

스크린 프린팅 기반 저가형의 플렉서블 칼륨 이온 센서 제조 및 이의 전기화학적 특성

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Fabrication of Low-cost and Flexible Potassium Ion Sensors based on Screen Printing and Their Electrochemical Characteristics

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초 록

본 연구에서는 스크린 프린팅 공정을 이용하여 저렴하고 유연한 칼륨 이온(K^+) 센서를 제작하였다. 전도성 잉크의 균일한 코팅은 주사 전자 현미경 및 광학 현미경 측정에 의해 입증되었다. K^+ 센서는 높은 감도, 빠른 응답 시간, 낮은 검출 한계를 보여주었다. 제조된 K^+ 센서의 감도는 기계적으로 구부러진 상태에도 여전히 유지되었다. 히스테리시스 효과가 없는 우수한 반복성과 우수한 장기 안정성이 K^+ 센서의 전기화학적 특성 분석에서 관찰되었다. 또한, K^+ 센서는 다른 간섭 양이온이 존재하는 경우에도 정확하게 K^+ 농도를 측정할 수 있어 우수한 선택성을 증명하였다. 또한, 실제 스포츠 음료 샘플에서 K^+ 농도의 성공적인 측정은 K^+ 센서의 K^+ 농도 값과 상용 K^+ 미터를 비교하여 증명되었다.

Abstract

A low-cost and flexible potassium ion (K^+) sensor was fabricated through a screen-printed process. Uniform and conformal coating of conductive inks was verified by scanning electron microscopy and optical microscopy measurements. The K^+ -sensors showed a high sensitivity, fast response time, and low detection limit. The sensitivity of K^+ -sensor was similar to that of both mechanically normal and bent states. The K^+ -sensor exhibited a good reproducibility with no hysteresis effect and excellent long term stability. In addition, the K^+ -sensor showed an excellent selectivity for K^+ concentrations in the presence of other interfering cation ions. Successful measurements of K^+ concentrations in sports drink samples were demonstrated by comparing K^+ concentration values from K^+ -sensor to those of using a commercial K^+ -meter.

Keywords: Screen printing, Potassium ion, Potentiometric ion sensor, Ion-selective membrane, Electrochemistry

1. Introduction

A potentiometric ion sensor consists of ion-selective electrode and reference electrode. They can accurately detect ion concentration in a solution sample has various potential applications in the growing field of clinical diagnosis, environmental, biological and chemical analysis, and healthcare[1-5]. Particularly, the continuous increase in concerning human health and safety, food and soil quality, and chemical and environmental protection requires the need for the development of low

cost, miniaturized, simple, and past ion sensors suitable for point of testing[4,5]. To date, high performance of potentiometric ion sensors has reported using ion-selective membrane-coated glassy carbon or gold rod electrodes[6-9]. In addition, some of the reports use glass-based silver/silver chloride (Ag/AgCl) reference electrode[8,9]. Although the sensitivity and stability of such ion sensors are accurate to approximately a millivolt, the design and configuration of ion sensors limit in applications that require robustness, flexibility, and limited space of sample[4,10-12].

Printing processes, including inkjet, screen, and roll-to-roll gravure, and flexographic printing, are widely used to transfer ink pigments onto the patterned surfaces of rigid, flexible and conformable substrates. These processes can be a promising candidate for high-throughput, simple, and inexpensive fabrication of flexible electronics, sensors, and

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energy storage devices[13-21]. As one of printing techniques, a screen printing is a mass-printing method realized by pressing an ink through a patterned stencil with a squeegee[17-21]. It has been widely employed for electronics and is compatible with a wide variety of functional inks and substrates[15-21]. Screen printing is a stencil process whereby ink is transferred on to the substrate through a stencil screen made of a fine, porous mesh of fabric, silk, synthetic fibres or metal threads. In addition, this process is simple, low-cost and scalable with various preparation conditions[18-21]. Although the screen printing technique is used for manufacturing of the conductive patterns and electrodes, its application to fabrication of flexible potentiometric ion sensors with a high reproducibility has been rarely reported.

