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A simple approach for fabricating solid-contact ion-selective electrodes using nanomaterials as transducers

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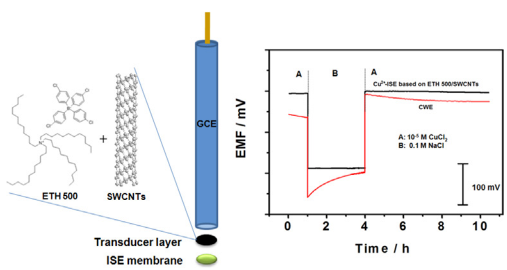
HIGHLIGHTS

- A general method for fabricating nanomaterials based solid-contact ISEs is developed.
- The mixture of an ionic liquid and a nanomaterial is used as intermediate layer.
- The detection limits of the proposed sensors are in the nanomolar range.
- The developed electrodes exhibit a good response time and excellent stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and robust approach for the development of solid-state ion-selective electrodes (ISEs) using nanomaterials as solid contacts is described. The electrodes are fabricated by using the mixture of an ionic liquid (IL) and a nanomaterial as intermediate layer, formed by melting the IL. Tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) is chosen as an model of IL to provide strong adhesion between the inner glassy carbon electrode and the intermediate layer. Nanomaterials including single-walled carbon nanotubes (SWCNTs) and graphene were used as active ion-to-electron transducers between the glassy carbon electrode and the ionophore-doped ISE membrane. By using the proposed approach, the solid-contact Cu^{2+}- and Pb^{2+}-selective electrodes based on ETH 500/SWCNTs and ETH 500/graphene as transducers, respectively, have been fabricated. The proposed electrodes show detection limits in the nanomolar range and exhibit a good response time and excellent stability.

1. Introduction

Ion-selective electrodes (ISEs) are most widely used chemical sensors in clinical diagnostics, process control and environmental monitoring due to their intrinsic advantages including excellent selectivity, low cost, ease of use, and high reliability [1–3]. Among these, solid-contact ISEs which eliminate the internal solution and are easily miniaturized have been recognized as the means by which the next ISE generation will be constructed. Solid-contact ISEs, known as coated-wire electrodes (CWEs), were introduced many years ago [4]. However, such electrodes lack long-term stability and they are only useful in specific applications such as chromatographic detectors [5] or in flow-injection analysis [6]. Potential instabilities of CWEs have been mainly attributed to the lack of a well-defined redox couple and the formation of a water layer at the membrane–metal interface [7]. The historical problem of poor potential stability between the ion-selective membrane and the conducting wire has been largely solved by the

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introduction of conducting polymers [8] such as poly(3-octylthiophene) (POT) [9,10], polypyrrole (PPy) [11], polythiophene [12], polyaniline [13], and poly(3,4-ethylenedioxythiophene) [14] as ion-to-electron transducers. Although the ISEs based on these transducing materials show benefits compared to those of traditional ISE with an internal solution, they also suffer from some drawbacks such as sensitivity to light, O_2, CO_2, and pH [3].

In recent years, nanomaterials have been extensively studied and widely exploited in chemsensors and biosensors, since they possess some unique chemical, physical and electronic properties that cannot be achieved by their bulk counterparts [15]. Especially, the exceptional electrical properties such as the high charge transfer, the extraordinary electrical capacities and good hydrophobicity make them suitable as transducing components in potentiometric sensors [16,17]. Recently, many nanostructured carbon materials including fullerene [18], graphene [19,20], carbon nanotubes (CNTs) [21–23], three-dimensionally ordered macroporous (3DOM) carbon [24] and colloid-imprinted mesoporous (CIM) carbon [25] have been utilized as ion-to-electron transducers in solid-contact ISE. The electrodes based on these nanomaterials as transducers exhibit excellent response performances such as long-term potential stability, and insensitivity to O_2. It has been well known that the transducer layer of solid-contact ISEs based on nanomaterials is usually formed by drop casting a suspension solution of nanomaterial onto the surface of the inner electrode (e.g., glassy carbon electrode, GCE) which is followed by heating the electrode surface to evaporate the solvent with a hot air stream or an infrared lamp. In order to obtain a homogeneous coverage of nanomaterials on the surface of the electrode, these processes have to be repeated for many times [18–22]. It is clear that such fabrication processes are somewhat complicated and time consuming. In addition, nanomaterials can easily peel off from the electrode surface owing to the poor adhesion between these nanomaterials and the surface of the GCE. This poses serious limits to their use in solid-contact ISEs.

