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Highly hydrophobic solid contact based on graphene-hybrid nanocomposites for all solid state potentiometric sensors with well-formulated phase boundary potentials

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ABSTRACT

The properties of solid contact (SC) transducer are crucial for obtaining stable solid state ion selective electrodes (ISEs). We report in this work that the hybrid nanomaterial composed of graphene and sliver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgTFPB), designated graphene&AgTFPB, can be sandwiched between an ion selective membrane (ISM) containing $TFPB^-$ and a silver conducting substrate (CS) and effectively work as the SC transducer to provide ion-to-electron translation. Thus developed solid state ISEs, designated Ag/graphene&AgTFPB/K^+-ISM electrodes, demonstrated a Nernstian response to K^+ with a slope of 56.46 (±0.25) mV/decade ($n = 5$) in a concentration range of $10^{-5.2}$–$10^{-2.9}$ M with a detection limit of $10^{-5.73}$ M, as well as a sufficient stability against O_2, CO_2 and light. Furthermore, the Ag/graphene&AgTFPB/K^+-ISM electrodes displayed a standard electromotive force (EMF) of 550.42 (±1.34) mV with a batch-to-batch deviation of 1.26 mV. We believe that the superior potential stability and reproducibility can be ascribed to the graphene&AgTFPB nanocomposites SC. We believe that the doped AgTFPB can provide the ion-to-electron transduction via the Ag/AgTFPB/$TFPB^-$ redox conversion at the SC/CS interface and the ion-exchange equilibrium of $TFPB^-$ at the ISM/SC interface. Thus, the overall potential difference across the potentiometric measurement cell can be theoretically formulated in terms of thermodynamic equilibrium at two interfaces. Moreover, the highly hydrophobic nature of graphene&AgTFPB nanocomposites can also substantially suppress the formation of water layer.

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1. Introduction

Ion selective electrodes (ISEs) are simple, routine tools for clinical blood electrolyte analysis, which comprises more than a billion of measurements per year and a large share in the *in vitro* diagnostic sensor market. Conventional liquid-contact (LC) ISEs, in which the ion-selective membrane (ISM) is sandwiched between the sample solution and the internal filling solution, have been widely applied [1–4]. However, due to the internal filling solution, LC ISEs require frequent maintenance and are not easily adapted to analysis in small sample volumes and *in vivo* conditions. Therefore, replacing the internal filling solution with a solid contact (SC) that provides the straightforward ion-to-electron transduction has been stimulated [1,5,6]. SC ISEs are in particularly promising for miniaturization and mass-production.

Since the properties of SC are crucial for obtaining stable and reliable SC ISEs, much research effort has been devoted to developing SC materials. In principle, an ideal SC material must fulfill the following requirements: (a) well defined phase-boundary potentials at the ISM/SC and SC/conducting substrate (CS) interfaces; (b) large redox capacity to accommodate sufficient amount of ion-to-electron transduction; (c) enough hydrophobicity of SC to reduce the formation of an aqueous film at the ISM/SC interface; (d) stable chemical composition; (e) easier to development [7,8]. Redox-active self-assembled monolayers (SAMs) [7,8], conductive polymers (CPs) [5,9,10] and nanostructured materials [11] have been investigated as the SC materials. However, the low redox buffer capacity of electroactive SAMs limits their real applications. Although CPs with high redox capacitance can effectively translate the flux of ionic analyte into electronic signal via redox transformation [9], their sensitivity to O_2, CO_2, pH and light makes the long-term potential instable [12]. Nanostructured materials [11], e.g., macroporous carbon [13,14], carbon nanotube [15–18] and graphene [19–21], can function as the ion-to-electron transducer layer via the charging capacitance, but the phase boundary potential at both ISM/SC and SC/CS interfaces cannot be easily formulated. The early work, utilizing the silver/silver tetraphenylborate

