Supporting information

Potentiometric sensor based on modified electrospun PVDF nanofibers – towards 2D ion-selective membranes

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Details of XPS experimental

The XPS instrument energy scale was calibrated to give a BE of 84.0 ± 0.1 eV for the $4f_{7/2}$ line of metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu $2p_{3/2}$ line of metallic copper. Energy resolution was examined on a silver sample. Survey (wide) spectra were collected with a quality corresponding to the full width at half maximum (FWHM) parameter for Ag 3d line equal to 0.71 eV at energy step size equal to 0.5 eV. For high resolution spectra the FWHM parameter for Ag 3d line was equal to 0.58 eV at step size of 0.1eV. Kratos charge neutralizer system was used to reduce charge compensation. The spectra were charge corrected by shifting all of the energy values in the way that the F 1s signal appears at the literature value of 688.2 eV [1,2]. The peaks fitting was conducted using CasaXPS software version 2.3.18 on a Shirley background based on Gaussian-Lorentzian (30) function.

Calculations related to core-shell nanofibers geometry

Increase of the diameter of nanofiber assumed to be ideal cylinder results only from "addition" of liquid layer. The volume of cylinder is given by formula $V_{cyl} = \pi r^2 h$, where r is radius of the base and h is the height of cylinder, in the case of nanofibers r is the radius of the nanofiber and h is the total length of modified nanofibers. Thus the amount of liquid modifying layer, V_{DOS};, resulting in increase of volume of nanofibers is given by the formula:

$V_{DOS} = V_{post\ modification} - V_{before\ modification} = \pi h (r^2_{post\ modification} - r^2_{before\ modification})$

V_{DOS} is known, whereas $r_{post\ modification}$ and $r_{before\ modification}$ can be estimated from TEM pictures Fig 1. Thus the length of nanofibers modified, h, can be calculated. For 42 ul of DOS used, $r_{post\ modification}$ = ½ of 105 nm (52.5 nm) and $r_{before\ modification}$ = ½ of 90 nm (45 nm), The resulting estimated length of nanofibers in herein proposed receptor is close to 18.3 km.

Assuming that length of nanofibers is 18.3 km, the surface area of core-shell nanofibers in the receptor can be calculated from the simplified formula assuming that surface area can be approximated by surface area of sides of cylinder, $P_{cyl} = 2\,\pi\, r_{post\ modification}\, h$, where all symbols used has meaning as defined above.

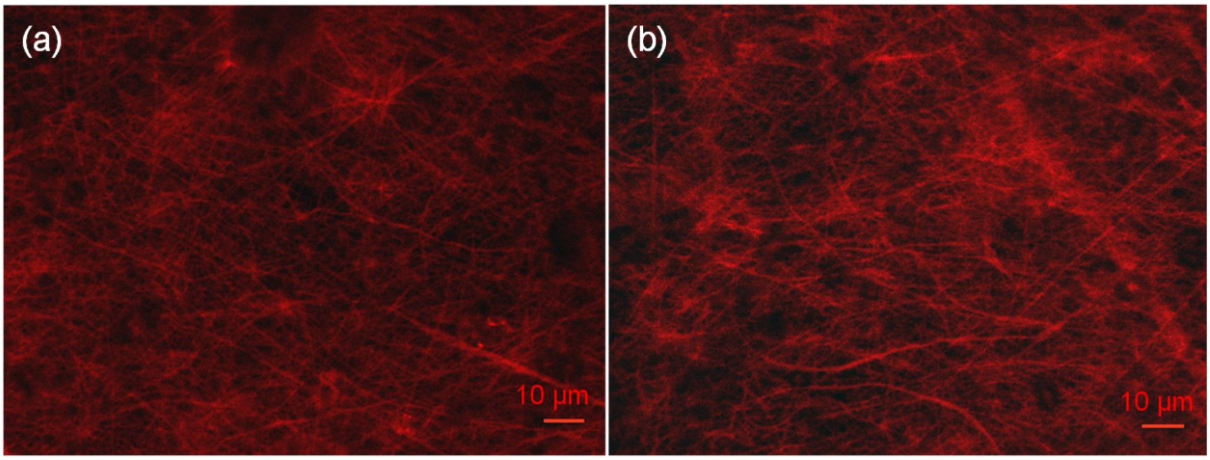
The resulting estimated surface area of nanofibers in herein proposed receptor is close to 60 cm^2. Taking into account that opening diameter of “Philips body” is equal to 3 mm – the area of nanofibers based membrane being in direct contact with solution (a fraction of total) is 15 cm^2.

