Trace Detection of Organic Amine with a PVDF Membrane Containing Mg(II) Based MOF

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Abstract: A composite membrane, containing Mg (II) based MOF and PVDF, was presented in this work. The resultant composite membrane exhibited good effect on trace detection of organic amine vapour, that a distinct colour variation (from yellow to black) was observed when the concentration of aniline and ethanediamine vapour was 10ppm and 5ppm, respectively. Besides that, fluorescence-quenching experiment further proved the good trace detection effect of composite membrane, and it was found that the peak intensity in curve decreased with the increase of organic amine vapor content.

Keywords: Organic amine; composite membrane; MOF; fluorescence-quenching

1. Introduction

Organic amines have enormous applications in the agrochemical, pharmaceutical, automotive chemical, cosmetics and food industries, etc [1]. These amines are also hazardous to the environment, and hence spillage of these materials should be sensed efficiently in order to prevent any probable harm. However, most of these amines are colorless, making their differentiation *via* visual inspection difficult [2, 3].

Traditional analytical methods were employed for determination of amines including titrimetry, ion selective electrodes, and UV-visible absorption spectrometry [4]. Such methods are typically employed for aqueous or liquid amine-containing samples but are not suitable for gas phase analysis or continuous monitoring applications. The electrochemical detection devices have also been developed based upon the interaction of the amine functionality, but a limitation of this type is that they usually require elevated operating temperatures [5-7].

Recently chemical sensors were employed for amine detection. The fluorescent sensing or probing has proved to be an expedient detection technique on account of the high signal output and detection simplicity. For instance, Zang reported several fluorescent nanofiber films of perylene bisimide derivatives as expedient sensors for detecting organic amines [8]. Xue proposed that fluorescence fibrous films of boron diketonate complexes can be used to detect organic amines [9]. Mohr studied the fluorescent dye-based membranes for probing lipophilic primary amines [10]. Except for the polymer fluorescent sensors, metal−organic frameworks (MOFs), as a new fluorescent sensor, have been widely studied. MOFs are a class of new crystalline porous materials, emerging as the most promising candidates for next-generation fluorescent sensors because of the advantages of tremendous structural flexibility, large pore volume, and pore size tenability [11-15]. These new types of functional materials could compete with the polymer chemical sensors but are immature for practical application because the majority of MOFs are powder. The workability of MOFs powder is rather poor than the polymer chemical sensors which are membranes. If we can make the MOF to be a membrane while keep its good performance, the practical application of MOF will be promoted.

The fabrication of MOFs into composite membranes is considered to be a significant step toward their practical application [16-19]. Herein we present a study of the chemical sensor on a Mg (II) based MOF (Mg-NDI), which possesses good effect to detect the organic amine. The composite membranes have further been easily and successfully fabricated using PVDF (it has excellent chemical and thermal stability) and crystalline particles of Mg-NDI. Remarkably, the composite membranes show considerable detection effect, reaching to 5ppm amine vapour.

2. Experimental

2.1. Preparation of Samples

2.1.1. The preparation of Mg-NDI

The sample Mg-NDI was solvothermally synthesized according to the previously reported procedure [20]. $Mg(NO_3)_2\ 6H_2O$ (24mg, 0.093mmol) and N,N-bis(5-isophthalic acid) naphthalenediimide (H_4BINDI, 21 mg, 0.035 mmol) were added to a mixture of DMF (4mL) and 3N HCl (0.2mL). The mixture was transfered to and sealed in a 25mL Parr Teflon-lined stainless steel autoclave and heated at 90 ℃ for 24h.

2.1.2. The preparation of composite membrane

The preparation process of composite membrane is described as follows: Firstly, PVDF (100 mg) was dissolved in DMF (2 mL). Secondly, Mg-NDI (10 mg) was added slowly to the DMF solution, followed by magnetic stirring at 60 ℃ for 6 h, becoming a viscous homogeneous suspension. Thirdly, the resultant suspension was poured onto a glass plate and dried under vacuum at 70 ℃ to remove the DMF. Finally, the obtained membrane was peeled off from the glass plate.

2.2. XRD

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5418 Å).

2.3. SEM

The morphologies of the powder and membranes were observed using a Hitachi SU8010 scanning electron microscope.

