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## Sensors and Actuators: B. Chemical



journal homepage: www.elsevier.com/locate/snb

# CeO<sub>2</sub>/NiO heterostructures for extremly-selective acetone detection: The critical role of the $Ce^{3+}/Ce^{4+}$ ratio in NiO nanodomes

Junho Hwang <sup>a,1</sup>, Jae Han Chung <sup>b,1</sup>, Hyeon Jae Kim <sup>b,1</sup>, See-Hyung Park <sup>b</sup>, Yun-Haeng Cho <sup>b</sup>, Sungwoo Sohn <sup>a</sup>, Seong-Jun Ro <sup>c</sup>, Hyojung Kim <sup>d</sup>, Kwangjae Lee <sup>c</sup>, Donghwi Cho <sup>e,f</sup>, Jung Hwan Seo <sup>g,\*</sup>, Young-Seok Shim <sup>b,\*</sup>, Jinho Lee <sup>h,\*</sup>, Wooyoung Lee <sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of Korea

<sup>b</sup> School of Energy, Materials and Chemical Engineering, Korea University of Technology and Education (KOREATECH), Cheonan 31253, Republic of Korea

<sup>c</sup> Department of Information Security Engineering, Sangmyung University, Cheonan 31066, Republic of Korea

<sup>d</sup> Department of Semiconductor Systems Engineering, Sejong University, Seoul 05006, Republic of Korea

e Thin Film Materials Research Center, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea

<sup>f</sup> Advanced Materials and Chemical Engineering, University of Science and Technology, Daejeon 34113, Republic of Korea

<sup>g</sup> Department of Mechanical Engineering, Hongik University, Seoul 04066, Republic of Korea

h Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

ARTICLE INFO

Keywords: NiO CeO<sub>2</sub> Nanostructure Catalysts Gas sensor

#### ABSTRACT

Exhaled breath analysis has emerged as a promising and non-invasive approach for diagnosing disease by detecting specific biomarkers. Acetone in exhaled breath can be used as a biomarker in diabetic patients, promoting the development of highly sensitive and selective acetone gas sensors. In this study, CeO<sub>2</sub>-decorated NiO nanodomes (NDs) were developed to enhance the response and selectivity for acetone detection. The optimal response was achieved using the NDs decorated with 5 nm thick CeO<sub>2</sub>, at 400 °C, affording about a 15.5-fold increase in the selective acetone response ( $R_{gas}/R_{air} - 1 = 25.4$ , 50 ppm). The enhanced gas response led to a ppb-level theoretical detection limit for the CeO<sub>2</sub>-decorated NiO NDs, even under humid conditions. This improvement is attributed to the formation of a p–n junction, as well as the increased contents of oxygen defects in sensing layers, driven by the higher Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio. These oxygen defects facilitate greater adsorption of oxygen ions on the CeO<sub>2</sub> and NiO surface, thereby enhancing the gas sensing performance. These results demonstrate the potential of CeO<sub>2</sub>-decorated NiO NDs for highly selective acetone detection, paving the way for non-invasive breath-based diagnostics.

1. Introduction

Diabetes is a prevalent metabolic disorder affecting an estimated 537 million adults globally and is linked to severe complications such as cardiovascular diseases, retinopathy, neuropathy, and nephropathy, which not only impair quality of life but also significantly reduce life expectancy [1–3]. Despite its widespread prevalence, nearly 50 % of adults with diabetes remain undiagnosed, primarily due to the reliance on invasive diagnostic methods with uncomfortable and time-consuming processes. In this respect, breath analysis has gained significant interest as a noninvasive diagnostic method that offers rapid diagnosis, is simple and pain-free, and has the potential for integration

with mobile devices for real-time monitoring systems. Breath analysis detects distinct volatile organic compounds (VOCs), called biomarkers, in exhaled human breath, indicating the presence of specific diseases [4, 5]. Recently, various studies have reported that breath acetone can serve as a biomarker for diagnosing diabetes, where the levels exceed 1.8 parts per million (ppm) in people with diabetes compared with levels ranging from 0.3 to 0.9 ppm in healthy people [6–9]. The detection of acetone gas in human exhaled breath at such extremely low levels requires high-performance gas sensors that can selectively detect acetone gas. Therefore, numerous attempts have been made to detect extremely low concentrations of acetone using various types of gas sensors, including electrochemical, catalytic combustion, and optical types [10–13].

\* Corresponding authors.

<sup>1</sup> These authors contributed equally to this work: J. Hwang, J.H. Chung, and H.J. Kim.

https://doi.org/10.1016/j.snb.2025.138070

Received 16 March 2025; Received in revised form 26 May 2025; Accepted 29 May 2025 Available online 1 June 2025 0925 4005 (© 2025 Elsavior B V. All rights are received including those for text and data mining. All training, and similar t

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E-mail addresses: gongzone@hongik.ac.kr (J.H. Seo), ysshim@koreatech.ac.kr (Y.-S. Shim), gonge3@kaist.ac.kr (J. Lee), wooyoung@yonsei.ac.kr (W. Lee).

