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Fabrication of an Electrochemical Sensor for NO_x Based on Ionic Liquids and MoS_2

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To improve the efficiency of the detection of NO_x, we propose a method using room temperature ionic liquids (RTILs) and nanomaterials. [Emim][BF_4] and [Bmim][BF_4] can absorb NO_x under normal atmospheric pressure, and the absorption rate can reach 14.07% and 10.04%, respectively. The electrochemical response of NO_x was studied in ILs by cyclic voltammetry using MoS_2-modified electrodes. MoS_2 can increase the effect of current density towords the reduction of NO_x because of its large surface area. By comparing the two ILs, we found that [Emim][BF_4] can absorb more NO_x than [Bmim][BF_4]. The electrochemical behavior of NO_x in [Emim][BF_4] shows relatively higher sensitivity and lower detection limits at the MoS_2-modified electrode.

Keywords: electrochemical sensor; NO_x; Ionic liquids; MoS_2; Nanomaterial

1. INTRODUCTION

In recent years, haze pollution has become increasingly serious in China. The main composition of haze includes nitrogen oxides (NO_x: NO, NO_2), and sulfur dioxide (SO_2). NO_x gas has a strong stimulating effect on the respiratory system and causes serious damage to the lungs, even leading to pulmonary edema and lung cancer. Therefore, it is necessary to monitor the concentration of NO_x in the environment and to control the exhaust gas from automobiles and factories. The separation and concentration of NO_x is required in order to achieve its recovery and to reuse and detect it in some processes. Ionic liquids are reagents that have the functions stated above. Room temperature ionic liquids (RTILs) have a near zero vapor pressure, high thermal and chemical stability, and can be tailored to their properties by changing the substituents. Therefore, ionic liquids can be used as environmental benign solvents for many applications. One of its most useful features is their ability to absorb and seperate certain gases, such as CO_2 [1], SO_2 [2,3] and NO_2 [6].The sensing and determination of nitrogen oxides in air is very important, as the gas is emitted from cars, boilers, and other combustion facilities. Several methods have been used to detect NO_x, including those based on electrochemistry [4,5]. Despite the interest in NO_x detection, there has been relatively little reported on NO_x gas dissolution in ionic liquids. Broder et al. [6] reported the electrooxidation of nitrite ions (from KNO_2) and the oxidation and reduction properties of NO_2 gas dissolved in the RTIL [Emim][NTf_2]. They explored and analyzed the reaction mechanisms and kinetics in this medium. They believe that NO_2 exists predominantly as a dimer, N_2O_4, at room temperature. The oxidation mechanism follows a CE(mono)process, which involves the initial dissociation of the dimer to the monomer, followed by a one-electron oxidation.

Recently, 2D nanomaterials have attracted increasing attention, especially MoS_2. MoS_2 is a graphene analogue constructed by stacking covalently bound S-Mo-S through weak van der Waals interactions [7], and it is a type of transition metal sulfide [8,9]. Many studies confirm that the HER activity of MoS_2 correlates with the number of catalytically active edge sites [10]. Molybdenum disulfide has its unique properties such as large surface area, significant electron mobility and high density of electronic states, so it exhibits superior biosensing properties in detecting nucleic acids [11,12] and biomolecules [13-18].

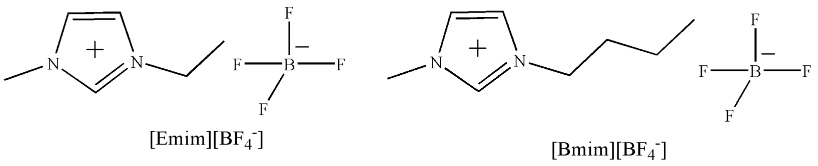

Figure 1. Structures of the two ionic liquids used in this study.

In this work, we demonstrated an electrochemical sensor based on MoS_2 for the detection of NO_x absorbed in two RTILs. The sensor shows better selectivity and good sensitivity for NO_2 due to the excellent absorption properties of ILs.

