Supporting Information

Solid-contact Ca^{2+}-selective electrodes based on two-dimensional black phosphorus as ion-to-electron transducer

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Reagents and materials

Black phosphorus powder (99.9%, pure) were purchased from Nanjing XFNANO Materials Tech Co.,Ltd (Nanjing, China). High molecular weight poly (vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), potassium chloride (KCl), calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were purchased from Sigma-Aldrich. Calcium ionophore IV N,N-Dicyclohexyl-N'N'-dioctadecyl-diglycolicdiamide (ETH 5234) and sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) were Selectophore from Fluka AG (Buchs, Switzerland). Tetrahydrofuran (THF) was freshly distilled prior to use. All other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All other reagents were analytical grade and used as received. Aqueous solutions were prepared by dissolving the appropriate salts in the freshly de-ionized water (18.2MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system.

Preparation of solid-contact Ca^{2+}-ISE

Ca^{2+}-selective membrane was prepared by dissolving 200 mg of components (in wt %) in 2.0 mL of THF: ionophore (ETH 5234), lipophilic cation-exchanger NaTFPB (0.5), PVC (33) and DOS (65.5). The membrane cocktail was degassed by sonication for 10 min before use.The glass carbon electrodes were carefully polished using alumina nanoparticles (500 nm), thoroughly rinsed with water and then bathed for 5 min in acetone. After that, they were completely air-dried. A mass of10 mg of black phosphorus powder was dispersed in 5 mL anhydrous ethanol filled with nitrogen and away from light. Then the conducting polymer black phosphorus powder was deposited on glass carbon surface by drop-casting 10 μL of a 2 mg/mL ethanol solution for 5 times and the solvent was left to evaporate at least 5 min in under nitrogen protection. The electrode was then introduced into a fitting PVC tube at a depth of 1 mm, allowing the casting of 100 μL of membrane cocktail on the top of the black phosphorus layer, and left to dry at room temperature. Before use, the electrodes were conditioned in 10^{-3} M $CaCl_2$ solution for one night.

Electromotive force (EMF) measurements

All electromotive force measurements (EMF) were carried out at 25 °C using a CHI 760D electrochemical workstation (Shanghai, China) in the following galvanic cell: SCE/1 M

LiOAC/sample solution/Ca^{2+}-sensing membrane/ blackphosphorus/glass carbon. The EMF values were corrected for liquid junction potentials using the Henderson equation, and ion activities were calculated according to the Debye-Hückel approximation.

Capacitance measurements

A three-electrode setup was used for measurements of the capacitance of black phosphorus. A solid-contact Ca^{2+}-ISE with or without a black phosphorus film was used as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl (3 M KCl) electrode as the reference electrode. Electrochemical impedance spectroscopy (EIS) experiments were carried out a 10^{-3} M $CaCl_2$ solution on a CHI 760D electrochemical workstation. The frequency range was 0.3 Hz to 10 kHz, with an excitation amplitude of 10 mV versus the open circuit potential.

Chronopotentiometric measurements

Chronopotentiometric measurements were performed in 10^{-3} M $CaCl_2$ by applying a constant current of +1 nA for 60 s and followed by a reverse current of the same magnitude for another 60 s. The capacitance of the electrode was calculated by using the constant current divided by the slope of the discharge curve in a potential versus time graph.

Table S1. Comparison of analytical characteristics of the solid-contact ISEs with the present GC/black phosphorus/Ca^{2+}-ISE

Electrode	Potential drift (μV/s)	LOD (mol/L)	Reproducibility (%)	Reference
GC/GO-PANI/ Ca^{2+}-ISE	87	5×10^{-8}	1.1%	1
GC/carbon nanotube/ Ca^{2+}-ISE	930	6.3×10^{-7}	Not shown	2
GC/MoS_2/ K^+-ISE	10	3.2×10^{-6}	Not shown	3
GC/black phosphorus/Ca^{2+}-ISE	72	4.6×10^{-7}	3.8%	Present

Table S2. Potentiometric selectivity coefficients ($\log K_{I,J}$) detected for solid-contact Ca^{2+}-ISE

Ion	Liquid contact[4, 5]	Solid contact Ca^{2+}-ISE[a]
H^+	-3.6	-3.5 ± 0.1
Na^+	-5.8	-6.1 ± 0.2
K^+	-6.5	-6.7 ± 0.1
Mg^{2+}	-9.5	-9.5 ± 0.2

[a] Standard deviations of 3 measurements given.

Table S3. Application of solid-contact Ca^{2+}-ISE to determination of Ca^{2+} in wine samples

Sample	Proposed sensor (10^{-3}M)[a]	AAS (10^{-3}M)[a]	Recovery results		
			Added (10^{-3}M)	Found (10^{-3}M)[a]	Recovery (%)
Wine sample1	2.0 ± 0.1	2.2 ± 0.1	0.40	2.5 ± 0.4	125
			1.0	2.9 ± 0.3	90
Wine sample2	2.6 ± 0.2	2.5 ± 0.1	0.40	3.0 ± 0.1	100
			1.0	3.7 ± 0.2	110

[a] Average of three measurements ± standard deviation.

References for the Supporting Information:

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