Development of solid phase colorimetric material for detecting formaldehyde in indoor environment

（ホルムアルデヒドの固相比色認識材料の開発）

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1.Introduction

Simple detection of formaldehyde (HCHO), which is a typical indoor air pollutant, has been attracting a great concern for realizing healthy and comfortable indoor air environment. Several methods have been previously used to determine the HCHO concentrations, such as detector tube method, and passive sampler and active sampler method. However, these methods require complicated procedures and professionals for operation. Then, the author developed a new material for colorimetric detection of HCHO. This material consists of co-precipitation of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT), ZnO and KIO_4. This discolors from white to purple when the material reacted with HCHO. In this study, optimization of preparing condition was carried out to maximize the detecting performance and the detector was tested to expose lower concentration of HCHO at guideline level.

2. Experimental

2.1 Preparation of detecting material

Powder of ZnO was dissolved into 0.2M-HCl containing AHMT. To the solution, KIO_4/0.2M-NaOH was added to give a co-precipitation. Molar ratio of HCl and NaOH in the mixed solution was kept from 0.87 to 0.95. The product was separated by centrifugation, and then taken out to a Petri dish(30mmφ, 15mm height). A solution of agar was added immediately to the product. The mixture was then cooled in a refrigerator.

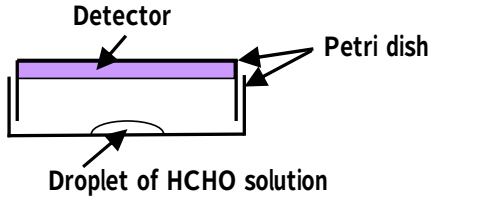

Fig.1 Exposure experiment in a closed Petri dish

2.2 Exposure experiment in a closed Petri dish

The detector was placed on a Petri dish(35mmφ, 15mm height) where 50μL of HCHO solution was dropped (Fig.1). The material was then exposed to HCHO gas diffused from the droplet for 24 hours.

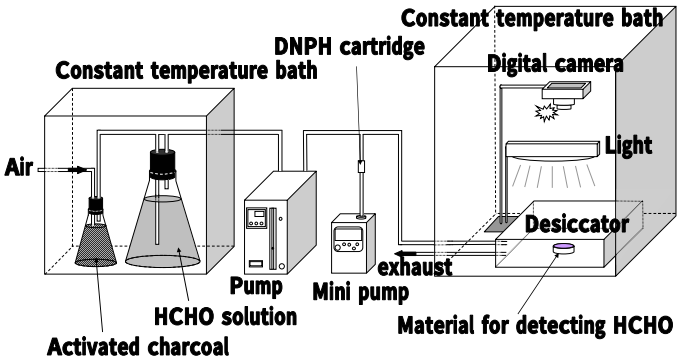

Fig.2 Layout of the small chamber experiment

2.3 Exposure experiment in a small chamber

The detector was placed in a small chamber and then exposed to the HCHO gas introduced from a constant gas generation system (Fig.2). The chamber was a transparent desiccator to allow observation of color change through the experiment.

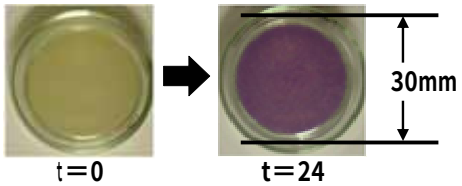

Fig.3 Typical color change of the detector before and after exposere

2.4 Measurement of color response

Fig.3 shows a typical color change of the detector exposed to the HCHO gas. The color was converted to a color value of green in a RGB color model. The color response of the detector was then expressed as a color degree defined by eq.①.

Color degree ＝ 255 － G value ・・・①

3. Results and Discussion

3.1 Effect of temperature on the color response

To investigate the effect of temperature, the materials were exposed to the HCHO gas from 0, 50, 100 and 2000 μg/mL-HCHO solutions at 10℃, 20℃ and 30℃. Fig.4 shows the result. The color degrees increased with time, and became constant. Although the color change rates varied with temperature, the final color degree became equivalent after 24 hours. Fig.5 shows relationship between color degree after 24 hours and concentration of HCHO of thedroplet. No difference was found among the curves obtained at 10℃, 20℃ and 30℃. This means the final color response is not influenced by the atmospheric temperature.