2. EXPERIMENTAL

2.1. Reagents

Ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) were purchased from the Center in Green Chemistry and Catalysis. Molybdenum disulfide (MoS_2) dispersions in NMP (N-methyl-2-

pyrrolidone) were purchased from Jining LeaderNano Tech L.L.C., with a maximum concentration of 40 mg/L. Nafion (5% in alcohol) was obtained from Sigma-Aldrich. All reagents and solvents were A. R. grade. All aqueous solutions were made with deionized water.

2.2. Instrumentation

Electrochemical measurements were performed with a CHI 660D electrochemical workstation (Chenhua Instruments Co., Shanghai, China). We used an electronic balance (EL 204, Mettler Toledo Instruments Co. Ltd., Shanghai) for weighing. Three-electrode system with a platinum wire counter and a saturated calomel reference electrode was employed in this study. All potentials were referred to the latter. The working electrode was the following modified GC electrode. The three electrodes were inserted into a 10 mL beaker through holes in the Teflon cover.

2.3. Procedures

2.3.1. Preparation of Nafion/MoS_2/GC

Carefully polish glassy carbon (GC, 3 mm diameter, CHI 104) electrode with 1.0, 0.3, and 0.05 mm alumina slurries and rinse thoroughly with deionized water between each polishing step. The electrode was then washed with ultrasonics in ethanol and deionized water and dried in air.Subsequently, 3 μL of the MoS_2 dispersion (in N-methyl-2-pyrrolidone) was cast onto the surface of the pretreated GC electrode with a microsyringe, and the solvent was allowed to dry at ambient temperature. Finally, 3 μL of the Nafion (0.1% in alcohol) solution was cast onto the MoS_2-modified GC electrode and dried to obtain the Nafion/MoS_2/GC electrode.

2.3.2. Preparation of Nafion/GC

3 μL of the Nafion (0.1% in alcohol) solution was cast onto the carefully polished and washed bare GC electrode. The modified electrode was dried before use.

2.3.3. Absorption of NO_x

Nitrogen oxides was prepared by chemical methods through a reaction of copper and concentrated nitric acid. The absorption experiment was carried out in several containers. There were three vials in each container containing one small beaker with some copper and two weighing bottles with the two ionic liquids both about 3.6 g . Then, excess nitric was added dropwise to the copper in the small beaker and soon after produced red brown gas, which is NO_x. After that, the container was quickly sealed and placed in a fume hood. The ionic liquids simultaneously absorbed NO_x. After a certain time, the two small weighing bottles in the same container were taken out and weighed. By recording the mass difference before and after absorption, we can determine the absorption mass of

NO_x in the ILs. The absorption rate can be determined by dividing the mass of NO_x by the mass of the ILs.

2.3.4. Detection methods

Electrochemical detection was carried out with a three-electrode system using a weighing bottle as an electrolytic cell. All the experimental procedures are carried out under normal atmospheric pressure at 25℃。

