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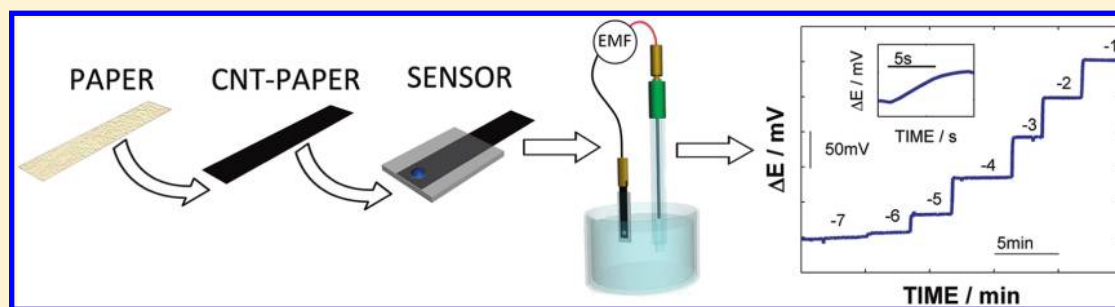
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Paper-Based Ion-Selective Potentiometric Sensors

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S Supporting Information



ABSTRACT: A new approach to develop ultra low-cost, robust, rugged, and disposable potentiometric sensors is presented. A suspension of carbon nanotubes in a water–surfactant mixture (carbon nanotubes ink) is applied on conventional filter papers to turn them into conductive papers, which are then used as a substrate to build ion-selective electrodes. The electrodes are made by drop casting a membrane on a small circular area of the conductive paper. In this way, the carbon nanotubes act as both electric conductors and ion-to-electron transducers of the potentiometric signal. Electrodes for sensing K^+ , NH_4^+ , and pH were built and tested using this approach, and the results were compared with classical solid-state ion selective electrodes using carbon nanotubes as transducers and glassy carbon as a substrate. In all cases, the analytical performance (sensitivity, linear ranges, limits of detection, selectivity, etc.) of these disposable paper electrodes was similar to that obtained for the more conventional type of ion-selective-electrodes. This opens new avenues for very low-cost platforms for generation of chemical information.

Having access to robust, rugged, and low-cost chemical sensors is becoming of paramount importance in a growing number of situations. There are well established needs, such as diagnostic tools for poor regions of the planet.¹ Additionally, the development of chemical sensing networks^{2,3} and the increasing role of approaches such as point of care^{4–6} and telemedicine^{7,8} are pushing the demand for fast access to bio(chemical) information. The term “vanguard analytical approaches”⁹ has been proposed to refer to these new platforms that allow low-cost, rapid, on site chemical analysis.

In these new platforms, traditional performance parameters, such as stability, detection limits, etc., must be balanced with the need for speed, cost, and simplicity. Under these new lenses, some techniques, such as potentiometry, are regaining new value. Potentiometry has traditionally displayed an unrivalled simplicity of operation and instrumentation.¹⁰ For this reason, it is still one of the workhorses in clinical laboratories and almost the universal approach to measure pH. Ion-selective electrodes have also become the standard procedure for measuring several ions. Furthermore, the development of solid contact ion-selective electrodes (SC-ISE) during the last few decades has produced a “silent revolution”¹¹ that has led to drastic improvements of the limits of detection (LOD), increased range of applications, and simplification of the sensor construction, operation, and maintenance. Recent works have also shown the advantages of miniaturization of the electrodes,¹² and the development of the electrode arrays^{13,14} that could be remotely operated. All in

all, potentiometric sensors are ideal “vanguard” tools for the remote, out of the lab generation of chemical information.

Some limitations, such as the cost of the sensors, still remain as a challenge when dealing with large scale applications. Despite being among the most affordable instrumental approaches, current potentiometric sensors are still too expensive for large scale operations. Screen-printed electrodes^{15,16} have partially addressed this problem, but the need for lower cost sensors still remains a challenge. The search for new substrates to build electrodes as well as the use of mass manufacturing techniques are crucial to further reduce the cost of the sensors. For this reason, recent breakthroughs in areas such as bendable electronics can be key to finding new substrates and processes to fabricate rugged, robust, and extremely low-cost potentiometric sensors.

