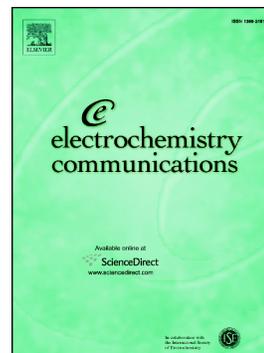


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Antimony tin oxide (ATO) screen-printed electrodes and their application to spectroelectrochemistry

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Abstract

Spectroelectrochemistry studies spectral changes as a function of applied potential or current. While there is no standard experimental setup, transparent electrodes are most typically used in transmission mode. Working in reflection mode forces light across the sample twice, resulting in higher sensitivities, but in turn requires the use of highly reflective electrodes. Here we present the production and characterization of screen-printed electrodes made from different antimony tin oxide (ATO) conducting particles. The resulting electrodes display excellent spectroelectrochemical properties, such as reflectivities up to 20 times higher than conventional graphite screen-printed electrodes, but with comparable electron transfer rates. These electrodes represent an attractive alternative to conventional materials and widen the choice of suitable electrode materials for electrochemistry in general and spectroelectrochemistry in particular.

1. Introduction

Among conducting oxides, tin oxides have the longest tradition as electrode materials [1]. Tin oxides have been mainly used as thin film coatings in the manufacture of transparent electrodes [2], and include indium–tin oxide (ITO) [3] and fluorine–tin oxide (FTO) [4]. In contrast, antimony–tin oxide (ATO) has been little used as a working electrode, perhaps due to its slightly darker appearance [5].

Over the past decade, screen-printed electrodes (SPE) have become a very interesting alternative to conventional solid electrodes in electroanalysis, thanks to the possibilities they offer in device miniaturization and integration, amenability to mass manufacture, and affordability [6,7]. In particular, SPEs can be easily used in spectroelectrochemistry because they simplify the experimental setup, enabling the use of this analytical technique for routine analysis [8].

In this work we present three different ATO-based SPEs as an alternative to conventional screen-printed carbon electrodes (SPCE). We have taken a series of commercially available clear conducting particles [9], formulated them into screen printing pastes, and made electrodes out of them. ATO-based SPEs have a white/gray appearance, providing superior spectroelectrochemical performance compared to more conventional SPCEs. In fact, they provide spectroelectrochemical performance levels comparable to screen-printed platinum or transparent ITO electrodes, at a significantly lower cost.

Spectroelectrochemistry (SEC) studies spectral changes as a function of applied potential or current, facilitating the determination of reaction intermediates and products [10,11]. There are a wealth of electrochemical and spectroscopic techniques, including UV-Vis-IR, EPR and ESR [12], or Raman scattering [13], as well as other less accessible methods based on NMR [14], X-ray absorption [15], and luminescence techniques [16].

In SEC, suitable electrodes not only need to display a sufficiently wide potential window and fast electron transfer kinetics, but they also need to be either highly transparent or highly reflective to the incident radiation [17]. Among reflective electrodes, metals such as gold, silver or platinum are the most common electrode materials [18-20]. For analytical purposes, and working in normal incidence configuration SEC, reflective electrodes improve the sensitivity of the method

because the solution volume over the electrode is sampled twice. Moreover, high reflectivity electrodes bring further sensitivity improvements by providing higher signal-to-noise ratios.

The clear appearance of the ATO electrodes presented in this work translates into dramatic increases in the signal-to-noise ratio of the spectroscopic signal, reducing experimental timescales and improving the detection limits. This provides obvious advantages not only from an electroanalytical viewpoint, but also to those interested in the study of reaction mechanisms.

