



Sub-second pyridine gas detection using a organometal halide perovskite functional dye



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ABSTRACT

We have investigated sub-second and reversible pyridine sensing using organometal halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite functional dye (PFD). Upon exposure of pyridine vapor, perovskite film showed a reversible visible color change with fluorescence switching driven by interactions between pyridine and perovskite. Perovskite functional dye also showed excellent durability by showing more than 100 times repeatability of reversible sensing. This study suggests a novel and practical sensing platform for highly sensitive and durable colorimetric/emission pyridine chemosensors.

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1. Introduction

Since the significant development of the world's industry and economy in recent years, detection and monitoring of pollutants with high sensitivity are of great social and environmental importance. In particular, volatile organic compounds (VOCs) such as alcohols, acetone, formaldehyde, and pyridine are widely known as the primary sources of indoor environmental pollutants and seriously harmful species to the human body [1]. Among them, pyridine ($\text{C}_5\text{H}_5\text{N}$), which is widely used as a versatile solvent in industrial organic synthesis, causes nausea, vomiting, coughing, asthmatic breathing, laryngitis and even cancers when inhaled, ingested, or absorbed through the skin. Even worse, because pyridine gas is colorless it is very difficult to recognize if we are exposed to it [2]. Thus, pyridine monitoring systems in various environments with both high sensitivity and reliability with quick detection is highly demanded for the protection of human body from harmful effects.

Various pyridine detection techniques have been reported so far such as barbituric acid spectrophotometry, liquid chromatography, gas chromatography, liquid chromatography-mass spectrometry,

and gas chromatography-mass spectrometry [3]. However, the reversible detection system exhibiting a dual mode (color/emission) signaling, which allows the simultaneous pyridine detection in the bright and dark condition, has not been reported yet.

As an excellent light harvester, organometal halide-type hybrid perovskites with a structure of ABX_3 (A = organic cation, B = metal cation, and X = halogen anion) have attracted considerable attraction because of their exceptional optoelectronic properties, such as intense broad-band UV/Vis light absorption (300–800 nm) and 10 times greater absorption coefficient ($\epsilon = 1.3 \times 10^5 \text{ cm}^{-1}$ at 550 nm) compared to that of the conventional light-absorbing ruthenium-based molecular dye [4]. By combining these unique optical characteristics with hydrogen bonding reactivity of perovskites with polar species, we have reported the application of perovskites functional dye (PFD) to the polarity chemosensor [5].

In this work, we suggest a simple but very effective pyridine chemosensor showing ultra-fast (<1 s) and reversible colorimetric/fluorescent respond to the polar pyridine vapor (polarity: $\text{ET} = 45.4 \text{ kcal/mol}$) using a polarity-recognizable organometal halide PFD. Compared to other reported sensing materials, preparation of perovskite layers are not only based on a very simple one-step synthesis but also highly compatible low-cost solution printing process, implying their applicability to the large-area chemosensor arrays.

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2. Experimental section

2.1. Materials

Chemical reagents used in this study were used without any further purification. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and lead (II) iodide (PbI_2) were purchased from Tokyo Chemical Industry (TCI). Dimethyl sulfoxide (DMSO) and pyridine were purchased from Sigma-Aldrich.

2.2. Film preparation and characterization

$\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite precursor solution was prepared using $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 following the reported method [6], and the perovskite films in this study were prepared on the glass substrates. The substrates were rinsed by sonication in detergent and deionized water, acetone and isopropyl alcohol before film coating. Then, uniform and large-area (10 cm^2) perovskite films were prepared in ambient condition by using a blade-coater and homogeneous $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution in DMSO. The wet films formed immediately after solution blading were kept at room temperature ($25\text{ }^\circ\text{C}$) for 40 min before annealing to wait for the majority of DMSO solvent to be dried and evaporated. Finally, the substrates were annealed at $100\text{ }^\circ\text{C}$ for 15 min to complete perovskite film fabrication. $\sim 400\text{ nm}$ -thick perovskite layers were obtained by blade-coating the precursor solution with a coating speed of 15 mm/s with the gap between blade and substrate of $10\text{ }\mu\text{m}$ (Blade-coating was performed using a knife-coating device (KP-3000H, KIPAE). UV-vis absorption and photoluminescence (PL) spectra were measured using an Agilent 8457 UV-vis spectrophotometer, a Shimadzu RF-5301PC Fluorescence spectrophotometer, and MCPD-3000 (Otsuka electronics). All the theoretical calculations were performed by DMol3 program in the Materials Studio 4.4 package which is the quantum mechanical code using density functional theory [7].

3. Results and discussion

Fig. 1(a) shows the crystal structure of perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) functional dye used in this study, which can be described by the general formula ABX_3 . All the perovskite films were prepared by a blade-coating mixed precursor solution ($\text{CH}_3\text{NH}_3\text{I}/\text{PbI}_2$ in DMSO) for uniform and large-area deposition as presented in Fig. 1(b). Crystalline perovskite films were formed by drying wet film, followed by $100\text{ }^\circ\text{C}$ annealing [6]. Scanning electron microscopy (SEM) image in Fig. 1(c) shows $\sim 5\text{ }\mu\text{m}$ sized uniform crystalline grains of the prepared perovskite film.