Regarding the search of new substrates, paper has been widely used to make simple, cost-effective analytical tools. Paper dipsticks and lateral flow systems have been used for decades for qualitative and semiquantitative analysis, and many new applications on this area are still being developed.^{17,18} Whitesides et al.^{19,20} have recently expanded the analytical usefulness of paper based devices exploiting the ability of papers to produce pump-free capillary flow of liquids. Through

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simple approaches to build planar and 3D paper based microfluidic devices, they demonstrated the power of these platforms as simple, fast, and cost-effective diagnostic tools. The use of electrochemical techniques has been proposed by Dungchai et al. as a way to overcome some limitations of the colorimetric detection.²¹ These authors used paper screen-printed electrodes to perform chronoamperometric measurements in paper microfluidic devices, achieving quantitative detection of several analytes of biological relevance. Apilux et al.²² followed a similar approach using square wave voltammetry on paper based electrodes to detect Au(III) in gold refining waste solutions, obtaining also accurate quantitative results. Karube et al.²³ pioneered the use of paper based electrodes by developing a disposable Clark-type oxygen sensor. The electrodes were fabricated by sputtering silver directly onto the paper substrate. All these results show that the combination of electrochemical detection on paper based devices is a promising route to generate robust and cost efficient quantitative analytical tools.

Some recent progress in bendable electronics using carbon nanotubes (CNTs) is opening new and attractive avenues in this area. CNTs are well-known for their outstanding electrical²⁴ and chemical properties, which have been extensively exploited in a plethora of different areas. During the past few years, dispersions of CNTs in aqueous solution (usually called CNT inks) have been used to generate conductive papers. CNT inks can be generated by functionalization of the CNTs (often through oxidation by acid treatment to generate carboxyl groups) or by the use of surfactants.²⁵ Surfactant-based inks, particularly using sodium dodecylbenzenesulfonate (SDBS), offer better electrical conductivity due to the higher weight fraction of CNTs that can be suspended.²⁶ Kordas et al.²⁷ printed a wide range of electrical circuits in paper using a conventional inkjet printer. Hu et al.^{28,29} developed paper based capacitors using CNT inks. Remarkably, it has been shown that CNT printed papers present enhanced charge storage capacity and ability to withstand mechanical work (such as folding or bending) better than metal coated paper. Indeed, because of the strong absorption onto the cellulose fiber, the CNT-conductive paper is in reality a 3D network of conductive fibers, not just a 2D conductive layer. Thus, CNT-conductive papers do not represent simply a replacement but a significant improvement of metal coated papers. Kotov et al.³⁰ pioneered the use of these CNT-conductive papers to make chemical sensors. These authors used resistive and amperometric measurements to detect antibodies and toxins in water using functionalized CNT-conductive papers.

Among their many advantages, during the past few years our research group has shown that CNTs can also act as very effective ion-to-electron transducers in solid-contact ion-selective electrodes (ISE).^{31,32} The use of CNTs, instead of conducting polymers, yields improved signal stability,³³ reduced light sensitivity, simplicity of construction and a great versatility. CNT-based potentiometric electrodes were used to detect inorganic and organic substances.^{34–36} This opens a very attractive opportunity to combine recent progress on CNT-conductive papers and CNT-based potentiometric sensors, which, to the best of our knowledge, has not yet been explored.

In this report, the development of solid contact ISEs based on conductive papers is presented. Conductive paper made by impregnation of CNT inks is used as a substrate where a conventional PVC based ion-selective membrane is deposited.

As proof of principle, electrodes for the determination of K^+ , NH_4^+ , and pH were constructed. The resulting paper electrodes show an analytical performance that is comparable to a conventional lab made ISE, opening the way to simple and cost-effective sensors that can be used outside the laboratory. Some limitations and potential future application of these novel sensors in real life scenarios are discussed.

■ EXPERIMENTAL SECTION

Reagents. Single-wall carbon nanotubes (SWCNTs) of 95% purity (1–2 nm outer diameter, 5–30 μ m length) were purchased from Chengdu Organic Chemicals Co. (ChengDu, SiChuan, China). The SWCNTs were used without further purification. Valinomycin (potassium ionophore I), nonactin (ammonium ionophore I), tridodecylamine (hydrogen ionophore), potassium tetrakis (4-chlorophenyl) borate (KTFP) with >98% purity, bis(2-ethylhexyl)sebacate (DOS) with >97% purity, polyvinyl chloride high molecular weight (PVC), tetrahydrofuran (THF), and sodium dodecylbenzenesulfonate (SDBS) were all purchased from Sigma-Aldrich. Analytical grade chloride salts of ammonium, calcium, lithium, magnesium, potassium, and sodium were purchased from Sigma-Aldrich.

CNT Ink Preparation. The carbon nanotube ink (CNT-ink) was prepared by adding SWCNTs to a 10 mg/mL sodium dodecylbenzenesulfonate (SDBS) aqueous solution, as reported by Cui et al.²⁹ A concentration of 3 mg/mL of SWCNTs was used since it gives optimum ink stability and adherence to the paper. SWCNTs were successfully dispersed using a tip sonicator (Ultrasonic processor UP200S, Hielscher Ultrasonics GmbH, Teltow, Germany) for 2 h (100 W, frequency of 24 kHz, 60% of amplitude and a cycle of 0.5 s). To avoid overheating and undesirable secondary reactions, the bath was always kept at 4 °C during the sonication. The CNT-ink, which shows a density of 0.99 g L⁻¹, was stored in a refrigerator at 6 °C to avoid destabilization. Under these conditions it has been observed that the CNT dispersion can be used for at least 3 months.