Metal-oxide-semiconductor (MOS)-based chemiresistive-type gas sensors are considered the most promising candidates for breath analysis due to their high response to VOCs, simple operation principle, and ease of fabrication in electronic devices [14]. However, the low selectivity and cross-selectivity issues that affect MOS gas sensors make it difficult to identify individual target gases accurately, especially in complex VOCs [15]. Notably, p-type MOS (e.g., CuO, NiO, Cr<sub>2</sub>O<sub>3</sub>, etc.) can also promote the surface decomposition of specific target gases through chemical sensitization, particularly via the spillover effect, where adsorbed molecules are transferred from the catalyst to sensing materials, further enhancing the gas selectivity and response time [16-18]. However, it is known that the gas response of p-type MOS is typically the square root of that of n-type MOS, which severely limits the utilization of p-type MOS for gas sensors [19-21]. To address these limitations, extensive efforts are being made to enhance the gas sensing performance through surface modification, incorporation of catalysts, and formation of p-n heterojunctions [22-24]. Among these approaches, the utilization of p-n heterojunction has been reported to be effective, as the interface between the respective MOS promotes charge transfer and alters the behavior of oxygen vacancies  $(V_0)$  on the surface, which is critical for enhancing the adsorption sites and response through electronic sensitization [18]. Therefore, investigating the decoration of p-type MOS with n-type MOS is essential for further enhancing the selectivity toward VOCs [21].

NiO ( $E_g = 3.6-4.2 \text{ eV}$ ) has been widely investigated due to its high selectivity toward acetone [25,26].  $CeO_2$  ( $E_g = 3.0-3.1 eV$ ) is an n-type rare-earth metal oxide with a unique Ce-4f electronic structure and abundant oxygen vacancies, allowing for reversible charge transfer between  $Ce^{4+}$  and  $Ce^{3+}$  [27]. These properties not only make  $CeO_2$  a notable gas-sensing catalyst for promoting various chemical reactions on surfaces, but also improve the kinetics of the gas sensing response. Moreover, the oxygen vacancies in CeO<sub>2</sub> facilitate easier adsorption and desorption of oxygen ions, further enhancing the gas sensing performance. These characteristics enable CeO<sub>2</sub> to effectively promote the oxidation of acetone, providing rapid and efficient gas sensing [28]. Accordingly, Lee et al. reported that coating CeO<sub>2</sub> onto In<sub>2</sub>O<sub>3</sub> hollow spheres in a layer-by-layer fashion enhanced the acetone sensing ability in humid environments, and the mechanism by which the CeO<sub>2</sub> coating mitigated performance degradation was discussed in detail [29]. Sinha et al. developed NiO/CeO2 p-n heterojunction nanofibers, reporting improved ammonia sensing at room temperature compared with that achieved with pure NiO fibers [28]. However, previous studies have primarily focused on humid or room temperature conditions, with no specific reports addressing the influence of the  $Ce^{3+}/Ce^{4+}$  ratio in  $CeO_2$ catalyst on gas sensing performance.

In this study, CeO2-decorated NiO-based gas sensors were developed to achieve enhanced gas response and selectivity. These effects are further maximized by fabricating nano-dome-like nanostructures using polystyrene (PS) beads as a simple soft-template. The gas sensing properties of the NiO NDs decorated with CeO2 at different thicknesses are investigated at various temperatures (250, 300, 350, and 400 °C) to optimize the operating temperature. When exposed to seven types of gases (CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C<sub>7</sub>H<sub>8</sub>, CO, H<sub>2</sub>, and NO<sub>2</sub>) at 400  $^{\circ}$ C, the CeO2 decorated NiO NDs exhibited a significantly enhanced response to acetone gas, compared with that of NiO NDs. The calculated theoretical detection limits (TDL) are as low as parts-per-billion (ppb) level even in high-humidity environments (80 % relative humidity (RH)) at 400 °C. The underlying mechanism of the gas sensing performance depending on the CeO<sub>2</sub> thickness is explained by the ratio of  $Ce^{3+}/Ce^{4+}$ , originating from electron transfer induced by the p-n junction. These results indicate the strong potential of CeO2-decorated NiO NDs for application in breath analyzers for the noninvasive diagnosis of diabetes.

#### 2. Experimental section

## 2.1. Fabrication of CeO2-decorated NiO nanodomes

Interdigitated electrodes (IDEs) with a width of 50 µm, a spacing of 5 μm, and a total of 20 fingers were created on SiO<sub>2</sub>/Si substrates (2000 Å thickness) using standard photolithography (Fig. S1). The procedure involved forming the electrode pattern, followed by the deposition of a 50 nm chromium (Cr) layer and a 100 nm gold (Au) layer using thermal evaporation. The SiO<sub>2</sub>/Si substrate with the Au/Cr-IDEs pattern was subjected to ultraviolet-ozone (UVO) treatment (AC-6, Ah Tech LTS) for 20 min to render its surface hydrophilic. NiO NDs were fabricated with PS beads (diameter: 500 nm; 5.0 % w/v, SPHERTM Polystyrene Beads, Spherotech) serving as a sacrificial template. The PS beads solution was mixed with ethanol in a 1:1 ratio and concentrated to 10 wt% for applying the Langmuir-Blodgett method. A single PS-beads layer was applied to the Au/Cr-IDEs-patterned SiO<sub>2</sub>/Si substrates by dispensing the mixture onto a glass slide set at an angle of  $45^{\circ}$  within a Petri dish filled with deionized water. For deposition of the NiO thin films and CeO<sub>2</sub> nanoislands (NIs), NiO and CeO<sub>2</sub> grains (99.99 %, Taewon Scientific Co.) were utilized. The crucible was positioned 50 cm below the substrate. Electron beam evaporation was conducted at a glancing angle of 15° and rotation speed of 3 rpm while maintaining a base pressure of  $5 \times 10^{-6}$  Torr and a growth rate of 1 Å/s. The thicknesses of NiO and CeO<sub>2</sub> were calculated using a quartz crystal microbalance (QCM), based on their densities and Z-ratios. The CeO2-decorated NiO NDs were annealed at 550 °C for 1 h under ambient atmosphere to improve their adhesion and crystallinity.

