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Fabrication and characterization of VOC sensor array based on SnO_2 and ZnO nanoparticles functionalized by metalloporphyrins

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Abstract

A volatile organic compound (VOC) sensor array based on metal oxide nanoparticles (MOX NPs) functionalized by metalloporphyrins (MPPs) was demonstrated. The VOC sensor array was composed of four single sensors based on SnO_2 NPs/cobalt-porphyrin, SnO_2 NPs/zinc-porphyrin, SnO_2 NPs/nickel-porphyrin and ZnO NPs/cobalt-porphyrin. The MOX NP/MPP-based sensors were fabricated by drop-casting the MOX NPs dispersion and MPPs solution onto a MEMS platform. The fabricated sensor successfully detected toluene at a concentration as low as 20 ppb, which is below the limit detection concentration of previously reported porphyrin-based VOC sensor arrays. We also confirmed the selectivity between benzene, toluene, ethylbenzene, and xylene (BTEX) by using principal component analysis in contrast to previous studies on MOX/MPP-based sensor. BTEX was classified from 1 to 9 ppm at a resolution of 2 ppm, and the sensor array showed stable performance even after considerable impact.

Keywords: Volatile organic compound, Metal oxide, Porphyrin, Gas sensor array, Principle component analysis

Introduction

Volatile organic compounds (VOCs), such as benzene, toluene, ethylbenzene and xylene (BTEX) are frequently used indoors, e.g., in adhesives or paints. VOCs are harmful when they are absorbed into the human body as they cause skin and respiratory diseases [1–4]. To prevent health risk caused by VOCs, it is necessary to measure the concentration of VOCs in the atmosphere.

Metal oxides (MOXs) change their resistance when a VOC is adsorbed, and thus have attracted significant attention as a VOC-sensing material [5]. A MOX-based VOC sensor has the advantages of easy processing and low cost, but it suffers from low selectivity and high operating temperature [6]. Recently, several studies were conducted to improve the sensitivity and selectivity to VOC through functionalization by porphyrin. Porphyrins are well-known as functionalizing substances that enhance the sensitivity of VOC-sensing materials owing to the various adsorption sites that can bind VOCs [7]. Belkova et al. improved the sensitivity by functionalizing zinc oxide (ZnO) and tin oxide (SnO_2) thin films with porphyrin [8]. Nardis et al. detected methanol at a low temperature by functionalizing a SnO_2 thin film prepared via the sol–gel method with cobalt porphyrin [9]. However, very few studies of MOX/porphyrin-based sensors have been performed to confirm the selectivity between various types of VOCs. VOCs must be selectively detected because the severity and nature of the hazards vary from one species to another [10]. Principal component analysis (PCA) uses orthogonal transformations to convert a set of correlated variables into a set of linearly uncorrelated variables, allowing the data to be mathematically or geometrically separated [10, 11]. The PCA method using a sensor array has been studied for the selective detection of VOC type. Shirsat et al. developed a sensor array consisting of several carbon nanotube/porphyrin-based VOC sensors with various metalloporphyrins (MPPs) and confirmed selectivity for acetone, ethanol,

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methanol, and methyl ethyl ketone [12]. Chen et al. used a sensor array consisting of various MOX nanomaterials and carbon nanotubes to obtain the selectivity between ethanol and other noxious gases [13]. However, the previous sensor arrays have the disadvantages of high detection limit and low concentration resolution.

In this study, a sensor array composed of four sensors was fabricated by functionalizing MOX nanoparticles (NPs) with various kinds of MPPs. The fabricated device exhibited a low detection limit of 20 ppb. Major VOCs such as BTEX were detected at a resolution of 2 ppm from 1 to 9 ppm, and selectivity was confirmed using PCA. Owing to the MPP functionalization, the sensors could react with a low concentration of VOCs, and the sensor response changed significantly even at small concentration changes. In addition, impact test confirmed that the sensor platform, MOX NPs, and MPPs were well bonded.