Ion Sensing Membrane Preparation. A potassium ion-selective membrane (ISM) contains 2 wt % (18 mmol/kg) of valinomycin, 0.5 wt % (10 mmol/kg) of potassium tetrakis (4-chlorophenyl) borate (KTFPB), 32.8 wt % of poly(vinyl chloride) (PVC), and 64.7 wt % of bis(2-ethylhexyl) sebacate (DOS).³⁷ Ammonium ISM contains 1 wt % of nonactin (13.6 mmol/kg), 32.2 wt % of PVC and 66.8 wt % of DOS.³⁸ Finally, pH sensing membrane contains 1 wt % (20.2 mmol/kg) of potassium tetrakis (4-chlorophenyl) borate (KTFPB), 2 wt % (38.3 mmol/kg) of tridodecylamine, 33.0 wt % of PVC, and 65.5 wt % of DOS.³⁹ All the membranes were prepared by dissolving 100 mg of the mixture into 1 mL of THF. The cocktails were stored at 4 °C and remain stable for about 2 weeks.

Conductive Paper. A conventional qualitative filter paper (10 cm diameter, 0.01 cm thick paper disk, 10–20 μ m fiber thickness) purchased from Ahlstrom (Barcelona, Spain) was used as the initial substrate. The conductive paper was made by painting a 7 cm side square with the CNT-ink using a conventional paintbrush. The ink is readily absorbed by the paper and, after the solvent evaporates (usually a few minutes), the paper is thoroughly rinsed with water. Some bubbles are observed during the rinsing process showing that, to some extent, the excess of surfactant is being washed out (there is still some controversy on whether this step is really needed²⁸). After

the rinsing, the paper is dried at room temperature or, to speed up the process, it can be placed in an oven at 60 °C for about 5 min. At this point the resistance is checked for optimization purposes using a four-point-probe method. This process of painting, drying, washing out the surfactant, and redrying is considered one cycle. The cycles are repeated until the resistance of the dried paper reaches a stable value, usually around 500 Ω /sq.

Paper Ion-Selective Electrode Construction. Once a suitable resistance has been achieved, the CNT conductive paper is cut into strips of 0.5 cm \times 2 cm and partially covered with plastic masks of 1 cm \times 1.5 cm on both sides. Details of the electrode components (conductive paper, mask, and membrane) and assembly are schematically shown in Figure 1. When glued together, the two plastic masks sandwich the

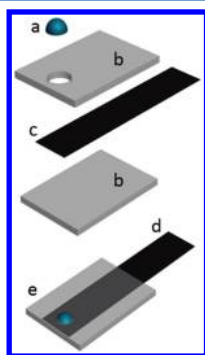


Figure 1. Scheme of the potentiometric paper based sensor: (a) ion selective membrane, (b) plastic mask, (c) carbon nanotube conductive paper, (d) area for electric contact, and (e) final sensor view.

conductive paper, avoiding any direct contact of the nanotubes with the solution. The front mask has a circular orifice with an area of approximately 2.8 mm². With this approach, the mask leaves one of the ends of the CNT conducting paper (approximately 0.5 cm long) exposed to make electrical contact with the reading instrument, while the small orifice in front the mask leaves room for casting the membrane. Finally, a volume of 15 μ L of the membrane cocktail is applied at once by drop casting onto the paper (into the orifice left by the plastic mask). The membranes usually dry in less than 10 min. The volume of membrane cocktail applied was optimized until maximum (Nernstian) sensitivity was reached. Under optimal conditions, the thickness of the membrane (measured with environmental scanning electron microscopy, ESEM) is approximately 20 μ m. These paper electrodes were used as conventional ion-selective electrodes (making sure that the membrane was always fully immersed into the solution). Electrodes were conditioned in 0.05 M solutions of the primary analyte overnight. Just before using them for the first time, they were preconditioned with a 10^{−4} M solution of the primary analyte for approximately 20 min.

Electrochemical Measurements. Electromotive force (EMF) was measured with a high input impedance (10¹⁵ Ω) EMF16 multichannel data acquisition device (Lawson Laboratories, Inc. Malvern) at room temperature (22 °C) in a stirred distilled water solution without any ionic strength adjuster. A double junction Ag/AgCl/KCl 3 M reference electrode (type 6.0726.100, Methrom AG) containing a 1 M LiAcO electrode bridge was used. The paper electrode is connected to the measuring instrument by means of a small clamp. The membrane is fully covered by the solution but there is no

direct contact between the exposed CNT-paper and the solution. The EMF values were corrected using the Henderson equation for the liquid-junction potential and the activity coefficients calculated by the Debye–Hückel approximation. After the measurements, the electrodes were air-dried and stored without using any storage solution.