2. Experimental

Potassium ferrocyanide, potassium chloride, and 2-butoxyethyl acetate were purchased from Sigma-Aldrich, and used as received without further purification. Conducting ATO-based materials Zelec 1410-T, Zelec 1610-S, and Zelec 3010-XC were kindly provided by Milliken Chemical, BE. Viton® fluoroelastomer (GBL-600S, DuPont) was purchased from Eagle Elastomer, USA. Carbon conducting paste ref. C2030519P4 was purchased from Gwent Electronic Materials Ltd, UK, and Electrodag PF-455B photocurable dielectric paste was obtained from Henkel (ES). 0.5-mm-thick PET sheets (Autostat WP20) were purchased from MacDermid, UK. Transparent ITO (ref. ITO10) and platinum (ref. 550) electrodes were acquired from Dropsens (ES).

Electrochemical measurements were carried out using an Autolab PGSTAT 12 (Metrohm) controlled by NOVA 2.0. Spectroelectrochemical measurements were done using a SPELEC instrument (Dropsens) controlled by DropView SPELEC software (version 3.0). Scanning electron microscopy images were obtained with an Auriga (Carl Zeiss) microscope.

Screen-printing pastes were prepared as described in [21], but a summary is given for convenience. Conducting particles were added to a 15–20% Viton solution in 2-butoxyethylacetate, to a final particle to binder ratio of 2.5:1. This mixture was thoroughly blended using a ball mill (1274 rpm for 2 hours), until a material with a honey-like texture was obtained. The paste presented a maximum particle size ranging between 10 and 15 μm , as measured with a 50 μm grind gauge (BYK Gardner, ES).

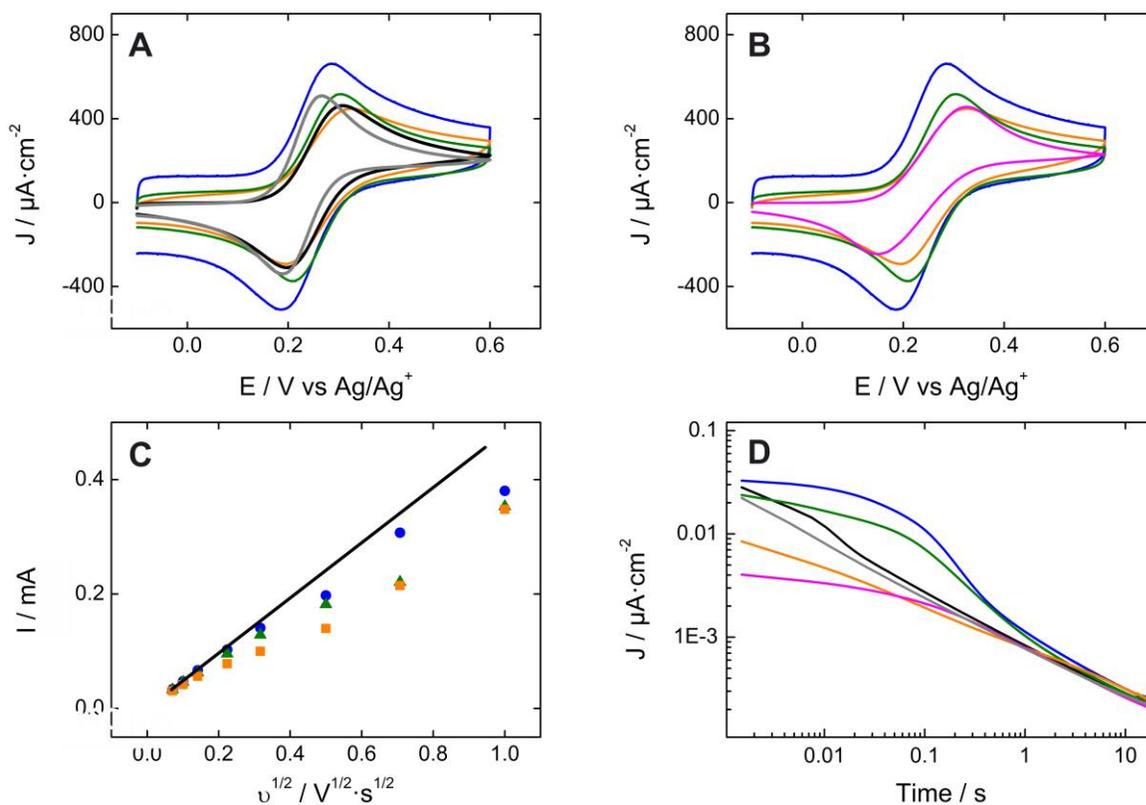
Electrodes were manually screen printed using a home-made setup [22]. First, conducting tracks and pseudo-reference electrode were printed on a PET substrate. Next, graphite was used to print the auxiliary electrode and a contact below the working electrode area to provide a conducting area. ATO-based working electrodes were then printed on these contacts, and finally a dielectric layer was applied to cover the conducting silver tracks.