## 2.2. Characterization and gas response measurements

The CeO<sub>2</sub>-decorated NiO NDs were analyzed by field-emission scanning electron microscopy (FE-SEM; JSM-7610 F-Plus, JEOL) and high-resolution transmission electron microscopy (HR-TEM; JEM-ARM 200F NEOARM, JEM-F200, JEOL). The elemental compositions of the fabricated samples were determined by energy-dispersive X-ray spectroscopy (EDS) combined with HR-TEM. XRD patterns were acquired by  $\theta$ -2 $\theta$  scanning using a high-resolution X-ray diffractometer (HR-XRD, Smartlab, Rigaku) with Cu-K<sub> $\alpha$ 1</sub> radiation ( $\lambda$  = 1.54056 Å) under ambient conditions. The surface binding energy spectrum and phase speciation of the material were analyzed through X-ray photoelectron spectroscopy (XPS) using monochromated Cu-K<sub> $\alpha$ 1</sub> radiation ( $h\nu$  = 8047.8 eV) under ambient conditions.

The measurement setup for the gas sensor included a mini-probe chamber equipped with an 8-channel probe system (MPS 4000, PHO-COS) and a mass flow controller (MFC, PHOCOS), with a heating line and bubbling system (Fig. S2). This configuration enabled precise adjustment of gas concentrations from 1 to 50 ppm. The target gases (CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C<sub>7</sub>H<sub>8</sub>, CO, H<sub>2</sub>, and NO<sub>2</sub>, all balanced with dry air, RIGAS) and humidified air were alternately injected in a repeating sequence using an automated gas control system, with both the dry air and the target gases injected at a constant flow rate of 1000 sccm. The 80 % RH condition was achieved by mixing dry air and water vapor. A silicon carbide heater was used to maintain the operating temperature at 250, 300, 350, or 400 °C to assess the gas response at various temperatures. Using a direct current bias of 1 V, the resistance was measured using a source meter (Keithley 237, KEITHLEY), whereas the current was precisely monitored using a high-density switch system (7001 switch system, KEITHLEY). To accurately evaluate the gas responses, the resistance changes were measured at 1 s intervals using the current-voltage solution software program, with the resistances of the samples recorded both in dry air and after full saturation upon exposure to the target gases.

## 3. Results and discussion

#### 3.1. Structural characterization

A schematic of the fabrication procedure is shown in Fig. 1a. Notably, nanostructured gas sensors fabricated using PS beads exhibit significantly improved transducer function and utility factors, as reported in our previous study [30]. The transducer function enables the conversion of electrical signals caused by the adsorption of a target onto the oxide surface into electrical signals, whereas the utility factor is related to the access of the target gas to the inner oxide grains. Accordingly, high-performance nanostructured gas sensors were fabricated with PS beads. Using the Langmuir–Blodgett method, a single PS-beads layer with hexagonal close packing was first formed on UVO-treated substrates with Au IDEs. Afterward, NiO and CeO<sub>2</sub> were sequentially deposited onto the single layer of PS beads via e-beam evaporation. After combustion of the PS beads during annealing, the CeO<sub>2</sub>-decorated, hollow, NiO NDs were obtained.

The SEM micrographs in Fig. 1b—e show the morphology of the CeO<sub>2</sub>-decorated NiO NDs, where CeO<sub>2</sub> with thicknesses of 1, 3, 5, and 10 nm correspond to Fig. 1b-e, respectively. The CeO<sub>2</sub>-decorated NiO NDs were arranged as a single layer with a highly ordered hexagonal close-packed structure and maintained contact with the adjacent NDs. The diameter of each ND was approximately 600 nm, which increased because of the deposition of a 150 nm thick NiO layer on the PS beads. Despite the CeO<sub>2</sub> deposition process, no notable changes in the morphology were observed. After annealing, the PS beads were completely removed, confirming the formation of a hollow structure (insets, Fig. 1b-e). The microstructure and crystallinity of the CeO<sub>2</sub>decorated NiO NDs were characterized by XRD and TEM. XRD was used to investigate the crystallinity of the CeO2-decorated NiO NDs (Fig. 1f-g). The XRD pattern shows distinct peaks at 37.2 and 43.3°, which are attributed to the (101) and (012) planes of NiO (JCPDS No. 00-044-1159), with no significant change in the intensity of the NiO peaks after decoration with CeO2. The presence of multiple peaks indicates that the CeO<sub>2</sub>-decorated NiO NDs are polycrystalline. The peak of CeO2 was observed in the pattern of the 10 nm-CeO2-decorated samples. For confirmation, the range from 24° to 32° was expanded. The CeO<sub>2</sub> (111) peak was first apparent in the pattern of the 5 nm-CeO<sub>2</sub>decorated NiO NDs, consistent with the reference data for CeO2 (JCPDS No. 01-075-0076). The weak peak intensity of CeO<sub>2</sub> observed in the 1 and 3 nm-CeO<sub>2</sub>-decorated NiO NDs can be explained by the formation of CeNi<sub>v</sub>O<sub>v</sub> compounds on the NiO NDs surface. This phenomenon is likely Ce ion doping into the NiO structure. The doping of Ce ion in NiO can change the surface electronic properties, leading to the formation of oxygen vacancies. As the deposition thickness of CeO2 increases, the CeO<sub>2</sub> film transitions to independent growth, as evidenced by the noticeable increase in peak intensity. This growth behavior primarily leads to the formation of nanoisland-like structures on the surface. The characteristic peaks of the NiO NDs are difficult to discern, indicating that the NiO NDs were deposited in a single layer without stacking. To observe the detailed structure of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs, the cross-sectional scanning transmission electron microscopy (STEM) image was acquired (Fig. 1h). When the PS beads (diameter: 500 nm) were completely removed, a hollow structure with a diameter of approximately 600 nm was formed. A distinct contrast layer also appeared on top of the NDs, indicating decoration with a heterogeneous material. To investigate the effect of CeO2 on the NiO NDs, EDS was used to map Ni, O, and Ce (Fig. 1i-k). The EDS analysis proves that NiO was consistently formed in a hollow ND structure, and CeO<sub>2</sub> was uniformly decorated on the surface. The HRTEM and fast Fourier-transform (FFT) images are shown in Fig. 1lm and n-o (NiO and CeO<sub>2</sub>, respectively). The peak position of NiO corresponds to the (111) plane of the NiO cubic phase with a 0.24 nm fringe interval.  $CeO_2$  had a fringe interval of 0.26 nm for  $d_{(200)}$  and 0.16 nm for  $d_{(311)}$ , corresponding to the peaks of the CeO<sub>2</sub> cubic phase, with the zone axis for these planes being [0, 1,

