SUPPLEMENTARY INFORMATIONS

Heavy metal ions detection at TiO_2 nanotubes and self-reduced TiO_2 nanotubes electrodes

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Abstract: TiO_2 nanotubes and self-reduced TiO_2 nanotubes semiconductor electrodes were used for electrochemically metal ions detection in open circuit under photo-accumulation conditions. Due to their surface properties, the electrodes showed different responses towards metal ions at different wavelengths of light radiation. Using TiO_2 nanotube-based electrodes, Pb(II) and Cu(II) ions were detected at irradiation wavelengths of 389 nm and 426 nm. Detection limits of 8×10^{-9} M and 5×10^{-9} M for Pb(II) and 3×10^{-8} and 7×10^{-9} M for Cu(II) were obtained at the two wavelengths, respectively. The self-reducing electrode showed response to Pb(II) and Cu(II) ions when irradiated with light 389 nm, while at 426 nm, Hg(II) ions along with Pb(II) and Cu(II) ions have been detected. The obtained detection limits with self-reduced TiO_2 nanotubes electrode for Pb(II) and Cu(II) at 389 nm were 2×10^{-7} M and 8×10^{-9} M, respectively. At the wavelength of 426 nm, the detection limits were 1×10^{-7} M, 3×10^{-9}, and 4×10^{-9} M for Pb(II), Cu(II), and Hg(II), respectively.

Keywords: TiO_2 nanotube electrode; self-reduced TiO_2 nanotube electrode; Heavy metal ions; Photo-accumulation; Electrochemical detection

Experimental section

Reagents

Titanium rod (99.99+%, Merck) with 8 mm in diameter was used to obtain Ti disks with 8 mm in diameter and 3 mm thickness which were subsequently employed as electrodes for obtaining TiO_2 nanotubes. Ethylene glycol (99+%, extra pure, Thermo Scientific Chemicals), NH4F (≥99.99% trace metals basis, Merck) and ultra-pure water (Millipore Direct − Q 3UV) were used as electrolyte for TiO2 nanotubes synthesis in order to avoid any contamination. K2SO4 (99.99% trace metals basis, Merck) was used as electrolyte (0.1M aqueous solution) for the recording of the anodic stripping curves. Sodium acetate (99.995% trace metals basis, Merck) and acetic acid (glacial, ≥99.99% trace metals basis, Merck) were used to prepare 0.1M aqueous acetic buffers. As source of metal ions were used: Pb(NO3)2 (≥99.95% trace metals basis), Cu(CH3COO)2 (99.99% trace metals basis), Cd(NO3)2 × 4H2O (99.997% trace metals basis), Hg(CH3COO)2 (ACS reagent, ≥98.0%), Zn(NO3)2 × 6H2O (reagent grade, 98%),were from Merck.

Apparatus

A direct current power supply (Matrix MPS-7505L-1) was utilized for potentiostatic anodizing of the titanium disks (6 mm in diameter of active area) derived from the 8 mm pristine disks which were placed in an custom electrode holder made from PEEK (8 mm in diameter) in order to be aglinied parallel with the counter-electrode. For recording the electrochemical experiments, the obtained electrodes were placed in an electrode holder (from Origalys) and connected with a static electrode (from Origalys)

An AUTOLAB PGSTAT 204 potentiostat (Metrohm) was used to record electrochemical experiments performed in a three-electrode cell (Ti/TiO_2 nanotube disk – working electrode; Pt mesh – counter electrode; Ag/AgCl, 3M KCl – reference electrode). IVIUM pocketSTAT2.LC potentiostat was used to perform the electrochemical impedance spectroscopy (EIS) and Mott-Schottky experiments (-1.0 V to +1.0 V range at a frequency of 1 kHz, with an amplitude of 0.01 V RMS].

A Switchable LED Light Source from Redox.me emitting light at a specific wavelength was used as source of photo-irradiation (25 mW/cm^2) of the electrodes.

UV–VIS spectral investigations were performed on a JASCO V-770 spectrophotometer equipped with an integrating sphere.

The SEM images and EDX spectra were acquired with a Hitachi SEM SU8230 scanning electron microscope at an acceleration voltage of 20 kV.

A Thermo Fisher K-Alpha instrument fitted with monochromatic Al Kα (1486.6 eV) X-ray was used for X-ray photoelectron spectroscopy (XPS). The survey spectra had a resolution of 200 eV, while the high-resolution spectra used 20 eV. The Shirley background was subtracted before applying a mixed Gaussian-Lorentzian function to deconvolve the spectra at the core level.

