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# A solid-contact potassium-selective electrode with $MoO_2$ microspheres as ion-to-electron transducer

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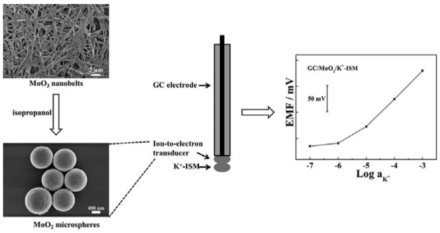
## HIGHLIGHTS

- A solid-contact ion selective electrode with $MoO_2$ microspheres as ion-to-electron transducer was fabricated.
- $MoO_2$ microspheres work as metallic analogues based on non-carbon and non-noble metal materials.
- $MoO_2$ microspheres were synthesized from $MoO_3$ with a certain morphology via a simple method.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A solid-contact ion-selective electrode (SC-ISE) for potassium with $MoO_2$ microspheres as ion-to-electron transducer is described. $MoO_2$ microsphers can be synthesized via the reduction of $MoO_3$ nanobelts in an isopropanol solvent with a mild process, and the obtained $MoO_2$ microspheres have been characterized by X-ray diffraction and field-emission scanning electron microscopy. With the application of $MoO_2$ microspheres, the newly fabricated SC-ISE for $K^+$ exhibits a stable and rapid potential response. A near Nernstian slope of 55 mV/decade to potassium activities in the range of $10^{-5} - 10^{-3}$ M is found and the detection limit is $10^{-5.5}$ M. Impedance spectra and chronopotentiometry results show that a smaller resistance together with a larger double layer capacitance is guaranteed due to the introduction of the intermediate layer of $MoO_2$ microspheres. Additionally, light, $O_2$ and $CO_2$ do not induce significant influences to the present SC-ISE, and a reduced water layer between the ion selective membrane and the underlying conductor is formed. Thus, it is clear that $MoO_2$ microspheres, as metallic analogues, can be used as a good candidate for the new type of transducing layer in SC-ISEs.

## 1. Introduction

Ion-selective electrodes (ISEs) have been widely applied as potentiometric sensors in chemical analysis for many decades [1]. Conventional ISEs, for which the ion-selective membrane (ISM) contacts electrically the inner reference electrode through an inner solution, suffer from problems of big volume, trivial maintenance and hard portability, thus restricting their wide applications [2,3]. In contrast, solid-contact ion-selective electrodes (SC-ISEs) exclude the usage of inner solution by making the ISMs coated directly onto solid conducting substrates, and therefore have drawn great attention [4].

Coated-wire electrodes (CWEs) invented in 1970s are the first examples for SC-ISEs [5]. However, these electrodes have the inherent disadvantage of poor long-term stability because of the indefinite phase boundary potential at the interface between the

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ISM and the underlying metallic conductor. To solve this problem, intermediate layers performing as ion-to-electron transducers have been employed between them, and consequently considerable efforts have been made for the investigation of effective transducer layers [6].

Hitherto, various solid-contact layers based on different transduction mechanisms have been reported [7]. On the one hand, conducting polymers, including polythiophene [8], polyaniline [9] and polypyrrole [10], are outstanding instances for the redox capacitance transduction mechanism. Unfortunately, these SC-ISEs may suffer from interferences of gases and light together with the formation of the unintended water layer between the conducting polymer and the ISM [11]. On the other hand, the double layer capacitance transduction mechanism has been illustrated for solid-contact layers mainly based on carbon [12], noble metal materials [13] as well as the hybrid composites of them [14]. Alternatively, to expand choices for this kind of transducing layer, materials with structures similar to graphite named as carbon analogues have been systematically investigated [15]. Considering the high cost and scarcity of these noble metal materials, we expect that cheap and available metallic analogues, can also be exploited as solid-contact layers. As a proof-of-concept study, a material with metallic properties can be chosen as a representative for a systematical study.

As a typical metallic transition metal oxide, monoclinic molybdenum dioxide ($MoO_2$) with a distorted rutile structure has drawn considerable attention due to its special physicochemical properties including low electrical resistivity, high melting point and good chemical stability [16]. $MoO_2$ materials with different morphologies perform well as electrochemical supercapacitors [17], battery anodes [18], catalysts [19] and transistors [20]. To synthesize these $MoO_2$ materials, various strategies have been explored. For example, $MoO_2$ nanotubes [21] and nanorods [22] were obtained via carbothermal and hydrogen reductions of $MoO_3$ at high temperatures, respectively. Yolk–shell $MoO_2$ microspheres were synthesized through a solvothermal process by using $MoO_2(acac)_2$ as the precursor [23]. In addition, mesoporous $MoO_2$ was fabricated by a nanocasting strategy, for which phosphomolybdic acid was used as the precursor while mesoporous silica KIT-6 used as hard a template [24]. However, drawbacks exhibited by the aforementioned preparation methods, such as the process of high temperature, the usage of expensive precursors and dangerous gases, as well as the requirement of templates, have largely impeded their wide applications. Thus, developing a facile and affordable method to fabricate $MoO_2$ materials with certain morphologies would still be an important and meaningful work. Moreover, to the best of our knowledge, $MoO_2$ materials have not yet been used as solid-contact layers for SC-ISEs.