-1]. Additionally, cross-sectional scanning transmission electron microscopy images of all CeO<sub>2</sub>-decorated NiO NDs samples are presented in Fig. S3.

## 3.2. Gas sensing performance

The operational mechanism of p-type MOS gas sensors is based on changes in the hole-accumulation layer (HAL) [31]. In p-type MOS, such as NiO, atmospheric oxygen is adsorbed on the surface, extracting electrons from the p-type MOS and forming ion states, creating an initial HAL on the MOS surface. Depending on the type of target gas, the gas either interacts with surface oxygen ions to donate electrons to the MOS (reducing gas) or removes electrons from the MOS (oxidizing gas). These interactions cause variations in the thickness of the HAL and subsequent changes in the electrical resistance of the MOS. The gas response (S) was evaluated by calculating the ratio of the resistance of the sensor in dry air  $(R_{air})$  to the resistance when exposed to the target gas  $(R_{aas})$ . As a typical reducing gas, CH<sub>3</sub>COCH<sub>3</sub> supplies electrons to the MOS upon adsorption on the surface, leading to a decrease in the resistance of the sensor. As a result, the gas response is calculated using the formula  $(R_{gas}/R_{air} - 1)$  for reducing gases and  $(R_{air}/R_{gas} - 1)$  for oxidizing gases. The formation of the HAL is influenced by the structure of the sensing material, and the p-n junction introduces an additional barrier to hole transfer, both of which directly affect the transducer function by modifying the extent of the HAL. When n-type CeO<sub>2</sub> is decorated on the surface of p-type NiO, electrons are injected from CeO<sub>2</sub> into NiO, which reduces the thickness of the HAL, leading to an increase in  $R_{air}$ . Therefore, the modulation of this p-n junction significantly influences the gas-sensing performance, especially by enhancing the selectivity and response to reducing gases such as CH<sub>3</sub>COCH<sub>3</sub>.

To simultaneously optimize the structural and catalytic effects, the response of the NiO thin film, NiO NDs, and 5 nm-CeO2-decorated NiO NDs to 50 ppm of CH<sub>3</sub>COCH<sub>3</sub> was investigated at an operating temperature of 400 °C (Fig. 2a). The Rair of all samples remained stable, with the 5 nm-CeO\_2-decorated NiO NDs (~3.5 k\Omega), exhibiting the highest resistance, followed in sequence by the NiO NDs ( $\sim$ 0.71 k $\Omega$ ) and NiO thin film (~0.18 kΩ). The increase in  $R_{air}$  observed in moving from the thin film to NDs is attributed to the formation of double Schottky barriers between the NDs, as reported in our previous study [30]. The data suggest that upon CeO2 decoration, p-n junctions with high barrier heights were established between the n-type CeO<sub>2</sub> NIs and p-type NiO, causing an increase in Rair, driven by electronic sensitization. When exposed to CH<sub>3</sub>COCH<sub>3</sub>, the resistance of NiO increased rapidly, indicating that NiO behaves as a p-type semiconductor. To clearly compare the gas-sensing properties, the responses of all the samples to 50 ppm CH<sub>3</sub>COCH<sub>3</sub> are presented in Fig. 2b. The responses of the NiO thin film, NiO NDs, and CeO<sub>2</sub>-decorated NiO were 1.6, 3.5, and 25.4, respectively. Notably, the response of the CeO2-decorated NiO NDs was about 7.3 times higher than that of the NiO NDs. This difference demonstrates that the gas-sensing properties of the CeO2-decorated NiO NDs were significantly enhanced by structural and catalytic effects.

The gas response is closely associated with the number of oxygen ions adsorbed on the metal-oxide surface [32]. As the operating temperature increases, the oxygen ions ( $O_2$ ,  $O^-$ , and  $O^{2-}$ ) adsorbed on the CeO<sub>2</sub>-decorated NiO NDs determine  $R_{air}$  [13]. The thickness of the CeO<sub>2</sub> layer affects both the catalytic effect and gas adsorption area of NiO, which modulates the adsorption of oxygen ions. Therefore, to identify the optimal thickness of CeO<sub>2</sub> for decoration, and the most effective operating temperature, the response of the NiO NDs decorated with CeO<sub>2</sub> of varying thicknesses (1, 3, 5, and 10 nm) to 50 ppm CH<sub>3</sub>COCH<sub>3</sub> at 250, 300, 350, and 400 °C was measured. The real-time resistance is graphically represented in Fig. 2c–f. The decrease in  $R_{air}$  for all samples as the operating temperature increased indirectly indicates that higher temperatures lead to enhanced adsorption of oxygen ions, which subsequently leads to the generation of more holes in NiO structure. The response of all samples was highest at 400 °C, which supports the



**Fig. 1.** (a) Schematic of procedures for fabricating CeO<sub>2</sub>-decorated NiO NDs. SEM images of CeO<sub>2</sub>-decorated NiO NDs with different thicknesses of CeO<sub>2</sub>; (b) 1 nm, (c) 3 nm, (d) 5 nm, and (e) 10 nm, with cross-sectional views shown in the insets. XRD patterns of (f) NiO NDs and CeO<sub>2</sub>-decorated NiO NDs with 1, 3, 5, and 10 nm, with a magnified view of the selected area shown in (g). (h) Cross-sectional transmission electron microscopy (TEM) image of CeO<sub>2</sub>-decorated NiO NDs. EDS mapping of 5 nm-CeO<sub>2</sub>-decorated NiO NDs displaying the distribution of (i) Ni, (j) O, and (k) Ce. (l—o) HR-TEM images of NiO and CeO<sub>2</sub> with FFT shown in the insets.



