>1</sup>, Clara Pérez-Ràfols <sup>1,2</sup>, Filipa M. Oliveira <sup>3</sup>, Rui Gusmão <sup>3,\*</sup>, Núria Serrano <sup>1,2,\*</sup>, Zdeněk Sofer <sup>3</sup>, and José Manuel Díaz-Cruz <sup>1,2</sup>

<sup>1</sup> Department of Chemical Engineering and Analytical Chemistry, Universitat de Barcelona (UB), Martí i Franquès 1-11, 08028-Barcelona, Spain; mtapia@ub.edu (M.A.T.); claraperezrafols@ub.edu (C.P.-R.); josemanuel.diaz@ub.edu (J.M.D.-C.)

<sup>2</sup> Water Research Institute (IdRA), Universitat de Barcelona (UB), Martí i Franquès 1-11, 08028-Barcelona, Spain

<sup>3</sup> Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic; filipa.oliveira@vscht.cz (F.M.O.); zdenek.sofer@vscht.cz (Z.S.)

\* Correspondence: rui.gusmao@vscht.cz (R.G.); nuria.serrano@ub.edu (N.S.)

## Materials and methods

### *Reagents and solutions*

Hydrochloric acid (Suprapur grade, 30%) was acquired from Merck (Darmstadt, Germany). Isopropanol (IPA) was supplied by Sigma-Aldrich (Germany). Gray antimony granules of 5 N purity were acquired from STREM (France).

Cd(II) and Pb(II) standard solutions were prepared daily by correct dilution of stock solutions 0.01 mol L<sup>-1</sup>, prepared from the corresponding nitrate salts, and standardized by complexometric titration.

Estuarine water sample LGC6016 was used as a certified reference material, acquired from LGC Standards (England, UK). According to the standard's specification, this water sample was collected from an industrialized area, the Severn Estuary (near Avonmouth, UK). The collected sample was filtered by using a membrane of 0.45 µm pore size, and was then acidified with HNO<sub>3</sub> until pH 2. The certified sample was stored under refrigeration prior to analysis. The certified values of constituents are: Cd= 101(2) µg Kg<sup>-1</sup>; Cu= 190(4) µg Kg<sup>-1</sup>; Pb= 196(3) µg Kg<sup>-1</sup>; Mn= 976(31) µg Kg<sup>-1</sup>; and Ni= 186 (3) µg Kg<sup>-1</sup>. Indicative values of other constituents are: Ca= 220 mg L<sup>-1</sup>, Mg= 570 mg L<sup>-1</sup>, K= 180 mg L<sup>-1</sup>, Na= 4700 mg L<sup>-1</sup>, and Zn= 55 µg L<sup>-1</sup>.

Ultrapure water (with a resistivity of 18,4 M Ω cm) obtained from a Milli-Q reference A+ water purification system (Millipore, France) was used in all experiments.

### *Electrochemical instrumentation*

Differential pulse anodic stripping voltammetric (DPASV) measurements were conducted with an electrochemical system arranged by a µAutolab potentiostat System type III acquired from Ecochemie (Utrecht, Netherlands), attached to a 663 VA Metrohm Stand (Herisau, Switzerland) and a personal computer with the GPES 4.9 software (Ecochemie, Netherlands) for data acquisition.

SPCE (Ref. DRP 110) and SPCNFE (Ref. 110 CNF) were purchased from Metrohm DropSens (Oviedo, Spain). The working electrode was connected to the electrochemical system by a flexible cable (ref. CAC) purchased from Metrohm DropSens.

### *Liquid-phase exfoliation of gray antimony*

Bulk antimony and isopropanol were added to an agar mortar and grounded for 10 min. Grinding solvent evaporation was compensated with the addition of extra

