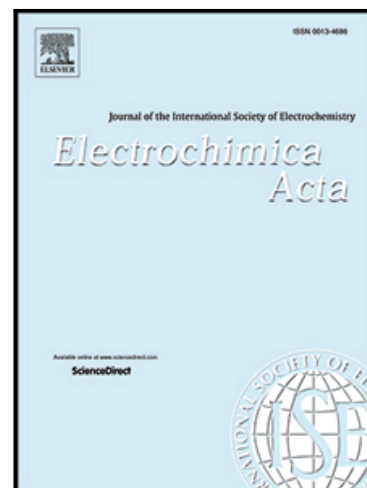


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All-solid state ion-selective carbon black-modified printed electrode for sodium detection in sweat

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Abstract

The synergic combination of printed electronics and printed electrochemical sensors has recently emerged as a new route for developing smart chemical wearable devices applied to sweat monitoring. Sodium ion is one of electrolytes monitored in sweat to evaluate sweating level for electrolyte replacement recommendations. Herein, we report the development of new designed screen-printed electrodes, in which working electrode has been easily modified by drop-casting with the nanomaterial carbon black and a selective membrane cocktail, and the reference electrode with a polyvinyl butyral-based membrane. Once optimised all conditions, the screen-printed electrochemical sensor demonstrated no aqueous layer formation between working electrode and selective membrane, long-term potential stability, good shelf life, and resistance to interferences from oxygen and light. The carbon black-based sensor allowed for the detection of sodium ions in range 10^{-4} M e 1 M with a slope of 58 ± 3 mV/decade and a detection limit of 63 μ M. The applicability for sweat analysis was evaluated by analysing three sweat samples collecting during running activity, obtaining concentrations of 44 ± 4 mM, 55 ± 6 mM, and 47 ± 3 mM, values in agreements with sodium ions content in healthy people, as well as using artificial sweat with recovery values of 90 ± 3 %, 94 ± 2 %, and 94 ± 5 %.

Keywords: modified screen-printed electrodes; carbon black; drop-casting; ion-selective membrane.

1. Introduction

Sweating usually occurs in response to external heat stimuli or internal chemical stimuli with the consequent loss of water and electrolytes, namely sodium, potassium, and chloride ions. Indeed, sweating has a well-known thermoregulatory role, but it is also related to other critical homeostatic functions, unconnected to thermoregulation [1]. As an example, sweat glands accomplish excretory functions, similar to that of the renal system, with the aim to eliminate the excess of micronutrients and metabolic waste from the body [2].

The need of biomedical analytical tools characterised by non-invasive analyses has boosted the scientific community to use easy-to-sample biofluids, as sweat for smart analysis in sports science and biomedical applications [3-5]. Indeed, the successful detection of sodium, potassium, and chloride ions, as well as glucose and lactate in this biofluid has demonstrated its suitability for non-invasive measurements by using sensing devices [6-8]. Furthermore, the huge advancement in printed electronics has allowed the application of electrochemical sensors in the sweat monitoring, enabling the realisation of flexible and miniaturised devices for on-line detection of biomarkers in sweat.

Gao et al. developed a fully integrated electrochemical (bio)sensor array for the simultaneous and selective measure of glucose, lactate, sodium and potassium ions, as well as of the skin temperature for sensor calibration. The electrochemical sensors were produced by photolithography and *ad hoc* modified with ion selective membranes or enzymes to quantify electrolytes or metabolites, respectively. The device was tested by measuring in continuous mode these biomarkers in sweat, demonstrating the capability of the electrochemical sensors to be used as wearable devices [3]. Gao's group has also developed a wearable device for smart detection of uric acid and tyrosine in sweat by using laser-engraved technique and graphene as nanomaterial for sensitive electrochemical sensor fabrication [9]. Among the diverse printing technologies, screen-

printed technique has demonstrated the suitability to deliver miniaturised, reproducible, and sensitive electrochemical sensing tools with the additional advantage of cost-effectiveness [10-12].

Screen-printed based electrochemical devices for sweat analyses have been reported in literature, for instance for pH or chloride ions measurements using screen-printed electrode modified with iridium oxide or ion selective membrane, respectively [13, 14].

Nanomaterials as working electrode nanomodifiers have improved the analytical features of merit of the screen-printed electrodes. Carbon nanotubes, graphene, metallic nanoparticles, among others have demonstrated the capability to improve the electrochemical features of the screen-printed electrodes, such as the enhancement of the electron transfer and the reduction of fouling problems [15-17]. Recently, carbon black (CB) has acquired a remarkable position in the carbonaceous nanomaterials, being characterised by high surface area and high number of defect sites, which confers improved electrochemical features in terms of reduced applied potential, resistance to fouling, increased sensitivity towards several analytes such as phenolic compounds, hydrogen peroxide, NADH, thiols, ascorbic acid [18-21]. The relevant features of CB as nanomodifier have been demonstrated for detection of nicotine, ascorbic acid, NADH, cysteine, even when compared with the more famous multiwalled carbon nanotubes [15, 22] or graphene [15, 23]. Furthermore, other benefits of CB rely on its usability without any further additional treatment, its cost-effectiveness, and the easy production of stable dispersion, which is a mandatory feature for scalable drop-casting modification of the working electrode surface. CB has been used the first time for the development of potassium potentiometric sensors by Paczosa-Bator in 2012 [24]. In detail, the author used CB as polymeric membrane component or as intermediate layer between the ionophore-containing membrane and glassy carbon electrode obtaining good Nernstian response (59.1-58.8 mV/decade) and detection limit equals to $10^{-6.4}$ M and $10^{-6.1}$ M, respectively. The same author investigated the effect of different types of carbon black as interlayer for nitrate detection.