Procedures

Electrodes preparation

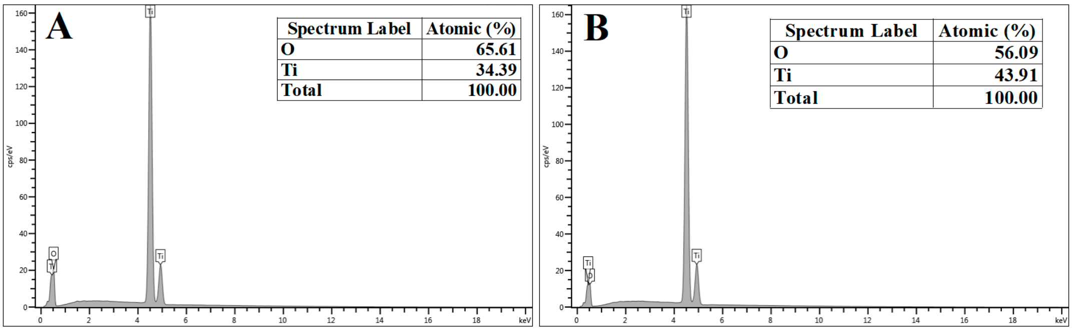
Titanium disks (99.99+%, Sigma Aldrich) with a diameter of 8 mm were polished with abrasive SiC paper up to a final porosity size of 4000 and the polishing finished with diamond paste (0.25 μm from Presi). Afterward, the Ti disks were meticulously cleaned through sonication in ethanol and acetone for 15 minutes each, followed by a thorough rinsing with ultrapure deionized water. The nanotubes of TiO_2 were grown under potentiostatic conditions at 30V for 1 hour in electrolyte of ethylene glycol + 0.5% HN_4F + 2% water followed by rinsing with purified water and drying under Ar [1, 2]. Further, for efficient photo- and electrochemical processes, the amorphous TiO_2 electrode was converted into crystalline phase by heating at 450 °C for 2 hours.

Self-reduced TiO_2 nanotubes (further denoted Ti/TiO_2-SR) were obtained through the electrochemical reduction of previously obtained Ti/TiO_2 nanotubes (further denoted Ti/TiO_2-NT) electrodes for 30 seconds at a potential of -1.5V (vs Ag/AgCl, 3M KCl) in a 0.1M aqueous solution of Na_2HPO4 at a pH of 10 (adjusted with 1 M NaOH) [3].

Sensing of metal ions

The photoaccumulation and reduction of metal ions on Ti/TiO_2-NT and Ti/TiO_2-SR electrodes was accomplished by their irradiation with light at a certain wavelenght. The electrodes were positioned in a quartz cuvette containing 25 mL aqueous solution of acetate buffer containing Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II) ions. Subsequently, the electrode was rinsed with purified water to eliminate the unbound ions and then transferred into a 0.1 M K_2SO_4 supporting electrolyte. The reduced ions on the electrode surface were stripped to metal ions using the differential pulse voltammetry (DPV) technique (20 mV s^{-1}, 25 mV amplitude, and 0.5 s pulse periods) under Ar atmosphere. To enhance the representation and interpretation of the DPV curves, a baseline extraction procedure was conducted beforehand. Determination of Pb(II), Cu(II), and Hg(II) ions was performed in triplicates for each solution used for the calibration curves. The calibration curves were plotted using mean value of the obtained results, and the concentration results were graphically represented with the standard deviation (Figures S2÷S4). The values of the standard deviations were situated in the range from 3% to 5% for all solutions.

Results and discussion



Spectrum Label	Atomic (%)
O	65.61
Ti	34.39
Total	100.00

Spectrum Label	Atomic (%)
O	56.09
Ti	43.91
Total	100.00

Figure S1. Energy dispersive X-ray spectra for (A) Ti/TiO_2-NT and (B) Ti/TiO_2-SR electrodes