3. RESULTS AND DISCUSSION

3.1. Characterization of MoS_2

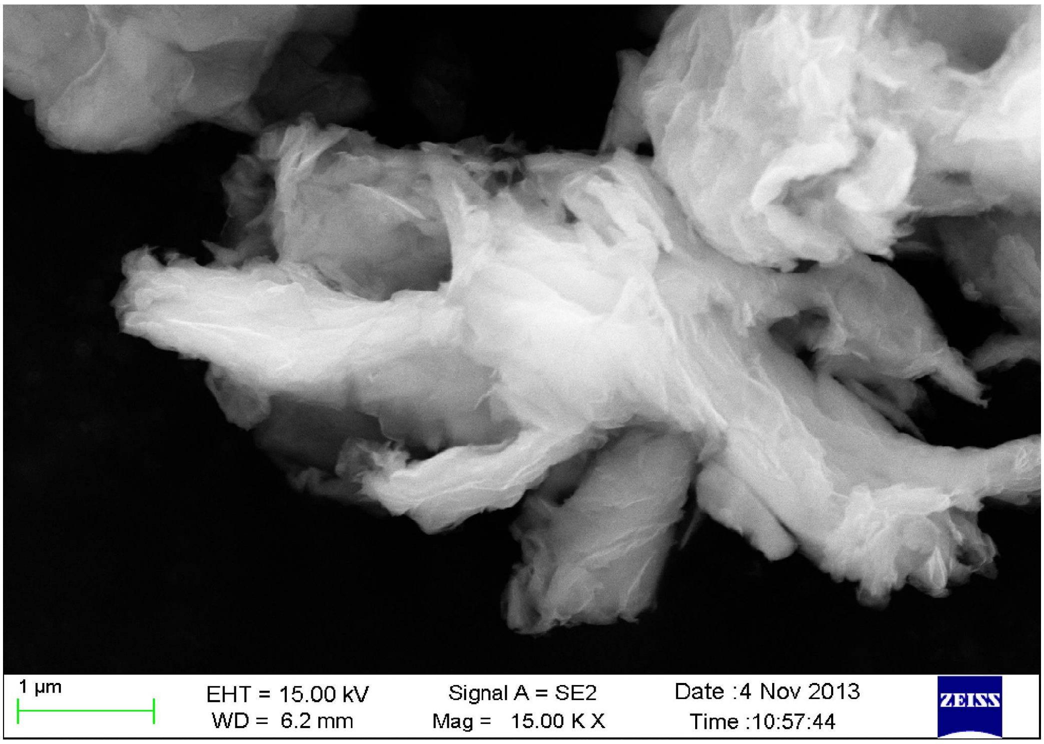

Figure 2. SEM image of MoS_2 nanomaterial.

The morphology of the as-obtained samples was examined by SEM. MoS_2 (Fig. 2) displays a typical layered nanosheet structure. We can clearly see the MoS_2 sheet is multilayer. This structure increases the contact area of the analytes. The overlapping or coalescing of the MoS2 can form an interconnected conducting network, and provided a feasible pathway for electron transfer. These properties would permit the construction of an electrocatalytic platform for biosensing [11].

3.2. Characterization of Nafion-MoS$_2$-GC

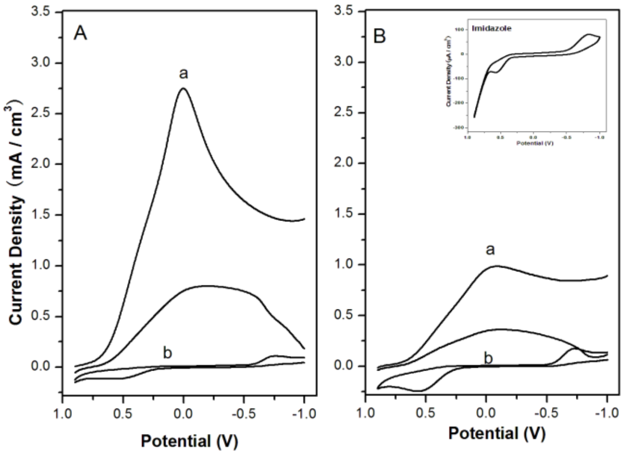

Figure 3. Cyclic voltammetric (CV) responses in [Emim][BF$_4$] (A) absorbed 1.79% NO$_x$ (a) and pure [Emim][BF$_4$] (b); [Bmim][BF$_4$] (B) absorbed 1.67% NO$_x$ (a) and pure [Bmim][BF$_4$] (b) detected at Nafion/MoS$_2$/GC electrode. Inset: the CV curve of pure imidazole. Scan rate: 50 mV/s.