Here, we report a low-cost, miniaturized, and flexible potassium ion (K^+) sensor based on screen printing process. The sensor electrodes were prepared by screen-printed carbon and Ag inks, resulting in two-electrode configuration for K^+ -sensors. The electrochemical performance of K^+ -sensors was evaluated by potentiometric technique. The screen-printed K^+ -sensors exhibited an ideal Nernstian behavior in a wide linear range with a fast response time and low detection limit. Under the mechanically bent state, the K^+ -sensor could measure accurately changes of K^+ concentration. In addition, the K^+ -sensors showed a good repeatability and long-term stability. This low-cost and high-performance K^+ -sensor provided accurate measurement of K^+ concentration of real sample (sports drink), and the values are comparable to those of commercial K^+ -meter equipped with glass-based electrodes.

2. Experimental

2.1. Materials

Valinomycin (potassium ionophore I), potassium tetrakis(4-chlorophenyl)borate (KTCIPB), bis(2-ethylhexyl)sebacate (DOS), polyvinyl chloride (PVC), BUTVAR[®] B-98 (polyvinyl butyral, PVB), tetrahydrofuran (THF), potassium chloride, calcium chloride, sodium chloride, magnesium chloride and ammonium chloride were purchased from Sigma-Aldrich (USA). An Ag paste (LS-405-5) and carbon paste (FTU-16) were obtained from Asahi Chemical Research Laboratory (Japan). An Ag/AgCl ink was purchased from Ercon (USA). Deionized water (18.2 M Ω -cm resistivity) was used in all experiments.

2.2. Preparation of screen-printed electrodes

The screen-printed electrodes of K^+ -sensor consisting of carbon and Ag inks were fabricated using a screen-printing system (Linesystem, LISD-60UV) and a custom stainless-steel mask developed using AutoCAD software. The carbon and Ag inks were screen-printed on the flexible polyethylene terephthalate (PET) substrate. The screen-printed electrodes, which are comprised of working electrode patterned using a carbon paste and reference electrode patterned from Ag paste, were cured at 85 °C for 30 min in a convection oven after screen print. To fabricate reference electrode, additionally screen printing Ag/AgCl paste on the Ag ink was conducted and left to dry at 85 °C for 30 min in a convection oven.

2.3. Fabrication of K^+ -sensor

A K^+ -selective membrane cocktail was prepared by mixing a valinomycin (2 %w/w), KTCIPB (0.5 %w/w), DOS (64.7 %w/w), and PVC (32.8 %w/w) in 1 mL of THF. The K^+ electrode was fabricated by drop-casting K^+ -selective membrane cocktail of 4 μ L onto the surface of carbon electrode and left to dry overnight at room temperature. The resultant K^+ electrodes were immersed in 10^{-3} M KCl for 1 day to eliminate interfering ions on the membrane before measurements were conducted. A reference cocktail consisting of 78 mg PVB, 50 mg NaCl in 1 mL of methanol was drop-casted on the electrode of Ag/AgCl paste (3 aliquots of 8 mL each, with 10 min drying at room temperature) and left to dry overnight at room temperature.

2.4. Characterization

Scanning electron microscopy (SEM) image were obtained using a field emission SEM (FE-SEM, Magellan 400, FEI company). Optical microscope (OM) images were obtained on an optical microscope (OM, BX53MTRF-S, Olympus). All electrochemical characterization was performed using a CHI760E (CH Instruments, USA) at room temperature (25 ± 4 °C) and obtained data were within the error range of $\pm 1\%$. The reference electrode of Ag/AgCl/KCl (sat.) (Model K0260, Ametek) was used for electrochemical measurements. In order to measure the electromotive force responses, 1 M KCl solution was diluted to prepare from 10^{-1} M to 10^{-4} M KCl solutions.