**Fig. 2.** (a) Resistance curves of NiO TF, NiO NDs, and 5 nm-CeO<sub>2</sub>-decorated NiO NDs exposed to 50 ppm  $CH_3COCH_3$  at 400 °C. (b) Gas response of NiO TF, NiO NDs, and 5 nm-CeO<sub>2</sub>-decorated NiO NDs to 50 ppm  $CH_3COCH_3$  at 400 °C. Resistance curves for 50 ppm  $CH_3COCH_3$  as a function of thickness of CeO<sub>2</sub> layer decorated on NiO NDs, at different temperatures; (c) 250 °C, (d) 300 °C, (e) 350 °C, and (f) 400 °C. Gas response for 50 ppm  $CH_3COCH_3$  as a function of thickness of CeO<sub>2</sub> layer decorated on NiO NDs, at different temperatures; (g) 250 °C, (h) 300 °C, (i) 350 °C, and (j) 400 °C.

increased adsorption of oxygen ions as a result of the elevated thermal energy (Fig. 2g—j). The gas response increased progressively with increasing CeO<sub>2</sub> thickness, reaching an optimal value at 5 nm, followed by a decrease at 10 nm. The 5 nm-CeO<sub>2</sub>-decorated NiO NDs demonstrated the highest response across all operating temperatures, with response values of 2.4, 4.1, 11.7, and 25.4 at 250, 300, 350, and 400 °C, respectively. The specific operating mechanism is explained in detail in

the following section.

To explore the gas selectivity of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs, the response to 10 ppm of various target gases (CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C<sub>7</sub>H<sub>8</sub>, CO, H<sub>2</sub>, and NO<sub>2</sub>) was measured at 400 °C under dry conditions. Fig. 3a—g show the real-time resistance curves of the NiO NDs and 5 nm-CeO<sub>2</sub>-decorated NDs for each target gas, for comparison. The decrease in resistance upon exposure to NO<sub>2</sub>, an oxidizing gas,



Fig. 3. (a–g) Resistance curves and (h) gas response of NiO NDs and 5 nm-CeO<sub>2</sub>-decorated NiO NDs under dry condition, exposed to 10 ppm of various gases (CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C<sub>7</sub>H<sub>8</sub>, CO, H<sub>2</sub>, and NO<sub>2</sub>) at 400 °C. (i–o) Resistance curves and (p) gas response of NiO NDs and 5 nm-CeO<sub>2</sub>-decorated NiO NDs under 80 % RH condition, exposed to 10 ppm of various gases at 400 °C.

further confirms that the NiO NDs function as a p-type sensing material. The responses of the NiO NDs to CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C<sub>7</sub>H<sub>8</sub>, CO, H<sub>2</sub>, and NO<sub>2</sub> gas were 1.6, 2.0, 1.0, 2.1, 0.53, 0.34 and 0.19, respectively (Fig. 3h). The NiO NDs could detect each target gas, but the gas response was in a similar range (0.2—2.1), resulting in low gas selectivity. On the other hand, the response of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs generally increased for all gases, compared with the response of the NiO NDs. Specifically, the gas responses were 10.3, 8.2, 4.4, 2.8, 1.3, 1.1 and 0.23, respectively, exhibiting high gas selectivity to CH<sub>3</sub>COCH<sub>3</sub>. To verify the humidity-resistant gas-sensing capability, all sensors were exposed to each target gas at 400 °C under 80 % RH conditions (Fig. 3i-o). The  $R_{air}$ 

value significantly increased in humid atmospheres (e.g., ~2.9 k $\Omega$  in dry, ~12.1 k $\Omega$  at 80 % RH, both at 400 °C), which were attributed to adsorption of water molecule at the surface of metal oxide sensing layer. Water molecules occupy the active site on oxide surface, thereby reducing oxygen ion adsorption. As a result, the thickness of HAL layer of the p-type NiO decreases, leading to an increase in the baseline resistance,  $R_{air}$ . The decrement of surface oxygen adsorption and competitive reaction of acetone and water molecule reduce the gas response [33,34]. Therefore, the overall response to each target gases also decreased in humid condition. This humidity-induced decrease in gas response was found to occur progressively as the relative humidity

increased (Fig. S4). These observations are typical properties associated with humidity dependence in p-type MOS-based gas sensors such as CuO and  $Co_3O_4$  [35,36]. Notably, even under a high relative humidity of 80 %, our gas sensor maintained a gas response that was 33 % of that in dry air, and it also exhibited high selectivity compared to other interfering gases (Fig. 3p).