Design and materials

We used commercially available ZnO NPs and SnO_2 NPs (Sigma Aldrich) as VOC-sensing materials. The functional materials were 5,10,15,20-Tetraphenyl-21H,23H-porphine zinc (ZnPP), 5,10,15,20-Traphenyl-21H,23H-porphine cobalt (CoPP), and 5,10,15,20-Tetraphenyl-21H,23H-porphine nickel(II) (NiPP) purchased from Sigma Aldrich. Deionized water and chloroform were used as solvents for the MOX NPs dispersion (0.1 wt%) and porphyrin solution (0.07 wt%), respectively.

Figure 1 shows the schematic of a single sensor. The proposed device consists of sensor electrodes, heater electrodes, and a central sensing part. A high temperature above 300 °C is required to adsorb oxygen ions on the surface of the sensing material to detect VOCs [14]. Therefore, a micro-heater is integrated on the platform. As the sensing part is suspended, the conduction of heat to the substrate and subsequent loss can be prevented.

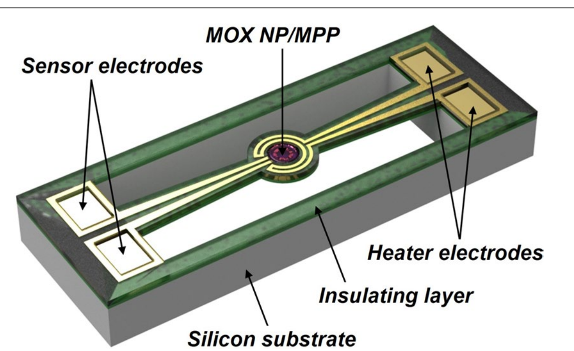

Fig. 1 Schematic of a single sensor. The sensing part is suspended to prevent conduction of heat to the substrate and its subsequent loss

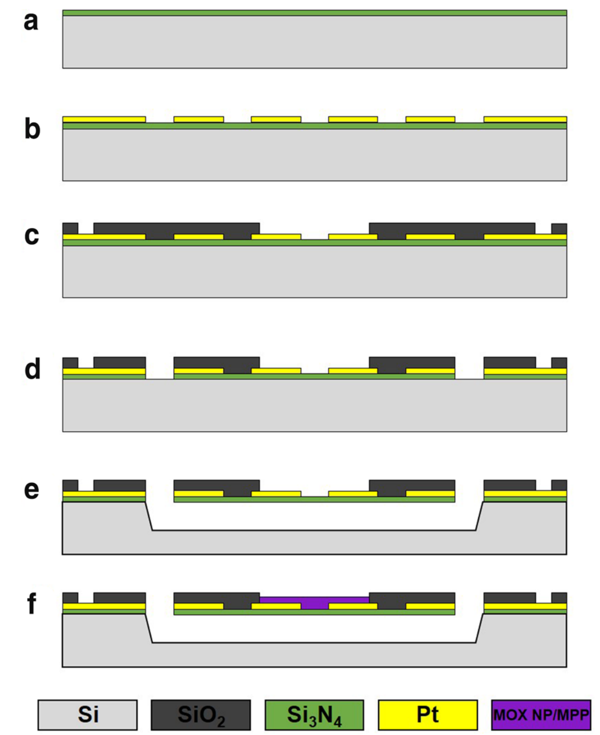

Fig. 2 Fabrication process flow. **a** Si_3N_4 film deposition on Si wafer. **b** Pt deposition and patterning. **c** SiO_2 deposition and patterning. **d** Si_3N_4/SiO_2 etching to form via hole. **e** Si wet-etching using TMAH. **f** Coating of sensing material

The fabrication process flow is depicted in Fig. 2. A 500-nm-thick Si_2N_3 film was deposited on a silicon substrate as a membrane for heaters and sensor electrodes through low-pressure chemical vapor deposition (CVD). After a 200-nm-thick Pt film was deposited onto the Si_2N_3 film via e-beam evaporation, it was patterned using photolithography and a lift-off process. A 100-nm thick SiO_2 film was deposited onto the surface via plasma enhanced CVD for a passivation layer; it was patterned using photolithography and etched using reactive ion etching (RIE). SiO_2 layer patterning followed the previous process to expose the sensor electrode. To form a suspended structure, the SiO_2 and Si_2N_3 layers at the front side were etched via RIE and the silicon substrate was wet-etched using tetramethylammonium hydroxide. After fabrication of the sensor platform, 1 μL of the MOX NPs (SnO_2 or ZnO) dispersion and MPPs (CoPP, ZnPP, or NiPP) solution was drop-casted onto the center of the sensor electrodes by using a micropipette.