Fig. 3 depicts the cyclic voltammetric (CV) responses of NO$_x$ at the Nafion/MoS$_2$/GC electrode in the two ionic liquids ([Emim][BF$_4$] is A and [Bmim][BF$_4$] is B). We compared the CV curves of the pure ILs (b) and NO$_x$-absorbed ILs (a). No obvious peak can be observed in either of the pure ILs, except for a pair of very small peaks at 0.5 V and -0.75 V, which were caused by imidazole. The CV curve of imidazole can be seen in the inset of FigB. However, there is an cathodic peak at 0.01 V in [Emim][BF$_4$] and -0.06 V in [Bmim][BF$_4$], and the peak current density is 2.507and 0.986 mA/cm^3, respectively. The completely irreversible cathodic peak observed in Fig. 3a certainly originate from the reduction of NO$_x$ at the Nafion/MoS$_2$/GC electrode.

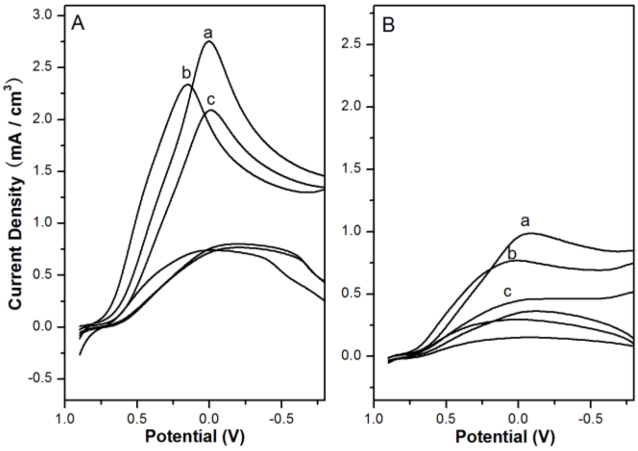

Figure 4. NO$_x$ detected at Nafion/MoS$_2$/GCE (a) compared with GCE (b) and Nafion/GCE (c). A was 1.79% NO$_x$ in [Emim][BF$_4$] and B was 1.67% NO$_x$ in [Bmim][BF$_4$]. Scan rate: 50 mV/s.

Although the absorption rate of NO_x in [Emim][BF_4] is only 0.12% higher than that in [Bmim][BF_4], the peak current density is 1.5 mA/cm^3 higher. From the cyclic voltammetry analysis, it can be seen that [Emim][BF_4] is more sensitive to NO_x than [Bmim][BF_4].

We also investigated the electrochemical behavior of NO_x on GC, Nafion/GC, and Nafion/MoS_2/GC electrodes in ionic liquids. To assess whether the preparation conditions (and not the MoS_2 or Nafion modifier itself) are responsible for the catalytic behavior, control experiments were conducted. For this purpose, the GC surface was coated with Nafion, which resulted in the lowest cathodic peak of NO_x at the Nafion/GC electrode (Fig. 4c). Therefore, the one well defined cathodic peak observed in the presence of MoS_2 (Fig. 4a) clearly indicates the essential role of MoS_2 may due to high surface activity and large specific surface area of MoS_2. The behaviors of these three electrodes are the same for the two ionic liquids. The higher response of NO_x to molybdenum disulfide is consistent with the results of SO_2 detection in our previously published article[19]. H song et. Have studied the electrochemical impedance spectroscopy of MoS2. they found molybdenum disulfide modified electrodes can reduce the electron transfer resisitance [13].

Comparing the two ionic liquids, we found that the peak current density of NO_x in [Emim][BF_4] was significantly larger than that in [Bmim][BF_4], and this behavior was the same for all three electrodes. Therefore, NO_x absorbed in [Emim][BF_4] shows better electrochemical property than in [Bmim][BF_4].

