Solid-contact Ca\textsuperscript{2+}-selective electrodes based on two-dimensional black phosphorus as ion-to-electron transducers\footnote{Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra07743b}

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A new type of solid-contact polymeric membrane Ca\textsuperscript{2+}-selective electrode has been developed by using black phosphorus as the transducing layer for the first time. The ion-to-electron transducing ability of black phosphorus was examined. The proposed electrode exhibits a good Nernstian slope with a detection limit of 4.0 × 10\textsuperscript{-7} M.

Black phosphorus (BP), a new member of two-dimensional (2D) materials, has recently attracted global interest for both its fundamental properties and its applications.\textsuperscript{16–21} Recently, it has been reported that black phosphorus displays high charge carrier mobility and electrical conductance.\textsuperscript{19,22} These properties, together with its better surface-to-volume ratio, make BP a promising candidate for chemical sensing applications. Several papers have appeared recently including field-effect transistors for nitrogen dioxide (NO\textsubscript{2}), electrochemical impedance spectroscopy for methanol and electrochemical sensing for humidity.\textsuperscript{23–25} However, without protection, black phosphorus flakes are reported to chemically degrade shortly with degradation of their electric properties and device performances.\textsuperscript{26} A recent theoretical paper demonstrated that black phosphorus flakes show improved stability for electrochemical sensing after being encapsulated by a hydrophobic polymeric membrane.\textsuperscript{27} Inspired by this, black phosphorus will be a very promising material for fabrication of SC-ISEs. As such, to the best of our knowledge, little is known about the performance of the black phosphorus as the ion-to-electron transducer of SC-ISEs.

Herein, we report here the first presenting of using black phosphorus for preparing the SC-ISEs. The Ca\textsuperscript{2+}-selective electrode was chosen as a model system. The main performance characteristics of black phosphorus based SC-ISEs were estimated. The fabricated sensors exhibit excellent Nernstian responses and potential stability. No water layer or interferences by light, O\textsubscript{2}, or CO\textsubscript{2} are observed.

The conducting film of SC-ISEs was prepared by drop-casting black phosphorus ethanol solution on electrode surface (see details in the ESI\footnote{Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra07743b}). The morphology of black phosphorus powder on the electrode was characterized with a scanning electron microscope (SEM) on a ZEISS EVO LS15 instrument at an accelerating voltage of 10 kV. A panoramic picture of the black phosphorus conducting polymer is illustrated in Fig. 1. It can be seen that obtained black phosphorus dispersion
material shows high dispersity from each other. In addition, black phosphorus has an irregular shape with an average size of approximately 10 nm. When used in a SC-ISE, these materials are bound together by the poly(vinyl chloride) (PVC) binder as well as the plasticized polymeric membrane.

To further characterize the quality of black phosphorus-based solid contact, electrochemical impedance spectroscopy (EIS) was performed. EIS was performed with a three-electrode setup (see details in the ESI†), where the glassy carbon electrode (GCE) coated with or without black phosphorus was connected as the working electrode, while an Au electrode as the auxiliary electrode and the Ag/AgCl electrode as the reference electrode. Impedance measurements of GCE/black phosphorus/Ca\(^{2+}\)-ISE and GCE/Ca\(^{2+}\)-ISE recorded in 10\(^{-3}\) M CaCl\(_2\) are shown in Fig. 2. The diameter of the high-frequency semicircle is related to the bulk membrane coupled to the contact resistance between GC or solid contact and the ion-selective PVC membrane. The resistance of the GC/black phosphorus/Ca\(^{2+}\)-ISE (0.64 MΩ) is smaller than that of the GC/Ca\(^{2+}\)-ISE (1.13 MΩ), which indicates that the charge transfer across the interfaces is facilitated due to the presence of black phosphorus.

Current-reversal chronopotentiometry was used to evaluate the short-term potential stability of the black phosphorus-based Ca\(^{2+}\)-ISE by recording potentials of the ISE under currents of 1 nA in 1 mM CaCl\(_2\) solution. Fig. 3 shows that the potential drift of the GC/black phosphorus/Ca\(^{2+}\)-ISE, derived from the ratio \(\Delta E/\Delta t\), is 72 \(\mu\)V s\(^{-1}\), which is much lower than that of the GC/Ca\(^{2+}\)-ISE under the same conditions (500 \(\mu\)V s\(^{-1}\)). These results indicate that the potential stability of the electrode can be obviously improved by using the black phosphorus film as the ion-to-electron transducer.