In detail, long-term potential stability was observed for glassy carbon electrodes modified with Printex XE2-B carbon black (BET surface area $1000 \text{ m}^2 \cdot \text{g}^{-1}$, average particle size: 30 nm), while glassy carbon electrodes modified with Vulcan XC-72 (BET surface: $240 \text{ m}^2 \cdot \text{g}^{-1}$; average size: 55 nm) demonstrated the most reproducible potential and the lowest detection limit for nitrate ($2.5 \cdot 10^{-7} \text{ M}$) [25]. Herein, at our knowledge, we reported the first CB-modified screen-printed electrode for potentiometric measurements, selecting sodium as selected target analyte, and taking into account that for sweat analysis the flexibility and miniaturization are necessary needs for the development of wearable sensors. Sodium ion is one of electrolytes measured in sweat to evaluate the dehydration of body, with physiologically relevant concentrations comprised between 10 and 160 mM. In detail, primary sweat is approximately isotonic with blood plasma (e.g. 135–145 mM); after the sweat flows through the duct, the sodium ions are passively reabsorbed via epithelial sodium channels, delivering hypotonic sweat with respect to sodium ions [26].

Furthermore, in the view to develop an easy to fabricate sensor, the classical configuration of screen-printed electrodes has been re-designed to create a reference electrode easily to be modified with a selected membrane by drop-casting method, which allowed an increased signal stability.

The suitability of the flexible and printed sensor for sweat analysis has been evaluated by measuring sodium in synthetic sweat samples as well as real samples, opening a further application of screen-printed electrode modified with CB in chemical wearable devices.

2. Experimental section

2.1. Materials

Sodium chloride, 4-tert-Butylcalix[4]arene (Sodium Ionophore X), Potassium tetrakis (4-chlorophenyl) borate (KTFPB), Polyvinyl chloride (PVC), Polyvinyl butyral (PVB), Methanol, 2-

Nitrophenyl octyl ether (O-NPOE), Dimethylformamide (DMF), Tetrahydrofuran (THF), Potassium chloride, Magnesium chloride, and Calcium chloride were purchased from Sigma Aldrich (USA). Carbon Black N220 was obtained from Cabot Corporation (Ravenna, Italy). Artificial sweat was prepared following the procedure described by Parrilla et al [27]. In detail, a cocktail composed of 6 mM KCl, 5 mM NH₄Cl, 0.08 mM MgCl₂, 2.6 mM NaHCO₃ and 0.04 mM Na₂HPO₄ was prepared in distilled water, pH= 5.3.

2.2. Fabrication of screen-printed electrodes

SPEs were produced using a 245 DEK (Weymouth, UK) screen-printing machine. Flexible polyester films (Autostat HT5), purchased from Autotype Italia (Milan, Italy), were used as substrate to print the electrodes. Silver/silver chloride ink (Electrodag 6038 SS) was used to print the pseudo-reference electrode, while graphite ink (Electrodag 423 SS) from Acheson (Milan, Italy) was used to print the working electrode, and grey dielectric paste (D2070423P5) from Gwent Electronic Materials (Pontypool, UK) for the insulating layer, to define the working electrode surface area. After each ink deposition, the electrodes were dried at 70 °C for 20 min for silver/silver chloride ink, 70 °C for 40 min for graphite-based ink and 80 °C for 40 min for grey dielectric paste. The resultant diameter of the working electrode was 0.3 cm with a geometric area equal to 0.07 cm².

2.3. Preparation of Carbon Black dispersion

CB powder was dispersed in a mixture of dimethylformamide/water in ratio 1:1 (v/v) at a final concentration of 1 mg/mL. In detail, 10 mg of CB were first dipped in 5 mL of dimethylformamide and then 5 mL of water were added. The dispersion was sonicated for 60 min at 59 kHz.

2.4. Preparation of ion selective membrane

The sodium selective membrane was fabricated following the procedure described by Cadogan et al. [28]. In detail, 300 mg of the membrane mixture contain 0.2% (w/w) potassium tetrakis (4-chlorophenyl) borate (KTFPB), 0.7 % (w/w) 4-tert-Butylcalix[4]arene, 33 % (w/w) polyvinyl chloride (PVC), and 66.1 % (w/w) 2-nitrophenyl octyl ether (O-NPOE). After the compounds were mixed, 3.3 ml of tetrahydrofuran (THF) were added to the mixture and left to stir for 1 h with magnetic stirrer.

2.5. Preparation of reference membrane

Reference membrane was prepared following the procedure described by Gao et al. [3]. In detail, 79.1 mg of polyvinyl butyral (PVB) and 50 mg of NaCl were dipped in 1 mL of methanol. The mixture was left under magnetic stirring for one hour.

2.6. Screen-printed electrode modification

Working and pseudo-reference electrodes were modified with the appropriate solutions using the drop-casting method.

Firstly, 6 μL of CB dispersion were added onto the working electrode surface in three successive steps of 2 μL , and left to dry for 1 hour after each step. Then, 7.5 μL of sodium selective membrane were drop-cast onto the CB-modified working electrode, and left to dry for 20 min. The pseudo-reference electrode was modified by casting 10 μL of the reference membrane solution, and left it to dry for 20 min.

All the steps, from screen-printing to SPEs modification, are schematized in Fig. 1.

2.7. Instrumentation

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potentiometry were performed using a portable PalmSens³ Instrument (PalmSens, Netherlands) connected to a laptop

and controlled by PSTrace 5.3 software. The measurement of sodium ions was carried out by dropping 100 μL of solution onto the working and reference electrodes (two-electrode system, being a potentiometric measurement), obtaining an output stable signal in less than 30 s.

CV and EIS measurements were performed by adding an external screen-printed graphite counter electrode (three-electrode system).

Micrographs of the working and reference electrodes were acquired by means of electron microscopy FEI Quanta 400. Field emission scanning electron microscopy was performed by a FEG-SEM, Leo Supra 35, UK.