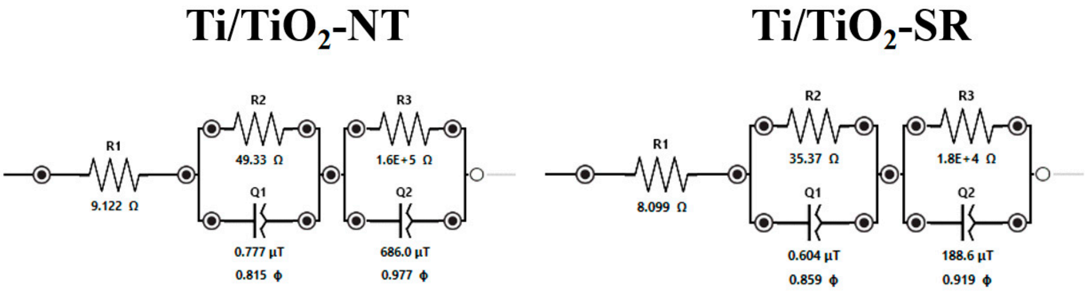
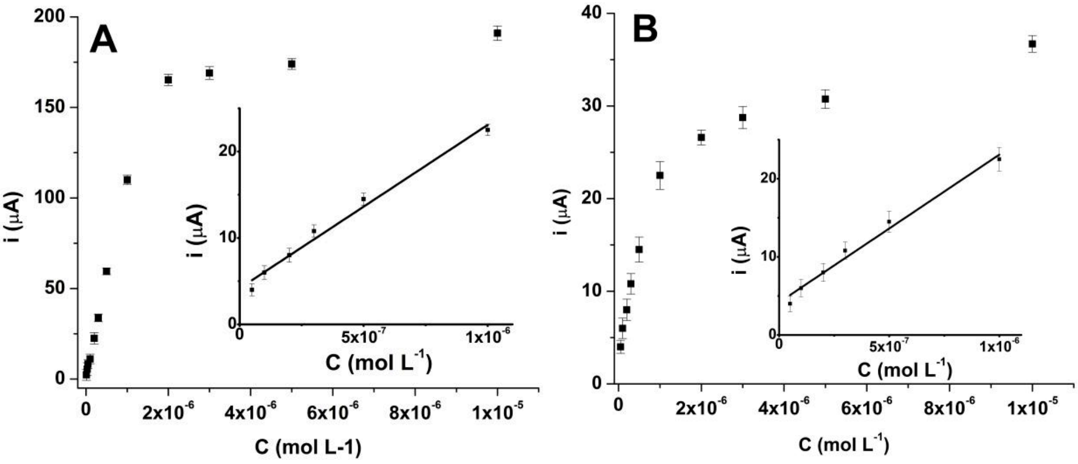


Figure S2 The equivalent circuit model used for fitting the EIS experimental data for Ti/TiO_2-NT and Ti/TiO_2-SR electrodes