For classical PVC based membrane placed in “Philips body”, of membrane opening diameter equal to 3 mm, $r_{classical\ membrane}$ = 1.5 mm, the surface area of membrane can be calculated using formula: $P_{classical\ membrane} = \pi\, r^2_{classical\ membrane}$.

The resulting surface area of classical membrane is equal to $7 \cdot 10^{-2}$ cm^2.

The ratio of P_{cyl} to $P_{classical\ membrane}$ is close to $2.1 \cdot 10^2$.

A)



B)

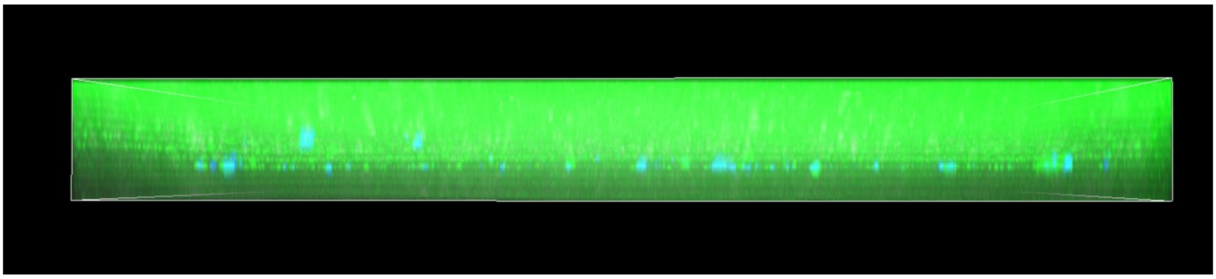


Figure S1 A) Confocal images of PVDF nanofibers coated with chromoionophore I and DOS: (a) top and (b) bottom part of nanofibers mat.

B) Cross-sectional confocal images of preconditioned PVDF nanofibers mat treated with KCl (10^{-3} M) fluorescein solution for 30 minutes.