3. Results and discussion

3.1 Electrochemical characterization

The electrochemical behavior of the SPEs was assessed by cyclic voltammetry and chronoamperometry, and compared to that of electrodes fabricated with a commercial screen-printing carbon paste as well as commercial Pt SPEs and ITO transparent electrodes. The electrodes were not pre-conditioned or activated prior to the experiments, which were carried out at room temperature.

First, voltammetric experiments were performed to study the electrochemical behavior of the ATO SPEs using ferrocyanide, a benchmark redox system that is highly sensitive to electrode surface quality. Different cyclic voltammograms were recorded using a 5 mM ferrocyanide solution in 1 M KCl at neutral pH (Fig. 1a and 1b). All ATO electrodes displayed higher background capacitive currents than their graphite, Pt and ITO counterparts, with the ATO-based electrodes showing a higher capacitance than SiO₂-ATO (Zelec 1610-S) and TiO₂-ATO (Zelec 1410-T) electrodes. These differences are likely due to a combination of material properties and surface roughness. Figure 1c shows the Randles–Sevčik plot obtained for the different ATO-based electrodes. The deviations at higher scan rates arise from electron transfer limitations.



The high capacitances observed in the 420–850 $\mu\text{F}\cdot\text{cm}^{-2}$ range are roughly two orders of magnitude higher than those of graphite, Pt or ITO electrodes, and make these materials potentially good candidates for the printing of capacitors [23].

