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Solid sensing

Pattern Recognition Using Chemical Sensor for Identification of Solid Materials by Responses to Multiple Probe Gases

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Abstract—A conventional approach to the analysis of solid materials generally focuses on their physical and chemical properties, and hence requires a corresponding analysis method. Recently, we have developed a novel sensing approach for materials analysis based on pattern recognition using chemical sensor arrays. Since sensing responses of a solid receptor material to gaseous molecules are unique to the combination of the solid materials and the gaseous molecules, solid materials can be identified by analyzing their response patterns to known "probe gases". Here, we demonstrated the identification of solid materials with their chemical or physical properties using this approach. Using a nanomechanical sensor as a sensing platform, we succeeded in simultaneously identifying differences between organic polymers and inorganic nanoparticles and their respective hydrophilicity. Moreover, we even identified the differences of polymer blends, which contain different amounts of plasticizers. Any kinds of gaseous and volatile molecules can be utilized as a probe gas, and hence, the number of response patterns can be tremendously increased by simply increasing the number of probe gases. Combined with a machine learning-based pattern recognition model, the present approach can be applied to a wide range of solid material analyses with high accuracy. This approach is expected to have potential applications in various fields such as materials science, chemistry, food, and environment.

Index Terms—Pattern recognition, solid sensing, chemical sensors, nanomechanical sensors, Membrane-type Surface stress Sensor (MSS)

I. INTRODUCTION

A pattern recognition-based chemical sensor array is a promising approach to identify, distinguish, and quantify odors, which are composed of a complex mixture of gaseous molecules [1–5]. In this approach, sensing signals are obtained by measuring chemical/physicochemical interactions induced by sorption of target analyte in sensing materials. Although large varieties of possible applications have been demonstrated in various fields including food, agriculture, environment, healthcare, and medicine [5–13], the usage of pattern recognition-based chemical sensors is basically limited to analyze gaseous or liquid samples.

Recently, we established a *reverse* approach: pattern recognition of solid materials by using multiple gases as a probe (Fig. 1) [14,15]. Since the signals of chemical sensors are based on the interaction between gases (i.e., analytes) and solids (i.e., receptors), a sensing element and a target analyte can be exchanged in theory. In this case, solid materials are the target analytes while the gaseous molecules are the sensing probes, allowing for the pattern recognition of solid materials coated on the sensing element. One of the advantages of this method is that almost all kinds of gaseous and volatile molecules can be utilized as a probe gas. Thus, the number of features can be tremendously increased by increasing the number of probe gases, leading to unlimited possibilities to differentiate solid materials.

In this study, we further investigated applicability of the pattern recognition-based solid sensing for identifying varieties of solid materials. For this purpose, we used a nanomechanical sensor as a model sensing platform because nanomechanical sensors have been confirmed that almost all kinds of solid materials can be used to obtain signals in response to gaseous molecules [5]. Among the nanomechanical sensors, we used a Membrane-type Surface stress Sensor (MSS) because of its high sensitivity and robustness. We demonstrated the identification of organic polymers and inorganic nanoparticles while simultaneously distinguishing differences in their hydrophilicity. In addition, we also revealed the applicability of this approach for identifying the amount of plasticizers in polymer blends. Detailed analysis using support vector machine (SVM)-based classification models suggests that the use of probe gases with wide range of chemical properties allows to discriminate the solid materials in high accuracy.

II. EXPERIMENTAL SECTION

A. Materials

Polystyrene (**PS**, Mw ≈ 350k), polycaprolactone (**PCL**, Mw ≈ 14k), poly(4-methylstyrene) (**P4MS**, Mw ≈ 72k), poly(vinylidene fluoride) (**PVF**, Mw ≈ 180k), polymethyl methacrylate (**PMMA**, Mw ≈ 15k), poly(ethylene glycol) (**PEG**, Mw ≈ 100k), and polyvinylpyrrolidone (**PVP**, Mw ≈ 360k) were purchased from Sigma Aldrich.