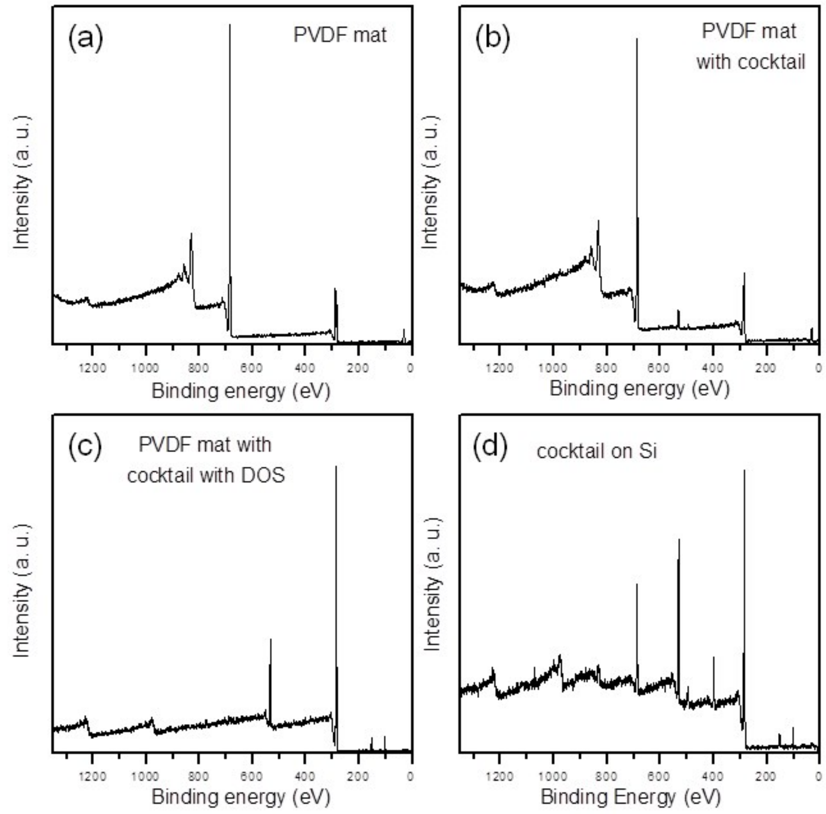


Figure S2 Survey XPS spectra of (a) PVDF mat, (b) cocktail deposited on PVDF mat, (c) cocktail and DOS mixture deposited on PVDF mat (d) DOS free cocktail deposited on Si substrate. The peak assignment was done as follow with increasing BE values: 32 eV– F2s, 103 eV – Si2p, 160 eV – Si2s, 285 eV – C1s, 400 eV – N1s, 534 eV – O 1s, 688 eV – F1s, 830 eV – F KLL Auger line, 980 eV – O KLL Auger line, 1072 eV – Na 1s, 1230 eV – C KLL Auger line.

Table S1. Atomic concentration of elements in samples: nanofibrous mat, cocktail (applied as chloroform solution) on the mat and cocktail with plasticizer DOS (applied as chloroform solution) on the mat, cocktail (applied as chloroform solution) on Si substrate.

Nanofibers	**C**	**F**	**O**
Mean:	62.9	36.1	1.0
d%	1.5	1.6	0.1

Components of cocktail, in the absence of DOS applied on nanofibers	**C**	**F**	**O**	**N**
Mean:	68.0	27.0	3.5	1.4
d%	0.6	0.7	0.2	0.1

Liquid, DOS based, receptor on nanofibers	**C**	**F**	**O**			**Si**
Mean:	85.4	0.3	8.6			5.8
d%	0.2	0.1	0.4			0.7

Components of cocktail, in the absence of DOS applied directly on Si	**C**	**F**	**O**	**N**	**Na**	**Si**
Mean:	74.2	4.2	12.1	4.6	0.3	4.6
d%	0.4	0.2	0.2	0.2	0.0	0.4