3. Results and discussion

The nanomaterials have established a new route in electrochemistry, due to their valuable features including high surface area and fast electron transfer. In the potentiometric electrochemical sensors, nanomaterial-based solid-state ion-selective electrodes have demonstrated improved characteristics in terms of potential drift, absence of aqueous layer, and effects of interferences on potential stability, thanks to the features as electrical properties and hydrophobicity. Furthermore, the immobilization of the ion-selective membrane on nanomaterials prevents its leaching [29].

The advantage of using CB in the potentiometric sensors was well reported by Paczosa-Bator [24, 25, 30] demonstrating long-term potential stability, good resistance to the interferences from O_2 , CO_2 and light, and preventing aqueous layer formation using CB-based glassy carbon potentiometric sensor. The presence of oxygen groups affects the electrochemical response because they may determine the wettability by the electrolyte solution or involve redox reactions. Herein, we have selected CB N220 because, among N220, N115, N375, N660, HP 160, HS20, MTN 990, PL6, Super P, XE2B, it is the one with low O1s XPS relative atomic concentration (as %, obtained from HR spectra), as well as for its good dispersibility, delivering a stable dispersion

needed for a reproducible fabrication by drop-casting [31]. For the modification of working electrode surface with CB, in our previous works we have investigated the electrochemical response of electrodes modified with CB during the screen-printing manufacturing adding CB to the ink in different amounts, or by drop casting using a CB dispersion. The morphological characterization by scanning electron microscopy analysis, carried out in an our previous work [20], has demonstrated that the modification of working electrode surface by drop-casting with 6 μL of CB dispersion 1 mg/mL is able to produce a working electrode homogenously, covered by CB thus this procedure with this volume of CB to cast on the working electrode surface has been used in this work. We would like to highlight that the presence of CB in the case of screen-printed electrodes, not only confers the previous cited features, but it is able to improve the repeatability of CB-modified screen-printed electrodes, exploiting its high area as well as its typical sponge-like structure, as well reported in literature [32-36].

3.1. Voltammetric, electrochemical impedance spectroscopy, and morphological characterization

Herein, we carried out a voltammetric investigation using cyclic voltammetry in the potential range comprised between -0.8 V and 1 V in 0.1 M NaCl solution, utilizing CB-modified screen-printed electrodes (CB-SPE) and bare screen-printed electrodes (SPE). As reported in Fig. 2A (continuous line), a higher capacitive current was observed in case of the CB-SPE (red line) in respect to the one obtained using the bare SPE (black line). In details, a capacitive current equal to ca. 500 nA was measured in case of CB-SPE and 5 nA in case of bare SPE at a potential close 0 V, demonstrating the increase of capacitive current using the SPE modified with CB. In addition, an increase of the cathodic current was observed using CB-SPE at potential ca. -0.4 V, due to the electrocatalytic properties of CB in the reduction of oxygen, in agreement with our previous work [37]. It has been reported in literature that an electrode modified with CB has a lower background current in respect

to electrodes modified with multiwalled carbon nanotubes [22], single walled carbon nanotubes [38], and thermally reduced graphene oxide [23]. In this work, we confirmed that the presence of CB onto the SPE working electrode surface allows for an increase of capacitive current in respect to bare electrode [22], with the advantages of using a cost-effective, robust, and easy dispersible nanomaterial [39], in respect to the more used carbon nanotubes and graphene. Indeed, even if for an ISE the most costly ingredient is usually the ionophore (Table S1), the use of cost-effective nanomaterial can benefit the cost production of the sensor at the industrial scale. To evaluate the effect of oxygen on cyclic voltammetry using CB-SPE, the same cyclic voltammograms were carried out in absence of oxygen (dashed line), demonstrating that in both cases the presence of oxygen does not affect the capacitive process, in agreement also with the data reported in literature using SPE modified with electrochemically reduced graphene oxide [40]. Furthermore, we estimated the capacitance at dc-potential 0.2 V obtaining a value of 66 μF . This value is in agreement with the one found in EIS 69 μF at low-frequency (0.1 Hz), demonstrating any significant discrepancy between the value found in CV and EIS. This behaviour is different than the ones obtained using conducting polymer-based sensors, because in that case a discrepancy between the values in CV and EIS is observed and elucidated by the conformational changes responsible for the amplitude dependence of the capacitance of conducting polymers as reported in literature [41].

Successively, we investigated the impedance plots of CB/SPE recorded in 0.1, 0.05, and 0.01 M NaCl solutions using Edc 0.2 V, potential selected in agreement with the literature [40, 42]. As depicted from Fig. 2B, the values of high-frequency intersection with the Z' axis are in function of the concentration of electrolyte and not to the ohmic resistance of CB film cast on the working electrode surface. Indeed, values of 0.18, 1.2, and 2.1 $\text{K}\Omega$ were observed using CB-SPE testing solution of NaCl at concentration of 0.1, 0.05, and 0.01 M, respectively, demonstrating that the different values of impedance measured in the presence of different concentrations of NaCl are

mainly ascribed to the resistance of the solution. Furthermore, as shed light in Fig. 2B (dashed line), the impedance values measured did not change in the absence and presence of oxygen, in agreement with the voltammetric results and with the literature [40]. Additionally, we modified CB-SPEs with Na^+ ion selective membrane (Na^+ ISM) and we recorded impedance measurements of SPE/ Na^+ ISM and SPE/CB/ Na^+ ISM as reported in Figure 2B (inset). In case of CB-SPE we observed a decrease of resistance of charge transfer which suggests that the presence of CB layer onto the working electrode surface facilitates the charge transport at the interface. This result highlighted that ion-to-electron transduction right happens between the electronically conducting CB-SPE and ionically conducting ionoselective membrane. Taking into account the higher capacitive current observed for CB-SPE in respect to bare SPEs as well as the facilitation of charge transport at the interface, CB-SPE was selected for the further studies of the optimization of the sensor.

