Electrochemical sensors: from the active material to the microfabrication of a device

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INTRODUCTION

Sensors find widespread uses from industrial production to security, food analysis and environmental monitoring.

The innovation in this area is driven by the search of systems that can provide lower detection limits, improved sensitivity, real-time on-site measurements and operation by non-specialists.

Electrochemical sensors are especially suitable because of their fast response, high sensitivity, simplicity of the instrumentation, as well as their relatively low cost and low power consumption.

Our project is focused on developing electrochemical sensors for the analysis of heavy metals.

Technological issues to be solved are the fabrication of inexpensive, robust, reliable and efficient miniaturized sensors free from hazardous elements.

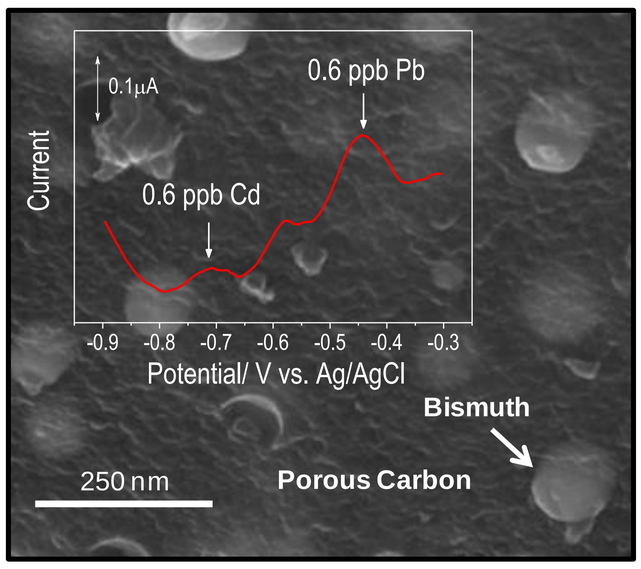
Active Material[1]:

Sol–gel chemistry was used to synthesize **composites of porous carbon containing bismuth nanoparticles.**
These materials displayed performance beyond the state-of-the art in the sensitive stripping voltammetric detection of heavy metals in water targeted by the recent EU regulations.

Specifically, for cadmium and lead we achieved the detection of 0.6 ppb, which is of the order of the maximum allowance concentration following the environmental quality standards (MAC-EQS) (i.e. between 0.45 ppb and 1.5 ppb Cd depending on water hardness class) and well below the threshold concentrations established for drinking water quality (5 ppb of Cd and 10 ppb of Pb).

The excellent behaviour of the nanocomposites is reflected by the low heavy metal concentration measured for a short accumulation time (180 s) in an overall assay time of less than 300 s.

Porous Bismuth-Carbon Nanocomposites for the Sensitive Detection of Heavy Metals

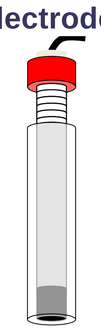


1 Facile Synthesis of Porous Bismuth-Carbon Nanocomposites for the Sensitive Detection of Heavy Metals
Marti Gich*, Cesar Fernandez-Sanchez*, Liviu Cosmin Cotet, Pengfei Niu, Anna Roig, Journal Materials Chemistry A 1 (2013) 11410-11418

Electroanalytical assessment of heavy metals in real water samples of different origins[2]:

Bismuth nanoparticle-porous carbon paste electrodes were employed in the analysis of real samples such as tap water, ground water, polluted waters from an influent and effluent of an urban wastewater treatment plant and polluted river water due to acid mine drainages.
Results are in good agreement with the reference values (see Table).

Working electrode



Paste of milled porous carbon + paraffin

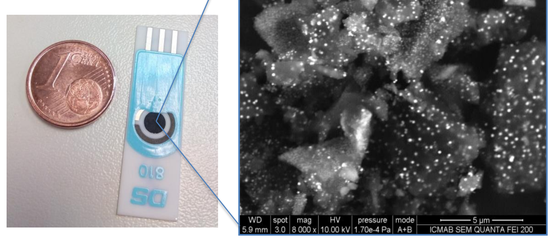
Results of the analyses of five real water samples using the Bi-CPE