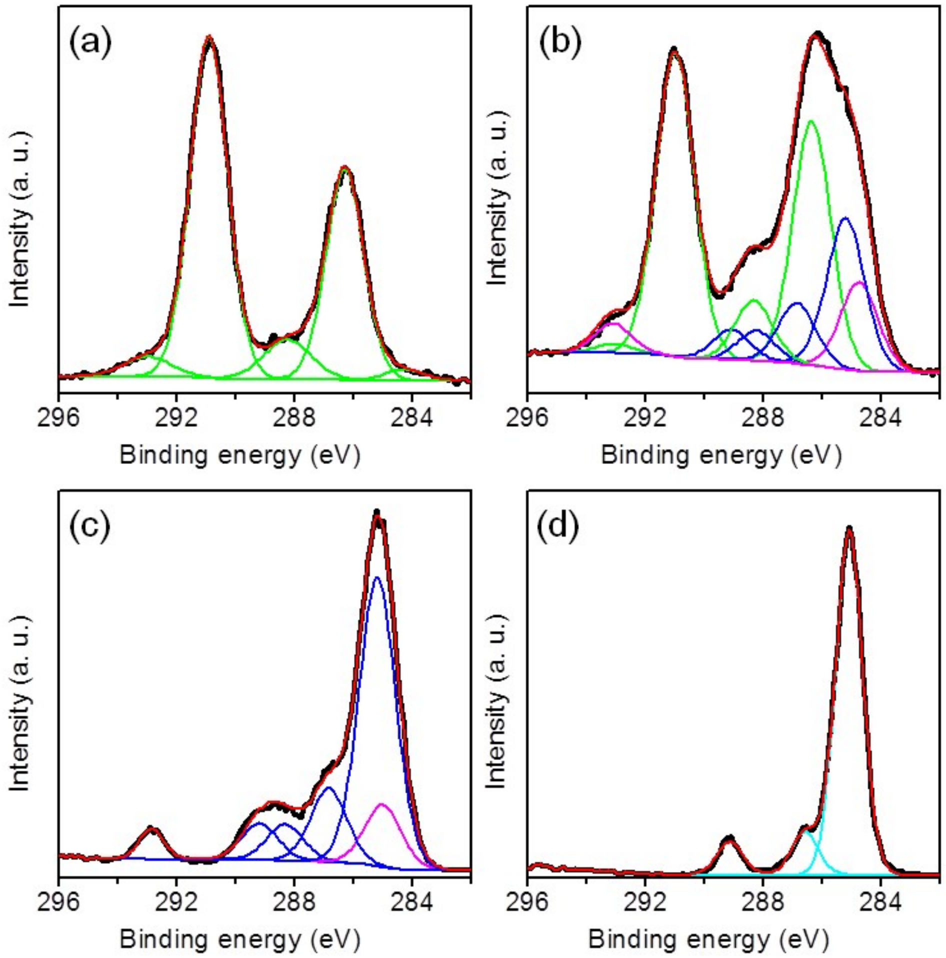


Figure S3 Results of XPS analysis and fitting: C 1s core level spectra of (a) as obtained PVDF mat; (b) PVDF mat covered with DOS free cocktail, system A. (c) DOS free cocktail on Si substrate, system B, and (d) PVDF mats covered with liquid, DOS based, ion-selective receptor layer. The black and red lines represent the experimental data and fitted curves. Individual components for nanofibrous mat, ionophore – valinomycin ($C_{54}H_{90}N_6O_{18}$), ion-exchanger NaTFPB ($C_{32}H_{12}BF_{24}Na$) and DOS ($[-(CH_2)_4CO_2CH_2CH(C_2H_5)(CH_2)_3CH_3]_2$) compounds are represented by green, blue, magenta and light blue fitting models, respectively.

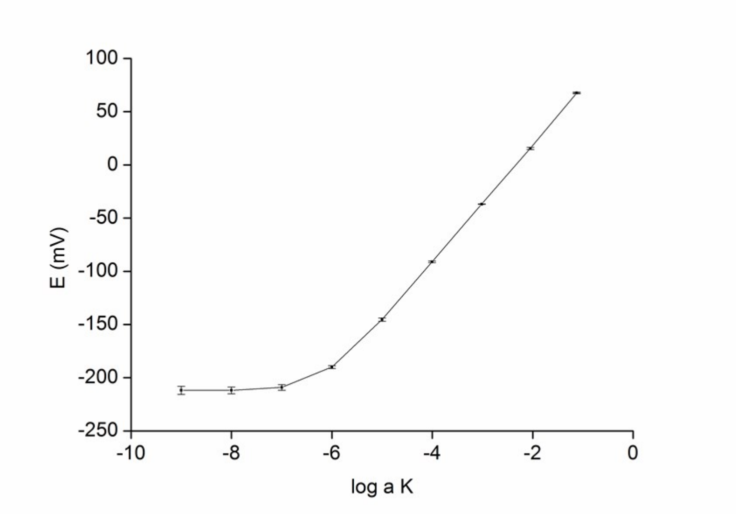


Fig S4. Mean ± SD of potential values recorded during calibrations performed between the first and thirty-fourth day, n = 21.