2.4. The Detection of Organic Amine

The color change of MOF-PVDF composite membranes under different organic amine vapor was recorded by camera. The equation for calculating the vapor concentration of organic amine was as follows:

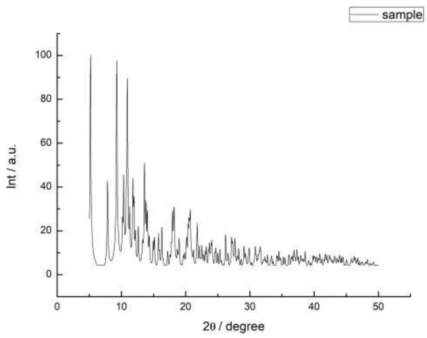
$$C = (P \times V) / V_0 \qquad (1)$$

Where C is vapour concentration (ppm); ρ is density of organic amines (g/cm^3); V is volume of organic amine liquid (μL); V_0 is volume of closed flask (L).

Horiba Jobin Yvon Fluorolog 3 spectrophotometer was used to study the fluorescence-quenching of MOF-PVDF composite membranes under different organic amine vapor.

3. Results and Discussion

PXRD profiles of Mg-NDI were illustrated in Fig. 1, together with simulated PXRD pattern of Mg-NDI. Both patterns show rather high similarity, indicating that we have successfully obtained the target sample of Mg-NDI. Thus, Mg-NDI has the same crystallographic texture with the standard sample, that is Mg-NDI crystallized in P2/c space group and the secondary building unit (SBU) contains two different hexacoordinated Mg(II) metal centers, two BINDI ligands, two coordinated DMF and one water molecule [20].



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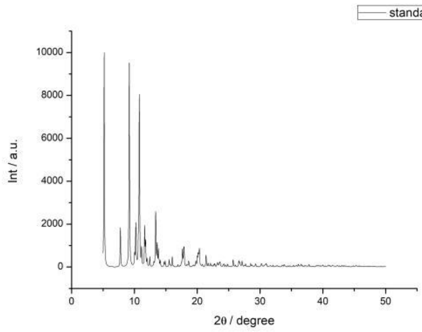
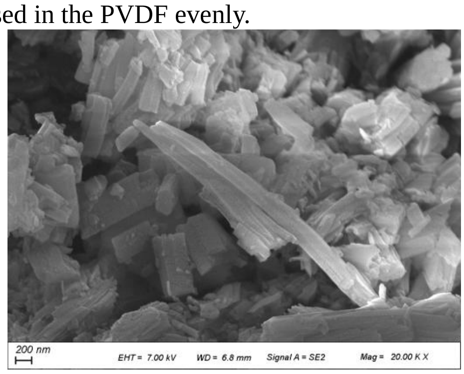


(b)

Figure 1. PXRD patterns of Mg-NDI(a), which correspond to the as-synthesized sample together with the simulated PXRD profile of Mg-NDI(b)

The composite membranes were fabricated using PVDF and particles of Mg-NDI. The SEM images of particles for Mg-NDI and its membranes were shown in Fig. 2, respectively. The pattern of Mg-NDI looks like schistose from Fig. 2a and 2b. The image of composite membranes and pure PVDF were shown in Fig. 2c and 2d, demonstrating that the particles of Mg-NDI have been dispersed in the PVDF evenly.



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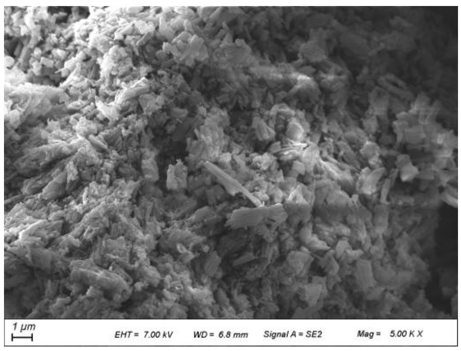

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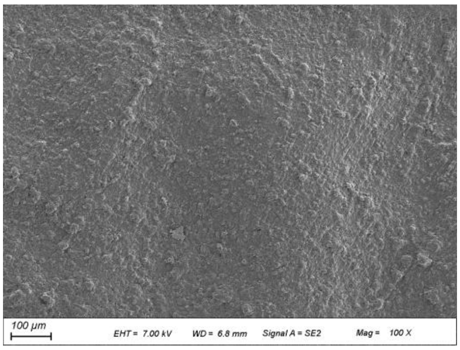