To deeply investigate the surfaces of the screen-printed electrodes, a morphological characterization was performed by scanning electron microscopy analysis for both working and reference electrode in absence and in presence of the drop-cast membrane. Fig. 3A and Fig. 3B show micrographs of bare reference electrode and polyvinyl butyral-membrane modified reference electrode, respectively. In detail, Fig. 3A displays silver particles and agglomerates with dimensions in the range between 5 μm and 10 μm and EDS spectrum confirm the presence of silver as the main component of printed reference electrode. Fig. 3B reveals the covering by the polyvinyl butyral-based membrane, and in EDS spectrum Carbon, Oxygen and Chlorine were mainly found. Fig. 3C shows the bare working electrode characterized by the typical graphite flakes and numerous small particles cross-linked by the agents present in the original ink [43]. Fig. 3D depicts the ion selective membrane covering the CB-modified working electrode, characterized by pore with diameters comprised between 2 μm and 5 μm . EDS spectrum also confirmed the presence of the PVC-based ion selective membrane, with the prevalence of Carbon, Oxygen and Chlorine atoms.

In order to deeply investigate the morphology of the ion-selective membrane, further analysis of the PVC-based membrane modifying the CB working electrode surface was performed by using a field emission SEM (FEG-SEM, Leo Supra 35, UK). The pictures obtained at higher magnification (Fig. 3F) depict a covering of the CB surface with the polymeric membrane having pore dimension in the range comprised between 2 μm and 10 μm . The presence of a porous membrane with an average pore size of $13 \pm 9 \mu\text{m}$ has also been observed by Roy et al. [44], in which paper the ion-selective membrane was drop-cast on a printed electrode modified with carbon nanotubes for sodium ion detection.

3.2. Optimisation of the selective membrane cocktail volume to cast on working electrode surface

The ion selective membrane was prepared using potassium tetrakis (4-chlorophenyl) borate, 4-tert-Butylcalix[4]arene, polyvinyl chloride, 2-nitrophenyl octyl ether, and tetrahydrofuran as reagents. The mixture prepared was then used to modify the working electrode surface by drop-casting. The correct volume to cast is a pre-requisite for homogenous coverage of the working electrode surface, thus the volume was optimized by evaluating the response at different concentrations of sodium ions in standard solution.

As depicted by Fig. S1, casting low volumes such as 2.5 and 5 μL onto the working electrode is not sufficient to give a response characterised by good repeatability, probably because these volumes are not enough for homogeneously covering the working electrode surface. Volumes of 7.5 μL and 10 μL gave comparable results, thus 7.5 μL were selected as a compromise between the repeatability and the minimum volume to use for modifying the working electrode surface.

3.3. Optimisation of the polyvinyl butyral-based solution volume to cast on reference electrode

The stability of the potentiometric measurements is one of challenges in electrochemical field. The reference electrode of screen-printed electrodes is produced by using silver or silver/silver chloride inks. For in continuous measurement, the use of silver/silver chloride ink enhances the stability of the electrochemical response [45]; however, for long-time analyses, the control of the chloride content is required to obtain a remarkable stability. In case of sweat measurements, the presence of samples with different chloride contents can affect the reference electrode potential and thus the accuracy of the measure. To be able to maintain a stable potential in working solutions characterized by different ionic strengths, a modification of the reference electrode with a membrane was carried out. With the final aim to deliver a flexible sensor easy to be mass-produced, a drop casting procedure was selected using a polyvinyl butyral-based solution reported in literature [3]. The effect of volume cast onto the reference electrode was evaluated, obtaining an improvement in terms of repeatability when using 10 μL as reported in Fig. S2, thus this volume was select for further studies.

3.4. Evaluation of condition process

The conditioning process is important to obtain a reproducible and stable signal. In our case, it was necessary only for the Ag reference electrode and it was carried out exposing just it to a KCl solution before the measurement. We utilised a solution of 3 M of KCl [46] and we evaluated the response of the sensor with and without this conditioning step for 18 and 24 hours. We observed an improved repeatability using a conditioning time of 18 hour (Fig. S3), thus this procedure before the measure was adopted for the rest of the work.

3.5 Potentiometric characterisation

Once optimised the fabrication of the sensor, we investigated its response in a range of Na^+ concentrations comprised between 10^{-5} M e 1 M, obtaining a linearity from 10^{-4} M to 1 M described by the following equation $y = (0.398 \pm 0.008) + (0.058 \pm 0.003) x$, $R^2 = 0.992$ (Fig. 4A). The repeatability was evaluated by triplicate measurements of the calibration curve, obtaining RSD % values equal to 12 %, 11 %, 8 %, and 2 % for, 10^{-3} , 10^{-2} , 10^{-1} and 1 M, respectively. The limit of detection (LOD) was calculated as the intersection of the two slope lines and found equal to 63 μM . The response reversibility of the CB-SPE-based sensors was also investigated by varying ion concentrations between of 10^{-1} and 10^{-3} M. As depicted in Fig. 4B no sensible effect was recorded when measuring with the same sensor concentrations going from 10^{-1} to 10^{-3} M and vice-versa, demonstrating the possibility to use the same electrode for continuous measurements, at several ion concentrations.

The light sensitivity and the evaluation of the formation of aqueous layer in CB-SPE-based sensors were also investigated, comparing the results obtained with no CB-modified SPE-based sensors, to confirm the advantage of using CB-SPE as platform for potentiometric sensor development. For the test of light sensitivity, the CB-SPE-based sensors were kept in the dark until the sensors were exposed either to room light or to UV light and the potential response was recorded in 0.1 M NaCl solution. No significant potential drift was observed during the measurement using CB-SPE-based sensor (Fig. 4C, continuous line) as well as using bare SPE-based sensor (Fig. 4C, dashed line). In detail, we observed a little bit more stable response of bare-SPE in respect to the one obtained using CB-SPE, however, this study confirms that the presence of CB does not affect significantly the response in different light conditions, taking into account the properties of CB to absorb light in the UV-Vis-NIR, as reported in the literature [47, 48].