Ionic liquids (ILs) refer to liquids composed entirely of ions that are fluid around or below 100 °C. They possess unique features, such as low volatility, tunable viscosity, high conductivity, large electrochemical window and low toxicity. These properties make ILs particularly suitable for their use in electrochemical sensors [26–29].

Herein, we propose a simple and robust approach for fabricating solid-contact ISEs based on nanomaterials as transducers. The transducer layer can be prepared by simply spreading the IL and nanomaterial composite on the GCE. Tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500) with a melting point of 79 °C, is a kind of IL but not a room-temperature IL. ETH 500 is utilized to provide strong adhesion between the GCE and the nanomaterial layer. In this work, single-walled carbon nanotubes (SWCNTs) and graphene have been chosen as the models of nanomaterials since they have been extensively used as solid contacts in potentiometric sensors. The chemical structure of ETH 500 and schematic structures of SWCNTs and graphene are shown in Scheme 1. By using the proposed approach, solid-contact Cu^{2+} and Pb^{2+}-selective electrodes based on ETH 500/SWCNTs and ETH 500/graphene as ion-to-electron transducers, respectively, have been fabricated. It shows that the proposed approach offers a simple way for fabrication of reliable and high-performance solid-contact ISEs based on nanomaterials as ion-to-electron transducers.

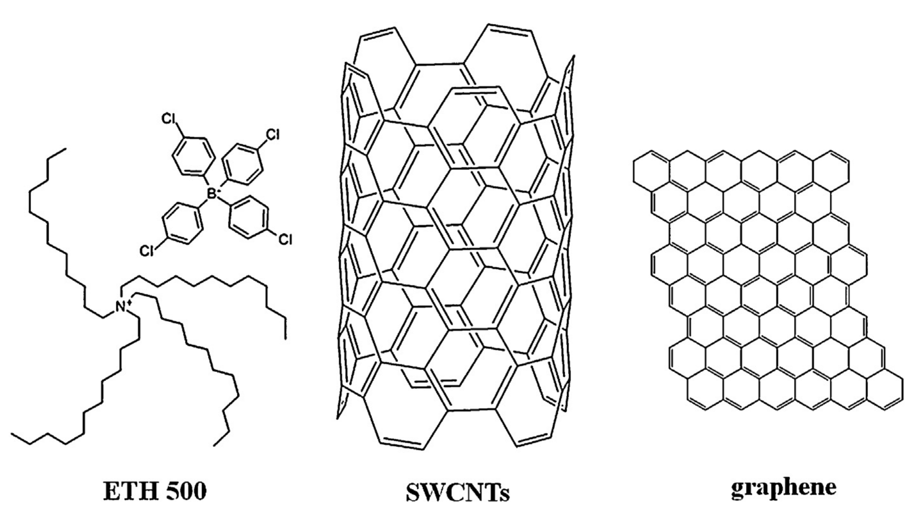
2. Experimental

2.1. Reagents

The ionophores *N,N,N′,N′*-tetradodecyl-3,6-dioxaoctane-dithioamide (ETH 1062, Cu^{2+} ionophore), tert-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) (lead ionophore IV), tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500), high molecular weight poly (vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl) sebacate (DOS), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), and dimethylformamide (DMF) were purchased from Fluka AG (Buchs, Switzerland). SWCNTs and graphene were obtained from XFnano Materials Tech Co., Ltd. (Nanjing, China). Aqueous solutions were prepared with freshly deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system. Tetrahydrofuran (THF) was freshly distilled prior to use. All other reagents were analytical grade and used without any further purification. A stock solution of 0.01 M Cu^{2+} or Pb^{2+} was prepared by dissolving $CuCl_2$ or $Pb(NO_3)_2$ in deionized water and then diluted to various concentrations of working solutions with deionized water prior to measurements.

2.2. Apparatus

All measurements of electromotive force (EMF) were performed at 20–21 °C using a PXSJ-216 pH meter (Leici, Shanghai) in the galvanic cell: saturated calomel electrode (SCE)//0.1 M LiOAc/sample solution/ISE membrane/nanomaterial layer/GCE. The external reference electrode employed was a double-junction



Scheme 1. Chemical structure of ETH 500 and the schematic structures of SWCNTs and graphene.