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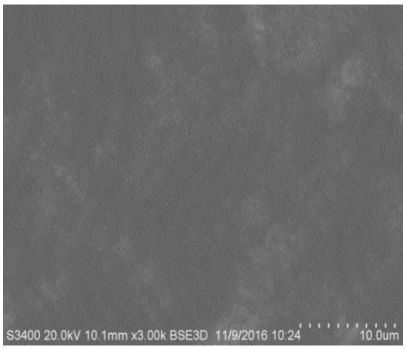


(d)

Figure 2. SEM images of Mg-NDI, (a and b) Prticles of Mg-NDI (c) membranes of Mg-NDI (d) membranes of pure PVDF

The variation of the colour of composite membrane in different amine vapour (vapor concentration of organic amine was 10ppm) was shown in Fig. 3. The colour of membranes changed obviously with time in ethanediamine and aniline vapour, respectively. Specially, the color changed from yellow to black. However, no distinct colour variation, from yellow to black, was observed in triethylamine vapour.

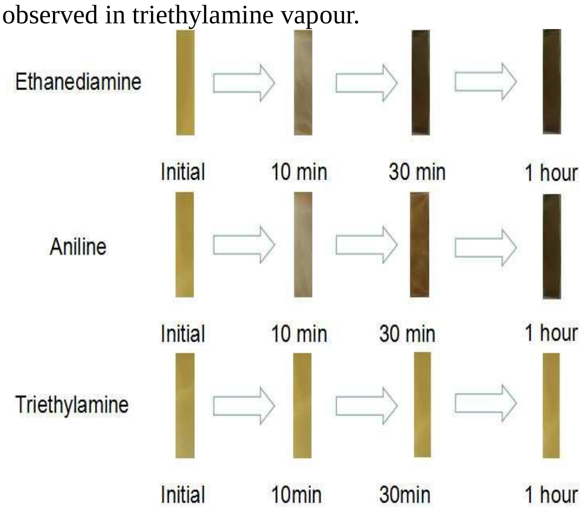
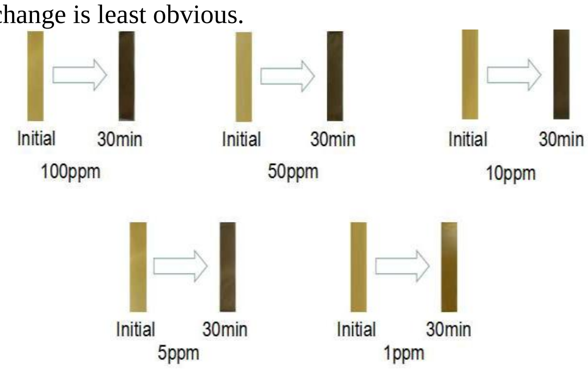


Figure 3. Variation of composite membrane's colour in different amine vapour with time

Besides that, to determine the trace detection of organic amine with the composite membrane, measurements of organic amine vapour in different concentration were carried out (shown in Fig. 4). Interestingly, the distinct colour change was observed even the concentration of ethanediamine vapour was 5ppm, indicating that this composite membrane has a good effect on trace detection of ethanediamine vapour. The same color conversion process (yellow to black) with ethanediamine was observed when the concentration of aniline vapour was 10ppm. But, the colour of the composite membrane still kept unchanged or just showed a little change in the atmosphere of triethylamine. MOF based sensors generally interact with the incoming analytes in three different ways: (i) analyte–luminescent metal ion interaction, (ii) analyte–luminescent organic linker interaction, and (iii) analytetrapped luminescent material interaction [14]. Among these, the most efficient way is to utilize the analyte–organic linker interaction, because each analyte produces distinct signal upon interaction with the luminescent MOF linkers. The Mg–NDI framework is electron decient in nature due to the presence of NDI chromophore. The small sized organic amines have electron rich chemical species. Thus, the electron rich organic amines can form charge transfer complex with the NDI moieties within the framework, resulting a change in color as well as photoluminescence property. In three small sized organic amines of this work, there are two, one and zero primary amine group in ethanediamine, aniline and triethylamine, respectively. So that, The charge transfer between triethylamine and NDI is worst in these three organic amines, and thus its colour change is least obvious.