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(AgTPB)/ISM (TPB^- as the additive) configuration to fix the phase boundary potentials [22], represented a very promising approach to construct SC ISEs. Nevertheless, the light sensitivity and the limited hydrophobicity of TPB^- discouraged the further study [23]. Although the incorporation of Ag^+ ion carrier into ISM [24] can fix the phase boundary at ISM/silver epoxy-based CS interface via reversible redox reaction, namely $AgL^+ + e \leftrightarrow Ag + L$ (where L refers to the Ag^+ ion carrier), the selectivity of the ISM containing mixed ionophores is challenging. SCs consisting of a redox couple, e.g., mixed-valent gold nanoclusters [25], cobalt [26,27], or osmium salts [28,29], have also been proposed for providing thermodynamically defined phase boundary potentials.

In this work, we synthesized hybrid nanocomposites of graphene and a lipophilic silver salt, namely sliver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgTFPB), which was subsequently sandwiched between a silver CS and ISM as the SC to prepare SC ISEs. The doped AgTFPB can provide an effective ion-to-electron transduction and fix the phase boundary potential at both ISM/SC and SC/CS interfaces, thus favoring the potential stability and analytical reproducibility of SC ISEs. Moreover, the highly hydrophobic nature of graphene&AgTFPB nanocomposites can also substantially suppress the formation of water layer. Indeed, the SC ISEs thus fabricated demonstrated a detection range of $10^{-5.2} \sim 10^{-2.9}$ M with a detection limit of $10^{-5.73}$ M, a sufficient inertness to O_2, CO_2 and light, and a standard EMF of 550.42 (±1.34) mV with a batch-to-batch deviation of 1.26 mV.

2. Theoretical Consideration

As shown in Fig. 1a, when a SC ISE based on the graphene&AgTFPB nanocomposite is utilized to measure a potential of an aqueous solution with respect to a calomel reference electrode (with an internal filling solution saturated by KCl), the equilibrium potential thus measured by the voltmeter is in fact the difference of the inner potentials between the two conducting copper wires (see Fig. 1b), namely,

$$\begin{aligned} \mathrm{EMF} &= \phi^{\mathrm{Cu^{II}}} - \phi^{\mathrm{Cu^{I}}} \\ &= (\phi^{\mathrm{Cu^{II}}} - \phi^{\mathrm{SC}}) + (\phi^{\mathrm{SC}} - \phi^{\mathrm{ISM}}) + (\phi^{\mathrm{ISM}} - \phi^{\mathrm{S}}) + (\phi^{\mathrm{IS}} - \phi^{\mathrm{Cu^{I}}}) \end{aligned} \quad (1)$$

The potential difference in Eq. (1) can be considered by taking into account the electrochemical equilibria at a series of interfaces. For simplicity, the liquid junction potential at the sample solution/internal filling solution interface, namely $\phi^{\mathrm{S}} - \phi^{\mathrm{IS}}$, is assumed to be negligible. First, at the Cu^{II}/Ag interface, the equilibrium between the copper wire and the silver CS is established by the equality of the electrochemical potential of electron in two phases,

$$\overline{\mu}_{e^-}^{\mathrm{Cu^{II}}} = \overline{\mu}_{e^-}^{\mathrm{Ag}} \quad (2)$$

At the Ag/SC interface, the redox equilibrium related to oxidation of silver and the solubility of AgTFPB give the following two equations,

$$\overline{\mu}_{\mathrm{Ag^+}}^{\mathrm{SC}} + \overline{\mu}_{e^-}^{\mathrm{Ag}} = \mu_{\mathrm{Ag}} \quad (3)$$

$$\overline{\mu}_{\mathrm{Ag^+}}^{\mathrm{SC}} + \overline{\mu}_{\mathrm{TFPB^-}}^{\mathrm{SC}} = \mu_{\mathrm{AgTFPB}} \quad (4)$$