Selectivity coefficients were calculated by the fix interference method (FIM), which is well reported in the literature.⁴⁰ Several calibration curves with the primary analyte in highly concentrated background interference solutions (10 mM) were done. From the limit of detection of each curve and knowing the concentration of the interference, the selectivity coefficient was obtained.

Electrochemical impedance spectroscopy (EIS) measurements were performed using a potentiostat/galvanostat AutolabPGSTAT128N with a frequency response analyzer electrochemical impedance module (FRA2) (AUTOLAB, Eco Chemie, B.V., Utrecht, The Netherlands) fitted with a three electrode electrochemical cell. The paper electrode was used as the working electrode, a glassy carbon rod with a diameter of 3 mm as the counter electrode, and a Ag/AgCl/KCl 3 M (type 6.0733.100, Methrom AG) single junction electrode as the reference electrode. The impedance spectra were recorded in a frequency range from 100 kHz to 0.01 Hz using an excitation amplitude of 10 mV in a 0.01 M solution of the target analyte.

RESULTS AND DISCUSSION

Conducting Paper. Figure 2 shows the result of the conversion of a conventional filter paper into conductive paper through successive applications of CNT-ink. The initial resistance of the untreated filter paper is extremely high, but it quickly decays with the application of the CNT-ink. Typically, values close to 500 Ω /sq are reached after the 4th to 5th cycle. Lower values of electrical resistance can be obtained through further application of the CNT-ink. However, values of a few hundred ohms are considered acceptable taking into account that the overall resistance of the system will be controlled by the ion-selective membrane. The pattern observed in Figure 2e is fairly reproducible, so no significant difference is found between the final values of electrical resistance obtained for different papers. These values are also in agreement with those already reported for the generation of CNT conductive papers. Cui et al.²⁸ reported a resistance of 30 Ω /sq using the Meyer rod coating method and one of 300 Ω /sq with the direct pen writing, which is more similar to our methodology. Any comparison, however, is relative, since these authors used Xerox paper, while filter paper has been used for our work. The ability to withstand mechanical stress, such as bending or twisting, is an attractive property that allows longer lifetime of the sensors. Cui et al.²⁸ demonstrated that, when subject to folding or bending, conducting papers using CNT-ink outperform other substrates, such as metal coated papers. In this work, no significant changes in both electrical resistance and mechanical properties were observed after bending and folding the papers many times.

The role of the surfactant used in the ink on the conductive paper is still a matter of debate. As suggested by Cui et al.,²⁸ because of the strong supramolecular interactions between the CNT and the cellulose, the SDBS is rearranged when the CNTs are absorbed onto the paper. These authors reported that there is no significant difference in the conductivity of the paper before and after washing. Some authors have suggested the use of an acid wash as a way to eliminate the surfactant.⁴¹ In