Fig. 4a, b displays the summarized gas responses of the NiO NDs and 5 nm-CeO2-decorated NiO NDs in a polar plot at 400 °C under dry and 80 % RH conditions. The response to CO, H<sub>2</sub>, and NO<sub>2</sub> remains low across all sensors due to their limited reactivity. Among the target gases, NiO NDs showed the highest response to C7H8, followed by C2H5OH and CH<sub>3</sub>COCH<sub>3</sub>. Notably, the 5 nm-CeO<sub>2</sub>-decorated NiO NDs exhibited the highest response to CH<sub>3</sub>COCH<sub>3</sub>. To verify the effect of CeO<sub>2</sub> deposition on the response to each gas species, the ratio  $(S_b/S_a)$  of the response of the NiO NDs ( $S_a$ ) to that of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs ( $S_b$ ) was calculated, clearly showing that CeO<sub>2</sub> deposition has the most significant effect on improving the detection of CH<sub>3</sub>COCH<sub>3</sub> (Fig. 4c). CH<sub>3</sub>COCH<sub>3</sub> recorded the highest  $S_b/S_a$  ratios of 6.5 and 2.3 at 400 °C under dry and 80 % RH conditions, respectively. To evaluate the chemical sensitization provided by decoration of the CeO<sub>2</sub>, the response times ( $t_{res}$ , defined as the time required to reach 90 % of the maximum response upon target gas injection) for 10 ppm of CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C7H8, CO, H2, and NO2 were determined, as summarized in Fig. 4d. The response times of the CeO2-decorated NiO NDs to CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, HCHO, C<sub>7</sub>H<sub>8</sub>, CO, H<sub>2</sub>, and NO<sub>2</sub> gases were approximately 295, 232, 210, 131, 120, 244 and 460 s, whereas the NiO NDs showed longer response times of 357, 265, 298, 145, 145, 339 and 486 s, respectively. Specifically, in the case of CH<sub>3</sub>COCH<sub>3</sub>, for which the 5 nm-CeO<sub>2</sub>-decorated NiO NDs demonstrated the highest increase in response, the response time decreased by approximately 87 s because CeO<sub>2</sub> facilitated the reaction with adsorbed oxygen on NiO surface, attributed to chemical sensitization (Fig. 4e, f). To improve gas selectivity, principal component analysis (PCA) was conducted based on five features, including Rair, Rgas, S, tres, and recovery time (trec, defined as the time required to reach 90 % of the baseline resistance upon air injection) of two curves for 10 ppm of each target gas (Fig. S5). The points for each gas were clearly distinguished, forming clusters that enable target gas identification.

For potential integration into breath analysis devices, the gas sensor requires both reliability and long-term stability. The 5 nm-CeO2-decorated NiO NDs were repeatedly exposed to dry air and 50 ppm of CH<sub>3</sub>COCH<sub>3</sub> over 15 cycles (Fig. 4g). During 15 cycles, the 5 nm-CeO<sub>2</sub>decorated NiO NDs exhibited a significantly smaller coefficient of variation (CV) value (0.94 %) in response, which represents the ratio of the standard deviation ( $\sigma$ ) to the mean ( $\mu$ ), calculated as  $CV = (\sigma/\mu) \times 100$ . This relatively low CV value confirms the highly reliable detection of CH<sub>3</sub>COCH<sub>3</sub> by the fabricated sensor, compared to commercial gas sensors, which typically exhibit CV values between 16.7 % and 41 % [37, 38]. Moreover, to investigate long-term stability, the response of 5 nm CeO<sub>2</sub>-decorated NiO NDs to 1 ppm CH<sub>3</sub>COCH<sub>3</sub> was measured six months after fabrication over eleven cycles (Fig. S6). After 6 months, the 5 nm CeO2-decorated NiO NDs retained approximately 82 % of their initial response (1.95–1.59), with a  $\sim$ 10 % reduction in response time showing no significant change and a notably low CV value of 3.5 %.

To confirm the trace-level gas-sensing capability, the TDL of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs was calculated. The responses of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs to 1—5 ppm CH<sub>3</sub>COCH<sub>3</sub> gas were measured under both dry and 80 % RH conditions at 400 °C to evaluate the concentration-dependence of the gas response (Fig. 4h, i). The TDL of the 5 nm-CeO<sub>2</sub>-decorated NiO NDs was calculated according to the following equation:

$$R_{x^2} = \sum (y_i - y)^2$$
 (1)

$$RMS_{noise} = \sqrt{\frac{R_{x^2}}{N}}$$
(2)

$$TDL = 3 \frac{RMS_{Noise}}{Slope}$$
(3)

 $y_i$  refers to the normalized resistance in the response curve prior to CH<sub>3</sub>COCH<sub>3</sub> exposure, and y represents the average of  $y_i$ . The  $R_{y^2}$  value was derived from a fifth-order polynomial fit applied to ten data points obtained from  $y_i$ . Here, RMS<sub>Noise</sub> represents the root mean square of the noise within the electrical resistance of the sensor under air exposure, and the slope is determined by extrapolating the linear relationship between the gas response and concentration (inset of Fig. 4h,i). The gas response of the 5 nm-CeO2-decorated NiO NDs gas sensor was proportional to the CH<sub>3</sub>COCH<sub>3</sub> concentration in the target range. The calculated TDL of the 5 nm-CeO2-decorated NiO NDs was 0.47 and 5.6 ppb at 400 °C under dry and 80 % RH conditions, respectively. In particular, the low detection limit under humid conditions, which has not been explored in previous studies, demonstrates the potential applicability of our sensor under humidity levels similar to real-world environments. To evaluate the potential of our CeO2-decorated NiO NDs gas sensor for CH<sub>3</sub>COCH<sub>3</sub> sensing in diabetes diagnosis, we exposed our gas sensors under 250 ppb of CH<sub>3</sub>COCH<sub>3</sub> gas condition (typical breath concentration: 0.3-0.9 ppm in healthy individuals, > 1.8 ppm in diabetic patients). Our gas sensor exhibited a mean gas response of 0.65 with five repeated gas exposure and a low CV value of 1.11 %, demonstrating its capability for reliable ppb-level CH<sub>3</sub>COCH<sub>3</sub> detection (Fig. S7). Consequently, the 5 nm CeO2-decorated NiO NDs exhibited excellent gas sensing performances for CH<sub>3</sub>COCH<sub>3</sub> gas compared to previously reported NiO-based CH<sub>3</sub>COCH<sub>3</sub> sensors, highlighting its potential as a promising candidate for exhaled breath sensors in non-invasive diabetes diagnosis (Table S1) [32,39-47].