Firstly, in order to explore the pyridine recognition abilities of perovskite films, we performed UV/Vis absorption spectral studies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film in the presence of pyridine vapor. The blade-coated $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was exposed to pyridine gas carried by nitrogen gas ($4.0 \times 10^{-2}\text{ mL/min}$) at room temperature ($25\text{ }^\circ\text{C}$). For this study, the time course of the reaction between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and pyridine was investigated by monitoring the absorption intensity changes of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. Broad-band ($400\text{--}800\text{ nm}$) absorption spectra featuring 745 nm peak, which indicates stoichiometric perovskite formation, was clearly observed from the blade-coated perovskite film, as shown in Fig. 2 (a) ($\lambda_{\text{onset}} = 795\text{ nm}$, $\Delta E_{\text{opt}} = 1.56\text{ eV}$) [8]. The exposure of pyridine vapor to these perovskite films resulted in an ultra-rapid ($<1\text{ s}$) and significant decrease not only in the intensity of perovskite's characteristic absorption band at 745 nm to 55.4% of its initial one, which indicates decomposition of the perovskite crystal structure, but also in that of entire visible spectra range (experimental setup for pyridine vapor exposure and optical measurements is presented in

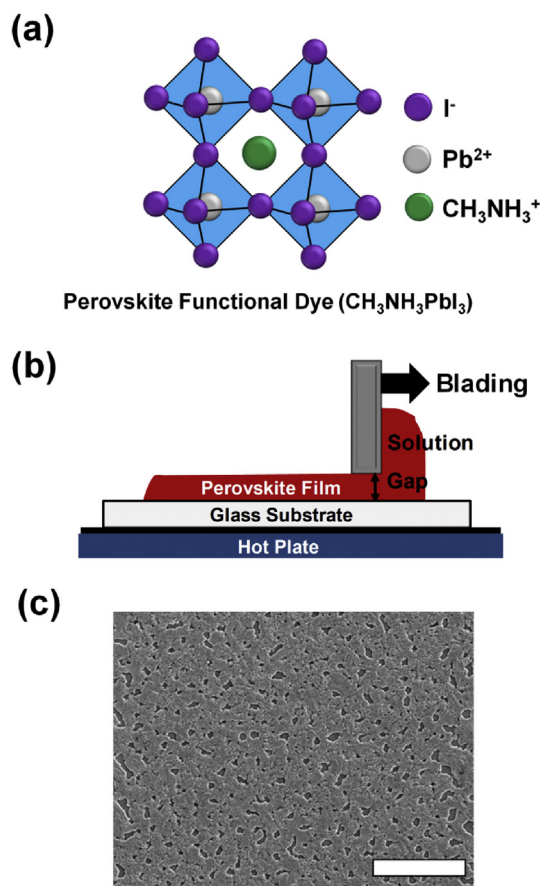


Fig. 1. (a) General (ABX_3) crystal structure of organometal halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$), (b) blade-coating process for perovskite film preparation, and (c) Scanning electron microscopy image of perovskite film (scale bar: $10\text{ }\mu\text{m}$).

Fig. 2(a)) [9]. Pyridine-induced transparency of the perovskite film is 55.3, 62.9, and 58.3% at 500, 600, 700 nm, respectively. This dramatic absorption and transparency changes are driven by crystal decomposition because of the hydrogen bond interaction between pyridine and CH_3NH_3^+ , consequently resulting in the color change of the films from dark brown to transparent (colorless), which is clearly visible to the naked eyes (see Figs. 2(a) and 6(a)). More interestingly, as shown in Fig. 2(b), complete recovery of both absorption spectrum and film color was clearly observed within 6 s after removal of pyridine vapor. Photography images in Fig. 3 presents the fast and reversible pyridine gas detection of perovskite film (recorded real-time movie is provided in Supplementary Information).

After then, we further investigated the effect of pyridine vapor on the emission properties of perovskite film. Fig. 4 compares PL spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film before and after pyridine exposure. 65.2% of its initial fluorescence intensity at 780 nm ($\lambda_{\text{exc}} = 600\text{ nm}$) remarkably quenched with exposure of the pyridine vapor in less than 1 s, and recovered with the removal of the pyridine vapor in a good accordance with absorption spectra changes. These results reveal that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite functional dye is capable of responding very fast and sensitively to pyridine vapor based on an emission signal as well.

Repeatability of reversible pyridine vapor detection was investigated by carrying out monitoring absorption and fluorescence intensity changes with repeated exposure and removal of pyridine vapor. As shown in Fig. 5, successive exposure cycles indicate that the interaction between pyridine and perovskite is fully reversible

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