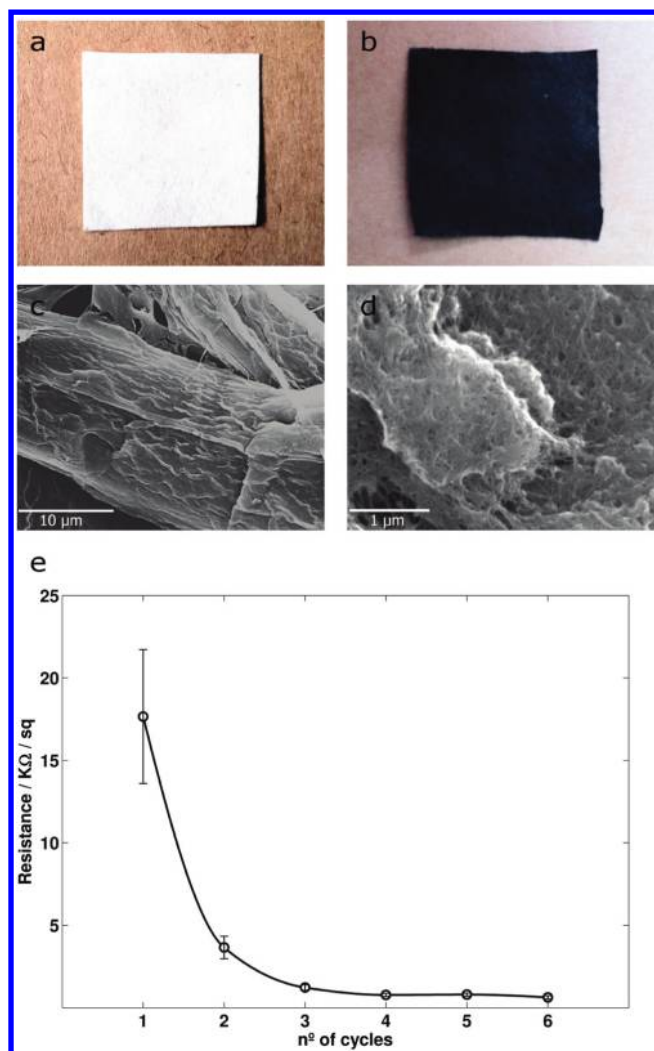


Figure 2. Conversion of filter paper into a conductive paper: (a) macroscopic image of filter paper, (b) macroscopic image of conductive paper, (c) SEM image of filter paper surface showing the paper fibers, (d) SEM image of filter paper impregnated with CNT-ink, and (e) electrical resistance of several filter papers as a function of the numbers of cycles of CNT-ink.

our work it is observed that the surfactant is, at least in part, washed during the careful rinsing of the paper. A quick way to evaluate the leaching of surfactant to the aqueous phase is by monitoring the concentration of surfactant in the rinsing water after each washing. This can be easily done by following the UV absorption spectrophotometry at different times using either one step or multi washing steps (see the Supporting Information, Figure 1.si). The experiment shows that, after some rinsing steps, the SDBS is practically extracted from the paper-CNT assembly (at least the concentration of SDBS should be lower than $1 \mu\text{M}$, which is the LOD of the technique). If those rinsing steps are avoided, letting the paper dry with the surfactant, the value of the electrical resistance obtained is slightly higher, and it can be decreased by proper washing. All in all, if some very low amount of surfactant remains, it seems that it does not produce a significant effect for the purpose of this work. Other type of inks, for example, using different surfactants, such as poly(sodium 4-styrene-sulfonate), to immobilize CNTs on cellulose have been reported. Nevertheless, for the purpose of this work the SDBS-CNT-

inks give satisfactory results, so no attempt to explore other surfactants were made.

The capillary effects due to the microstructure generated by the cellulose fibers produces a very quick impregnation of the papers with the CNT-ink. The papers acquire a gray-black color almost instantly, which darkens with successive ink applications. Figure 2 shows an image of the paper before (part a) and after (part b) the application of the CNT ink. Apart from the color change, the conductive paper does not show any visible sign of the CNT deposition. In fact, the conductive sheet can be bent and folded as normal, untreated paper, without affecting the electrical resistance. Scanning electron microscopy images of the untreated (part c) and CNTs covered (part d) cellulose fibers show that conductive papers are covered by a widespread randomly interconnected network of CNTs. It is important to remark that, due to this impregnation and diffusion of the ink, the CNT-paper forms an individual entity which does not present defined layers. It has been suggested that this structure results from the great stabilization of CNTs on the cellulose fibers by supramolecular interactions, which impedes their detachment when the papers are rinsed with water. This intimate interaction between CNTs and cellulose fibers gives conductive CNT-papers a 3D microstructure that is not present in metal covered papers and that is responsible for two important features. First, the enhanced effective area gives good electrical conductivity. This has been exploited for the development of supercapacitors. Second, improved mechanical stability allows withstanding bending, folding, etc., without significantly affecting the electrical conductivity.²⁹ This is a significant advantage when compared to metal coated papers. It is noteworthy that when the CNT-ink is deposited and dried onto substrates such as glassy carbon or metals, most of the CNTs are washed away simply by rinsing with water.

Paper-based ion-selective electrodes for three target species, namely, K^+ , NH_4^+ , and H^+ , were prepared and individually tested. Figure 3 shows the time trace of the potentiometric response for the three paper SC-ISE when the activity of the primary analyte is increased. The corresponding calibration plots for each one of the analytes (Figure 3) show a Nernstian response between 10^{-5} and 10^{-1} M indicating that the membrane is working as expected. In all cases, error bars cannot be seen in the calibration plots due to the scale. The standard deviation of a single, continuous measurement is well below 1 mV, as with conventional glassy carbon CNT ISE. The reproducibility of several repeated measurements of the same solution with the same electrode is close to 1 mV. Furthermore, since the slopes are fairly reproducible (1–2% RSD), the largest source of variability between sensors arises from the “ E_{exp}^0 ” value (i.e., intercept of the calibration plot). Typically, a series of electrodes will show intercepts that will not differ in more than a few millivolts, although it is found that eventually one electrode may show values that differ from the others is as much as 30 mV (while the slope remains Nernstian), thus increasing the uncertainty of this value. The observed intercept value is a function of the individual interface potential between the paper/CNTs layer, CNTs layer/ion selective membrane, and the rest of the constant potentials along the potentiometric cell (see eqs 1–4 in the Supporting Information). It is evident that those potentials will depend intrinsically on the construction of the electrodes (amount of CNTs, homogeneity of CNT-layers, membrane, and CNT-layer thickness, etc). This variability in the intercept indicates that there some factors in the construction procedure of the electrodes that are not totally