## 3.3. Characterization of surface chemical states

To elucidate the role of CeO2 in gas-sensing using the CeO2-decorated NiO NDs, the atomic states of CeO2 and NiO were comprehensively analyzed using XPS, where the thickness of the deposited CeO<sub>2</sub> was varied (Fig. 5). The Ni 2p spectra of the NiO NDs and CeO<sub>2</sub>-decorated NiO NDs with different CeO<sub>2</sub> thicknesses are presented in Fig. 5a. Specifically, the peaks at 853.8 and 855.8 eV in the Ni 2p<sub>3/2</sub> region are assigned to  $Ni^{2+}$  and  $Ni^{3+}$ , respectively [48]. The other peaks at 860.6 and 864.5 eV are Ni satellite peaks. Significantly, the Ni 2p peak shifted toward a lower binding energy after CeO<sub>2</sub> deposition. This pronounced binding-energy shift is attributed to electron transfer from n-type CeO<sub>2</sub> to p-type NiO, resulting in the formation of p-n heterojunctions at the interfaces. The shift in the binding energy was largest with the deposition of 3 nm thick CeO<sub>2</sub> (0.66 eV, decreased as the CeO<sub>2</sub> thickness increased). Fig. 5b shows the Ce 3d spectra of the NiO NDs and CeO2-decorated NiO NDs. Nine characteristic peaks were observed in the Ce 3d spectrum, including the Ni satellite peak at 879.3 eV. These peaks were observed in the Ce 3d spectrum of the CeO2-decorated NiO NDs. The other peaks in the Ce 3d spectra at 881.7, 884.9, 884.5, 897.9, 900.4, 902.9, 907.0, and 916.1 eV (Fig. 5b) are assigned as v, v', v'', v'' u, u', u'', and u''' peaks, respectively [49]. The v-series peaks are assigned to Ce<sup>3+</sup>, and the u-series peaks correspond to the Ce<sup>4+</sup> state. As the thickness of CeO2 increased, the peak height and area also increased. The valence states of Ni and Ce were determined from the Ni 2p and Ce 3d spectra. The Ni (Ni<sup>3+</sup>/Ni<sup>2+</sup>) and Ce ion (Ce<sup>3+</sup>/Ce<sup>4+</sup>) ratios in the NiO NDs and CeO2-decorated NiO NDs were calculated. With the deposition of 1 nm thick CeO<sub>2</sub>, the interaction between Ce and NiO led to the formation of CeNi<sub>x</sub>O<sub>v</sub>-like structure at the interface, resulting in a decrease in the Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio compared to that of the NiO NDs. Surprisingly, as the thickness of the deposited  $CeO_2$  increased, the Ni<sup>3+</sup> ion ratio increased until 5 nm of CeO2 was deposited, suggesting electron transfer from the Ni to Ce ions. The data in Fig. 5a confirm that the binding-energy shift for Ni 2p was largest with the deposition of 3 nm  $CeO_2$  (-0.66 eV) and was reduced with even thicker (5 and 10 nm)  $CeO_2$ (-0.61 and -0.39 eV, respectively), which is consistent with this result.



**Fig. 4.** Polar plot showing the response of (a) NiO NDs and (b) 5 nm-CeO<sub>2</sub>-decorated NiO NDs to 10 ppm of various gases under dry and 80 % RH condition at 400 °C. (A: CH<sub>3</sub>COCH<sub>3</sub>, E: C<sub>2</sub>H<sub>5</sub>OH, F: HCHO, T: C<sub>7</sub>H<sub>8</sub>, C: CO, H: H<sub>2</sub>, and N: NO<sub>2</sub>) (c) Response ratio ( $S_b/S_a$ ) for NiO NDs versus CeO<sub>2</sub>-decorated NiO NDs.  $S_a$  and  $S_b$  represent gas responses of NiO NDs and 5 nm-CeO<sub>2</sub>-decorated NiO NDs, respectively. (d) Enhanced chemical sensitization was realized by decorating CeO<sub>2</sub> onto NiO NDs. (e—f) Response time ( $t_{90}$ %) of NiO NDs and 5 nm-CeO<sub>2</sub>-decorated NiO NDs, respectively. (g) Resistance curves of 5 nm CeO<sub>2</sub>-decorated NiO NDs to CH<sub>3</sub>COCH<sub>3</sub> at 400 °C measured over 15 cycles, toward 1, 2, 3, 4, and 5 ppm CH<sub>3</sub>COCH<sub>3</sub> at 400 °C under (h) dry air and (i) 80 % RH (Inset: response of 5 nm CeO<sub>2</sub>-decorated NiO NDs as a function of CH<sub>3</sub>COCH<sub>3</sub> concentration under, including the calculated theoretical detection limit (TDL)).



**Fig. 5.** XPS profiles of NiO NDs and CeO<sub>2</sub>-decorated NiO NDs with different CeO<sub>2</sub> thickness. (a) Ni 2p, (b) Ce 3d, and (c) O1s spectra of pristine NiO NDs and 1, 3, 5 and 10 nm CeO<sub>2</sub>-decorated NiO NDs. (d) Ni<sup>3+</sup>/Ni<sup>2+</sup> and Ce<sup>3+</sup>/Ce<sup>4+</sup> ion ratio of pristine NiO NDs and 1, 3, 5, and 10 nm-CeO<sub>2</sub> decorated NiO NDs.

