



Solid-contact K^+ -selective electrode based on three-dimensional molybdenum sulfide nanoflowers as ion-to-electron transducer



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ABSTRACT

Three-dimensional (3D) molybdenum sulfide (MoS₂) nanoflowers have been synthesized via a novel hydrothermal method and applied as ion-to-electron transducer for solid-contact ion-selective electrodes (SC-ISEs). The morphology and elemental composition of the prepared nanomaterials have been characterized. The performance of the developed K^+ -SC-ISE has been demonstrated by determining K^+ in solution with a polymeric membrane containing valinomycin as the ionophore. A Nernstian slope of 55.8 mV/decade with a detection limit of $10^{-5.5}$ M can be obtained. Using the 3D flowerlike MoS₂ as solid contact, the fabricated K^+ -SC-ISE exhibits a smaller impedance and more stable potential response than the coated-wire electrode. In addition, the novel SC-ISE behaves well in the water layer test and shows good resistance to interferences from light, O₂ and CO₂. It is believed that the 3D MoS₂ nanoflowers can be a good alternative as solid contact in SC-ISEs.

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1. Introduction

With a long history in the field of chemical sensors, ion-selective electrodes (ISEs) have been widely used in routine analysis [1]. The coated wire electrodes (CWEs) with ion selective membranes (ISMs) attached directly on the metal substrates were introduced in 1971, and have greatly simplified the volume of the ISEs evoking the development of solid state ISEs [2]. However, their long-term stability has been found rather poor due to the lack of well-defined interfacial potential between the ISM and the underlying conductor. Consequently, intermediate layers working as ion-to-electron transducers have been proposed, which promotes the development of solid-contact ion selective electrodes (SC-ISEs) [3].

During the past decades, various intermediate layers have been developed. Conducting polymers such as polyaniline [4], polythiophene [5], and polypyrrole [6] with redox capacitances have been investigated. Nevertheless, some of these SC-ISEs suffer from problems of the formation of water layers [7] and the interferences from oxygen, carbon dioxide and light [8]. On the other hand, nanostructured materials, mainly based on carbon (e.g., carbon nanotubes [9], colloid-imprinted mesoporous carbon

[10], graphene [11], and fullerene [12]) and noble metals (e.g., nanoporous gold film [13] and platinum nanoparticles [14]), have been reported as ion-to-electron transducers owing to their special physicochemical properties. It has been shown that the large interface area between nanostructured materials and the ISM leads to a high double-layer capacitance, thus minimizing the potential drift. In particular, the water layer existing between the ISM and the underlying conducting substrate can be largely reduced because of the intrinsic hydrophobicities of the nanomaterials. Due to the booming development of nanochemistry, new nanomaterials based on non-carbon and non-noble-metal materials as ion-to-electron transducers are highly desired to develop novel SC-ISEs.

Layered transition metal dichalcogenides have similar structures to graphite and exhibit promising applications [15]. As a typical example, molybdenum disulphide (MoS₂) has shown its excellent performances as supercapacitors [16], transistors [17] and catalysts [18]. Until now, MoS₂ nanomaterials with various morphologies synthesized by different methods have been reported. For example, MoS₂ nanotubes can be synthesized at a high temperature in a floating hydrogen–thiophene atmosphere [19]. MoS₂ nanoribbons have been obtained by a thermally decomposed phosphomolybdic acid in the presence of H₂S/H₂ [20]. However, the high temperature processes as well as the use of gases may restrict their wide applications. Hydrothermal processes own their unique advantages with controllable synthesis procedures in mild

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and facile ways [21,22], which could be used to synthesize MoS₂ with certain morphologies.

In this work, the 3D MoS₂ nanoflowers have been synthesized through a novel hydrothermal method and applied for the first time as ion-to-electron transducer for a SC-ISE. Due to the excellent electrochemical properties of the 3D flowerlike MoS₂, the constructed K⁺-SC-ISE exhibits high stability and small impedance. In addition, the developed SC-ISE behaves well in the water layer test and shows good resistance to interferences from light, O₂ and CO₂. It will be shown that the 3D MoS₂ nanoflowers can be used as an excellent ion-to-electron transducer for SC-ISEs.

2. Experimental

2.1. Reagents

Poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), and the potassium ionophore-valinomycin were purchased from Sigma-Aldrich. All other chemical reagents were purchased from Sinopharm Chemical Reagent with analytical grade and were used without further purification. Deionized water with a specific resistance of 18.2 MΩ cm obtained with a Pall Cascada laboratory water system was used to prepare aqueous solutions.