Figure 3a shows an optical image of the sensor platform before MOX NPs/MPP coating. The sensing area of the sensor platform has a circular shape with a diameter of approximately 140 μm and the external heater resistor

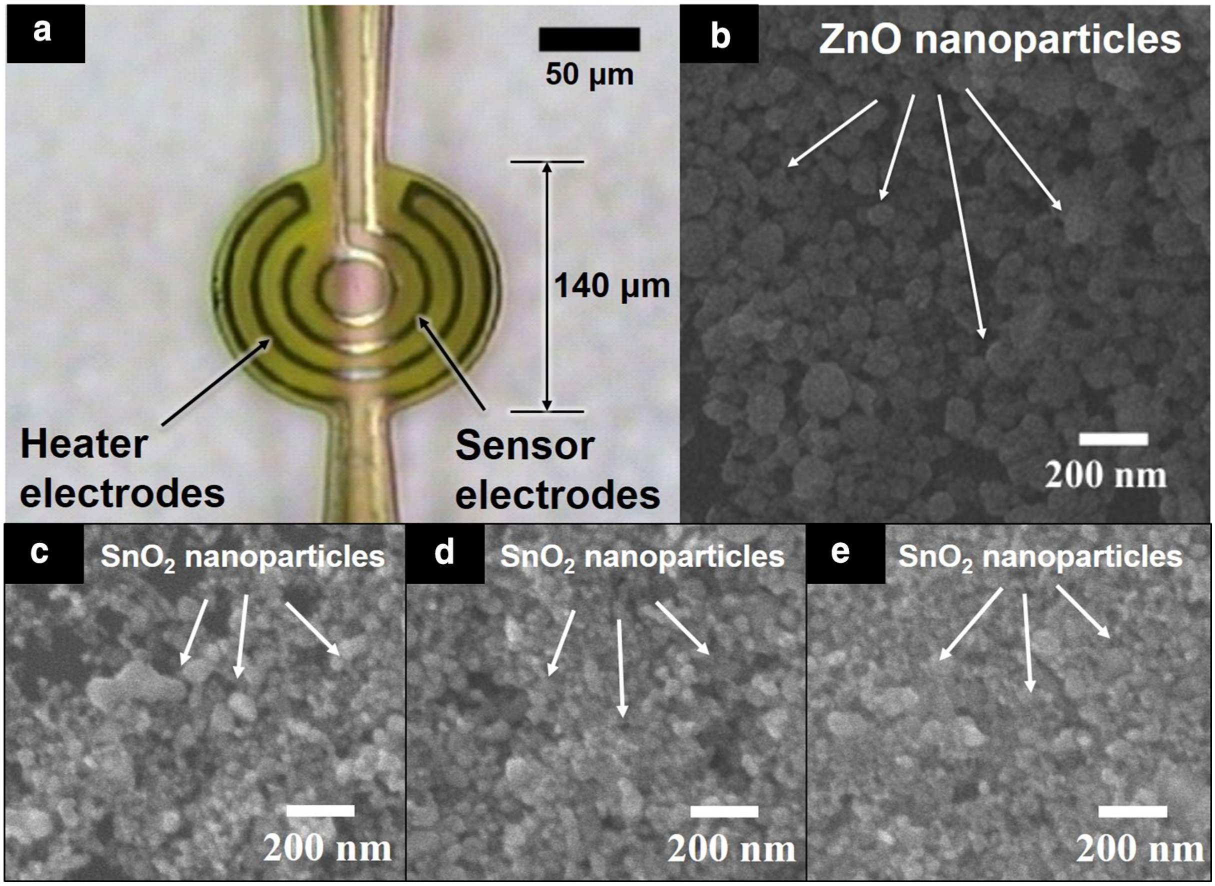

Fig. 3 **a** Optical image of the fabricated sensor platform. Scanning electron microscope image of **b** ZnO NPs/CoPP, **c** SnO_2 NPs/CoPP, **d** SnO_2 NPs/ZnPP, and **e** SnO_2 NPs/NiPP

surrounds the sensor electrodes inside. Figure 3b–e presents a scanning electron microscope image of ZnO NPs/CoPP, SnO_2 NPs/CoPP, SnO_2 NPs/ZnPP, and SnO_2 NPs/NiPP, respectively. The MOXs used as the sensing material are composed of NPs of diameter less than 100 nm.

