

Supplementary Information

Improved Performance of Printed Electrochemical Sensors via Cold Atmospheric Plasma Surface Modification

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Water contact angle

Table S1. Water contact angle change for the screen-printed carbon electrodes (SPCEs) by plasma treatment using different plasma power and oxygen flow.

Applied plasma power (W)	Applied oxygen flow rate (mL.min ⁻¹)	Water contact angle (°)
200	0	84.1 ± 2.86
	80	23.8 ± 1.15
	100	21.5 ± 1.1
	120	17.6 ± 1.0
	140	13.9 ± 1.0
300	0	58.3 ± 3.4
	80	19.1 ± 1.1
	100	15.8 ± 1.0
	120	12.8 ± 0.3
	140	12.4 ± 0.8
400	80	18.1 ± 1.0
	100	15.8 ± 1.0
	120	14.2 ± 0.9
	140	12.1 ± 0.5
500	80	16.4 ± 0.9
	100	14.0 ± 0.7
	120	12.3 ± 0.2
	140	12.1 ± 0.3

An increase in both plasma power and applied oxygen flow rate resulted in a decrease in WCA values. Increasing plasma power and oxygen flow rate could effectively activate SPCE surface by decontaminating the surface and adding oxygen-based functional groups, respectively.

SEM micrographs of SPCE surface

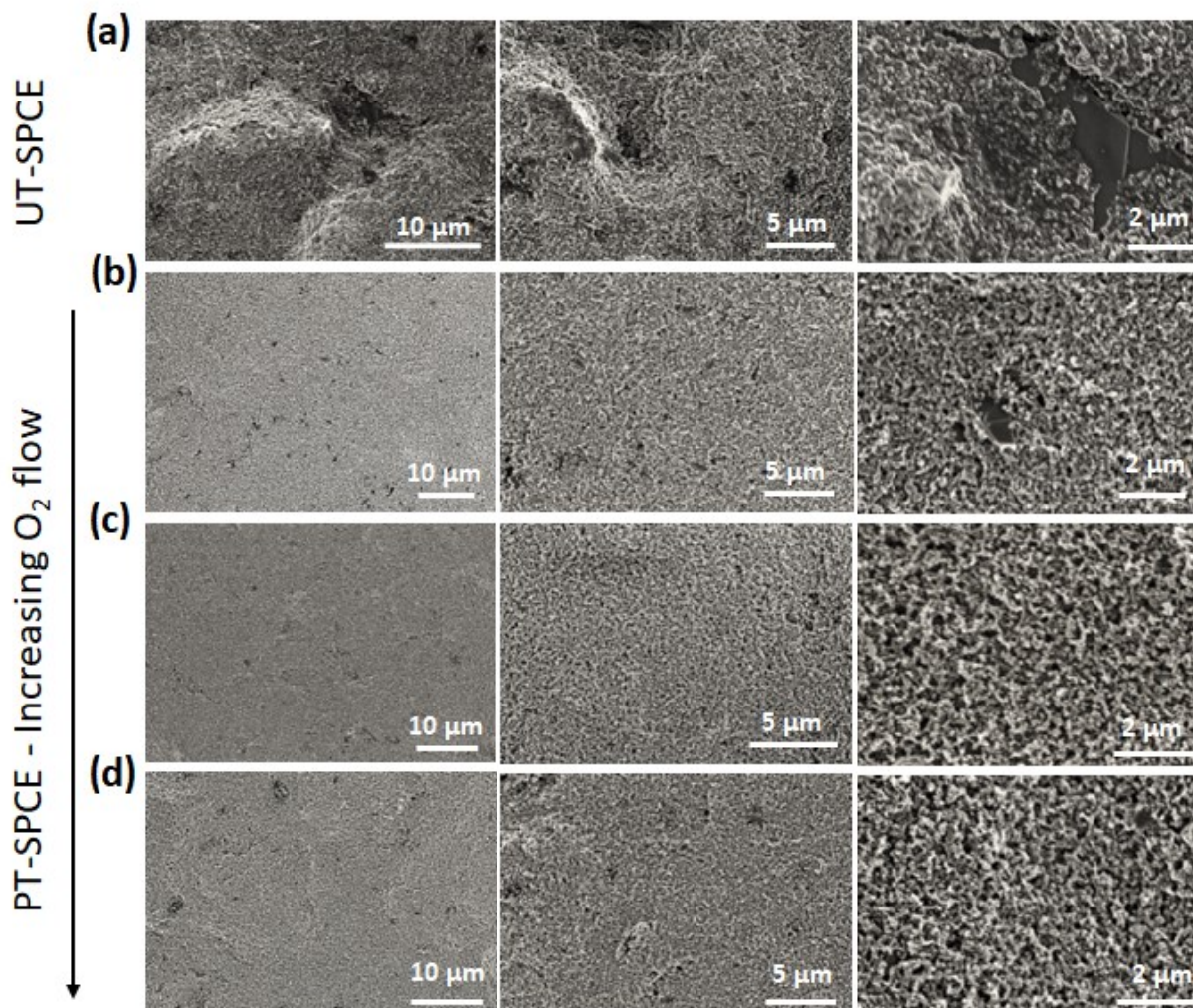


Fig. S1. Surface micrographs. SEM images of (a) untreated SPCE surface and Plasma-treated SPCE by applying (b) 300W- 80 mL/min O₂ flow, (c) 300W- 100 mL/min O₂ flow, (d) 300W- 120 mL/min O₂ flow, (e) 300W- 140 mL/min O₂ flow, and (f) 500W- 120 mL/min O₂ flow CAP treatment.

As shown in **Fig. S1(a)**, the UT- SPCE surface consists of a non-uniform morphology including fabrication residues and contaminating particles. CAP treatment improved the microstructure of the SPCE surface via removal of contamination and binder remnants from the surface and between the graphitic particles of the SPCE (**Fig.S1 (b-d)**). Increasing the oxygen flow rate enhanced the CAP effect by providing more active species. Oxygen-based components could actively connect to the superficial hydrophobic contaminations and remove them from the surface through decomposition, leaving a nano porous pristine graphitic structure on the SPCE. **Fig. S1(c)** represents the SPCE surface that resulted in the minimal WCA with the lowest plasma processing power 300W and O₂ flow of 120 mL.min⁻¹.

Selectivity coefficients

Table S2. Selectivity coefficients ($\text{Log } K_{\text{NO}_3,j}$) of developed nitrate ISEs with and without plasma treatment at 1 mM interfering anions (j). Given mean (n=5) deviation. values are \pm standard

Ion, j	$\log K_{\text{NO}_3,j}^{\text{Pot}}$	
	Untreated ISE	Plasma-treated ISE
H_2PO_4^-	-1.28 ± 0.04	-1.45 ± 0.02
