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

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Supplementary Information

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A This journal is The Royal Society of Chemistry 2013



S1 Size distribution of the powder of (C-Bi)_{IM} composite used to prepare test electrodes measured by optical microscopy image analysis with Morphologi G3 equipment by Malvern Instruments.

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S2 (a) XPS spectrum of (C-Bi)_{IM} composite in the region of the Bi $4f_{7/2}$ and $4f_{5/2}$ photoelectrons. The peak energies centered at 159.06 and 164.36 eV are characteristic of Bi₂O₃. (b) Z-contrast Transmission Electron Microscopy image revealing that the Bi nanoparticles present a core-shell structure.

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S3. Backscattered electrons SEM images of composites $(C-Bi)_{CS_L}$ (a) and $(C-Bi)_{CS_H}$ (c) showing Bi nanoparticles. From the detailed analysis of more than 10 images, bimodal particle size distribution histograms were obtained for both materials (b) and (d).

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S4 Backscattered electrons SEM image of composite $(C-Bi)_{IM}$ (a) and particle size distribution histograms obtained from the detailed analysis of more than 10 images (b).



S5. Nitrogen adsorption and desorption isotherms of the nanocomposites $(C-Bi)_{IM}$ and $(C-Bi)CS_L$ (a) and the cumulated volume of pores as a function of the pore size for the same materials and (C-Blank), calculated for the adsorption isotherm from the BJH model (b).



Figure S6. Cyclic voltammograms recorded with carbon paste electrodes fabricated with (a) $(C-Bi)_{IM}$ and $(C-Bi)_{CS_L}$ in a 0.1 M KNO₃ solution containing 1 mM ferricyanide. Scan rate: 50 mV/s.

The detection of heavy metals by Square Wave Anodic (Cathodic) Stripping Voltammetry

The detection of heavy metals using Bi-based electrodes is commonly based on the application of Square Wave Anodic Stripping Voltammetry. The working principle of the technique is as follows: A constant negative cathodic overpotential is applied, at which the different heavy metal ions present in solution are reduced and deposit on the electrode surface, in a process analogous to electroplating. This first step of the process in which heavy metal ions in solution are reduced and form alloys with the Bi metal is called accumulation and the corresponding electrochemical reaction is represented in equation (1). Subsequently a potential scan towards positive anodic potentials induces the heavy metal oxidation and strips off the heavy metal atoms from the Bi nanoparticles into the solution. This process is accompanied by a release of electrons that can be measured as a current peak and is used as the analytical signal. This occurs at different potentials for each metal depending on their standard redox potential and enables the simultaneous detection of several of these pollutants. The electrochemical reaction of the stripping part of the process is expressed by equation (2)

(1) Under constant V<0 : $Bi + M^{n+} + ne^- \rightarrow Bi(M)$ (2) Under a scan towards V>0 : $Bi(M) \rightarrow Bi + M^{n+} + ne^-$

In the detection of some heavy metals the so-called Square Wave Cathodic Stripping Voltammetry is applied in which the accumulation step is carried out by applying a potential at which the heavy metal ions are not reduced but adsorbed on the electrode surface with the aid of a complex agent present in solution. Then, a cathodic potential scan is applied, at which the adsorbed heavy metal ions are reduced and give rise to the corresponding analytical signal. **S8**



Figure S8. SWASV signals recorded in 0.1 M acetate buffer solutions at different accumulation times using (C-Bi)_{IM} based CPEs. Baselines were corrected in order to superimposed all signals.



Figure S9. Pb and Cd calibration curves plotted using SWASV signals recorded with the $(C-Bi)_{CS_H}$ material. Accumulation step: -1.4 V for 4 min. Other conditions detailed in the text.



Figure S10. SWASV signals recorded in 0.1 M acetate buffer solution pH 4.5 containing (a) 0 and (b) 50 ppb Cu and Hg, using CPE prepared with the (C-Blank)_{CS_H} material. Other conditions detailed in the text.