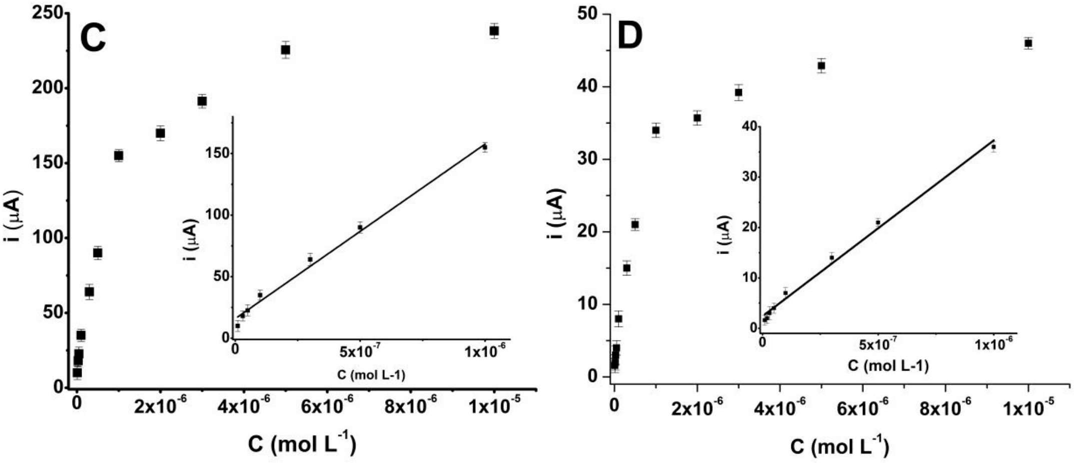
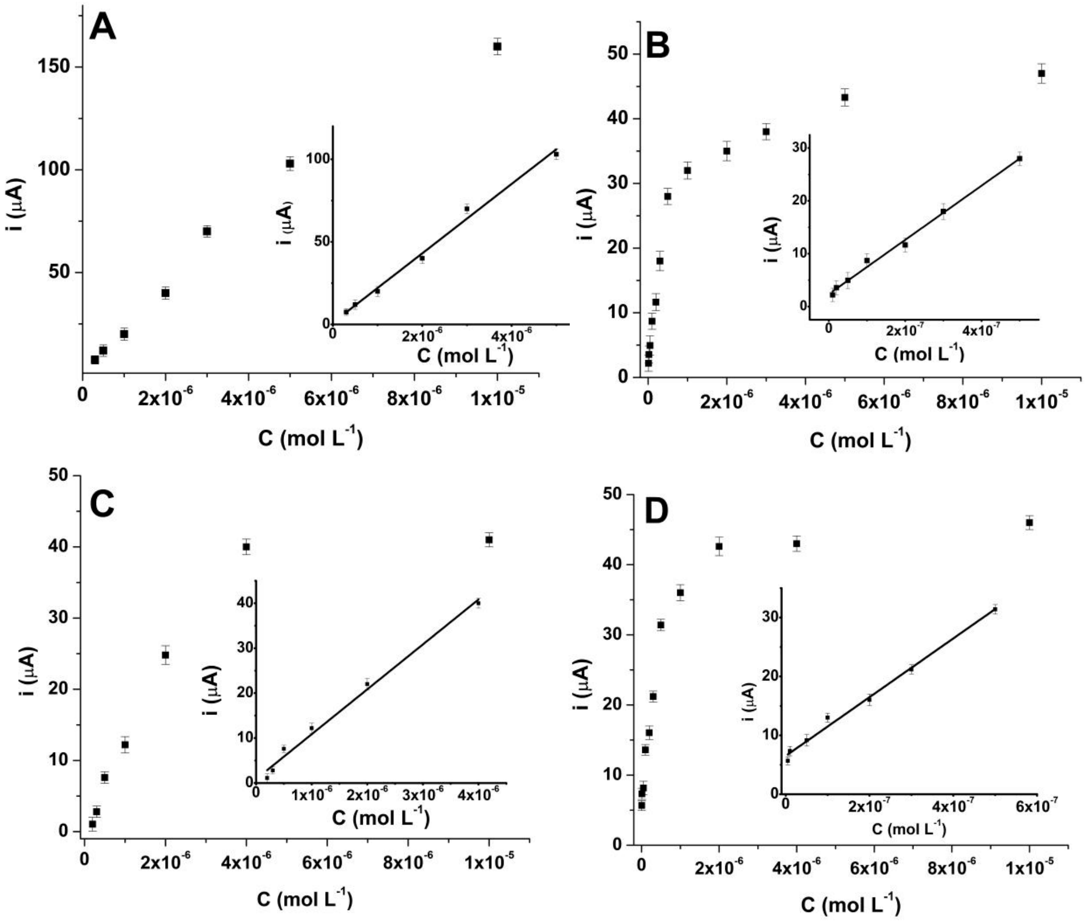


Figure S3 Calibration curves obtained with Ti/TiO$_2$-NT electrodes for different concentrations of (A, C) Pb(II) and (B, D) Cu(II) ions. Accumulation of metal ions was performed under light irradiation at 389 nm (A, B) and 426 nm (C, D). Insets: the corresponding linear domain of concentration.



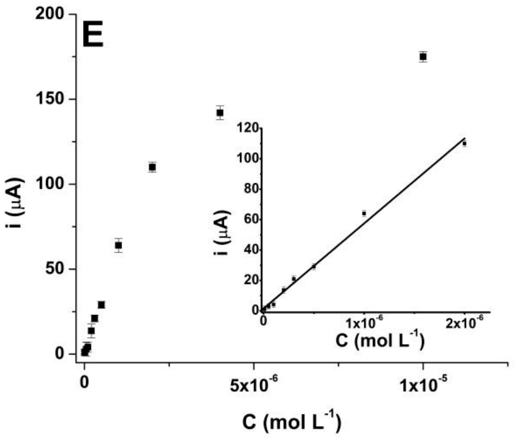


Figure S4 Calibration curves obtained with Ti/TiO_2-NT electrodes for different concentrations of (A, C) Pb(II), (B, D) Cu(II), and (E) Hg(II) ions. Accumulation of metal ions was performed under light irradiation at 389 nm (A, B) and 426 nm (C, D, E). Insets: the corresponding linear domain of concentration.

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