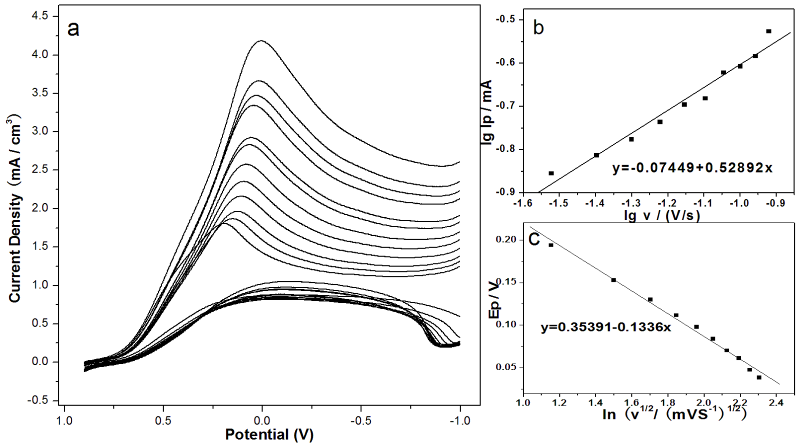

Figure 5. (a): Cyclic voltammetric (CV) responses of 1.70% NO_x in [Emim][BF_4] detected at Nafion/MoS_2/GC electrode at different scan rate(10-120 mV); (b): Experimental variations of the logarithmic of the peak current vs. the logarithmic of the scan rate; (c): Experimental variations of peak potential vs. the natural logarithmic of the scan rate.

3.3. Kinetic characteristics of the Nafion/MoS_2/GC electrode

Fig. 5 shows cyclic voltammetric (CV) responses of 1.70% NO_x detected at the Nafion/MoS_2/GC electrode at different scan rates in [Emim][BF_4]. As seen in Fig. 5a, the curves gradually increased with an increase in scan rate in [Emim][BF_4], while there was no distinct increase in [Bmim][BF_4] (the figure is not shown). We determined the logarithm of the peak currents (lg I_p) as a function of the logarithm of the potential scan rate (lg v) and the magnitudes of the peak potentials (E_p) as a function of the natural logarithm of the potential scan rate. From Fig. 5, we find that lg I_p increases linearly with increasing lg v, and the slope is 0.5. This indicates that the electrode process is a diffusion-controlled process.

For an irreversible diffusion-controlled reaction, the relationship between peak potential and the scan rate follows the Nicholson equation [20]:

$$E_p = E^0 - \frac{RT}{\alpha nF}\left[0.78 + \ln\left(\frac{D_0^{1/2}}{k^0}\right) + \ln\left(\frac{\alpha nFv}{RT}\right)^{1/2}\right] \qquad (1)$$

where F is the Faraday constant, n the number of electrons transferred, α is the electron-transfer coefficient, k^0 the standard rate constant of the electrode reaction, E^0 is the formal potential, D_0 is the coefficient of diffusion, and v is the scan rate. We can see from the equation and from Fig. 5b that the plots of E_p vs. ln $v^{1/2}$ are linear, αn was estimated to be 0.195 from the slope, and k^0 was estimated to be 0.9044 $cm\cdot s^{-1}$ from the intercept at 25°C. This indicates that the reaction rate of NO_x at the MoS_2-modified electrode is relatively slow. Some literature has reported that SO_2 is purely physically absorbed in ILs. Riisager et al studied some kinds of normal ILs and it showed a physical absorption of the gas without any new chemical bond between the ILs cations and SO_2 [21]. We believe that the absorption of NO_x in ILs should be similar to that of SO_2, which is physical absorption. This should be the reason why the reaction rate between MoS_2 modified electrode and NO_x is slow.

3.4. Interference detection of Nafion/MoS_2/GC electrode

We studied the interference of several kinds of gases such as SO_2, NH_3, H_2S and CO_2. In addition to other gases other than SO_2 have no effect on the detection of NO_x. When NO_x was absorbed in the presence of SO_2, the absorption concentration was unaffected. The cyclic voltammetric (CV) responses of the two gases absorbed in [Emim][BF_4] has been studied with two peaks in the curve (it can be seen in Fig.6). The peak of NO_x was at 0.05V, while a small peak at 0.7V was caused by SO_2 according to reports in the literature of detection of sulfur dioxide[19]. The two peaks were far enough, so SO_2 has no effect on the detection of NO_x.