In this work, a facile and cost-effective solvothermal strategy is used to synthesize $MoO_2$ microspheres. The obtained $MoO_2$ microspheres can work as metallic analogue and have been firstly applied as ion-to-electron transducer layer for SC-ISEs. The electrochemical properties of the fabricated SC-ISEs have been characterized by chronopotentiometry, AC impendence and open circuit potential-time techniques. It has been found that using $MoO_2$ microspheres as intermediate layer, the new proposed SC-ISE exhibits good potential response and stability, which indicates that $MoO_2$ microspheres can be employed as a new ion-to-electron transducer for solid state potentiometric sensors.

## 2. Experimental

### 2.1. Reagents and materials

Reagents including high molecular weight poly(vinyl chloride) (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), and the potassium ionophore valinomycin were obtained from Sigma-Aldrich. Other chemical reagents with analytical grade were purchased from Sinopharm Chemical Reagent, and were used without further purification. Deionized water (resistance 18.2 MΩ cm) obtained by a Pall Cascada laboratory water system was used to prepare aqueous solutions.

### 2.2. Synthesis of $MoO_2$ microspheres

To synthesize $MoO_2$ microspheres, $MoO_3$ nanobelts were prepared firstly as described before [25,26]. The resultant $MoO_3$ nanobelts were dispersed in an isopropanol solvent for further experiments. In a typical process for the synthesis of $MoO_2$ microspheres, 25 mg of $MoO_3$ nanobelts dispersed in 30 mL of isopropanol were firstly added into a 50 mL of Teflon-lined stainless steel autoclave. Then, the autoclave was placed in an oven and heated at 180 °C for 36 h. After being cooled, the resulting black product was centrifuged and washed with water and ethanol, respectively. Eventually, the obtained material was dried at 80 °C in vacuum for 12 h.

### 2.3. Fabrication of the solid-contact $K^+$-ISEs

The glassy carbon (GC) electrodes with a diameter of 3 mm were polished in aqueous dispersions of alumina (0.3 and 0.05 μm, respectively). Then, the GC electrodes were washed with water and ethanol via an ultrasonication process for 5 min, respectively. 2 mg of the as-synthesized $MoO_2$ microspheres were dispersed in 1 mL of distilled tetrahydrofuran (THF) through ultrasonication for 30 min to form $MoO_2$ dispersion. Subsequently, 20 μL of the $MoO_2$ dispersion was drop-cast onto the cleaned GC electrode and a solid contact layer was formed after the evaporation of THF.

The $K^+$-selective membrane contained 1.0 wt% valinomycin, 0.6 wt% NaTFPB, 32.8 wt% PVC, and 65.6 wt% *o*-NPOE. To obtain the membrane, 200 mg of membrane components were dissolved in 1.6 mL of distilled THF to form the cocktail solution for the potassium ISM. In order to fabricate this newly developed SC-ISE, 100 μL of the potassium membrane cocktail was drop-cast onto the intermediate layer of $MoO_2$ microspheres, and was left to dry overnight.

### 2.4. Characterization of $MoO_2$ microspheres

To determine the crystallinity and phase purity of the prepared products, the X-ray diffraction (XRD) measurements were performed by using a Shimadzu XRD-7000 X-ray diffractometer, operated at 40 kV and 50 mA under a Cu Kα radiation with a scanning rate of 2°/min. A field-emission scanning electron microscope (FESEM, Hitachi, S-4800) was utilized to characterize the size and morphology of the synthesized material.

### 2.5. Electrochemical measurements

For electrochemical tests, a CHI 760D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) was used. The potentiometric assays were performed using a galvanic cell: Ag/AgCl(3 M KCl)/0.1 M LiOAc/sample solution/ISM/$MoO_2$ layer/GC electrode. The impedance spectra were recorded in a solution of 1 mM KCl with a frequency range of $10^6$–$10^{-1}$ Hz and an amplitude of 100 mV. Chronopotentiometric measurements were performed by successively applying constant currents of ±1 nA for 60 s, respectively, in 1 mM KCl solution. The electrochemical impedance spectroscopy and chronopotentiometry tests were done in 1 mM KCl solution by using a conventional three electrode system including the ISE as working electrode, a Ag/AgCl (3 M KCl) as the