The VOC sensing tests were performed by measuring the changes in the electrical resistance of the sensors as the sensors were exposed to air-diluted VOC and dry air alternately at atmospheric pressure and room temperature. While the sensor was operating, the microheater was driven at a fixed bias voltage of 3.5 V. The power consumption of the heater was 28 mW, and the corresponding temperature measured by a resistance temperature detector was approximately 353 °C. The concentration of VOC was adjusted by changing the mixing rate using a mass flow controller, and the total flow rate of VOCs diluted in air was maintained as 500 sccm. The response is defined as R_a/R_g, where R_a and R_g are the resistances of the sensors before and after the exposure to VOCs, respectively. For measuring R_a/R_g, a current was monitored using a sourcemeter (KEITHLEY 2400) under a fixed bias voltage of 1 V.

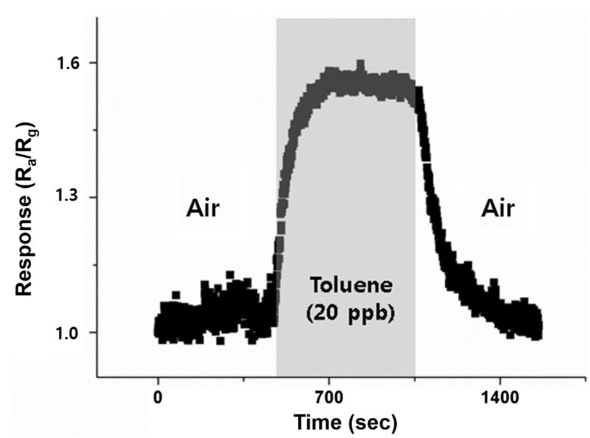

Fig. 4 Transient response graph of the sensor based on ZnO NPs functionalized by CoPP for toluene

Results and discussions

Figure 4 shows the transient response of toluene to MOX NP/MPP-based sensors. The sensing material of the tested sensor is ZnO NPs functionalized by CoPP. When the sensor was exposed to 20 ppb of toluene, the resistance of the sensing material decreased and showed a response of 1.6. The sensor could detect toluene at a low concentration of 20 ppb at a signal-to-noise ratio greater than 10, as CoPPs improve the response to VOCs by providing a variety of interacting adsorption sites to ZnO NPs [7, 15].

Figure 5 shows the concentration–response graph of the fabricated sensor array composed of four sensors based on SnO_2 NPs/CoPP, SnO_2 NPs/ZnPP, SnO_2 NPs/NiPP and ZnO NPs/CoPP for BTEX. The order of response to BTEX was different for all sensors. The sensors based on SnO_2 NPs/CoPP and SnO_2 NPs/NiPP exhibited the same order of response for BTEX, but the sensor functionalized by CoPP was more sensitive to toluene than the one functionalized by NiPP.

Figure 6 shows a PCA graph with experimental data measured using the sensor array composed of the manufactured four kinds of sensors. It was confirmed that 20 data values measured for BTEX 1–9 ppm with resolution 2 ppm were dispersed without overlap in the three-dimensional PCA graph. This indicates that the fabricated sensor array is selective between BTEX