Sample	Added/Reference/ICP-MS values (ppb)			Bi-CPE sensor values (ppb)		
	Cd(II)	Pb(II)	Ni(II)	Cd(II)	Pb(II)	Ni(II)
Tap water	10	10	10	9.2 ± 1.0	9.1 ± 0.7	9.4 ± 0.9
Polluted water - influent	5	5	10	4.7 ± 0.6	5.1 ± 0.8	≤ LOD
Certified water	2.78	7.98	27	≤ LOD	7 ± 2	25 ± 4
Polluted water – effluent	< 2	< 2	7.8	3.7 ± 0.8	1.3 ± 0.4	≤ LOD
Heavily polluted–mine drainages	55 ± 3	38 ± 2	273 ± 14	≤ LOD	40.9 ± 0.6	262 ± 73*

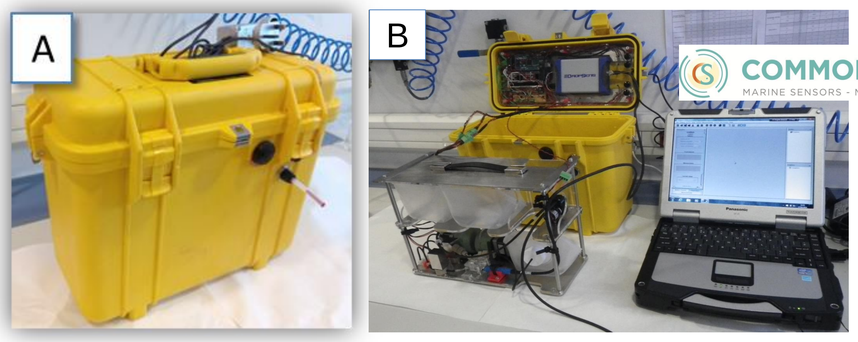
* analyzed by the interpolation method

2 Highly Sensitive, Fast Electrochemical Detection of Heavy Metals in Waters with Bismuth Nanoparticle-Porous Carbon Electrodes
Pengfei Niu, César Fernández-Sánchez*, Martí Gich*, Carlos Ayora and Anna Roig, *Electrochimica Acta* 165 (2015)155-161

Bismuth nanoparticle-porous carbon paste electrodes were processed as screen-printed electrodes[3] and tested in a marine sensor prototype



Screen-printed electrodes based on porous carbon-Bi & porous carbon-Au for the simultaneous detection of below 0.5 ppb of Pb, Cd, Hg, Cu in seawater.



A) Water tight cage with the fluidic system prototype. B) Fluidic system containing a wall-jet electrochemical fluidic cell where the screen-printed electrode is placed and connected to a laptop.

3 Screen-printed electrodes made of a bismuth nanoparticle porous carbon nanocomposite applied to the determination of heavy metal ions
Pengfei Niu, César Fernández-Sánchez,* Martí Gich,* Carla Navarro-Hernández, Pablo Fanjul-Bolado, Anna Roig Microchimica Acta 183, 2 (2016) 617

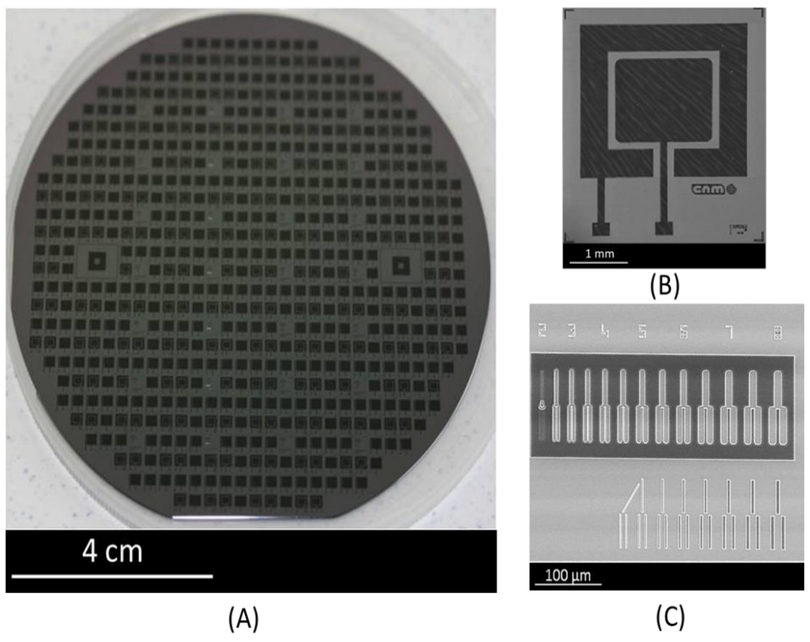
Miniaturized thin-film carbon-silica electrodes to produce highly robust electrochemical microdevices[4,5]

Carbon-silica thin films on silicon substrates could be subjected to several processes that combined lithography, etching, and pyrolysis to yield thin film electrodes at wafer scale.