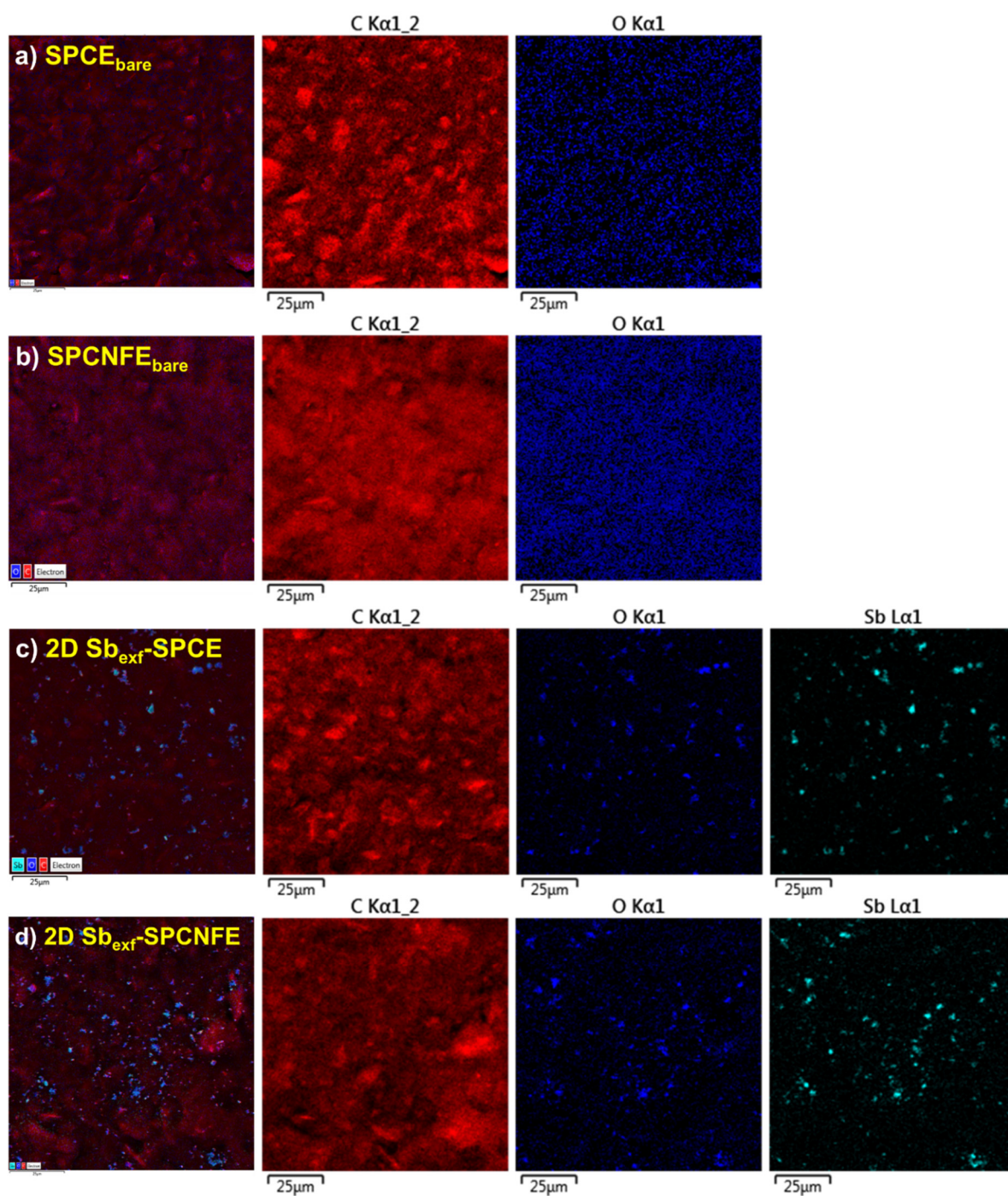
isopropanol. The obtained sample (*ca.* 500 mg) was added to 100 mL of IPA 1:1 H<sub>2</sub>O previously deaerated with N<sub>2</sub>, and then submitted to high shear rate force using a T 18 digital Ultra-Turrax mixer (IKA, Wiesenweg, Germany) with a dispersion stainless-steel foot S18N-19 G at 18 krpm for 120 min. In order to prevent overheating, the exfoliating procedure was conducted under an inert atmosphere and kept at room temperature by water circulation. The obtained suspension was centrifuged at 1.5 krpm for 10 min, and then filtered with a 0.20  $\mu$ m pore size nylon filter. The resulting material was dried and stored under a vacuum until further use.