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Silica/titania-based hybrid nanoparticles (STNPs) bearing different organic functional groups (aminopropyl-functionalized STNPs, **NH_2-STNPs**; octadecyl-functionalized STNPs, **C_{18}-STNPs**; phenyl-functionalized STNPs, **Ph-STNPs**) were synthesized by a multistep nucleation-controlled growth method according to our previous literatures [3,16,17]. Pristine fullerene (C_{60}) (>99.9%) was purchased from Materials Technologies Research, Ltd. (USA). *N,N*-Dimethylformamide (DMF) and 1,1,2,2-tetrachloroethane (TCE) were purchased from Wako Pure Chemical Industries and used as a solvent to prepare polymer solutions for inkjet spotting. Ethanol (99.5%), 1-hexanol (≥99.0%), hexanal (>98.0%), *n*-heptane (>99.0%), methylcyclohexane (>99.0%), toluene (>99.5%), ethyl acetate (>99.5%), acetone (99.7%), chloroform (>99.0%), aniline (≥99.5%), and propionic acid (≥99.5%) were purchased from Sigma Aldrich, Tokyo Chemical Industry, Wako Pure Chemical Industries, and Kanto Chemical, and used as probe gases. All chemicals were used as purchased. To obtain water vapor, MilliQ water was used (Merck MilliPore).

B. Experimental Procedure

To identify solid materials, they were coated onto an MSS chip by inkjet spotting. The detailed fabrication process of the MSS chip was described in the previous literatures [18,19]. An inkjet spotter (LaboJet-500SP, MICROJET Corporation) equipped with a nozzle (IJHBS-300, MICROJET Corporation) was used. To identify the plasticizer-containing polymers, pristine C_{60} fullerene was used as an example [20]. Fullerene was added to a solution of **PS** in the mixture of DMF and toluene (vol/vol = 1/1; 1 mg/mL) in the range of 1 to 10 w/w%. The resulting solutions were deposited onto each channel of MSS. Each solid material was coated onto at least 3 different channels to investigate the coating quality and discrimination accuracy: **PS**, N = 11; **PCL**, N = 11; **P4MS**, N = 11; **PVF**, N = 11; **PMMA**, N = 7; **PEG**, N = 3; **PVP**, N = 3; **NH_2-STNPs**, N = 7: **C_{18}-STNPs**, N = 8; **Ph-STNPs**, N = 11; **PS-C_{60}(1%)**, N = 3; **PS-C_{60}(2%)**, N = 3; **PS-C_{60}(4%)**, N = 3; and **PS-C_{60}(10%)**, N = 3.

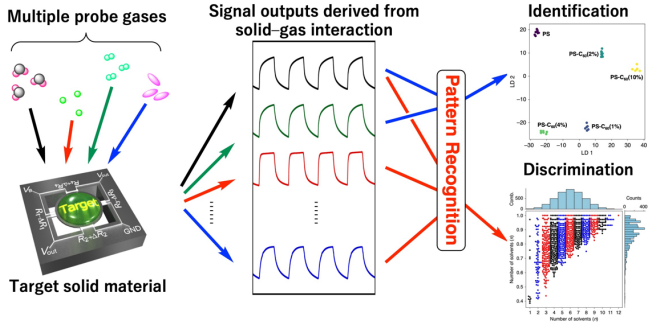

Fig. 1. Schematic illustration of pattern recognition of solid materials by multiple probe gases.

For sensing experiments, a handmade setup is used [14]. The coated MSS chips were placed in a Teflon chamber. Temperatures of incubators 1 and 2 were set at 15.00 ± 0.02 °C and 25.00 ± 0.02 °C, respectively. The vapor of each solvent was produced by bubbling of carrier gas with a fixed concentration of 10% of each saturated vapor. Pure nitrogen was used as carrier and purging gases. The total flow rate was kept at 100 mL/min during the experiments. Before measuring MSS signals, pure nitrogen gas was flowed through the MSS chamber for 2 min. Subsequently, mass flow controller (MFC)-1 (injection line) was switched on/off at each duration time (10 s) with a controlled total flow rate of 100 mL/min using MFC-2, and the cycle was repeated five times. The signal output of the MSS (V_{out}) is given by the total resistance changes from the Wheatstone bridge circuit as [18]