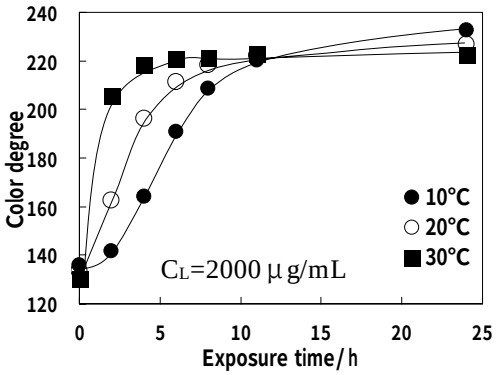

Fig.4 Time courses of color degree of the detector exposed in a Petri dish

3.2 Exposure to lower concentration of HCHO gas

Fig.6 shows the time course of color degrees of the detector exposed to the 0.1mg/m³ of HCHO gas under the constant gas flow system, comparing with that of the unexposed sample (blank). This shows the detector can be practically used for checking the indoor air guideline level set by the Ministry of Health, Labor and Welfare.

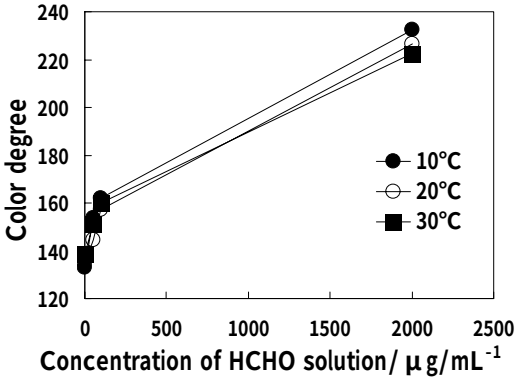

Fig.5 Relationship between color degree after 24 h and aqueous HCHO concentration

3.3 Langmuir-Hinshelwood model

The reaction of the detection with HCHO was described by Langmuir-Hinshelwood mechanism(eq.②).

$$\frac{1}{r}=\frac{1}{kK}\frac{1}{Cg}+\frac{1}{k} \quad \cdots ②$$

r : reaction rate (/h)
k : reation rate constant(/h)
K : adsorption equilibrium constant(m³/mg)
Cg : air concentration of HCHO(mg/m³)

The reaction rates were derived from the slopes of color degrees at 10 and 25℃ against the exposure time, show in Fig.7. Subsequently, the k and K were obtained as shown in Table 1. This means the temperature should be considered in measurement of color degree of the detector.

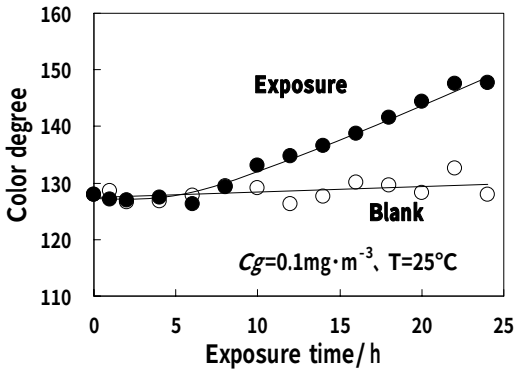

Fig.6 Time courses of color degree of the detector exposed in a small chamber

Table 1 Calculated k and K

T/℃	k/h^{-1}	K/m³·mg^{-1}
10	2.3	20
25	9.4	1.6

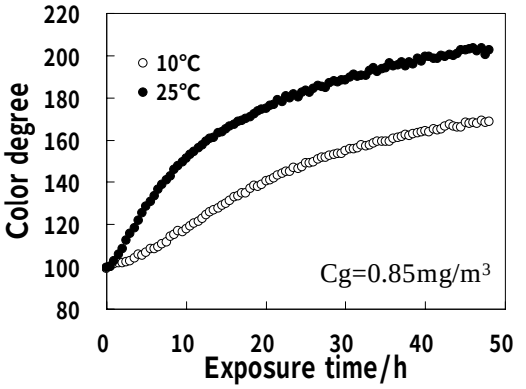

Fig.7 Time courses of color degree of the detector when exposed to the HCHO gas at 10℃ and 25℃

4. Conclusion

The author successfully developed a simple material for detecting gaseous HCHO by visual change. This detector will be practically used for determing HCHO emission flux from building material and indoor air concentrations of HCHO in houses, schools and offices.