2.2. Synthesis of 3D flowerlike MoS₂

MoS₂ nanoflowers were synthesized through a two-step hydrothermal process. In a typical procedure, MoO₃ nanomaterials were prepared firstly according to the literature [23] with some modifications. 3.36 g Na₂MoO₄·2H₂O was firstly dissolved in 70 mL of distilled water, and then 5 mL of 4 M nitric acid was added into the solution. After being stirred for 5 min, the mixture was treated under hydrothermal conditions at 180 °C for 24 h. The resulting white product was then collected and dried at 80 °C for 12 h under a vacuum.

To synthesize the 3D MoS₂ nanoflowers, 2.5 mmol MoO₃ was dispersed in 30 mL H₂O, and then 2 mL of 4 M HCl was added. The resulting solution was stirred for 30 min. Then 6.25 mmol NaSCN was added into the solution. After being stirred for 10 min, the resulting suspension was treated via a hydrothermal process at 180 °C for 24 h. The black product was collected by centrifugation and dried in vacuum at 80 °C for 12 h.

2.3. Preparation of potassium ion selective electrodes

The membrane cocktail was prepared by dissolving 200 mg membrane component (1.0 wt% valinomycin, 0.6 wt% NaTFPB, 32.8 wt% PVC, and 65.6 wt% *o*-NPOE) in 1.6 mL of tetrahydrofuran (THF). The K⁺ SC-ISEs were fabricated according to the literature [24] with some modifications using the 3D MoS₂ nanoflowers as the ion-to-electron transducer. Typically, the glassy carbon (GC) electrodes (i.d. 3 mm) were polished with alumina (0.3 and 0.05 μm) and then rinsed in water and ethanol. 2 mg of 3D MoS₂ nanoflowers was ultrasonicated in 1 mL of freshly distilled THF for 30 min to form a uniform dispersion. 20 μL of the 3D MoS₂ dispersion was drop-cast onto the GC electrodes and left to dry, forming a solid contact layer with a thickness of approximately 5 μm. Finally, 100 μL of membrane cocktail was drop-cast on the top of the 3D MoS₂ layer and left to dry overnight to generate an ISM with a thickness of approximately 100 μm. All the ISEs were conditioned in 10⁻³ M KCl for 24 h before use.

2.4. EMF measurements

Electrochemical measurements were performed at 20 ± 2 °C using a CHI 760D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China). Potentiometric detection was conducted in the galvanic cell: Ag/AgCl(3 M KCl)/0.1 M LiOAc/sample solution/ISM/MoS₂ layer/GC electrode. Electrochemical impedance spectroscopy (EIS) and chronopotentiometry measurements were carried out with Ag/AgCl (3 M KCl) and platinum wire as the reference and auxiliary electrodes, respectively. Activity coefficients were calculated according to a two-parameter Debye-Hückel approximation and electromotive force values were corrected for liquid-junction potentials with the Henderson equation.

3. Results and discussion

3.1. Characterization of the synthesized MoO₃ and MoS₂

The morphology of the sample was observed with a field-emission scanning electron microscope (FESEM) on a Hitachi S-4800 instrument at an accelerating voltage of 5 kV. In addition, the elemental composition of the as-synthesized material was confirmed by the energy dispersive spectroscopy (EDS). The corresponding results are shown in Fig. 1. A panoramic picture of the as-prepared intermediate product of MoO₃ is illustrated in Fig. 1a. It can be seen that the obtained MoO₃ materials are composed by nanobelts with high dispersity from each other. Fig. 1b demonstrates the overall view of the synthesized MoS₂ nanomaterials with a uniform morphology. A high resolution image (Fig. 1c) indicates that the synthesized MoS₂ has a flowerlike morphology in three dimensions. The EDS data confirm the as-synthesized materials are composed by Mo and S with a molar ratio of 1:2, as shown in Fig. 1d.

3.2. Performance of the 3D flowerlike MoS₂-based K⁺-SC-ISE

The potential response of the 3D flowerlike MoS₂-based SC-ISE was tested in KCl solutions at concentrations ranging from 10⁻² to 10⁻⁷ M. The dynamic potentiometric response trace and the corresponding calibration curve are shown in Fig. 2a and b, respectively. As can be seen, a fast response time as well as a high stability of the proposed K⁺-SC-ISE can be obtained for higher concentrations of 10⁻²–10⁻⁵ M, while a small potential drift could occur for lower concentrations of 10⁻⁶–10⁻⁷ M. It is also shown that a Nernstian response with a slope of 55.8 mV/decade in the activity range of 10⁻²–10⁻⁵ M can be obtained with a detection limit of 10^{-5.5} M.