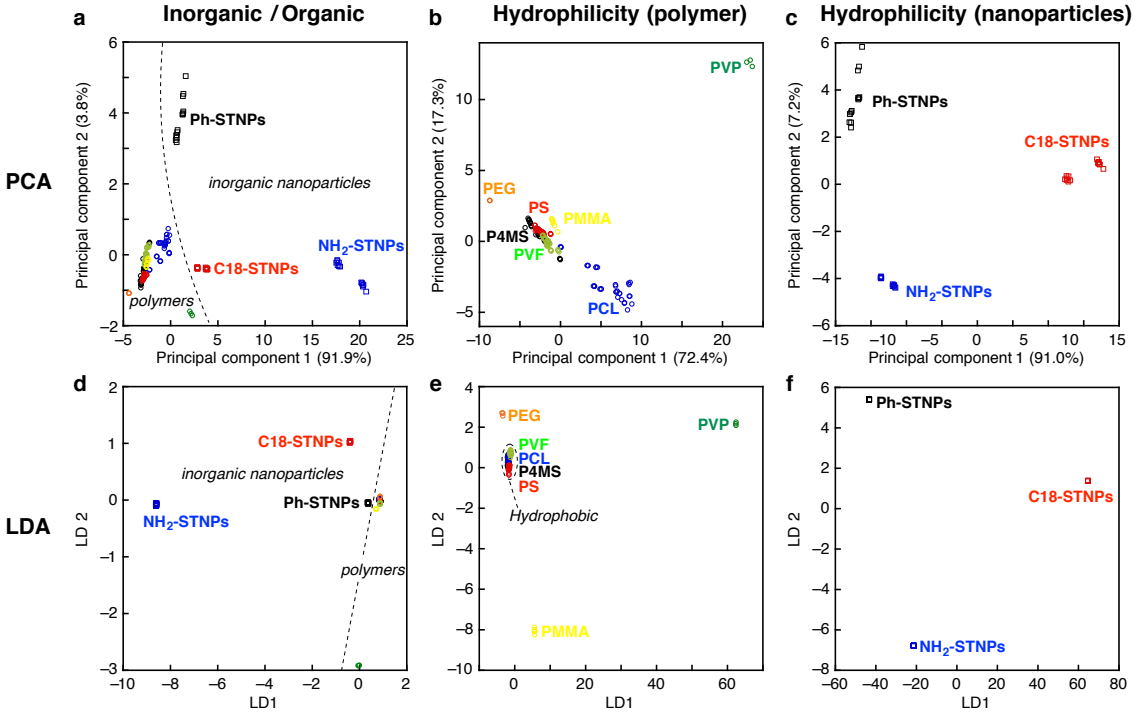

Fig. 2. Identification of polymers and STNPs by pattern recognition using 12 different probe gases. (**a–c**) PCA score plots and (**d–f**) LDA score plots. (**a,d**) All solid materials including nanoparticles and polymers. (**b,e**) Identification of polymers. (**c,f**) nanoparticles.

$$V_{\text{out}} = \frac{V_B}{4}\left(\frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_2} + \frac{\Delta R_3}{R_3} - \frac{\Delta R_4}{R_4}\right), \quad (1)$$

where V_B is the bridge voltage applied on the Wheatstone bridge circuit, and $\Delta R/R_i$ (i = 1–4) is the relative resistance change in each sensing beam [18]. Data were measured with the bridge voltage of –0.5 V and recorded with a sampling rate of 10 Hz. The data collection program was designed using LabVIEW (NI Corporation).

C. Pattern Recognition Procedure

Pattern recognition analyses were performed according to our previous study [14]. Briefly, principal component analysis (PCA) and linear discriminant analysis (LDA) were utilized for reducing the dimensionality of the datasets. Feature sets were extracted from each decay curve of a normalized MSS signal measured with 12 different gases. Three different slopes m_i were extracted from the i-th gas according to the following equation [21]:

$$m_i(t_n) = \frac{V_i(t_0) - V_i(t_0 - t_n)}{t_n} \ (n = 1, 2, 3), \quad (2)$$

where $V_i(t)$ and t_0 denote the signal output at time t and the time when the signal response starts to decay, respectively. In this study, we chose three time points for t_n: t_1 = 0.5, t_2 = 1.0, and t_3 = 1.5 [s]. The PCA and LDA were performed by using scikit-learn package for Python 3.

Classification models based on a non-linear support vector machine (SVM) were also developed using scikit-learn package for Python 3 according to our previous study [14]. Briefly, to optimize and evaluate the models, we employed 5 × 2 cross-validation with optimizing the hyperparameters of the SVM (i.e., C and γ).