#### *Characterization of materials and electrodes*

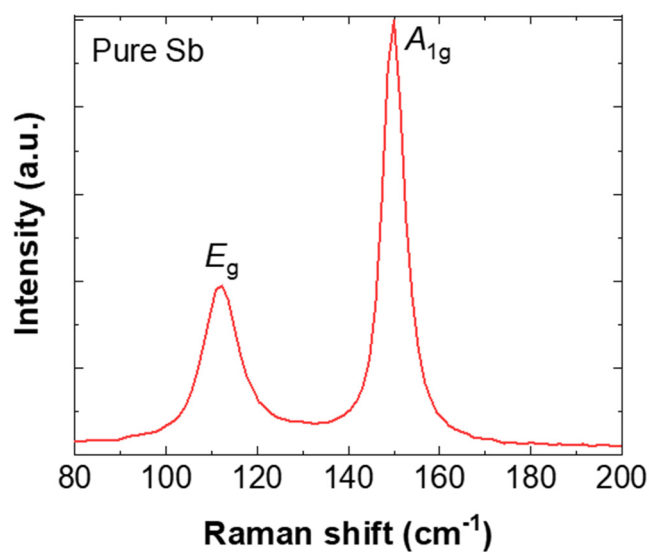
The morphology of 2D materials and SPEs was examined by scanning electron microscopy (SEM) with a FEG electron source (Tescan Lyra dual-beam microscope) with a 5 kV acceleration voltage. Elemental composition was investigated by energy-dispersive X-ray spectroscopy (EDX) using an X-Max<sup>N</sup> detector from Oxford Instruments and the AZtecEnergy software with a 20 kV acceleration voltage. SEM-EDX analysis was directly performed from modified SPEs.

An InVia Raman microscope (Renishaw, England) was used for Raman spectroscopy measurements in backscattering geometry with a charge-coupled device (CCD) detector. An Nd:YAG laser (532 nm, 50 mW) with an applied power of 1% and 20 $\times$  objective were used for the measurements. The data were directly collected from modified SPEs in the Raman range of 40–1800 cm<sup>-1</sup> at room temperature.

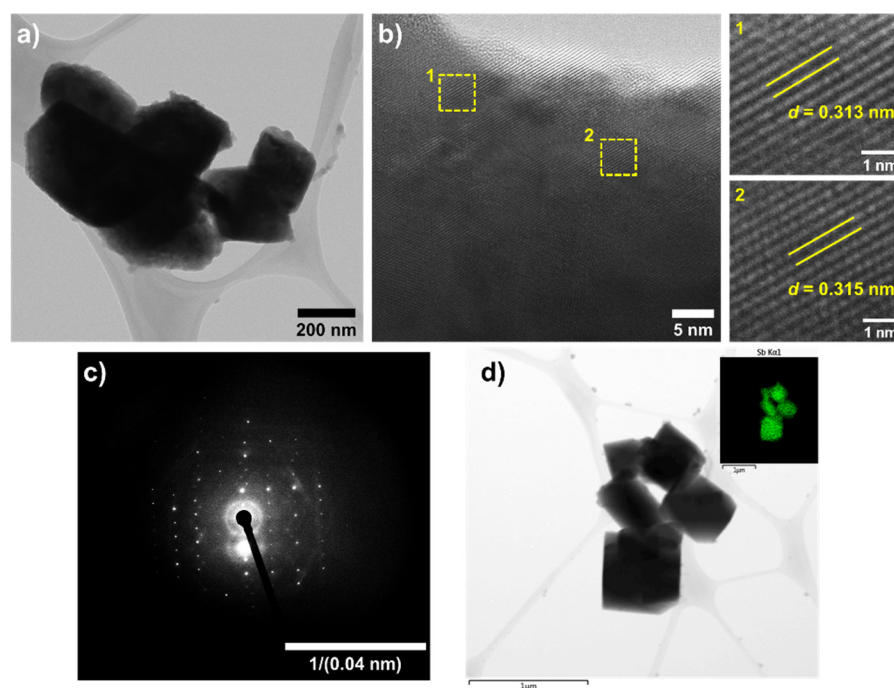
Transmission electron microscopy (TEM) micrographs were obtained using a JEOL JEM-1010 instrument at an accelerating voltage of 200 kV. Pictures were taken by SIS MegaView III digital camera (Soft Imaging Systems) and analyzed by AnalySIS v. 2.0 software. Elemental maps were acquired with an SDD detector X-MaxN 80 TS from Oxford Instruments (England). A suspension was prepared from the exfoliated material, and 3  $\mu$ L were drop-casted on a TEM grid (Cu, 200 mesh, Formvar/carbon from TED PELLA, Inc.) and dried overnight in a vacuum oven at 50 °C.