An additional study was also carried out to evaluate the formation of aqueous layer between the surface of CB-SPE and the cast ion-selective membrane, which is the main reason of instability in

long-term measurement. To evaluate the formation of water film, the potentiometric test was carried out recording the potential response for both bare SPE and CB-SPE-based sensors, using the procedures reported in the literature [24, 40, 49]. As shown in Fig. 4D (dashed line), a substantial potential drift was observed when changing back from K^+ to Na^+ using bare SPE-based sensor, confirming the presence of a water film in case of unmodified SPE. Instead, any drift was obtained using CB-SPE-based sensor, demonstrating the absence of water film and boosting the use of CB modified SPE as platform to fabricate smart sensors for long-term potentiometric measurement. The achieved results demonstrate that the water layer is absent in CB-SPE-based sensors owing to the high hydrophobic character of CB, highlighting the advantage of using CB-SPE in respect to bare SPE for potentiometric sensor fabrication. To confirm the suitability of CB-SPE-based sensor for long time analysis, we evaluated the working stability by measuring the potential of 0.1 M NaCl for 24 consecutive hours (Fig. 5A), observing a stable signal that confirms the previous results. The calculated drift of SPE/CB/ Na^+ ISM which was equal to 0.6 mV/h during the 24 hours tested. The value obtained is in the range of drift reported in the literature; indeed, it is lower than the one obtained using gold nanowire electrode modified with sodium Ionophore X (2.2. mV/h) [50] and higher than the values in case of gold chip electrode modified sodium Ionophore X (0.22 mV/h) [51], paper-based electrode modified with graphene and sodium Ionophore X (0.18 mV/h) [52], and screen-printed electrode modified with sodium Ionophore VI and nanocomposite constituted of Prussian Blue and chitosan (1.3 μ V/h) [53].

Together with working stability, also storage stability was investigated by measuring 0.1 M NaCl the same day of ion selective and reference membrane deposition, and after 5, 7, and 15 days, demonstrating good shelf life when the sensors are stored dry in the dark at room temperature (Fig. 5B).

3.6. Sweat analysis

With the aim to apply this sensor for Na⁺ measurement in sweat, an interference study was carried out evaluating the response of Na⁺ 100 mM solution in presence of Mg²⁺ 0.2 mM, K⁺ 10 mM, Ca²⁺ 1 mM, electrolytes usually present at these concentrations in sweat [54], observing a negligible interference (Fig. 5C). To evaluate the suitability of the developed sensor, three samples of sweat collected during running activity were measured, obtaining 44 ± 4 mM, 55 ± 6 mM, and 47 ± 3 mM, values in agreements with sodium ions content in healthy people. To evaluate the accuracy, a synthetic artificial sweat was prepared according to Parrilla et al. [27]. Firstly, we have investigated the response of the sensor in this artificial matrix in a range up to 500 mM, taking into account that the concentration of sodium ions in sweat is usually found between 10 and 160 mM, obtaining a linearity described by the following equation $y = (0.499 \pm 0.005) + (0.076 \pm 0.004)x$, $R^2 = 0.989$ (Fig. 5D). To deeply investigate the super-Nernstian behaviour of this sensor, the measurements were carried out by using an external Ag/AgCl reference electrode or the printed solid-state Ag/AgCl reference electrode. The response of the sensor in standard solutions was evaluated in the range of sodium ions comprised between 10⁻⁵ M and 1 M, obtaining linearity in both cases comprised between 10⁻⁴ M and 1 M, with a slope equal to 0.058±0.003 mV and 0.053±0.004 mV, respectively for solid-state and external reference electrodes (Figure S4-A). In the case of artificial sweat, linearity between 8 mM and 0.5 M was observed with a slope equal to 0.076±0.004 mV and 0.071±0.005 mV, respectively for the solid-state and external reference electrodes, as reported in Figure S4-B. The obtained data demonstrated the suitability of the solid-state reference electrode, while further another investigation is needed to understand the super-Nernstian behaviour. Then, the recovery study was carried out by spiking sweat sample 25 mM, 50 mM and 75 mM with recovery values equal to 90 ± 3 %, 94 ± 2 %, and 94 ± 5%. When compared with the literature, this CB-based ion selective sensor has demonstrated comparable analytical performances in respect to

other ion-selective sensors based on nanomaterials including graphene, gold nanodendrites, vertically aligned gold nanowires, and carbon nanotubes (Tab. 1), with the advantage that this sensor was conceived with cost-effective material e.g. carbon black and procedures (e.g. screen-printing technique, drop-casting) with the aim to deliver an easy mass-producible sensor to apply in wearable device sector.

4. Conclusion

The use of nanomaterials has had a huge impact in the electrochemistry field including in the potentiometric sensors. Among carbonaceous materials, carbon black in the last years have acquired a relevant position due to its relevant electrochemical features as well as its low cost and easiness to prepare a stable dispersion useful for modification of sensors by drop-casting procedure. The printed electrochemical sensors modified with carbon black has demonstrated the capability to detect several analytes with improved analytical features. Herein, we exploited the features of carbon black in potentiometric sensors to develop a printed electrochemical sensor for sodium ions detection. The optimisation of drop-casting modification of working and reference electrodes as well as the conditioning process allowed for a sensor characterised by no aqueous layer formation with long-term potential stability, good shelf life, and resistance to the interferences from oxygen and light. The results achieved demonstrated the suitability of screen-printed electrode as platform for developing a carbon black-based potentiometric sensor for sodium ions detection in standard and artificial sweat samples, opening a further application of screen-printed electrodes modified with carbon black for potentiometric measure to apply in wearable device sector.