The presence of silica in the electrode material promotes strong interfacial adhesion to the substrate, dramatically increasing the number of measurements a single electrode can withstand without loss of performance. The modification of the electrode surface with metal nanoparticles allowed the sensitive detection of heavy metal ion pollutants.

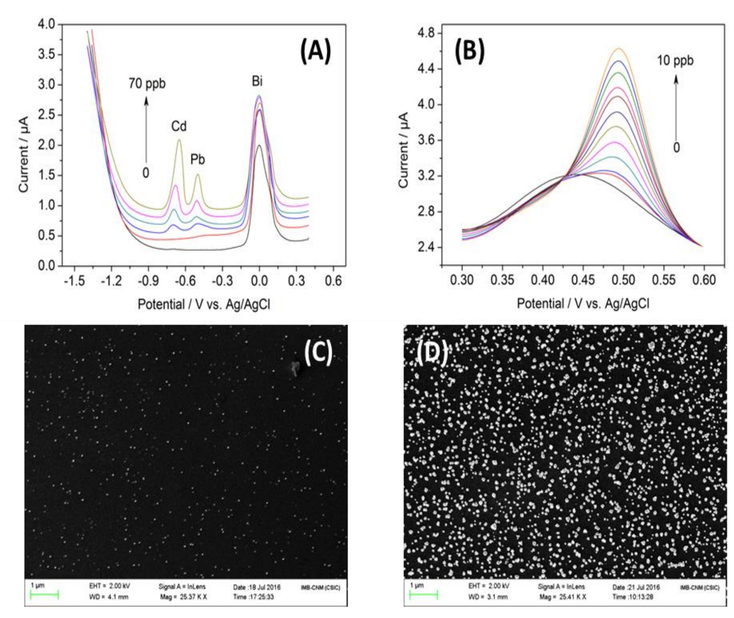
Overall, the C/SiO_2 thin-film electrodes show clear advantages of ease-of-use, robustness, reusability, long-term stability, and reproducibility, which make them ideal sensing platforms for analytical applications and may find uses in other areas such as energy conversion and storage or electrocatalysis.

Thin-film electrode patterns prepared by photolithographic patterning of C/SiO_2 thin films



(A) digital image of a 4-inch SiO_2/Si wafer containing around 600 electrodes, (B) SEM image of a representative electrode feature, (C) Detail of several small features produced.

Square-wave anodic stripping voltammograms recorded with C/SiO_2 electrodes



(A) 0.1 M H_2SO_4 solutions containing 2 ppm Bi(III) ions and different concentrations of Cd(II) and Pb(II) (from bottom to top signals: 0, 5, 10, 20, 40 and 70 ppb). (B) in 0.1 M HCl solutions with Hg(II) concentrations varying from 0 to 10 ppb (from bottom to top signals: 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ppb), previously modified with Au nanoparticles generated on the electrode surface by applying a +0.18 V for 15 s in a 0.5 M H_2SO_4 solution containing 0.2 mM $HAuCl_4$. (C) and (D) are SEM images showing the surface of a C/SiO_2 thin-film electrode modified with Bi and Au nanoparticles,

4.Electrochemically Active Thin Carbon Films with Enhanced Adhesion to Silicon Substrates
Pengfei Niu, Laura Asturias-Arribas, Martí Gich*, César Fernández-Sánchez*, Anna Roig, Applied Materials & Interfaces 8, 45 (2016) 31092–31099.

5. Carbon–Silica Composites to Produce Highly Robust Thin-Film Electrochemical Microdevices
Pengfei Niu, Laura Asturias-Arribas, Xavier Jordà, Alejandro R. Goñi, Anna Roig, Martí Gich*, César Fernández-Sánchez*, Adv. Mater. Technol. 1700163 (2017).

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