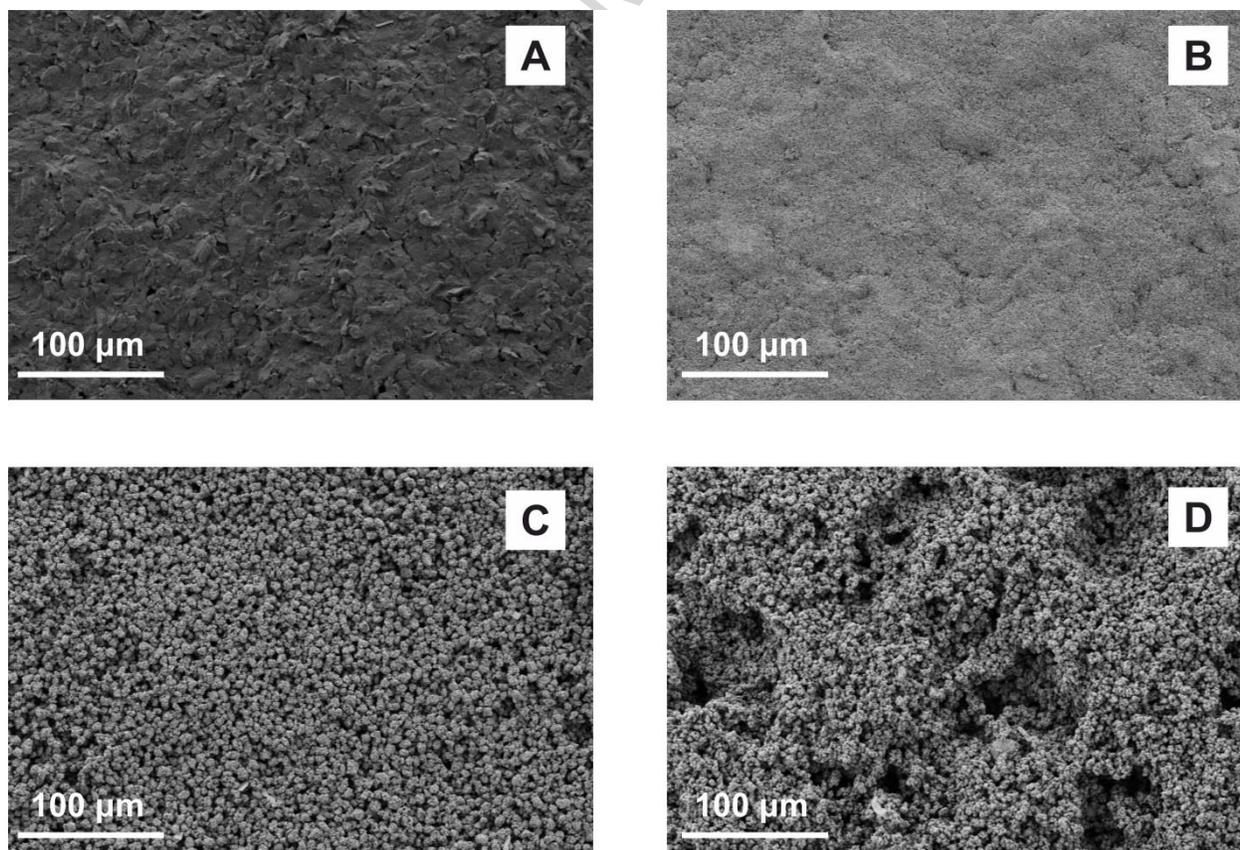
Table 1 shows the basic electrochemical parameters extracted from the cyclic voltammetry experiments. ATO-based electrodes are worse than Pt electrodes, quite similar to graphite electrodes, but better than the ITO electrodes tested. The worse performance of SiO₂-ATO-based electrodes was attributed to the higher resistivity of its particles compared to the other two ATO-based materials (2–25 Ohm cm vs 1–5 Ohm cm, according to the manufacturer).

In addition to this, the electrode surface morphology is also likely to play a part. Figure 2 shows SEM images of the SPE. Graphite and ATO electrodes present very similar surfaces, while

TiO₂-ATO, and SiO₂-ATO electrodes are rougher. The size of the microparticles combined with the fluoroelastomer binder results in a marked hydrophobic surface, which hinders the electrochemical process by diminishing the contact area between the electrode surface and the solution. However, the roughness of these electrodes makes them of particular interest in applications where a high surface area is needed [13].

Next, we probed the electrode-solution interphase by means of “fast” chronoamperometry. The goal was to determine whether this electrode roughness/porosity translated into thin-layer [24,25] or other effects. Figure 1d shows a logarithmic plot of current density (J) vs time. Surprisingly, following double-layer discharge after the first few milliseconds, the slope of the curves differed from the expected $-1/2$, consistent with thin-layer diffusion effects accruing from the electrode roughness [26]. In fact, only the graphite electrode showed this kind of behaviour. After longer times, however, all electrodes display transient currents consistent with Cottrellian behavior.

That the slope of the current transients in Figure 1d approaches 0 at time less than half a second, suggests that the current is controlled either by hemispherical diffusion, or by a surface-bound process. Using the Einstein-Smoluchowskii expression for the estimation of diffusion distances, $\delta \approx \sqrt{2Dt}$, yields a distance of about 25 μm between electrocatalytic centres which, based on the SEM images in Figure 2, seems rather unlikely. We find it more plausible that the current observed after short times corresponds to the mild oxidation of the ATO at the working potential. This is hardly surprising, considering that tin oxides are known to display a small degree of electroactivity and electrochromism [27-30].