3. Result and Discussion

Figure 1(a) displays the schematic illustration for preparing miniaturized K^+ -sensor based on screen printing process using carbon and Ag inks. The K^+ -sensor consists of two-electrode configuration with a dimension of 1×6.7 cm². The K^+ -selective sensing electrode was prepared by a dip-casting the K^+ -selective membrane cocktail onto the surface of carbon electrode. For a reference electrode, Ag/AgCl paste was printed onto Ag electrode, followed by coating with NaCl-containing PVB. The screen-printed electrodes are highly flexible [Figure 1(b)]. This process is desirable for fabricating large-scale and low-cost ion sensors. Cross-sectional SEM image shows strong adhesion of carbon and ion-selective membrane without no cracks or pinholes [Figure 1(c)]. When observing surface morphologies, the carbon ink and ion-selective membrane were uniformly distributed to the substrates [Figure 1(d) and (e)].

The electrochemical performance of the K^+ -sensor was evaluated using a potentiometric technique. The response of electromotive force (EMF) between sensing and reference electrodes was recorded in KCl solutions with the decreasing K^+ concentration from 10^{-1} to $10^{-6.5}$ M. Figure 2(a) shows a calibration curve of EMF versus $\log[K^+]$. The sensitivity of slope was calculated from the calibration plot in a linear range of $10^{-1} \sim 10^{-4}$ M to be 54.58 mV/decade ($R^2 = 0.99$), which is close to an ideal Nernstian behavior[1,2,18]. Based on the intersection of the two slope lines in the calibration curve, the K^+ -sensor had a low detection limit of $10^{-4.7}$ M. To investigate the repeatability of K^+ -sensor, the sensor was tested repeatedly in KCl solutions with concen-

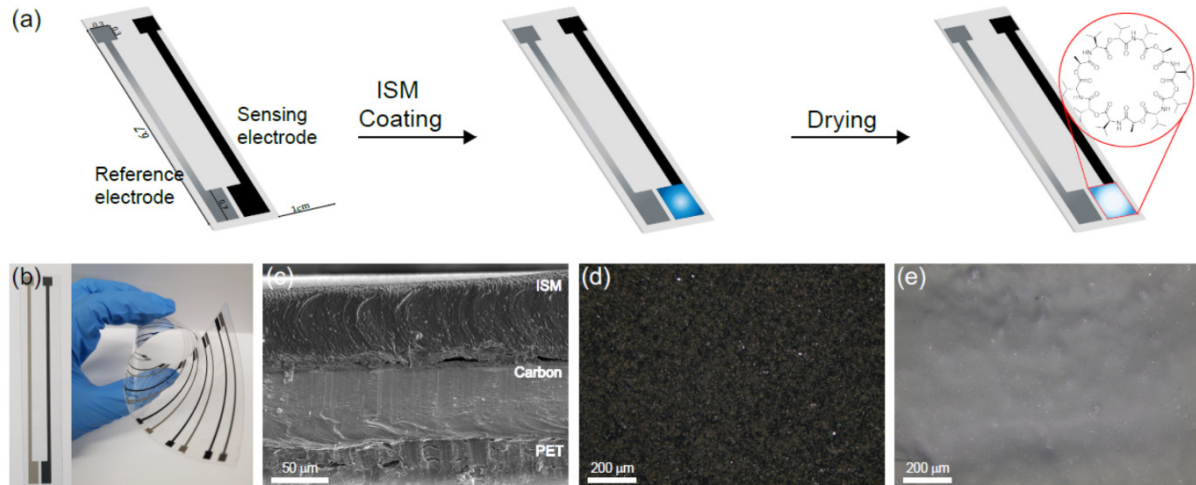


Figure 1. (a) Schematic illustration for preparing K^+ -sensor based on a screen-printing process, (b) photograph images of K^+ sensor, (c) cross-sectional SEM image of K^+ -sensor, (d) and (e) optical images of K^+ -sensor.