The potentiometric performance characteristics such as the working concentration range, the limit of detection, the slope of the linear curve and response time were determined. The results of these measurements are summarized in Fig. 4. As can be seen, a linear range of the developed GC-BP-Ca\(^{2+}\)-ISE from 1.0 \(\times\) 10\(^{-8}\) to 1.0 \(\times\) 10\(^{-3}\) M is observed with a Nernst slope of 28.3 ± 0.7 mV decade\(^{-1}\) \((R^2 = 0.99)\). The detection limit calculated as the intersection of the slope line is 4.0 \(\times\) 10\(^{-7}\) M. The response time of the electrode was measured after successive immersion of the electrode in a series of Ca\(^{2+}\) solutions. A response time of about 10 s was required to achieve a steady potential within 0.7 mV for measuring Ca\(^{2+}\) at concentrations ranging from 1.0 \(\times\) 10\(^{-1}\) to 1.0 \(\times\) 10\(^{-6}\) M. In addition, experiments also show that the potential response of the proposed electrode can be fully reversible with a relative standard deviation of 3.8% \((n = 5)\). The comparison of the analytical
The performance of the developed sensor with some of other reported solid-contact ISEs is summarized in Table S1 in the ESI. As illustrated, the response characteristics of the proposed electrode are comparable with those of other solid-contact ISEs. The potentiometric selectivity coefficients were obtained in an alkali metal or alkaline earth metal chloride solutions using the separate solution method. The results are presented in Table S1. As can be seen, GC-black phosphorus-Ca\textsuperscript{2+}-ISEs exhibited a high selectivity over interfering ions, which are all very close to the values reported in the literature. These phenomena indicate that the selectivity of the developed Ca\textsuperscript{2+}-ISEs is not affected by the ion-to-electron transducing layer, but is dependent on the ionic sensing polymeric membrane itself. This selectivity satisfied the requirements for calcium assay in the wine samples.

A potentiometric water layer test was conducted with all electrodes to evaluate the water layer formation between the polymeric ion-selective membrane and its solid contact. The electrode was first immersed in 0.1 mol L\textsuperscript{-1} of CaCl\textsubscript{2} solution. Then the solution was changed to 0.1 mol L\textsuperscript{-1} NaCl solution. After 2 h the NaCl solution was replaced by 0.1 mol L\textsuperscript{-1} of CaCl\textsubscript{2} solution. The potential responses of the tested electrodes are shown in Fig. 5. As can be seen, a negative EMF change is observed for both electrodes upon replacing the CaCl\textsubscript{2} solution with the NaCl solution. Such EMF change reflects the change in the outer phase boundary potential as a consequence of the selectivity behavior of the Ca\textsuperscript{2+}-selective membrane. In this process, the electrode based on black phosphorus exhibits a stable potential response while an obvious positive potential drift is observed for the electrode without solid contact. These results demonstrate that no undesirable water layer is formed for the GC/black phosphorus-Ca\textsuperscript{2+}-ISE while there was a water layer at the sensing polymer/electrode interface in case of absence of the ion-to-electron transducer layer.

It has been reported that light, oxygen, and carbon dioxide may cause interference to several SC-ISEs. Oxygen or carbon dioxide can permeate plasticized PVC membranes which affect the boundary potential or alter the local pH. In addition, SC-ISE can be photosensitive if the solid contact is an organic conductor. In this study, the effect of O\textsubscript{2} and CO\textsubscript{2} was tested by bubbling both gases into 10\textsuperscript{-3} M CaCl\textsubscript{2} solution for 25 min respectively followed by purging with N\textsubscript{2} to remove O\textsubscript{2} or CO\textsubscript{2} for 25 min. In addition, the effect of light on the GC/BP-Ca\textsuperscript{2+}-ISE was investigated by recording the potential response in a 10\textsuperscript{-3} M CaCl\textsubscript{2} solution while turning on/off the ambient light. As clearly illustrated in Fig. 6, no significant potential changes are observed during the measurements, indicating that the black phosphorus film-based solid contact has no light, O\textsubscript{2} or CO\textsubscript{2} sensitivity.

The proposed GC/black phosphorus/Ca\textsuperscript{2+}-ISE was finally applied to determination of Ca\textsuperscript{2+} in wine samples that are widely consumed by the local public. It should be noted that alcohol was removed from wine samples using rotary evaporators and the samples were diluted 10 times with deionized water before potentiometric detection. In order to illustrate its accuracy, the comparison between the proposed sensor and the atomic absorption spectrophotometry (AAS) method was performed. The results are given in Table S2. It can be seen the data obtained by the proposed electrode agree well with those obtained by the AAS method, indicating that the proposed GC/black phosphorus/Ca\textsuperscript{2+}-ISE has a promising potential for real sample analysis.

**Conclusions**

In summary, we have for the first time used a few-layer black phosphorus film as the ion-to-electron transducer in solid-contact Ca\textsuperscript{2+}-ISE. The presence of this layer significantly reduces the resistance of membrane compared to coated disk electrode. There are also many other important advantages, including long-term potential stability, no undesirable water layer and their insensitivity to O\textsubscript{2} or CO\textsubscript{2} and light. In addition, the electrodes demonstrate excellent sensing properties including fast response time, a wide dynamic response range, low detection limit and good selectivity. Moreover, this robust sensor was successfully applied for Ca\textsuperscript{2+} determination in the wine samples with similar results to AAS.

**Conflicts of interest**

There are no conflicts to declare.
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