SO_4^{2-}	-2.86 ± 0.01	-2.89 ± 0.01
HCO_3^-	-1.90 ± 0.01	-1.98 ± 0.01
Cl^-	-0.89 ± 0.01	-1.05 ± 0.01

Anti-interference behavior of the proposed electrodes was calculated in the presence of phosphate, sulfate, bicarbonate, and chloride ions. The data are provided in **Table S2** (Supplementary Information). While the highest interference was recorded for Cl^- ion in both UT-ISE and PT-ISE, the PT-ISE showed a slightly improved selectivity. This behavior can be explained by the modified interface between SPCE and ISM which led to a consistent potential reading and minimized water-layer-formation effect.

Comparison table

Table S3. Comparison of some of the reported surface modification techniques and/or materials for the development of solid-state nitrate ion-selective electrodes.

Surface modification technique or material	Stability	LOD (M)	Cost	Fabrication complexity	Scalability	Ref
Cold atmospheric plasma treatment of solid contact	Improved water-layer resistance, -0.1 mV/day	1×10^{-5}	Low	Low	High	This work
Graphene implementation on solid contact	Improved water-layer resistance	3×10^{-5}	Medium	High	Low	¹
Laser-induced graphene as solid contact	Improved, 5 weeks	6×10^{-6}	Low	Medium	Medium	²
Graphene/tetrathiafulvalene nanocomposite on solid contact	Improved water-layer resistance, 15 mV/h	$1 \times 10^{-6.2}$	Medium	High	Low	³
Nanohybrid composite films with Au nanoparticles on solid contact	Improved water-layer resistance, 65 days	$1 \times 10^{-5.2}$	High	High	Low	⁴
Polyaniline nanoparticles on solid contact	Improved, 30 days, 0.7 mV/h	2.1×10^{-7}	Medium	High	Low	⁵
Multiwall carbon nanotube on solid contact	Improved, 50 days	1×10^{-5}	Medium	High	Low	⁶
tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) solid contact	Improved potential stability	$1 \times 10^{-5.5}$	Medium	High	Low	⁷

A comparison of our proposed surface modification technique with some of the recently reported methods for developing nitrate ISEs is provided in **Table S3** (Supplementary Information). ISE fabricated through surface modification via CAP treatment not only provided a noticeably decreased processing and manufacturing complexity, but also represented a comparable potential stability with previously reported methods. CAP can be an alternative green technique to improve the performance of various solid-contact ISEs in wearable health care or environmental monitoring applications where long-term stability of the ISE is required.

References

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