where $\overline{\mu}_{\mathrm{Ag^+}}^{\mathrm{SC}}$ and $\overline{\mu}_{\mathrm{TFPB^-}}^{\mathrm{SC}}$ are the electrochemical potential of Ag^+ and $TFPB^-$ in the SC phase, respectively. μ_{AgTFPB} and μ_{Ag} are the chemical potential of AgTFPB salt and Ag CS, respectively. Eqs. (3) and (4) can be combined to yield,

$$\mu_{\mathrm{Ag}} + \overline{\mu}_{\mathrm{TFPB^-}}^{\mathrm{SC}} = \overline{\mu}_{e^-}^{\mathrm{Ag}} + \mu_{\mathrm{AgTFPB}} \quad (5)$$

which can be expressed as,

$$\mu_{\mathrm{Ag}} + \mu_{\mathrm{TFPB^-}}^{\ominus,\mathrm{SC}} + RT \ln a_{\mathrm{TFPB^-}}^{\mathrm{SC}} - F\phi^{\mathrm{SC}} = \mu_{e^-}^{\mathrm{Ag}} - F\phi^{\mathrm{Ag}} + \mu_{\mathrm{AgTFPB}} \quad (6)$$

where $\mu_{\mathrm{TFPB^-}}^{\ominus,\mathrm{SC}}$ and $a_{\mathrm{TFPB^-}}^{\mathrm{SC}}$ are the standard chemical potential and the activity of $TFPB^-$ in the SC phase, respectively. $\mu_{e^-}^{\mathrm{Ag}}$ is the standard

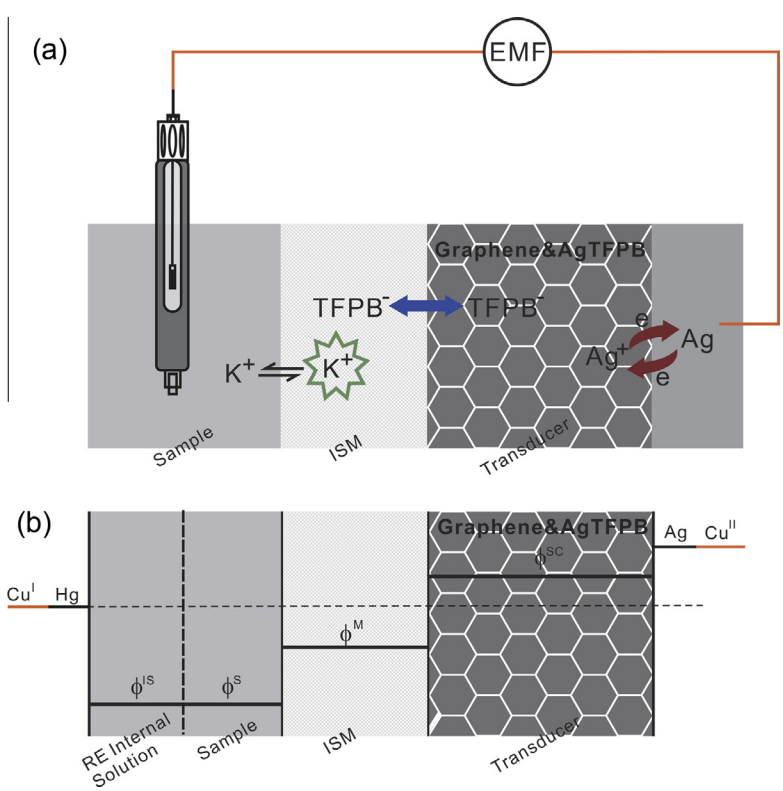

Fig. 1. (a) Schematic illustration of the potentiometric measurement with a solid state K^+-ISE using the graphene&AgTFPB nanocomposites as the ion-to-electron transducer, where the phase boundary potentials at both SC/Ag and SC/ISM interfaces are well-defined by Ag^+/Ag redox couple and $TFPB^-$ distribution, respectively. (b) The potential distribution across the cell used to analyze an aqueous solution with respect to a calomel reference electrode.

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