3.3. Characterization of the fabricated K⁺-SC-ISE

The EIS and chronopotentiometry experiments were done to characterize the fabricated SC-ISE. The EIS measurements were performed with a frequency range of 10⁵–0.01 Hz. The semicircle at the high-frequency region represents the bulk resistance of the ISM together with the contact resistance between the ISM and the underlying conductor in parallel with the combined geometric capacitance. As shown in Fig. 3a, the MoS₂-based K⁺-ISE has a smaller impedance compared to that of the CWE, which is probably due to the facilitated charge transport across the interface induced by the 3D flowerlike MoS₂ layer. Additionally, in the low-frequency region, a smaller semicircle is observed for MoS₂-based K⁺-ISE, indicating a higher capacitance and lower charge-transfer resistance at the buried interface. By recording potentials of the ISE under currents of ± 1 nA in 1 mM KCl solution, a potential drift up to 0.78 mV/s was found for the CWE, while a much smaller drift of 10.0 ± 2.7 μV/s (n = 3) could be obtained for the MoS₂-based K⁺-ISEs (Fig. 3b). The high potential stability of the proposed ISE may

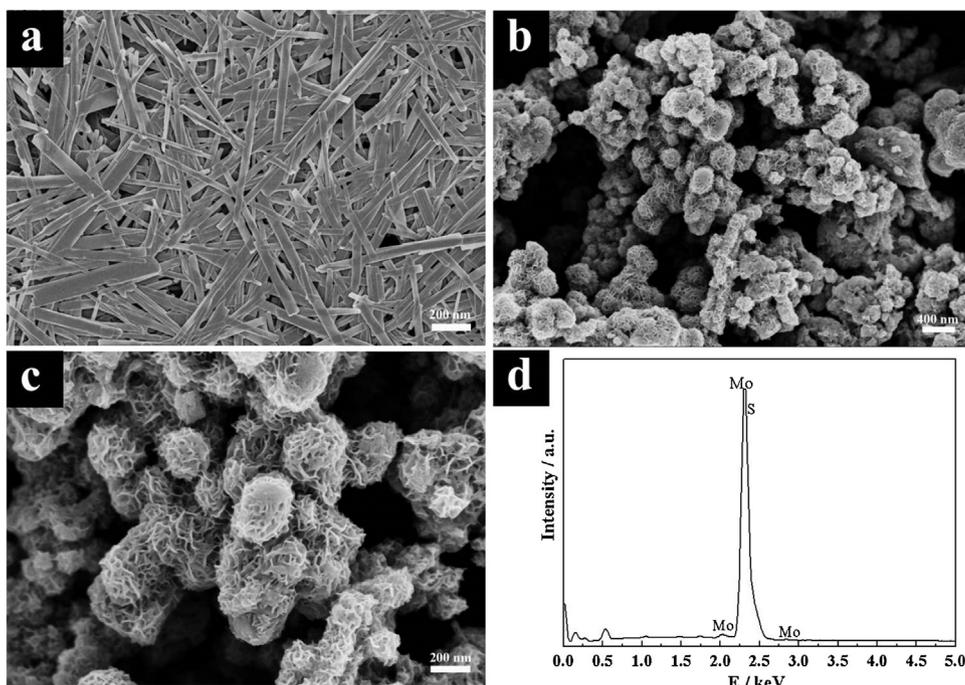


Fig. 1. FESEM images of the obtained MoO₃ (a) and MoS₂ (b–c) nanomaterials; EDS spectrum of the MoS₂ nanomaterials (d).

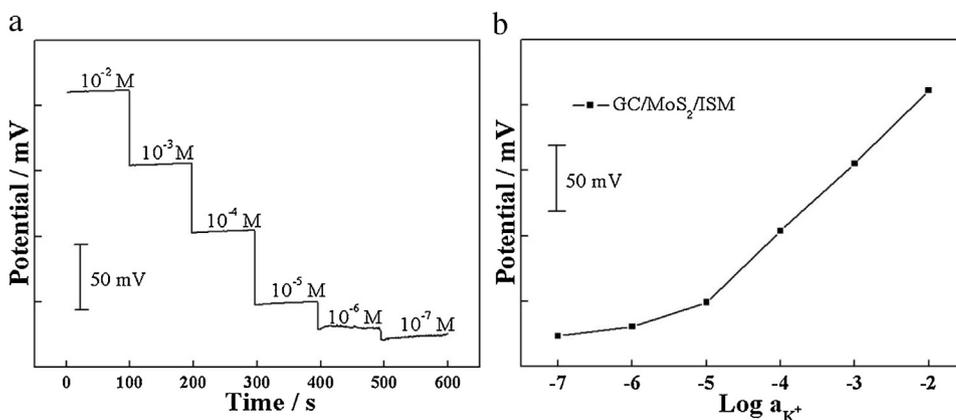


Fig. 2. (a) Time-dependent potential response trace and (b) calibration curve of the 3D flowerlike MoS₂-based K⁺-ISE.