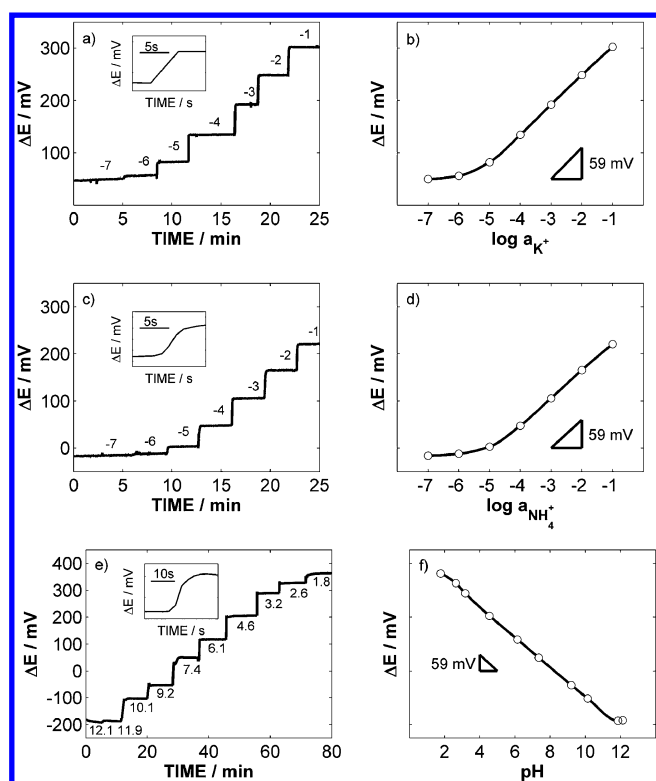


Figure 3. Potentiometric response for three different paper ISEs. Time trace (left) and corresponding calibration plots (right) after addition of the primary analyte for ammonium (a, b) potassium (c, d), and pH (e, f). The inset on the plots a, c, and f shows a detail of the time response for a single addition of the analyte.

under control. However as with many other solid contact ion-selective electrodes manually prepared,^{33,42} the variability on the intercept values is the same order of magnitude. In any case, after the intercept has been corrected by proper calibration, the calibration plots overlap well enough so that the error bars cannot be easily seen. Calibration is always necessary since, as it was mentioned before, changes over time occur when electrodes are used intensively (see Figure 2.s*i* in the Supporting Information). It should be expected that improvements on the electrode manufacturing approach, especially the membrane deposition, will help in the future to overcome this issue. In any case, the results show that the CNT-paper based electrodes emulate conventional ion-selective electrodes.

Table 1 summarizes the most relevant parameters of the analytical performance for the three sensors. Limits of detection (LOD) found for K^+ and NH_4^+ are in the micromolar range. These values are satisfactorily taking into account the scope of this work, i.e., the development of out of the lab chemical sensing platforms. Indeed, handling submicromolar concentrations of these ions in field analysis is not a simple task. Additionally, although SC-ISE reported in the literature show a significantly lower LOD, this is usually achieved through strict

conditioning protocols or using additional approaches to compensate for the undesirable fluxes from the phase boundary membrane to the aqueous solution.⁴³ These complex procedures require facilities and expertise that fall beyond the expected field of application of these sensors. Thus, these limits of detection were considered satisfactory for field analysis. No attempts to further decrease these values were yet made, although it will be interesting to evaluate the real limitations of these sensors.

The selectivity of the membranes was calculated using the fixed interference method. The selectivity coefficients, $\log K_{ij}^{pot} \pm$ standard deviation ($n = 3$) (Table 2) are comparable with similar membranes cast on glassy carbon instead of CNT-ink papers.³⁵ Different values can be due to the different methodology used for the experimentation.