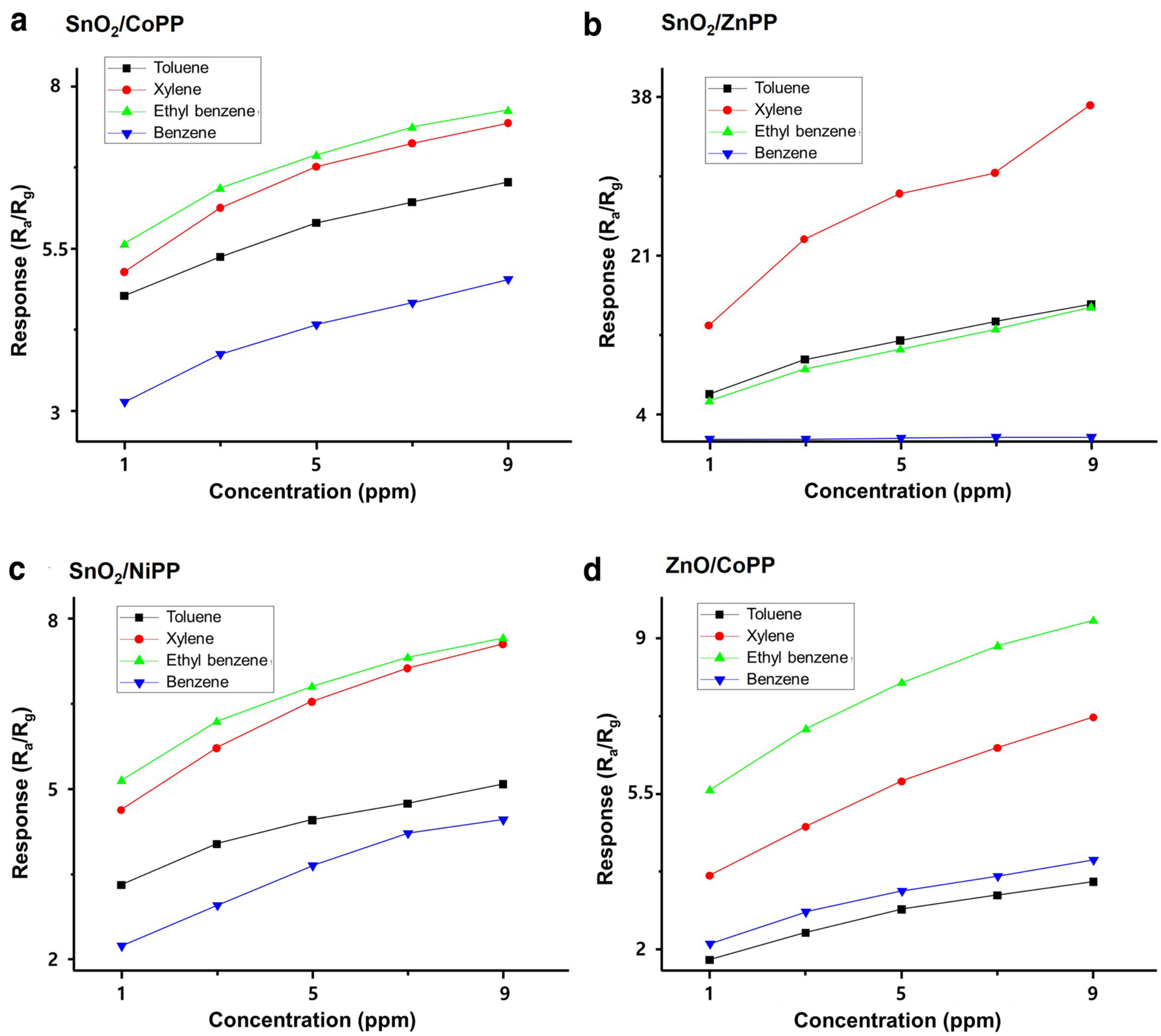

Fig. 5 Concentration-response graphs of the sensor array composed of 4 MOX NP/MPP-based sensors for BTEX. **a** SnO_2/CoPP, **b** SnO_2/ZnPP, **c** SnO_2/NiPP, and **d** ZnO/CoPP

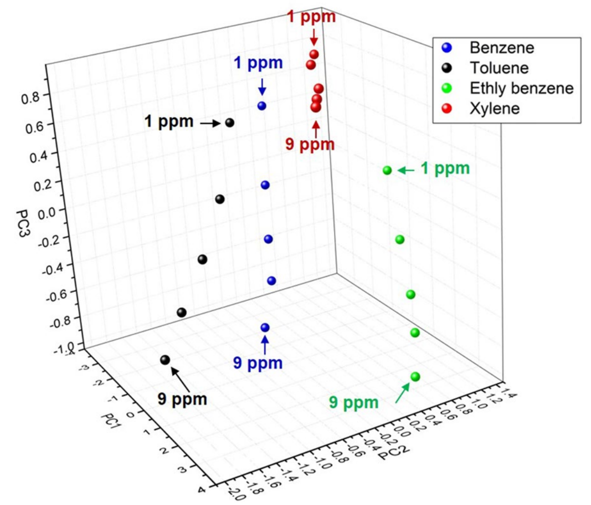

Fig. 6 PCA result with experimental sensing data measured using a sensor array composed of four kinds of sensors