III. RESULTS AND DISCUSSION

A. Identification of polymers and nanoparticles

In the previous study [14], we have revealed that the polymers composed of different monomers were discriminated, while the number of polymers is still limited. We coated three hydrophilic polymers in addition to four hydrophobic polymers used in our previous study [14]. Moreover, we also coated a series of the inorganic nanoparticles: STNPs [16]. Each STNPs has different surface functionalities, i.e., hydrophilic aminopropyl (**NH_2-STNPs**), aromatic hydrophobic phenyl (**Ph-STNPs**), and aliphatic hydrophobic octadecyl groups (**C_{18}-STNPs**). To identify these ten different solid materials, we performed the pattern recognition of solids by using 12 different probe gases, which cover a wide range of chemical properties. Upon exposure to each probe gas, each solid material shows unique responses, which reflects the differences in chemical and physical affinity, such as sorption kinetic parameter, partition coefficient, and viscoelastic parameters [22]. By using the extracted dataset, we conducted unsupervised and supervised analyses. Differences between polymers and inorganic nanoparticles are shown in Fig. 2a and d, forming well-separated clusters on PC plane and LDA. When we performed the identification of polymers and STNPs separately, they were clearly distinguished according to their hydrophilicity as shown in Fig. 2. These results indicate that this solid sensing approach distinguished not only the differences between the polymers and inorganic nanoparticles but also the differences in their hydrophilicity by tuning the dataset.

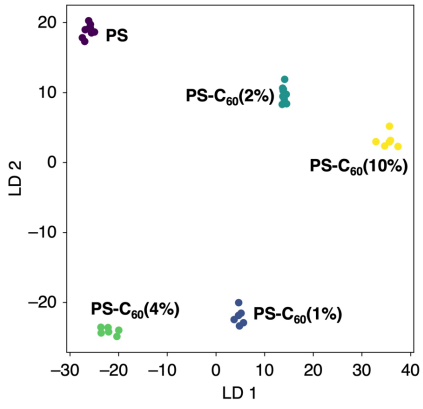

Fig. 3. LDA score plots of polystyrenes with different amounts of C_{60} plasticizer.

B. Identification of plasticizers in polymer blends

To evaluate further the possibility of this approach, we performed the identification of plasticizer amounts in polymer blends. Pristine C_{60} is known as a plasticizer and the addition of C_{60} to **PS** leads to subtle effects in glass formation [20]. We prepared four different polystyrene blends containing different amounts of C_{60} plasticizer (**PS-C_{60}**) at the concentration of 1, 2, 4, and 10 w/w% in DMF/toluene mixture. Subsequently, the resultant solutions were deposited on each channel of MSS by inkjet spotting. The MSS signal responses of **PS-C_{60}** to 12 different probe gases were measured. To differentiate subtle differences between each **PS-C_{60}** with different amount of C_{60}, we performed LDA using feature dataset extracted from 12 different probe gases. As shown in Fig. 3, each polystyrene blend was distinguished in well-separated clusters. Notably, the order of each cluster does not follow the concentration of plasticizers; this fact may reflect the nonlinear effects of C_{60} plasticizer on polystyrene, such as glass transition temperature T_g (the order of T_g: **PS** < **PS-C_{60}(10%)** < **PS-C_{60}(1%)** < **PS-C_{60}(2%)** < **PS-C_{60}(4%)** in the range of 100 to 110 °C) [20].

For efficient application of this approach, it is important to find appropriate probe gases [14]. To evaluate the discrimination accuracy, we also developed machine learning models for discriminating polystyrenes with different amounts of plasticizers based on an SVM classifier with a nonlinear kernel [14]. To optimize and evaluate the model, we employed 5 × 2 cross-validation. We developed SVM models of all combinations of probe gases (i.e., $2^{12} - 1 = 4095$). The results are shown in Fig. 4. In our previous study [14], we demonstrated two cases, i.e., discrimination of polymers having different molecular weight and polymers composed of different monomers. In such cases, it is possible to identify 100% accuracy by properly selecting two probe gases. In the present case, on the other hand, the combination of two selected probe gases can achieve up to 98% discrimination accuracy, i.e., in the case of [water, toluene] (Fig. 4, n = 2), because of subtle differences of **PS-C_{60}** [20]. It should be noted that appropriate selection of three probe gases leads to 100% accuracy (Fig. 4, n = 3). For example, in this case, four different combinations of three probe gases achieved 100% accuracy. These combinations can be divided into two groups: (1) water, polar, and non-polar combinations: [water, hexanal, n-heptane] and [water,