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Figures

Figure 1

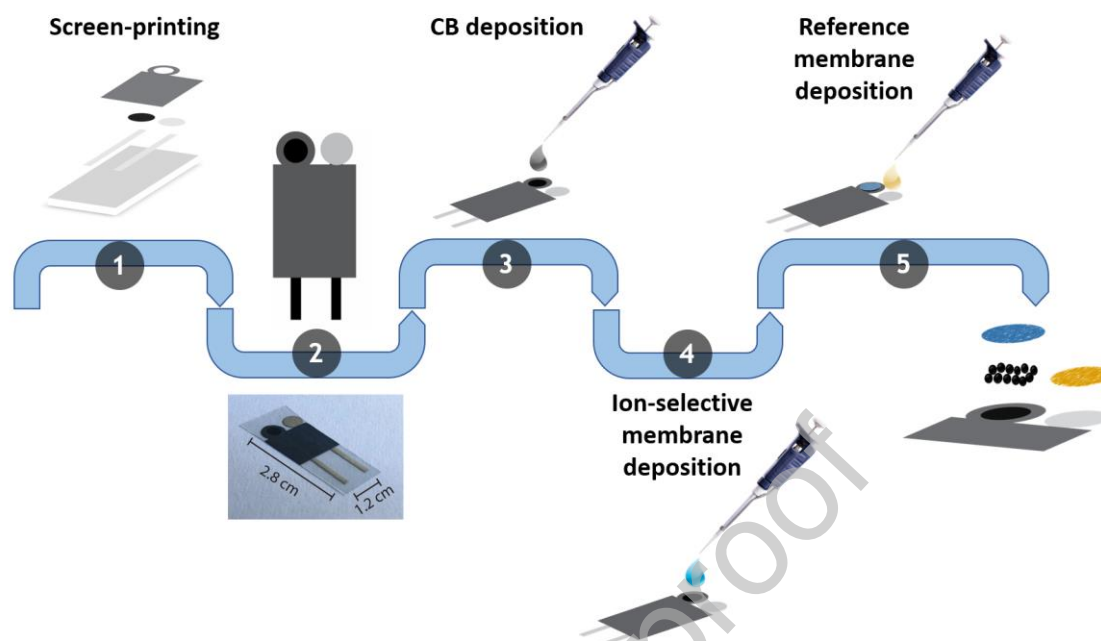


Figure 2

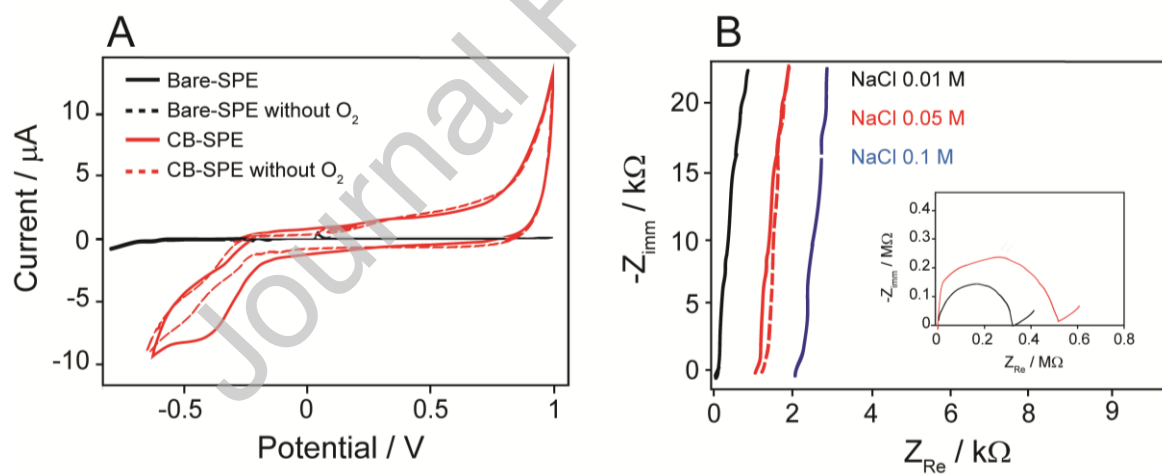


Figure 3

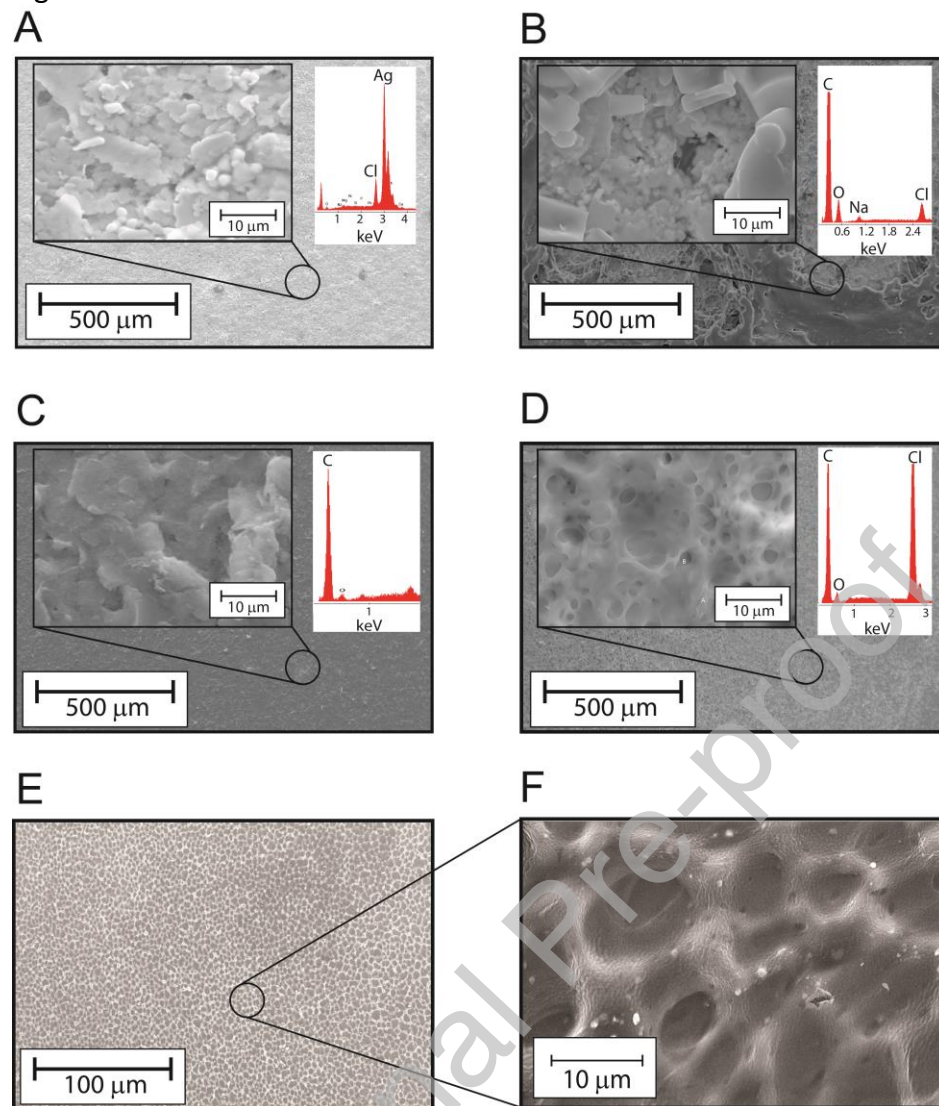


Figure 4

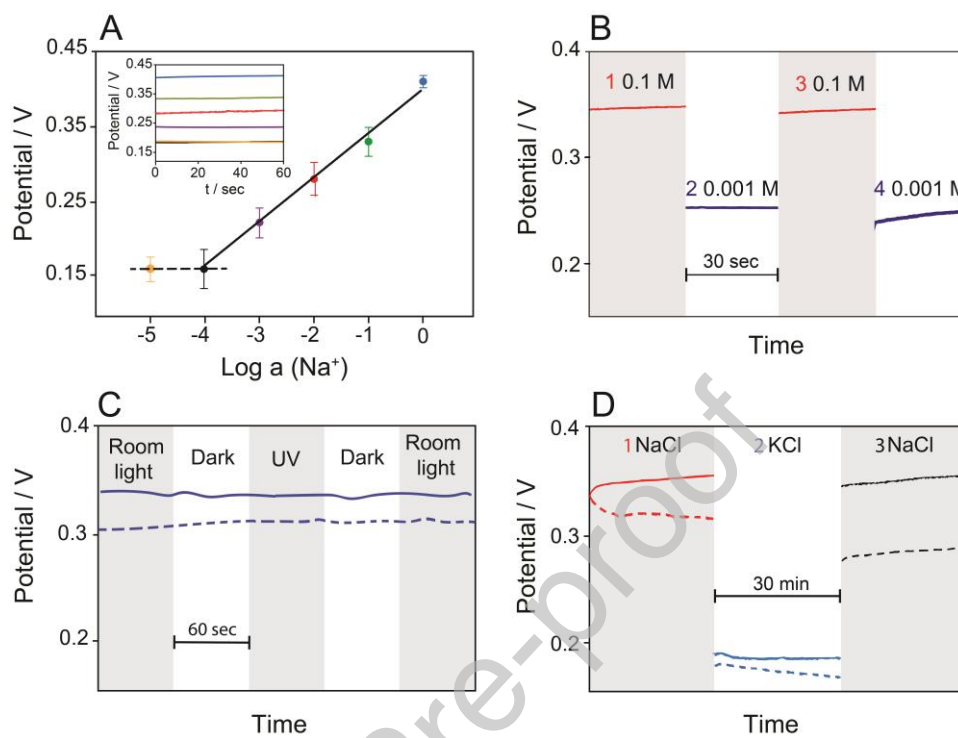


Figure 5

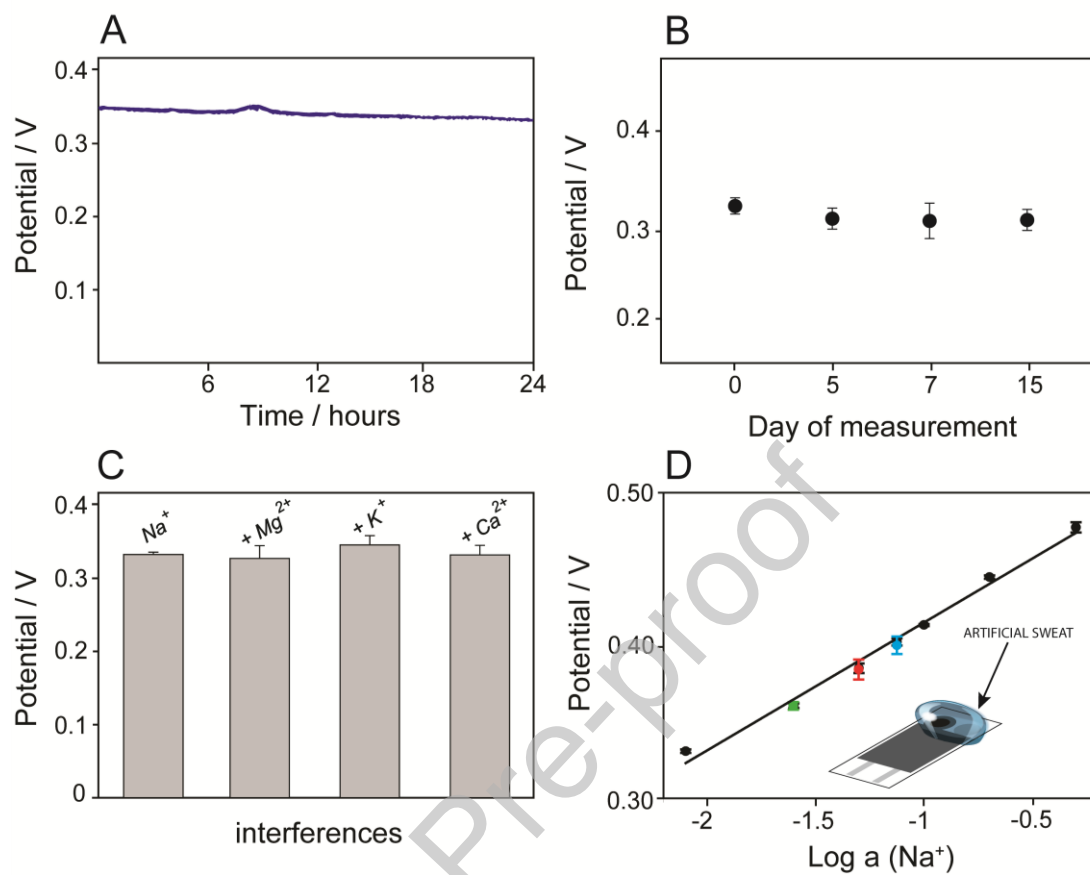


Table 1

Sensor	Nanomaterial	Modification procedure	Analyte	Linear Range (M)	Slope (mV / decade)	LOD	Matrix	drift	Ref
v-AuNW electrodes	v-AuNW	Dipping in precursor solution	Na ⁺	10 ⁻³ -10 ⁻¹	58.2		sweat	2.2 mV/h	50
Au chip electrode	AuNDs	Electrodeposition	Na ⁺	10 ⁻⁶ -10 ⁻¹	56.6	0.8 μM	sweat	0.22mV/h	51
Paper based electrode	Graphene	Spray	Na ⁺	10 ⁻⁶ -10 ⁻¹	55.7	---	sweat	0.18 mV/h	52
SPE	CS/PB nanocomposite	Dropcasting	Na ⁺	10 ⁻⁴ -1	52.4	---	---	1.3 mV/h	53
Textile screen-printed	CNT	Ink mixing	Na ⁺	10 ⁻⁴ -10 ⁻¹	56.5	13 μM	---	---	54
SPE	CB	Dropcasting	Na ⁺	10 ⁻⁴ -10 ⁻¹	58.4	63 μM	Artificial sweat	0.6 mV/h	This work

Figure captions

Fig. 1. Schematic representation of the various steps of fabrication of modified SPEs used in this work. Screen-printing (A) and final conformation electrode (B), CB deposition onto working electrode surface (C), ion selective membrane deposition onto CB-modified working electrode (D), reference membrane deposition onto pseudo-reference electrode (E).