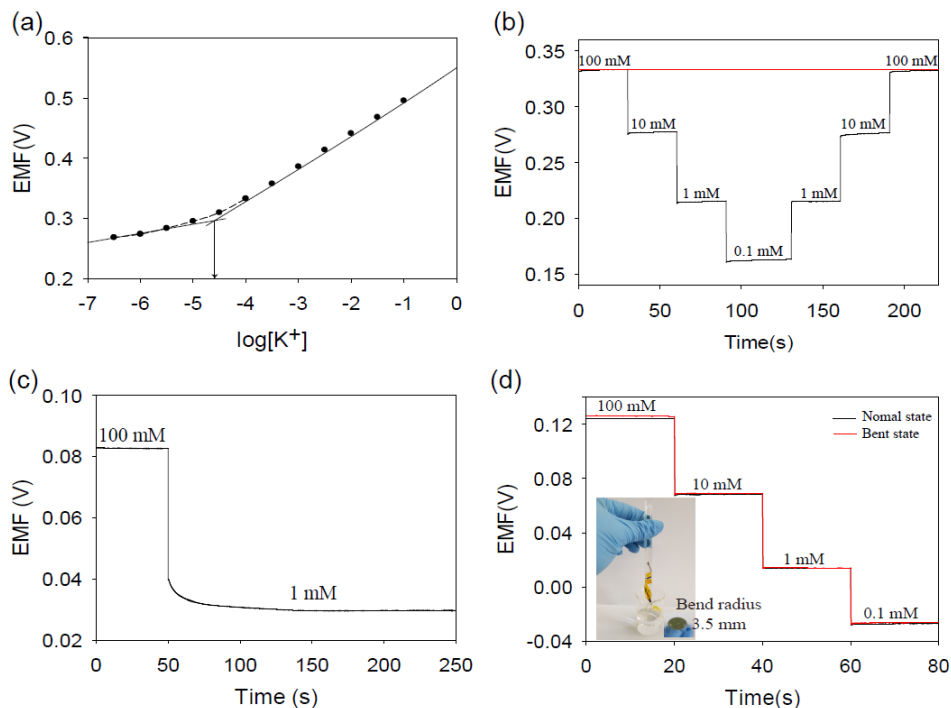


Figure 2. (a) A plot of EMF responses versus $\log[K^+]$ for the K^+ -sensor, (b) repeatability curve for the K^+ -sensor with varying K^+ concentration, (c) response time test by diluting KCl solution from 100 mM to 1 mM, (d) EMF responses of K^+ -sensor under mechanically normal and bent states.

trations from 10^{-1} to 10^{-4} M [Figure 2(b)]. The sensors exhibited the sensitivity for forwards and backwards directions of 57.23 and 56.83 mV/decade, respectively. In addition, the initial EMF value at 100 mM KCl for K^+ -sensor was almost retained with a hysteresis width of 1 mV. These results indicate that K^+ -sensor fabricated in this work had a good repeatability. The K^+ -sensor showed a response time of < 1 s, measured on decreasing K^+ concentration from 10^{-1} to 10^{-3} M [Figure 2(c)]. A flexibility of K^+ -sensor was also tested by measuring EMF response under a mechanically bent state [Figure 2(d)]. The EMF re-

sponses of K^+ -sensor recorded in different concentration of KCl solutions were consistent with those of K^+ -sensor measured under a mechanically normal state. The K^+ -sensors showed sensitivities of 51.2 and 50.8 mV/decade for mechanically normal and bent states, respectively. This result implies that K^+ -sensor has a strong mechanical resistance.

The long-term analysis on K^+ concentration in real samples cause the variation in the actual measurement results due to the potential drift. The potential drift of K^+ -sensor was investigated by measuring