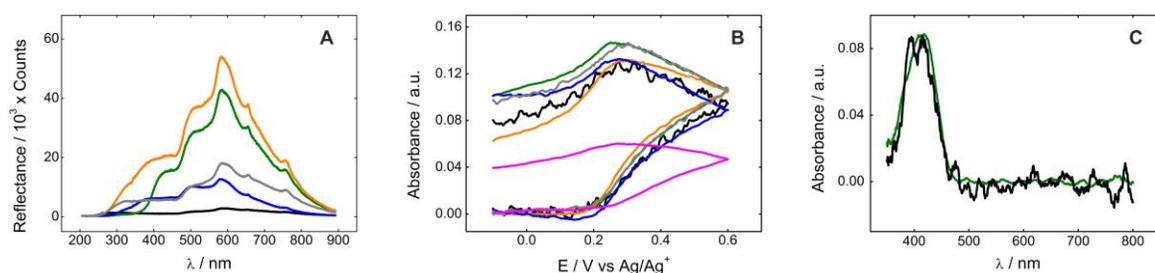


3.2 Spectroelectrochemical characterization

We studied the suitability of these electrodes for spectroelectrochemical experiments. Carbon SPEs are routinely used in SEC experiments in spite of their noisy signals and requirement for long integration times. Other materials, such as gold or platinum, can also be used, but they are more expensive. Affordable, high-reflectivity electrodes are desired because they allow for shorter integration times, providing access to faster processes.

The ATO electrodes presented here display good electrochemical behavior, but a much higher optical contrast than conventional materials. The blue colour of the ATO paste electrodes and particularly the clear grey-white look of the TiO_2 -ATO and SiO_2 -ATO electrodes gives them a significant spectroelectrochemical advantage over conventional electrode materials, including transparent ITO electrodes.

Figure 3a shows reflectance UV-VIS spectra registered in 1 M KCl. ATO-based electrodes reflect up to 20 times more light than carbon ones. Figure 3b shows well-defined voltabsorptograms at 420 nm, for the six different materials tested in a 2.5 mM ferrocyanide solution in 1 M KCl. At 420 nm there is negligible absorption by ferrocyanide, whereas ferricyanide absorbs with a known extinction coefficient around $1020\text{--}1040\text{ M}^{-1}\text{cm}^{-1}$ [31]. The voltabsorptogram recorded at carbon is much noisier than those from ATO-based electrodes. Figure 3c shows absorption spectra obtained at graphite and SiO_2 -ATO electrodes polarized at 0.4 V vs. Ag/Ag^+ in a 2.5 mM ferrocyanide solution in 1 M KCl. The spectrum from the graphite electrode is significantly noisier than that from the clear, ATO-based electrode. Moreover, these new electrodes are also less noisy than Pt electrodes. Noise affects the spectroelectrochemical performance in two ways. First, it makes it more difficult to relate the electrochemical and the spectroscopic signals to the same process as clean derivative voltabsorptograms are harder to obtain. Second, since the signal-to-noise ratio is worse at low reflectivity electrodes, their spectroscopic analytical performance is consequently poorer. To evaluate this, the oxidation of ferrocyanide solutions of different concentrations was studied using chronoabsorptometry by applying 0.5 V vs Ag/Ag^+ for 30 seconds.



As shown in Table 1, the electrochemical and spectroscopic sensitivities are similar regardless of electrode material, except for ITO, where the spectroscopic measurement was done in transmittance mode. Although the electrochemical detection limits are better for C, Pt and ITO commercial electrodes than for ATO-based electrodes, the spectroscopic detection is better for ATO electrodes. The LODs, which have been estimated from the standard deviation in the signal recorded in the absence of electrochemical oxidation, are similar to those of transparent ITO and Pt electrodes and markedly lower than those of graphite electrodes.