Fig. 2. (A) Cyclic voltammetry obtained measuring 100 μL of NaCl 100 mM with Bare-SPE (black) and CB modified SPE, in absence (dashed line) and in presence of oxygen (solid line), scan rate: 25 mV/s (B) Electrochemical impedance spectroscopy obtained with and CB-SPE in different concentrations of NaCl: 0.1 M (blue), 0.05 M (red), 0.01 M (black), in absence (dashed line) and in presence of oxygen (solid line); Frequency range: 10 kHz to 0.1 Hz, E_{dc} : 0.20 V, ΔE_{ac} : 10 mV. Inset: Nyquist plot depicting response obtained using SPE/ Na⁺ ISM (red) and SPE/CB/ Na⁺ ISM (Black), measuring NaCl 0.1 M. Frequency range: 10 kHz to 0.1 Hz, E_{dc} : 0.20 V, ΔE_{ac} : 10 mV

Fig. 3. SEM micrographs of bare Ag/AgCl reference electrode (A), Ag/AgCl reference electrode modified with polyvinyl butyral-based solution (B), bare graphite working electrode (C), graphite working electrode modified with CB and ion selective membrane (D) and graphite working electrode modified with CB and ion selective membrane performed with FE-SEM (C,D). (insets: higher magnification micrographs and EDS spectrum).

Fig 4. (A) Calibration curve and potentiograms (inset) obtained using CB-SPEs modified with 7.5 μL of mixture for ion selective membrane and 10 μL of polyvinyl butyral-based solution for reference membrane, measuring 100 μL of a solution containing Na⁺ 10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M and 1 M; (B) Reversibility test obtained measuring 0.1 M NaCl (red) and 0.001 M NaCl (blue) using CB-