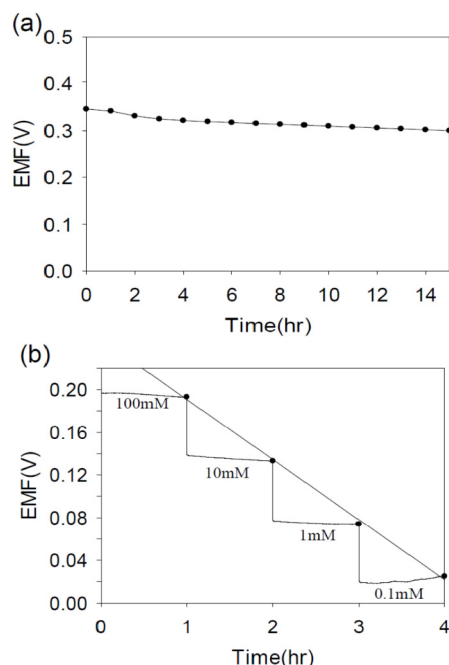


Figure 3. (a) Long-term stability of K^+ -sensor measured in 100 mM KCl, (b) EMF responses of K^+ -sensor measured in a range of 100–0.1 mM KCl.

the EMF responses over 15 h [Figure 3(a)]. The K^+ -sensor exhibited a low potential drift of 1.9 mV/h in EMF responses measured at 100 mM KCl. This result implies that the K^+ -sensor has a small deviation of approximately 3.4% over an hour of continuous measurement. The stability of K^+ -sensor was also tested under $10^{-1} \sim 10^{-4}$ M KCl solution for a total of 4 h [Figure 3(b)]. Based on the calibration curve, the K^+ -sensor showed a Nernstian behavior with a sensitivity of 53.1 mV/decade. Basis on the results, the K^+ -sensor has a long-term stability during the electrochemical measurements.

The ion sensors should accurately measure the target concentration in the presence of interfering ions. In order to check the ion selectivity of K^+ -sensors, we evaluated selectivity coefficients (K) using the separate-solution method (SSM)[22,23] in the presence of Na^+ , NH_4^+ , Ca^{2+} , and Mg^{2+} as interfering ions [Figure 4(a)]. As shown in Table 1, all K values were < 1 , which is indicative of a good selectivity of K^+ -sensors against the interfering cations. Figure 4(b) shows a good selectivity of K^+ -sensor, in which interfering EMF signals were not observed when adding interfering electrolytes of 0.1 mM $MgCl_2$, 0.1 mM $CaCl_2$, 1 mM NH_4Cl , and 10 mM $NaCl$.

The K^+ -sensors were used for determining the K^+ concentration of real samples, including a commercial sports drink of Pocari SweatTM. The obtained K^+ levels were compared with those obtained using a commercially available potassium ion meter (OrionTM Versa Star ProTM). Figure 5 shows the K^+ concentration of sports drink (Pocari SweatTM) measured by K^+ -sensor and K^+ -meter. The obtained values are almost similar even after adding high-concentration KCl solution into sports drink. The K^+ -sensors showed relative small variations from the K^+ -meter.

Table 1. Selectivity coefficients of the K^+ -sensor using a SSM with the interference ions of Na^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}

Ions (J)	$\log K_{IJ}^{POT}$	K_{IJ}^{POT}
Na^+	-0.695	2.02×10^{-1}
NH_4^+	-1.653	2.22×10^{-2}
Ca^{2+}	-4.564	2.56×10^{-5}
Mg^{2+}	-5.159	6.93×10^{-6}

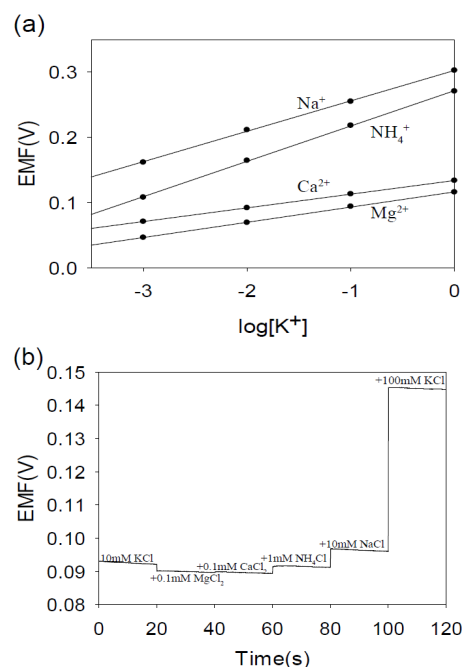


Figure 4. (a) EMF responses of K^+ -sensors with different ions of NH_4^+ , Na^+ , Ca^{2+} , and Mg^{2+} , (b) EMF responses of K^+ -sensors in the presence of different ion concentrations of 10 mM KCl, 0.1 mM $MgCl_2$, 0.1 mM $CaCl_2$, 1 mM NH_4Cl , 10 mM $NaCl$, and 100 mM KCl.