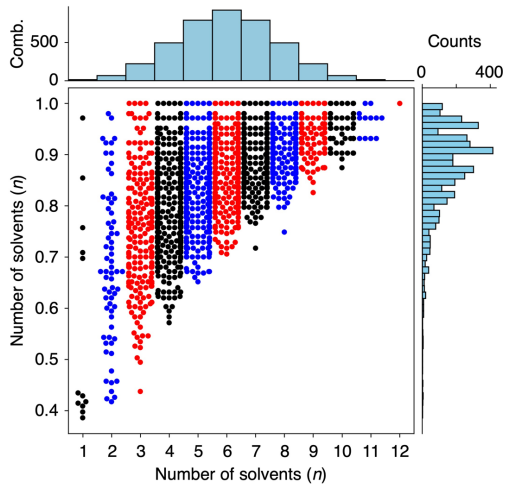

Fig. 4. SVM classification for the identification of polystyrenes with different amounts of C_{60}. Dot plots of classification accuracy calculated by SVM as a function of the number of probe gases (*n*) used for the calculation. Histograms show the number of combinations (top) and classification accuracy (right).

hexanal, toluene]; (2) water-miscible, water-immiscible polar, and water-immiscible non-polar combinations; [hexanal, *n*-heptane, acetone], and [hexanal, toluene, acetone]. These results suggest that probe gases selected from a wide variety of chemical properties can achieve the high discrimination accuracy.

IV. CONCLUSION AND OUTLOOK

We have demonstrated the further applicability of the solid sensing approach, that is, the pattern recognition of solid materials by multiple probe gases. This approach can distinguish a large variety of solid materials including organic polymers and inorganic nanoparticles with differentiating their hydrophobicity at the same time. In addition, we have also successfully identified the subtle differences of polystyrene blends with addition of plasticizer, C_{60} at 100% discrimination accuracy by using appropriately selected three probe gases combinations. An SVM-based model suggested that the probe gases with different chemical properties yield wide range of signal responses, resulting in the high discrimination accuracy.

Since the number of data is limited in the present study (in the case of plasticizer, $N = 22$), it is difficult to sufficiently train a machine learning model to predict the concentration of plasticizers by using regression models, such as kernel ridge regression [3] and Gaussian process regression [17]. By increasing the amount of data, this approach has potential to predict not only chemical and physical parameters, such as Young's modulus, viscoelastic parameters, sorption kinetic parameters, and partition coefficient, but also the concentration of target components in solid samples, such as the concentration of gluten in flour for quality assessment, in a single method. Therefore, this pattern recognition-based solid sensing can be utilized as a new way of analyzing solid materials in various fields including materials science, chemistry, food, and environment.

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REFERENCES

[1] K. J. Albert, et al., "Cross-reactive chemical sensor arrays," *Chem. Rev.*, vol. 100, pp. 2595–2626, 2000, doi: 10.1021/cr980102w.

[2] G. Imamura, K. Shiba, G. Yoshikawa, "Smell identification of spices using nanomechanical membrane-type surface stress sensors," *Jpn. J. Appl. Phys.*, vol. 55, p. 1102b3, 2016, doi: 10.7567/jjap.55.1102b3.

[3] K. Shiba, R. Tamura, G. Imamura, G. Yoshikawa, "Data-driven nanomechanical sensing: specific information extraction from a complex system," *Sci. Rep.*, vol. 7, p. 3661, 2017, doi: 10.1038/s41598-017-03875-7.

[4] H. Xu, et al., "Determination of quasi-primary odors by endpoint detection," *Sci. Rep.*, vol. 11, p. 12070, 2021, doi: 10.1038/s41598-021-91210-6.

[5] K. Minami, G. Imamura, R. Tamura, K. Shiba, G. Yoshikawa, "Recent advances in nanomechanical membrane-type surface stress sensors towards artificial olfaction," *Biosensors*, vol. 12, p. 762, 2022, doi: 10.3390/bios12090762.

[6] A. D. Wilson, M. Baietto, "Applications and advances in electronic-nose technologies," *Sensors*, vol. 9, pp. 5099–5148, 2009, doi: 10.3390/s90705099.