**Figure S1.** EDX elemental mapping of the elements in a) SPCE<sub>bare</sub>, b) SPCNFE<sub>bare</sub>, c) 2D Sb<sub>exf</sub>-SPCE, and d) 2D Sb<sub>exf</sub>-SPCNFE.



**Figure S2.** Raman spectrum of pure bulk antimony with a representation of phonon frequencies of the  $E_g$  and  $A_{1g}$  modes at 112.2 and 150.0  $\text{cm}^{-1}$ , respectively.



**Figure S3.** Characterization of 2D  $\text{Sb}_{\text{exf}}$ : a) TEM and b) HRTEM images with a detail showing well-defined layered phases in 2D  $\text{Sb}_{\text{exf}}$ . c) SAED pattern. d) STEM image with inset of mapping of Sb element. Scale bars represent 1  $\mu\text{m}$  in STEM and EDX images.

**Table S1.** Summary of various electrodes based on the use of antimony nanomaterials, carbon nanomaterials, and the hybrid bismuthene/graphene-modified GC electrode for the determination of Cd(II) and Pb(II).

Electrode	Technique	Linear range ( $\mu\text{g L}^{-1}$ )		LOD ( $\mu\text{g L}^{-1}$ )		Deposition time (s)	Ref.
		Cd(II)	Pb(II)	Cd(II)	Pb(II)		
Bulk SbNP-MWCNT-CPE	SWASV	10-60	10-60	0.77	0.65	120	[1]
<i>In situ</i> Sb-SPCE	DPASV	9.5-100.3	17.5-100.9	2.8	5.3	120	[2]
<i>In situ</i> Sb-SPGPHE	DPASV	13.2-100.3	28.8-100.9	4.0	8.6	120	
<i>In situ</i> Sb-SPMWCNTE	DPASV	8.6-100.3	14.7-100.9	2.6	4.4	120	
<i>In situ</i> Sb-SPCNFE	DPASV	3.7-100.3	6.9-100.9	1.1	2.1	120	
<i>In situ</i> Sb-GO-SPCE	SI-SWASV	33.7-168.6	20.7-269.36	6.07	5.39	100	[3]
Bulk Sb <sub>2</sub> O <sub>3</sub> -MWCNT-CPE	LSASV	80-150	5-35	16.77	6.12	600	[4]
Sb <sub>2</sub> Te <sub>3</sub> -SPCE	DPASV	89.5-161.5	57.5-157.3	26.9	17.3	240	[5]
Sb <sub>2</sub> Se <sub>3</sub> -SPCE	DPASV	14.5-18.5	9.8-49.4	4.3	3.0	240	
Sb <sub>2</sub> S <sub>3</sub> -SPCE	DPASV	15.4-104.0	6.0-49.4	4.6	1.8	240	
2D Sb <sub>exf</sub> -SPCE	DPASV	9.1-132.7	1.1-128.3	2.7	0.3	240	
2D bismuthene-graphene/GCE	SWASV	1-30	1-30	0.3	0.3	180	[6]
2D Sb <sub>exf</sub> -SPCNFE	DPASV	2.9-85.0	0.3-82.0	0.9	0.1	240	This work

CPE: carbon paste electrode; DPASV: differential pulse anodic stripping voltammetry; GCE: glassy carbon electrode; GO: graphene oxide; LSASV: linear sweep anodic stripping voltammetry; MWCNTs: multiwall carbon nanotubes; 2D Sb<sub>exf</sub>: antimonene; SbNP: antimony nanoparticles; SI: sequential injection; SPCE: screen-printed carbon electrode; SPCNFE: screen-printed carbon nanofiber electrode; SPGPHE: screen-printed graphene electrode; SPMWCNTE: screen-printed multiwalled carbon nanotubes electrode; SWASV: square wave anodic stripping voltammetry.

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