	ΔE_p / mV	$k^0_{\text{apparent}} \times 10^3 / \text{cm} \cdot \text{s}^{-1}$	Amperometric		Spectroscopic	
			Sensitivity / $\mu\text{A} \cdot \text{cm}^{-2} \cdot \text{mM}^{-1}$	LOD / mM	Sensitivity / $\text{a.u.} \cdot \text{mM}^{-1}$	LOD / mM
ATO	122	2.25	41.0	0.043	0.030	0.07
TiO₂-ATO	127	2.15	32.2	0.054	0.028	0.04
SiO₂-ATO	160	1.22	35.9	0.055	0.028	0.09
Graphite	115	2.47	40.3	0.014	0.027	0.24
ITO	143	1.69	27.0	0.013	0.014	0.07
Pt	68	35.5	31.7	0.016	0.033	0.07

Table 1. Data extracted from the voltammetric and spectroelectrochemical experiments. Peak-to-peak separations were registered for a scan rate of 50 mVs^{-1} for $n = 4$ electrodes. The heterogeneous electron transfer rate constants were calculated using Nicholson's method [32], taking a value of $6.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ as the diffusion coefficient of ferrocyanide. The spectroelectrochemical calibration was done with concentrations ranging from 0.5×10^{-3} to $10 \times 10^{-3} \text{ mol L}^{-1}$. $E_{\text{app}} = 0.5 \text{ V}$; $\lambda = 420 \text{ nm}$.

4. Conclusions

We have presented new screen-printed electrodes with excellent spectroelectrochemical performance compared to conventional materials. These new electrodes exhibit a high reflectivity that helps to improve the signal-to-noise ratio in the spectroscopic signal, without compromising their electrochemical performance. These electrodes may open new opportunities in the field of spectroelectrochemistry but also in other, perhaps more conventional, areas of electroanalysis. For instance, the materials presented here can improve optical contrast in electrochromic devices if they are used as an undercoat of the main electrochromic layer. These materials may also be useful in other electroanalytical applications where the surface chemistry of these oxides may be exploited to facilitate the anchoring of other molecules in the development of modified electrodes, such as in the field of biosensors.

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Captions to Figures

Figure 1. (A-B) Cyclic voltammograms obtained at 20 mV s^{-1} in $5 \times 10^{-3} \text{ M}$ ferrocyanide in 1 M KCl at pH 7 at different electrodes: ATO (blue), $\text{TiO}_2\text{-ATO}$ (green), $\text{SiO}_2\text{-ATO}$ (orange). (A) Comparison with commercial C (black) and Pt (grey) SPE; (B) Comparison with commercial ITO electrode (magenta) (C) Peak current as function of the square root of the scan rate for different cyclic voltammograms in the same ferrocyanide solution, compared to the theoretical prediction by the Randles–Sevcik equation (solid line). (D) Chronoamperograms for the same ferrocyanide solution $E_{\text{app}} = 0.5 \text{ V}$ vs Ag/Ag+.