Table 2. Selectivity Coefficients for Potassium ($\log K_{Kj}^{pot}$), Ammonium ($\log K_{NH_4j}^{pot}$), and Proton ($\log K_{Hj}^{pot}$) Compared to the Ones Reported by Other Authors,^{35,47,48} Respectively

ion <i>j</i>	K^+ -paper ISE	K^+ -ISE ³⁴
Li^+	-2.7 ± 0.1	-4.4 ± 0.1
Mg^{2+}	-4.1 ± 0.1	-4.9 ± 0.2
Ca^{2+}	-3.9 ± 0.1	-4.7 ± 0.1
Na^+	-2.8 ± 0.1	-3.2 ± 0.2
NH_4^+	-1.9 ± 0.1	
ion <i>j</i>	NH_4^+ -paper ISE	NH_4^+ -ISE ⁴⁷
Mg^{2+}	-3.8 ± 0.5	-4.0
Ca^{2+}	-4.7 ± 0.1	-3.7
Li^+	-4.7 ± 0.1	-3.5
Na^+	-3.0 ± 0.1	-2.4
K^+	-1.2 ± 0.1	-1.0
ion <i>j</i>	pH-paper ISE	pH-ISE ⁴⁸
K^+	-9.3 ± 0.8	-7.86
NH_4^+	-10.1 ± 0.3	-8.90
Na^+	-10.2 ± 0.1	-8.90
Li^+	-10.1 ± 0.1	-8.90
Ca^{2+}	-10.4 ± 0.1	-8.36
Mg^{2+}	-9.8 ± 0.1	-9.40

A comparison between these paper-based and glassy carbon (using CNTs as transducers) ISE shows no differences between the electrodes in terms of the time response characteristics. Also, paper-based sensors show good short and medium term stability. In fact, it is observed that the baseline drift is less than 3 mV h^{-1} and $5\text{--}10 \text{ mV h}^{-1}$ for potassium and ammonium, respectively (based on a continuous 5 h period). Considering that the sensors are expected to be used for short time readings, these variations of potential can be considered satisfactory. For conventional CNT SC-ISE on glassy carbon, significantly better values, below $50 \mu\text{V h}^{-1}$, have been reported.⁴⁴ It is not yet clear what are the main factors affecting signal stability for these paper electrodes, although it should be expected that both electronic and chemical factors might be playing some role. In

Table 1. Analytical Parameters of the Three Sensors

	ammonium	potassium	pH
sensitivity	$56.4 \pm 0.8 \text{ mV/dec } a_{NH_4^+}$	$58.1 \pm 0.7 \text{ mV/dec } a_{K^+}$	$56.6 \pm 1.1 \text{ mV/unit of pH}$
linear range	$10^{-5}\text{--}10^{-1} \text{ M}$	$10^{-5}\text{--}10^{-1} \text{ M}$	$4\text{--}10$
limit of detection	$7.2 \times 10^{-6} \text{ M}$	$4.1 \times 10^{-6} \text{ M}$	----
response time	$10\text{--}50 \text{ s}$	$10\text{--}50 \text{ s}$	$50\text{--}100 \text{ s}$

the first case, it should be remembered that CNTs are playing a double role, as ion-to-electron transducers and as an electrical conductors. In other words, the body of the electrode, which in conventional approaches is glassy carbon, is now made by CNT-covered paper. This substrate shows higher resistance (a few hundreds of ohms) than conventional electrodes and it is not shielded, so it might be prone to suffer higher electronic noise. This kind of high frequency noise, however, can be filtered. In a long period of time, more than 1 h, the instability could be related to a parasitic process of the nanostructured interface with a large time constant. This kind of effect is almost neglected in conventional CNT SC-ISE on glassy carbon and, therefore, the paper-CNT assembly seems to be the cause. On the chemical side, factors affecting the membrane stability (membrane composition variation, adherence (see below), paper degradation, etc.) and its electrical connection to the paper might also be involved. In any case, the stability values obtained seem adequate for the scope of these electrodes.

A topic that deserves a particular discussion is the membrane adherence to the conductive papers. Two sets of experiments were performed to evaluate this point: the well-known water layer test⁴⁵ and spectroscopy impedance measurements when the membrane was sequentially torn using a plastic tape. On one hand, the water layer test shows the absence of water between the membrane and the paper-CNT layer (see Figure 3.si in the Supporting Information, insignificant changes in the slope are observed when the sensor is subsequently placed in 0.1 M KCl, 0.1 M NaCl, and 0.1 M KCl). In contrast, the presence of water is evidenced when glassy carbon/membrane (i.e., with a classical coated wire electrode configuration) was used. Therefore, as it has been reported,³¹ the presence of CNTs helps to avoid the water layer due to their hydrophobic features. On the other hand, the initial impedance measurement shows a well-defined semicircle indicating the absence of holes or channels or inward sample flows (see Figure 4.si in the Supporting Information). When the membrane is carefully torn, step by step, the total resistance and length of the semicircle decrease from mega-ohms up to a few hundred ohms at least five times. All in all, this suggest that the membrane sticks strongly to the CNT-paper under normal conditions.

