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Electrochemical properties of a 2D-molybdenum disulfide–modified electrode and its application in SO_2 detection

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ABSTRACT

Sulfur dioxide (SO_2) emissions must be efficiently controlled owing to environmental demands. An interesting approach for SO_2 concentration is the use of ionic liquids (ILs) and subsequent detection by electrochemical methods. In this study, two kinds of IL ([EMIM][TfO] and [EMIM][BF_4]) have been shown to absorb and desorb SO_2, and the electrochemical behavior has been investigated by using nanoscale molybdenum disulfide (nano-MoS_2)–modified electrodes. The corresponding absorption results showed that the MoS_2-modified electrode is a good sensor for SO_2 and that the ILs have a high SO_2 absorption capacity. According to the SO_2 desorption results, it was shown that desorption can be completed at approximately 140 °C under vacuum. Based on the high response signal of this modified electrode to SO_2, it was utilized to detect the SO_2 in haze. The results suggested that [EMIM][TfO] is able to absorb SO_2 from haze with a higher selectivity and capacity than [EMIM][BF_4]. Meanwhile, the MoS_2-modified electrode was used to detect the concentration of SO_2 in the air, which was consistent with the official results.

1. Introduction

Air pollution has drawn worldwide attention due to its seriousness. Sulfur dioxide (SO_2) is a significant atmospheric pollutant that is mainly emitted from burning fossil fuels, such as coal and oil [1–3]. Owing to the formation of smog and acid rain in the process of SO_2 emission, it threatens both the environment and human health [4,5]. Although traditional methods such as flue-gas desulfurization (FGD) and limestone scrubbing can effectively control SO_2 emissions, they also have limitations including their byproducts and the volatilization of solvents [5]. Research has found that carbon nanotubes [6], TiO_2 nanotubes [7], and graphene-based sensors [8] show good response to SO_2. Electrochemical sensors also have been used to detect various air pollutants (e.g., formaldehyde, ammonia, SO_2) in recent years [9–11]. Analysis by this method requires that the target is in an aqueous solution, but some air pollutants are water insoluble. Therefore, it is important to find a material for the reversible and selective absorption of air pollutants from the flue gas.

Recently, ionic liquids (ILs) have been widely applied in the field of electrochemical sensors [12–14]. They can potentially be used to preferentially absorb hazardous gasses (such as SO_2 and CO_2) because they are considered as environmentally benign solvents for a variety of chemical processes [1,3,15]. ILs are a promising replacement for traditional organic solvents due to their unique properties, including their high ionic conductivities, negligible vapor pressures, wide electrochemical windows, ion-exchange properties, extraction and catalytic activities, good thermal and chemical stabilities, and ability to tune their properties by substituting their functional groups [15–17]. Accordingly, ILs have various applications in the field of applied electrochemistry, such as in fuel cells, photoelectron-chemical cells, and electrocatalysis [17].

Molybdenum disulfide (MoS_2) possesses a layered structure and has a high surface activity and large specific surface area [18,19]. It can promote the selectivity and sensitivity of electroanalysis methods [20]. In this work, a modified glassy carbon electrode coated with nano-MoS_2 was prepared and used to investigate the properties of two ILs ([EMIM][TfO] and [EMIM][BF_4]) in the absorption and desorption of SO_2 gas. The sensitivity of MoS_2/Nafion/glassy carbon electrode (MoS_2/NF/GCE) is higher than that of NF/GCE and GCE. The haze absorption experiments were also investigated. It was shown that [EMIM][TfO] can absorb SO_2 from haze with a higher selectivity and capacity than [EMIM][BF_4]. A possible explanation is related to the molar volumes of the ILs, as those with larger molar volumes would have a greater ability to dissolve SO_2. According to the absorption and enrichment abilities of

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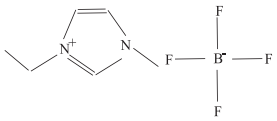
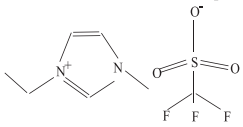
Table 1
Ionic liquids used in the current study.

Ionic liquid	Structure	Short name
1-Ethyl-3-methylimidazolium tetrafluoroborate		[EMIM][BF_4]
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate		[EMIM][TfO]

ILs, and the good response of the MoS_2-modified electrode to SO_2, the concentrations of SO_2 in fog and haze are also obtained. The results are in good accordance with the official test data, suggesting that this is a good method for quantifying the air quality.