be attributed to the high double layer capacitance of the 3D flowerlike MoS₂. The capacitance was calculated to be 100 μ F, which is comparable to those of other SC-ISEs with transduce layers such as graphene and carbon nanotubes [9,11]. The water layer test was done by immersing the electrode in 0.1 M KCl, 0.1 M NaCl and 0.1 M KCl sequentially. As shown in Fig. 3c, when the NaCl solution is used to replace the KCl solution at $t = 1.5$ h, a positive potential drift of 36 mV is obtained for the GC/ISM electrode while no significant potential drift is found for the GC/MoS₂/ISM electrode. In addition, when the electrode is immersed back in 0.1 M KCl solution, there is no significant potential drop for the MoS₂ based K⁺-ISE, but an apparent negative potential drift is observed for the CWE. These results indicate that a reduced water layer forms at the interface between the ISM and MoS₂. To investigate the effects of O₂ and CO₂, measurement were done by bubbling both gases into 10⁻³ M KCl solution for 30 min, respectively, which was followed by purging with N₂ for another 30 min. For the light sensitivity test, the potentials were recorded while immersing the fabricated SC-ISEs into 10⁻³ M KCl in the presence and absence of the ambient light. As shown in Fig. 3d, no significant potential drift is observed when

the sensor is exposed to light, O₂ and CO₂, indicating the good robustness of the MoS₂-based K⁺-ISE.

4. Conclusions

The 3D MoS₂ nanoflowers can be prepared by a novel hydrothermal method and applied as the ion-to-electron transducer for SC-ISEs. It has been found that the as-synthesized MoS₂ has a uniform 3D flowerlike morphology. The fabricated K⁺-SC-ISE based on the 3D MoS₂ nanoflowers shows good Nernstian response, small impedance, high stability, and has excellent resistances to interferences from O₂, CO₂ and light and to water layer formation.

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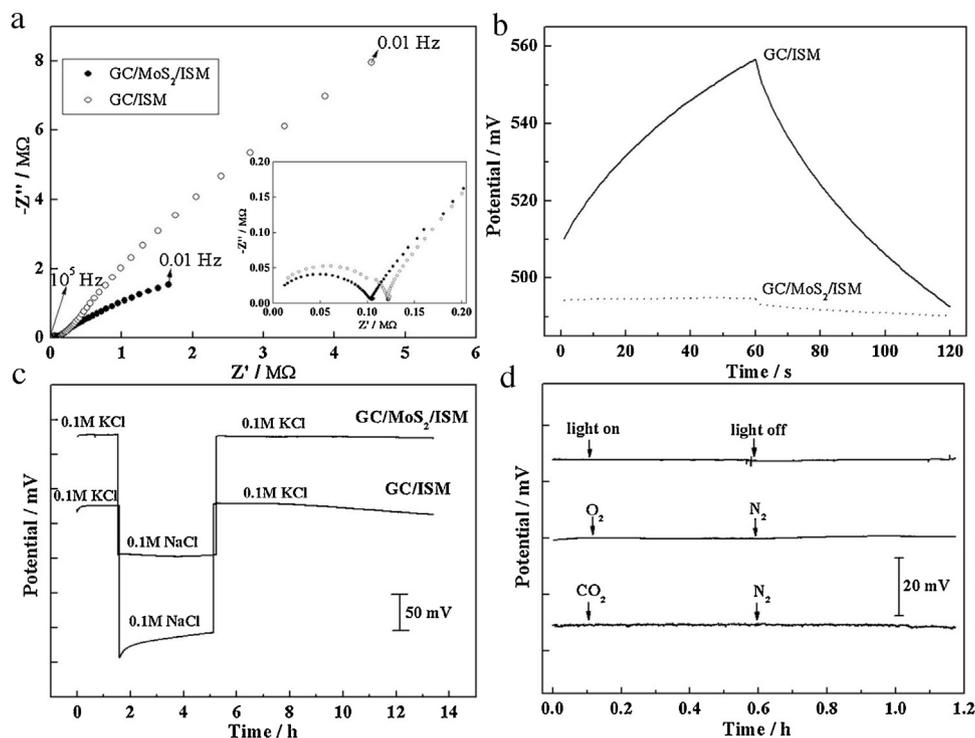


Fig. 3. Impedance plots (a), chronopotentiograms (b), and water-layer tests (c) for the K^+ -ISE with and without MoS_2 as the solid contact; effects of light, O_2 , and CO_2 for the MoS_2 based K^+ -SC-ISE (d).

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