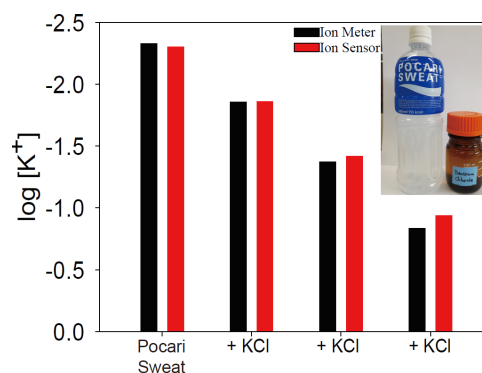


Figure 5. K^+ concentration of sports drink (Pocari SweatTM) measured by K^+ -sensor and commercial K^+ -meter.

The high-performance of the K^+ -sensors can be understood by an important role of carbon-based electrode as a solid contact between ion selective membranes and current collectors. The carbon-based electrode is an effective ion-to-electron transducers because they generate the

electrical double layer capacitance at the interface of ion selective membrane and solid contact. This solid contact of carbon electrode results in improved potential stability, sensitivity, selectivity, and reproducibility.

4. Conclusion

A low-cost and flexible screen-printed K^+ -sensor was fabricated to accurately measure K^+ concentration in electrolyte solution samples. The screen-printing is scalable manufacturing techniques for potentiometric ion sensor substrates with uniform and conformal coating, resulting in a high reproducibility. The potentiometric measurements using K^+ -sensors resulted in the high sensitivity of 54.58 mV/decade, low detection limit of $10^{-4.7}$ M, and fast response time of < 1 s. In addition, the fabricated K^+ -sensors showed a good repeatability and long-term stability. The electrochemical performance of K^+ -sensor withstood under mechanically bent state. The K^+ -sensor could measure accurately K^+ concentration in the presence of other interfering cation ions, demonstrating a good selectivity. When measuring real sample of sports drink, the K^+ -sensor showed similar K^+ concentration values compared to commercial K^+ -meter.