2. Experimental

2.1. Materials and instruments

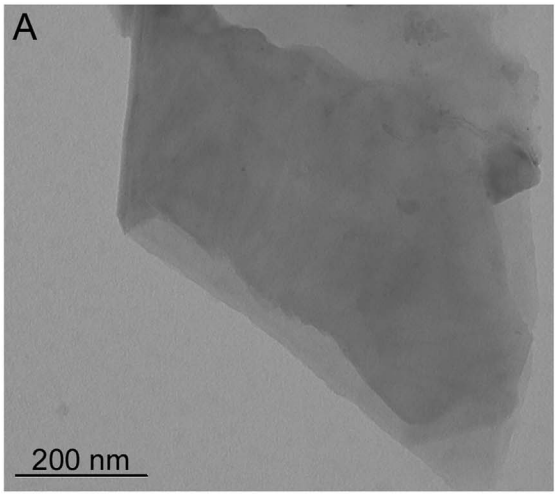
Sulfur powder (precipitated, purity ≥99.5%) and α-aluminum oxide polishing powder (purity ≥99.0%) were purchased from Alfa Aesar. Molybdenum disulfide (MoS_2) and *N*-methyl-2-pyrrolidone (NMP) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Potassium ferricyanide (purity ≥99.5%) was purchased from Sigma-Aldrich. 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4], purity ≥99%) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][TfO], purity ≥99%) were supplied by the Center of Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (see Table 1 for the structures). The Nafion solution (5 wt% alcohol solution) was supplied by Fluka Chemica. Deionized water was purified by a Milli-Q reagent water treatment system (Millipore, Milford, MA). All the chemical reagents used in the experiments were of analytical grade and were used without any further purification.

Cyclic voltammetry (CV) was performed with a CHI-660D electrochemical workstation (CH Instruments, Shanghai, China). The electrochemical measurements were carried out with a three-electrode system including a bare or modified glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. The weight experiments used an EL-204 electronic balance (Mettler Toledo). The absorption experiments were carried out in a DZF-6050 vacuum oven (Shanghai, China). The air was collected by a GH-5C02 collector (Wuhan, China).

2.2. Preparation of the MoS_2-NMP dispersion and modified electrodes

The MoS_2-NMP dispersion was obtained by lithium intercalation according to a literature method [21], and was used without further modification. The morphological information of the MoS_2 was obtained by using transmission electron microscopy (TEM). This experiment was carried out on a JEM-1011 instrument operated at an accelerating voltage of 100 kV. Sample for TEM characterization were prepared by placing a drop of ethanol containing nanomaterial onto a carbon-coated copper grid and dried in air before characterization. The typical TEM image of MoS_2 was shown in Fig. 1A.

The glassy carbon electrode was pretreated by first polishing with alumina powder. Then, it was rinsed with deionized water, ultrasonically cleaned with ethanol and deionized water to remove any remaining alumina, and rinsed again with abundant deionized water.



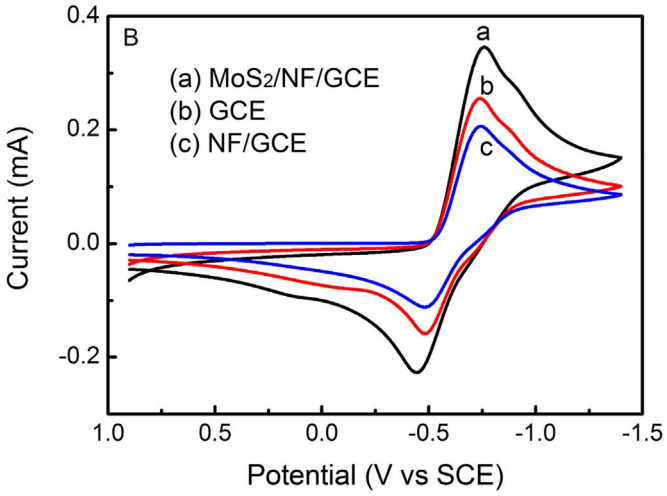


Fig. 1. (A) TEM micrographs of MoS_2. (B) Cyclic voltammograms of [EMIM][TfO] with 0.47% absorbed SO_2 obtained on (a) MoS_2/NF/GCE, (b) GCE, and (c) NF/GCE.

Next, the electrode was pretreated by cycling the potential from 0.6 V to −0.2 V *vs*. SCE in a 10 mM potassium ferricyanide-potassium ferrocyanide solution, until reproducible voltammograms were obtained. Afterwards, the electrode was rinsed with deionized water and left to dry at room temperature.

The modified electrodes were obtained by a drop coating method, and the detailed processes are as follows. For the MoS_2-free electrode, 3.0 μL of 0.2% w/w Nafion (NF) solution diluted in ethanol was placed on the surface of the pretreated GCE and allowed to dry at room temperature. This was named NF/GCE. For the MoS_2-modified electrode, 3.0 μL of the MoS_2-NMP solution was coated onto the GCE surface and allowed to dry at room temperature. Then, the Nafion-ethanol solution (3.0 μL, 0.2% w/w) was placed on the above modified electrode and left to dry at room temperature. This electrode was named MoS_2/NF/GCE.

2.3. SO_2 absorption and desorption procedures

The absorption experiments were carried out by igniting sulfur powder in a sealed container at ambient pressure and room temperature. A small bottle containing an IL was put into the sealed container on an electronic balance with an accuracy of 0.1 mg. The amount of absorbed SO_2 was calculated by the weight difference of the IL-containing bottle before and after ignition. The absorption ratio of SO_2 to IL was calculated from the quantity of absorbed SO_2/quantity of IL. Cyclic