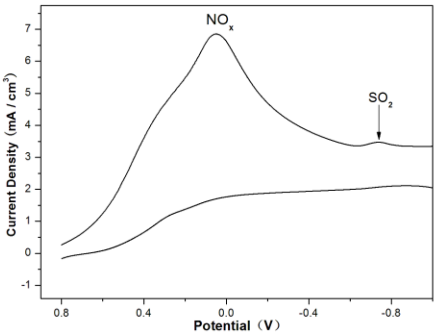

Figure 6. Cyclic voltammetric (CV) responses of NO_x and SO_2 absorbed in [Emim][BF_4] at Nafion/MoS_2/GC electrode. Scan rate: 50 mV/s.

3.5. Electrochemical detection of NO_x absorbed in ILs

A constant amount of copper (1 g) was reacted with excess concentrated nitric acid (4 mL) in the closed container to gradually extend the absorption time of NO_x in the two ionic liquids (both were 3.6 g). After that, we obtained the following data.

Table 1. Relationship between absorption time and absorption rate of NO_x in ILs.

Absorption time	Absorption rate (wt. %) (NO_x in [Emim][BF4])	Absorption rate (wt. %) (NO_x in [Bmim][BF4])
15 min	1.79	1.67
30 min	3.40	2.66
45 min	4.75	4.26
1.0 h	4.99	4.97
2.0 h	10.23	7.25
3.0 h	14.07	10.04

To test the potential electrochemical activities of the Nafion/MoS_2/GC electrode, cyclic voltammetric responses were recorded in the ILs with different concentrations of absorbed NO_x. Fig. 7 further demonstrates the excellent catalytic activity of Nafion/MoS_2/GCs towards the reduction of NO_x in different concentrations.

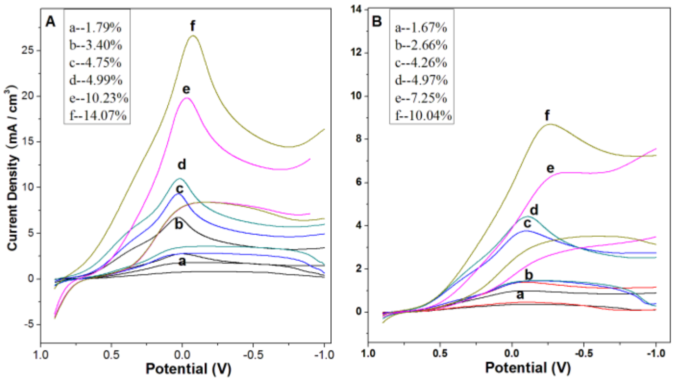

Figure 7. Cyclic voltammetric (CV) responses of different absorption rate of NO_x in [Emim][BF_4](A) and [Bmim][BF_4](B) detected at Nafion/MoS_2/GC electrode. Scan rate: 50 mV/s.

Fig. 7 A and B further demonstrates the excellent electrochemical behaviors of NO_x at the Nafion/MoS_2/GC electrode in the two ILs. It is easily found that the amperometric response increases gradually with increased absorption rate. The cathodic peak current densities increased in both ILs, exhibiting the excellent electrocatalytic activity of MoS_2 towards the reduction of NO_x. However, comparing the two ionic liquids, the peak current density of NO_x in [Emim][BF_4] was much higher than that in [Bmim][BF_4] at the same Nafion/MoS_2/GC electrode. From Fig. 8 we can see the linear relationship of the absorption rate of NO_x and the peak current densities. We found that the correlation coefficient of NO_x in [Emim][BF_4] was better than that in [Bmim][BF_4]. According to the linear equation, the sensitivity of NO_x was 1.906 mA/(cm^3•%) in [Emim][BF_4] and 0.951 mA/(cm^3•%) in [Bmim][BF_4]. At three times the signal-to-noise ratio, the detection limits of NO_x were estimated to be approximately 0.0255% and 0.0544% for in [Emim][BF_4] and [Bmim][BF_4], respectively.