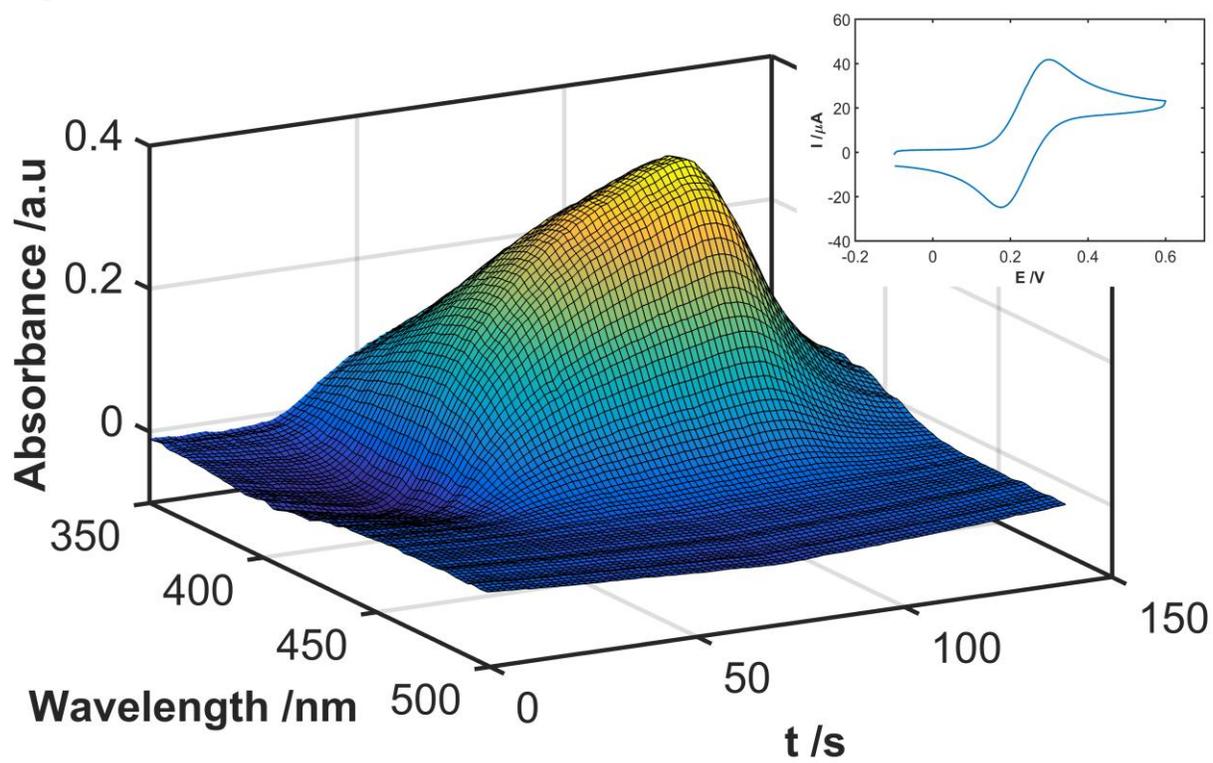
Figure 2. SEM images of the working electrode surfaces manufactured with (A) graphite, (B) ATO, (C) $\text{TiO}_2\text{-ATO}$, and (D) $\text{SiO}_2\text{-ATO}$ pastes.

Figure 3. (A) UV-vis reflectance spectrum in a KCl 1 M solution. (B) Voltabsortograms of a 2.5 mM ferrocyanide solution in 1 M KCl pH = 7. $\lambda = 420 \text{ nm}$. Graphite (black), ATO (blue), $\text{TiO}_2\text{-ATO}$ (green), $\text{SiO}_2\text{-ATO}$ (orange), ITO (magenta), Pt (gray). (C) Absorbance spectra obtained at graphite (black) and $\text{TiO}_2\text{-ATO}$ (green) electrodes.

Captions to Table

Table 1. Data extracted from the voltammetric and spectroelectrochemical experiments. Peak-to-peak separation were registered for a scan rate of 50 mVs^{-1} for $n = 4$ electrodes. The heterogeneous electron transfer rate constants were calculated using Nicholson's method [32] taking a value of $6.5 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ as the diffusion coefficient of ferrocyanide. The spectroelectrochemical calibration was done with concentrations ranging from 0.5×10^{-3} to $10 \times 10^{-3} \text{ mol L}^{-1}$. $E_{\text{app}} = 0.5 \text{ V}$; $\lambda = 420 \text{ nm}$. The LOD was estimated using 3 times the standard deviation of the signals recorded in the absence of an electrochemical reaction.

Graphical abstract



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HIGHLIGHTS

- New screen-printed electrodes based on antimony tin oxide microparticles are presented.
- The electrodes display good electron transfer properties, which makes them suitable for electroanalytical applications.
- The electrodes are clear in colour and provide much higher optical contrast than conventional graphite electrodes in spectroelectrochemical applications.

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