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References

1. J. H. Yoon, S. B. Hong, S. O. Yun, S. J. Lee, T. J. Lee, K. G. Lee, and B. G. Choi, High performance flexible pH sensor based on polyaniline nanopillar array electrode, *J. Colloid Interface Sci.*, **490**, 53-58 (2017).
2. J. H. Yoon, K. H. Kim, N. H. Bae, G. S. Sim, Y. J. Oh, S. J. Lee, T. G. Lee, K. G. Lee, and B. G. Choi, Fabrication of newspaper-based potentiometric platforms for flexible and disposable ion sensors, *J. Colloid Interface Sci.*, **508**, 167-173 (2017).
3. M. Cuartero and G. A. Crespo, All-solid-state potentiometric sensors: A new waver for *in situ* aquatic research, *Curr. Opin. Electrochem.*, **10**, 98-106 (2018).
4. M. Parrilla, M. Cuartero, and G. A. Crespo, Wearable potentiometric ion sensor, *TrAc Trends Anal. Chem.*, **110**, 303-320 (2019).
5. M. Cuartero, M. Parrilla, and G. A. Crespo, Wearable potentiometric sensors for medical applications, *Sensors (Basel)*, **19**, 363 (2019).
6. C. Jiang, Y. Yao, Y. Cai, and J. Ping, All-solid-state potentiometric sensor using single-walled carbon nanohorns as transducer, *Sens. Actuator B*, **283**, 284-289 (2019).
7. J. Hu, X. U. Zou, A. Stein, and P. Buhlmann, Ion-selective electrodes with colloid-imprinted mesoporous carbon as solid contact, *Anal. Chem.*, **86**, 7111-7118 (2014).
8. E. Jaworska, W. Lewandowski, J. Mieczkowski, K. Maksymiuk, and A. Michalska, Critical assessment of graphene as ion-to-electron transducer for all-solid-state potentiometric sensors, *Talanta*, **97**, 414-419 (2012).
9. R. Hernandez, J. Rju, J. Bobacka, C. Valles, P. Jimenez, A. M. Benito, W. K. Maser, and F. X. Rius, Reduced graphene oxide films as solid transducers in potentiometric all-solid-state ion-selective electrodes, *J. Phys. Chem. C*, **116**, 22570-22578 (2012).
10. J. Bobacka, A. Ivaska, and A. Lewenstam, Potentiometric ion sensors, *Chem. Rev.*, **108**, 329-351 (2008).
11. J. Hu, A. Stein, and P. Buhlmann, Rational design of all-solid-state ion-selective electrodes and reference electrodes, *Trends Anal. Chem.*, **76**, 102-114 (2016).
12. A. Michalska, All-solid-state ion selective and all-solid-state reference electrodes, *Electroanalysis*, **24**, 1253-1265 (2012).
13. F. Tehrani, M. B. Gastelum, K. Sheth, A. Karajic, L. Yin, R. Kumar, F. Soto, J. Kim, J. Wang, S. Barton, M. Mueller, and J. Wang, Laser-Induced graphene composites for printed, stretchable, and wearable electronics, *Adv. Mater. Technol.*, **4**, 1900162 (2019).
14. J. Bian, L. Zhou, X. Wan, C. Zhu, B. Yang, and Y. Huang, Laser Transfer, Printing, and assembly techniques for flexible electronics, *Adv. Electron. Mater.*, **5**, 21800900 (2019).
15. K. Arapov, E. Rubingh, R. Abbel, J. Laven, G. de With, and H. Friedrich, Conductive screen printing inks by gelation of graphene dispersions, *Adv. Funct. Mater.*, **26**, 586-593 (2016).
16. W. J. Hyun, E. B. Secor, M. C. Hersam, C. D. Frisbie, and L. F. Francis, High-resolution patterning of graphene by screen printing with a silicon stencil for highly flexible printed electronics, *Adv. Mater.*, **27**, 109-115 (2014).
17. S. Bellani, E. Petroni, A. E. Del Rio Castillo, N. Curreli, B. M. Garcia, R. O. Nunez, M. Prato, and F. Bonaccorso, Scalable production of graphene inks via wet-jet milling exfoliation for screen-printed micro-supercapacitors, *Adv. Funct. Mater.*, **29**, 1807659 (2019).
18. H. J. Park, J. H. Yoon, K. G. Lee, and B. G. Choi, Potentiometric performance of flexible pH sensor based on polyaniline nanofiber arrays, *Nano Converg.*, **6**, 9-15 (2019).
19. Z. Chu, J. Peng, and W. Jin, Advanced nanomaterial inks for screen-printed chemical sensors, *Sens. Actuator B*, **243**, 919-926 (2017).
20. F. Bonaccorso, A. Bartolotta, J. N. Coleman, and C. Backes, 2D-crystal-based functional inks, *Adv. Mater.*, **28**, 6136-6166 (2016).
21. G. Hu, J. Kang, L. W. Ng, X. Zhu, R. C. T. Howe, C. G. Jones, M. C. Hersam, and T. Hasan, Functional inks and printing of two-dimensional materials, *Chem. Soc. Rev.*, **47**, 3265-3300 (2018).
22. C. Macca, The current usage of selectivity coefficients for the characterization of ion-selective electrodes. a critical survey of the 2000/2001 literature, *Electroanalysis*, **15**, 997-1010 (2003).
23. Y. Umezawa, P. Buhlmann, K. Umezawa, K. Tohda, and S. Amemiya, Potentiometric selectivity coefficients of ion-selective electrodes, *Pure Appl. Chem.*, **72**, 1851-2082 (2000).