[7] A. D. Wilson, M. Baietto, "Advances in electronic-nose technologies developed for biomedical applications," *Sensors*, vol. 11, pp. 1105–1176, 2011, doi: 10.3390/s110101105.

[8] A. D. Wilson, "Review of electronic-nose technologies and algorithms to detect hazardous chemicals in the environment," *Proc. Technol.*, vol. 1, pp. 453–463, 2012, doi: 10.1016/j.protcy.2012.02.101.

[9] G. Konvalina, H. Haick, "Sensors for breath testing: from nanomaterials to comprehensive disease detection," *Acc. Chem. Res.*, vol. 47, pp. 66–76, 2014, doi: 10.1021/ar400070m.

[10] J. Gutierrez, M. C. Horrillo, "Advances in artificial olfaction: sensors and applications," *Talanta*, vol. 124, pp. 95–105, 2014, doi: 10.1016/j.talanta.2014.02.016.

[11] R. A. Potyrailo, "Multivariable sensors for ubiquitous monitoring of gases in the era of internet of things and industrial internet," *Chem. Rev.*, vol. 116, pp. 11877–11923, 2016, doi: 10.1021/acs.chemrev.6b00187.

[12] J.-W. Yoon, J.-H. Lee, "Toward breath analysis on a chip for disease diagnosis using semiconductor-based chemiresistors: recent progress and future perspectives," *Lab Chip*, vol. 17, pp. 3537–3557, 2017, doi: 10.1039/c7lc00810d.

[13] C. Kim, et al., "Recent trends in exhaled breath diagnosis using an artificial olfactory system," *Biosensors*, vol. 11, p. 337, 2021, doi: 10.3390/bios11090337.

[14] K. Minami, G. Imamura, T. Nemoto, K. Shiba, G. Yoshikawa, "Pattern recognition of solid materials by multiple probe gases," *Mater. Horiz.*, vol. 6, pp. 580–586, 2019, doi: 10.1039/c8mh01169a.

[15] K. Minami, G. Yoshikawa, "Pattern recognition of solid materials by multiple probe gases," *ECS Meet. Abstr.*, vol. MA2020-01, p. 2260, 2020, doi: 10.1149/MA2020-01302260mtgabs.

[16] K. Shiba, T. Sugiyama, T. Takei, G. Yoshikawa, "Controlled growth of silica-titania hybrid functional nanoparticles through a multistep microfluidic approach," *Chem. Commun.*, vol. 51, pp. 15854–15857, 2015, doi: 10.1039/c5cc07230a.

[17] K. Shiba, et al., "Functional nanoparticles-coated nanomechanical sensor arrays for machine learning-based quantitative odor analysis," *ACS Sens.*, vol. 3, pp. 1592–1600, 2018, doi: 10.1021/acssensors.8b00450.

[18] G. Yoshikawa, T. Akiyama, S. Gautsch, P. Vettiger, H. Rohrer, "Nanomechanical membrane-type surface stress sensor," *Nano Lett.*, vol. 11, pp. 1044–1048, 2011, doi: 10.1021/nl103901a.

[19] G. Yoshikawa, et al., "Two dimensional array of piezoresistive nanomechanical Membrane-type Surface Stress Sensor (MSS) with improved sensitivity," *Sensors*, vol. 12, pp. 15873–15887, 2012, doi: 10.3390/s121115873.

[20] A. Sanz, H. C. Wong, A. J. Nedoma, J. F. Douglas, J. T. Cabral, "Influence of C_{60} fullerenes on the glass formation of polystyrene," *Polymer*, vol. 68, pp. 47–56, 2015, doi: 10.1016/j.polymer.2015.05.001.

[21] K. Minami, K. Shiba, G. Yoshikawa, "Discrimination of structurally similar odorous molecules with various concentrations by using a nanomechanical sensor," *Anal. Methods*, vol. 10, pp. 3720–3726, 2018, doi: 10.1039/c8ay01224e.

[22] K. Minami, K. Shiba, G. Yoshikawa, "Sorption-induced static mode nanomechanical sensing with viscoelastic receptor layers for multistep injection-purge cycles," *J. Appl. Phys.*, vol. 129, p. 124503, 2021, doi: 10.1063/5.0039045.