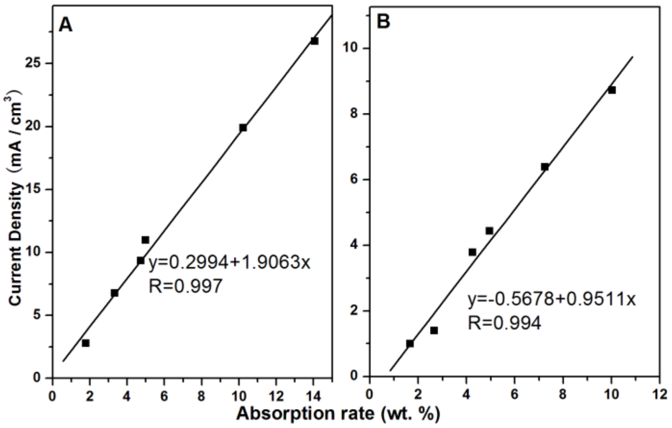

Figure 8. Calibration curves for NO_x in [Emim][BF_4](A) and [Bmim][BF_4](B) detected at Nafion/MoS_2/GC electrode.

Table 2. Comparison of the parameters of similar NO_x sensors.

Electrode	Test gas	Linear range	Sensitivity	Detection limit
Au/PVC electrode [4]	NO_2		400 nA/ppm	50 ppb
Carbon-fluorocarbon gas memeable electrode [5]	NO_2		-1.9 μA/ppm	
Graphene/AuNPs/GCE [22]	NO	36 nM to 20 μM		18 nM
Au@Qc/PEGDGE/Hb/GCE [23]	NO	0.9 to 16 μM		12 nM
Nafion/MoS_2/GC electrode (this work)	NO_x	0.105% to 14.07%	1.906mA/(cm^3 •%)	0.0314%

From these various comparisons, [Emim][BF_4] is much better than [Bmim][BF_4] for NO_x absorption with better electrochemical detection performance. The same anion imidazole-based ionic liquids has been studied in previous literature [1] and it reported that the longer the alkyl chain, the higher the solubility of the gas, but the difference is slightly. That is to say, the solubility of [Emim][BF_4] and [Bmim][BF_4] to NO_x is not very different. The absorption rate of NO_x in [Emim][BF_4] is higher than in [Bmim][BF_4] at the same absorption time, probably because the molar mass of [Emim] is smaller than [Bmim]. In the case of little difference in absorption rate, the electrochemical responses of NO_x in [Emim][BF_4] is better than in [Bmim][BF_4].

The proposed Nafion/MoS_2/GC electrode for NOx determination was compared with other kinds of electrochemical electrodes, and the results were illustrated in Table 2. Although our sensor is somewhat inferior in sensitivity and detection limit, detection can be accomplished by increasing the absorption time and the gas volume because of the enrichiment of the ILs. Our linear response can reach 14.07%, so we can detect high concentrations of NO_x gas. The common three-electrode system used in our sensor devices uses less material and is cheaper and easier to obtain than other gas sensors.

The repeatability and stability of the Nafion/MoS_2/GC electrode were tested. Eight experiments were carried out in the presence of 5.34% NO_x absorbed in [Emim][BF_4] use cyclic voltammetry. The results demonstrated the Nafion/MoS_2/GC had a great reproducibility with a relative standard deviation of 4.2%. The operational stability was studied in 10 hour, and repeated the test per hour. The current density response decreased by only about 16% within 10 h, which indicated the Nafion/MoS_2/GC electrode has a good operational stability and enough for continuous usage for hours.