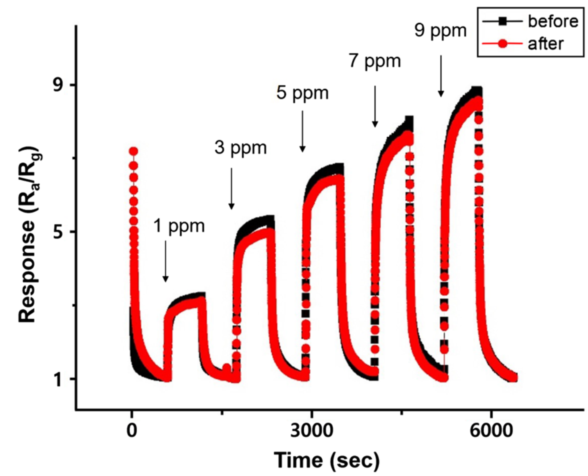

Fig. 8 Transient response graph of SnO_2 NPs/ZnPP-based sensor before and after impact test at toluene environment. The sensor was dropped five times from a height of 150 cm

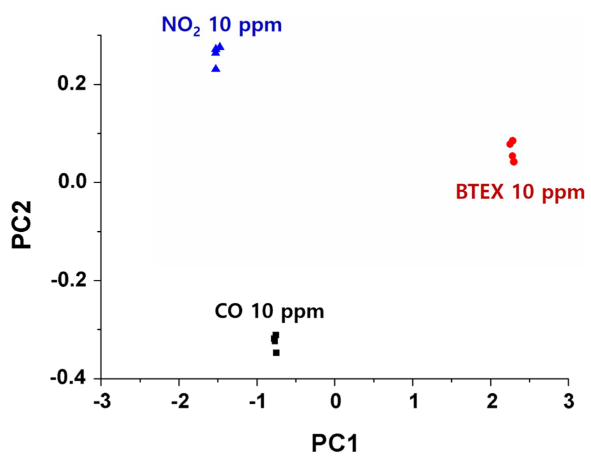

Fig. 7 PCA result for BTEX mixture, NO_2, and CO

concentrations ranging from 1 to 9 ppm. The selectivity of our sensor array is attributed to the metal ion, which selectively interacts with the VOC through coordination bonds, located at the center of porphyrin.

In addition, additional experiments were conducted to determine whether the sensor array is selective for NO_2 and CO, the harmful gases generated indoors. Figure 7 shows the PCA graph of the sensor array for BTEX mixture, NO_2 and CO. Based on the two-dimensional PCA, we confirm that the sensor array can selectively discriminate BTEX mixture gas, NO_2, and CO of 10 ppm.

Figure 8 shows the results of stability test for the impact of the fabricated sensor. Even after dropping the fabricated sensor 5 times from a height of 150 cm, the response of SnO_2 NPs/ZnPP based sensors for toluene ranging from 1 to 9 ppm was changed within 10% compared with before the drop.

Conclusions

A VOC sensor array composed of SnO_2 NPs/CoPP, SnO_2 NPs/ZnPP, SnO_2 NPs/NiPP and ZnO NPs/CoPP was developed and its sensing characteristics were evaluated. A single sensor in the sensor array was fabricated by coating MOX NP solutions and solvent-dispersed MPP onto a platform fabricated through a MEMS process. The fabricated device successfully detected toluene at a concentration as low as 20 ppb. We also confirmed the selectivity between BTEX using the arrays via the three-dimensional PCA. BTEX of 1–9 ppm was classified at a resolution of 2 ppm, and the fabricated device showed stable performance even after considerable impact. The fabricated VOC sensor array can be used in indoor environments, such as houses or hospitals, which require low concentration detection and need to distinguish VOCs.

Authors' contributions
BC and KL performed the experiments, analyzed the data, and wrote the manuscript. SP supported the data analysis and reviewed the manuscript. JK supervised the research and reviewed the manuscript. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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