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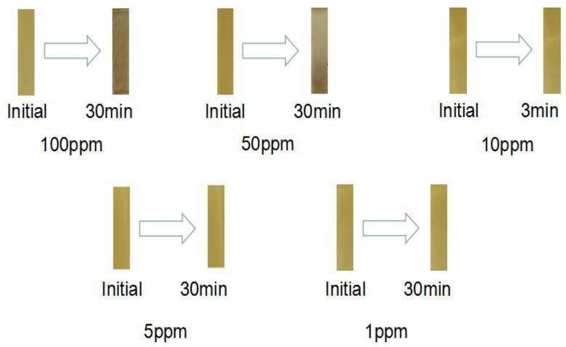
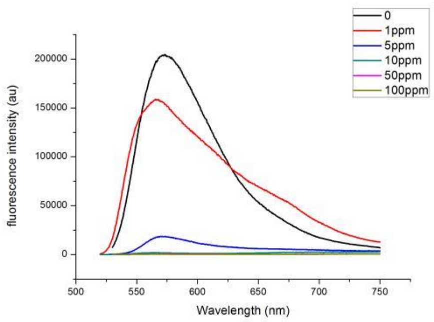


(c)

Figure 4. Variation of composite membrane's colour in different amine vapour (a) Ethanediamine (b) Aniline (c) Triethylamine

To further explore the ability of Mg–NDI to sense a trace quantity of amine, fluorescence-quenching experiment in aniline and ethanediamine were performed, respectively. The results were illustrated in Fig. 5 and 6. The strong fluorescence quenching was observed upon increasing the concentration of both amine vapour. In the cases of aniline, the rate of color change was found to be relatively slow because of their bulky size. The fluorescence quenching can be attributed to the donor–acceptor electron transfer between amines and MOF. The electron transfer happens because the HOMO energy (-6.02eV) of Mg–NDI is lower than that of amine analytes (ethylenediamine: -5.60eV, aniline: -5.63eV) [20]. The electron transfer from ethylenediamine to Mg–NDI is faster than other amines because of energy difference as compare to other amines.



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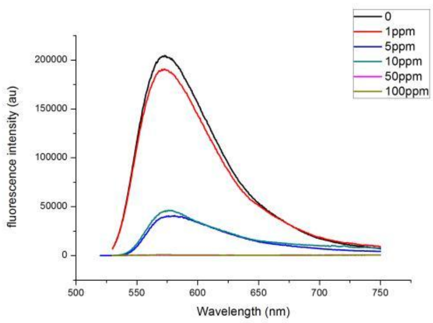
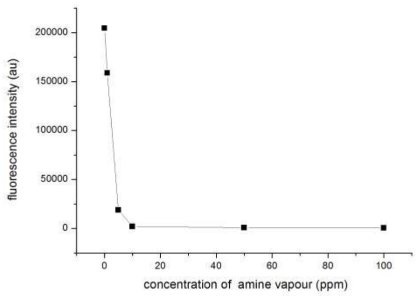


(b)

Figure 5. The fluorescence-quenching of composite membrane in different amine vapour (a) Ethanediamine (b) Aniline



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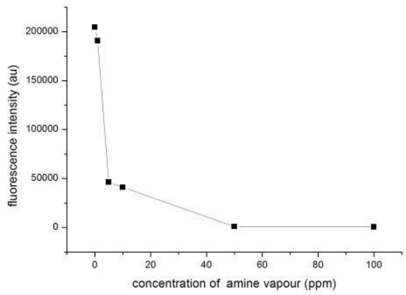

(b)

Fig.6 The variation of fluorescence intensity with the change of organic amine vapor content (a) Ethanediamine (b) Aniline

4. Conclusion

In summary, we presented a composite membrane containing Mg–NDI and PVDF, and found that this composite membrane exhibited good trace detection effect on organic amine vapour, especially the ethanediamine vapour, that a distinct colour variation (from yellow to black) was observed even the concentration of ethanediamine vapour was 5ppm. The fluorescence-quenching experiment demonstrated that the peak intensity of composite membrane decreased with the increase of organic amine vapor content. Such composite membrane has promising application in trace detection of organic amine vapour.

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