modified

SPE. Ion selective membrane: 7.5 μL , reference membrane: 10 μL ; (C) Effect of light on the potential

stability of the CB modified-SPE in 0.1 M NaCl solution. Ion selective membrane: 7.5 μL , reference membrane: 10 μL ; (D) Water layer test performed with Bare-SPE (dashed line) and CB-modified SPE (solid line) switching between 0.1 M NaCl and 0.01 M KCl. Ion selective membrane: 7.5 μL , reference membrane: 10 μL .

Fig 5. (A) Working stability study obtained measuring 0.1 M NaCl for 24 consecutive hours using CB-modified SPE. Ion selective membrane: 7.5 μL , reference membrane: 10 μL ; (B) Shelf-life test performed by measuring 0.1 M NaCl the same day of ion selective and reference membrane deposition and after 5, 7 and 15 days. Reference membrane storing condition: 0.01 M KCl; (C) Histogram bars obtained measuring 100 μl of a solution containing Na^+ 100 mM, in presence of Mg^{2+} 0.2 mM, K^+ 10 mM, Ca^{2+} 1 mM; (D) Recovery studies performed in artificial sweat by spiking the matrix with 25 mM (green) and 50 mM (red) and 75 mM (cyan) of NaCl.

Table 1. Electrochemical sensors for the detection of sodium ions

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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