3.6. Application

We simulated a NO_x-containing environment in the laboratory for actual testing. Adding a certain amount of NO_x in a closed container makes the ambient NO_x concentration about 27 ppm. 4.6 g of [Emim][BF_4] was added to the vessel to absorb NO_x, and after 2 hours electrochemical detection was performed using the MoS_2-modified electrode. According to the measured electrichemical response and linear relationship, the absorption rate can be calculated as 0.146%. In order to verify the accuracy of our test results, we performed a comparative test using spectrophotometry and use the “China National Environmental Protection Standard HJ-479-2009” method to detect the content of NO_x. The test result was 8.5% RSD compared with the electrochemical method. This indicates that the MoS_2-modified electrode has some potential for electrochemical detection of NO_x in practical applications.

4. CONCLUSIONS

The electrochemical detection of NO_x absorbed in [Emim][BF_4] and [Bmim][BF_4] was studied by cyclic voltammetry using MoS_2-modified electrodes. MoS_2 can increase the effect of current density towords the reduction of NO_x because of its large surface area. By comparing the two ILs, we found that [Emim][BF_4] has better ability to absorb NO_x than [Bmim][BF_4]. The electrochemical behavior of NO_x in [Emim][BF_4] shows relatively higher sensitivity and lower detection limits at the MoS_2-modified electrode. Our method can detect high concentrations of NO_x gas, so the detection can be accomplished by increasing the absorption time and the gas volume when the concetration of NO_x in the environment is low. Therefore the MoS_2-modified electrode has some potential for electrochemical detection of NO_x in practical applications.

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References

1. J. Huang, T. Rüther, *Aust. J. Chem*., 62 (2009) 298.
2. K. Y. Lee, Chang Soo Kim and Honggon Kim, *B. Korean Chem. Soc*., 31 (2010) 1937.
3. S. Ren, Y. Hou and W. Wu, *J. Phys. Chem*. B., 114 (2010) 2175.
4. Z. Hohercáková, F. Opekar, *Sens. Actustors* B., 97 (2004**)** 379.
5. Y. Mizutani, H. Matsuda and T. Ishiji, *Sens. Actuators* B., 108 (2005) 815.
6. T. L. Broder, R. G. Compton, *J. Phys. Chem*. B., 111 (2007) 7778.
7. H. Matte , A. Gomathi and A. K. Manna, *Angew. Chem. Int. Ed*., 49 (2010) 4059.
8. H. E. Jeong, S. H. Lee and P. Kim, *Nano Lett*., 6 (2006) 1508.
9. X. Li, Y. Li, *J. Phys. Chem*. B., 108 (2004) 13893.
10. J. Xie , H. Zhang and Sh. Li, *Adv. Mater*., 25 (2013) 5807.
11. K. Huang, Y. Liu and H. Wang, *Biosens. Bioelectron*., 55 (2014) 195.
12. X. Wang, F. Nan and J. Zhao, *Biosens. Bioelectron*., 64 (2015) 386.
13. H. Song, Y. Ni and S. Kokot, *Biosens. Bioelectron*., 56 (2014) 137.
14. K. Huang, L. Wang and J. Li, *Sens. Actuators* B., 178 (2013) 671.
15. Zh. Zheng, Q. Feng and J. Li, *Sens. Actuators* B., 221 (2015) 1162.
16. Q. Feng, K. Duan and X. Ye, *Sens. Actuators* B., 192 (2014) 1.
17. H. Wang, P. Chen and F. Wen, *Sens. Actuators* B., 220 (2015) 749.
18. X. Lin, Y. Ni and S. Kokot, *Sens. Actuators* B., 233 (2016) 100.
19. X Xu, Zh Du and Y Wang, *J. Electroanal. Chem*., 815 (2018) 220.
20. R. S. Nicholson, *Anal. Chem*., 37 (1956) 1351.
21. J Huang, A Riisager and P Wasserscheid, *Chem. Commun*., 38 (2006) 4027.
22. Y Wang, B Song and J Xu, *Microchim. Acta*., 182 (2015) 711.
23. F Li, M Nie and X He, *Microchim. Acta*., 181 (2014) 1541.