The ability of the electrodes to withstand long-term storage without affecting the analytical performance will be relevant for the applications in mind. Preliminary tests were conducted by using the electrodes, storing them in a dry place, and retesting their performance after a given time. The only requisite was to precondition the electrodes for 20 min in a 10^{-4} M primary analyte solution before reusing them. The results show that electrodes can be used, dried, stored, and reused every day for a week without detecting significant changes in the analytical performance (Figure 5.si in the Supporting Information). The same experiment has been repeated for longer periods of time, and reusing periods of at least 4 weeks have been tested. It has been noticed that after 2 weeks of daily use, the limit of detection may increase up to 1 order of magnitude, while still keeping the Nernstian response (see Figure 2.si in the Supporting Information). The reasons for this decrease of performance are not yet clear. One possibility is the leaching of the ionophore out of the membrane, a problem that is commonly found with ISE. Approaches such as the immobilization of the ionophore might in this case be a solution,⁴⁶ since the CNTs are an excellent backbone to link supramolecular receptors. Further work is needed to understand the process of aging of the membrane on the conductive

paper and its analytical implications. In any case, considering the disposable nature of these electrodes, long-term performance is not considered a big problem.

Electrical characteristics of the membranes were evaluated by electrochemical impedance spectroscopy (EIS). The results show that the bulk resistances are on order of 2–2.5 M Ω for the K⁺ and NH₄⁺ membranes and 3 M Ω for the pH membrane (see Figure 6.si in the Supporting Information). This confirms the overwhelming contribution of the membrane to the total resistance of the system that makes the contribution of the conductive paper negligible. It should be noticed that these resistances (values 2–3 M Ω) are higher than those reported for solid contact CNT-ISEs on glassy carbon with 10 times thicker PVC membrane (values 150–180 k Ω).⁴⁶ This could be, at least in part, due to the smaller effective area used for the paper electrodes (see Table 1.si in the Supporting Information, resistivity values) (area 2.8 mm²) in comparison with the glassy carbon/CNTs/ion selective membrane classical approach (area 14 mm²). A higher resistance could also explain the higher susceptibility of these paper electrodes to different sources of noise, thus decreasing their long-term stability, as it was mentioned above. Figure 6.si in the Supporting Information shows the typical EIS spectra for three membranes, demonstrating that there are not electrical channels between the transducer and the aqueous phase. For the expected application of these sensors, noise has not been seen as a significant problem. However, if noise due to higher impedance values were an issue, different ways to solve it, such as the use of lipophilic salts (such as ETH 500), could be used. Alternatively, working on the electronics of the detection device to achieve very high input impedance is also possible. Therefore, this factor should not be considered a serious issue in the future.

Paper vs Classical Ion Sensors. Labmade ISE were built on glassy carbon to compare the performance of the paper electrodes with these more “conventional” electrodes under similar conditions. The results obtained show similar analytical parameters for paper-based ion sensors and classical electrodes (limit of detection, selectivity, response time, stability) within a range of concentrations relevant for many different field applications. Thus, paper-based electrodes might be used instead of conventional ISE as a low cost, disposable alternative for those applications where conventional electrodes are not affordable.

Some challenges still remain to fully address the problem of affordability and simplicity of operation. In this work, the paper electrodes have been used just as a replacement of working electrodes. Further work is needed to develop suitable reference systems that allow a simple, integrated approach. Recent work on printed reference electrodes may help to solve this issue. Also, the development of integrated potentiometric cells, where these electrodes could be easily mounted, could help to solve problems regarding the simplicity of operation.

Conclusions and Future Work. In summary, this work has demonstrated that through the combination of recent trends in bendable electronics and carbon nanotubes based potentiometric sensors, a new type of simple, rugged, low-cost sensor with good analytical performance can be built. The evidence suggests that, when compared to metal coated paper, CNT-papers show superior performance for making robust field potentiometric sensors, first, because of their excellent electrical properties and second, because of the already demonstrated optimal performance of the CNTs as ion-to-electron signal

transducers. Also, the effect of the paper porosity, which provides an increased effective area, may yield additional benefits, such as better conductivity and higher surface area in contact with the membrane. Last but not least, the simplicity of the fabrication should be stressed. The conductive paper can be simply made by a dying process, so the whole electrode can be built using mass manufacturing techniques, which helps to further reduce the costs.

From a technological perspective, there are still many paths to explore, including the development of integrated potentiometric cells (including a reference system) and the use of printing technologies to speed up the construction of the sensors and further decrease their cost. The analytical problem regarding the calibration of the sensor must not be overlooked. There is still considerable work to be done in this area, particularly in factors affecting the reproducibility in the manufacturing process, in order to minimize complex calibration steps. In any case, these sensors open new and attractive avenues to merge the analytical science with recent trends in bendable devices, chemical sensing networks, user generated information platforms, telehealth, etc.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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