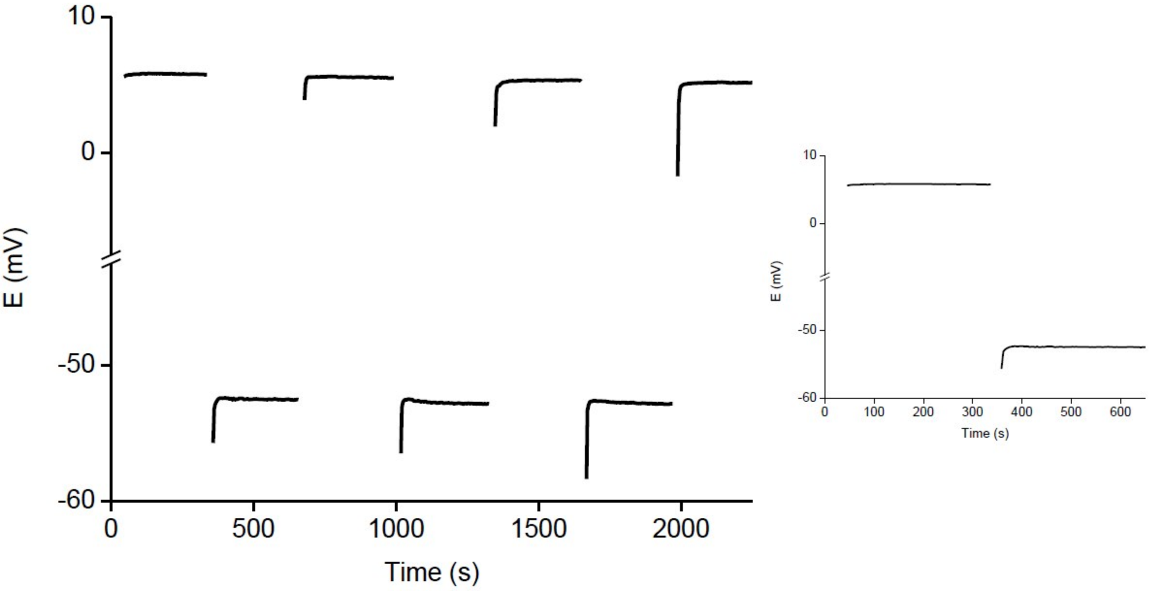


Fig S5. Response time of core-shell nanofibers based sensors obtained at first day of sensor testing for K^+ concentration repeated change between $10^{-2.5}$ and $10^{-3.5}$ M. The electrode was repeatedly placed in solutions of different concentration, in-between was briefly rinsed with water.

Inset: magnification of first 600 s of measurement.

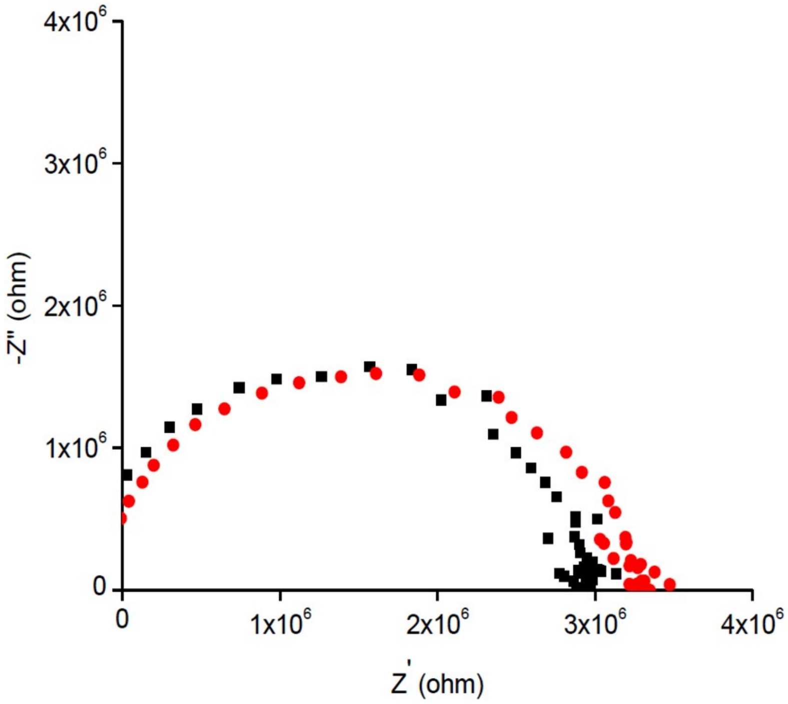


Figure S6 Complex plane impedance spectra of potassium ion-selective sensor prepared using (■) liquid ion-selective receptor layer supported on nanofibers or (●) PVC membrane, recorded in 0.1 M KCl solution at 0.2 V, using amplitude 50 mV in the frequency range from 0.01 Hz to 10^5 Hz in 0.1 M KCl.

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(1) A.M. Ferraria, A. J. D. Lopes da Silva and A. M. Botelho do Rego, *Polymer (Guildf)*, 2003, **44**, 7241–7249.

(2) G.Beamson and D. Briggs, *SurfaceSpectra Ltd.* 2000.