Notably, this type of electron transfer is in the opposite direction of the initial electron transfer (n-type CeO<sub>2</sub> to p-type NiO). The valence states of the oxygen species in the NiO NDs and CeO2-decorated NiO NDs were also determined from the O1s spectra (Fig. 5c). Three peaks were present in the O1s spectra, which are assigned to lattice oxygen in the oxide (529.4 eV), adsorbed oxygen ions (oxygen defects) (531.5 eV), and surface hydroxyl groups (532.4 eV). The atomic ratios of each oxygen state are summarized in Table 1, with the highest surface oxygen ratio observed for the 5 nm-CeO $_2$  decorated NiO (O $_{surface}/O_{lattice} = 0.76$ ), contributing to the enhanced gas response due to the oxygen-defective surface. As the thickness of the CeO<sub>2</sub> increased, the atomic ratio of the adsorbed oxygen ions increased. The atomic ratio of the Ni and Ce ions was calculated according to the Ce thickness. The  $Ce^{3+}/Ce^{4+}$  ratio increased as the thickness of the CeO<sub>2</sub> layer increased, indicating an increase in the number of oxygen defects in the CeO<sub>2</sub> NIs. Therefore, initially, the introduction of Ce atoms promoted electron transfer to the

## Table 1

Oxygen states and  $O_{\rm surface}/O_{\rm lattice}$  ratio of CeO\_2-decorated NiO NDs. The oxygen contents calculated from O1s spectra.

Thickness of CeO <sub>2</sub>	Lattice Oxygen (at%)	Surface O <sup>2-</sup> (defect) (at%)	Surface water (at%)	O <sub>surface</sub> / O <sub>lattice</sub>
1 nm	0.514	0.303	0.184	0.59
3 nm	0.516	0.325	0.158	0.63
5 nm	0.478	0.364	0.158	0.76
10 nm	0.504	0.322	0.174	0.64

NiO NDs, where Ce acted as a dopant. However, as the CeO<sub>2</sub> particles gradually formed, oxygen defects were generated in CeO<sub>2</sub>, which increased the Ce<sup>3+</sup>/Ce<sup>4+</sup> ion ratio. With 10 nm Ce decoration, the Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio decreased because of the decrease in the surface area of CeO<sub>2</sub> with larger CeO<sub>2</sub> NIs.

## 3.4. Role of CeO<sub>2</sub> as a catalyst in acetone sensing

CeO<sub>2</sub> deposition improved the acetone-sensing characteristics of the NiO NDs; the mechanisms are shown in Fig. 6. The NDs structure clearly improved the gas sensing performance due to electronic sensitization, as demonstrated in our previous studies [30]. As shown in Fig. 6a, the overall resistance of the sensor consists of the contact resistance ( $R_c$ ) at the electrodes and the resistance of the individual NDs ( $R_{ni}$ ), including the potential barriers between the NDs, which are modulated when the sensor is exposed to the target gas [50]. When CeO<sub>2</sub> NIs were decorated onto NiO NDs, an initial p–n junction forms a depletion region at the surface of NiO, which leads to a reduction in the thickness of the HAL, as shown in the band diagram of the CeO<sub>2</sub>-decorated NiO NDs before and after junction formation (Fig. S8). Thus, the sample with CeO<sub>2</sub> decoration exhibited the maximum potential barrier due to the formation of a NiO–CeO<sub>2</sub> p–n junction.

The expansion of the depletion region resulting from  $\text{CeO}_2$  decoration is also reflected in the  $R_{air}$  values in Fig. 2a. The diminished thickness of the HAL amplifies the gas response of the NiO NDs to changes in the electrical resistance induced by the adsorption of oxygen ions and the subsequent gas reaction at the surface of the NiO NDs. As





the thickness of the CeO<sub>2</sub> decoration increases, the depletion region expands; however, there is a trade-off as the surface area of NiO available for gas interactions decreases (Fig. 6b). This balance results in a specific thickness at which the catalytic effect is optimized. In the present experiments, the response progressively improved when the thickness of the CeO2 decoration was increased from 1 to 5 nm. However, when the CeO2 thickness was further increased to 10 nm, the response decreased. Additionally, measurement of Rair for the NiO NDs decorated with CeO<sub>2</sub> at each thickness showed that the highest resistance was observed with the 5 nm CeO<sub>2</sub> decoration, whereas the lowest resistance was recorded with the 10 nm thick CeO<sub>2</sub> decoration. These observations can be explained by two effects: (1) CeO2 NIs form additional current paths, and (2) the depletion regions were not overlapped due to the large size of the NIs, limiting the catalytic effects of CeO<sub>2</sub>, indicating that the optimal thickness for maximizing the catalytic effect is 5 nm [51].

decorated NiO NDs with various  $Ce^{3+}/Ce^{4+}$  ratios, showing the formation of the depletion layer.

Furthermore, the ionic state of Ce varied with the thickness of the CeO<sub>2</sub> decoration, which in turn affected the catalytic effect. As previously described, the Ni 2p and Ce 3d XPS profiles revealed significant shifts in the binding energies of the Ni ions with varying CeO<sub>2</sub> thickness. These shifts indicate electron transfer from n-type CeO<sub>2</sub> to p-type NiO,

forming a p–n heterojunction that expands the depletion region and increases the electrical resistance. As the thickness of the CeO<sub>2</sub> layer increased, the Ni<sup>3+</sup>/Ni<sup>2+</sup> and Ce<sup>3+</sup>/Ce<sup>4+</sup> ratios changed, where the most pronounced effects were observed with the deposition of 5 nm thick CeO<sub>2</sub>. These observations suggest a complex interaction between the Ni and Ce ions at the interface, which influences the gas-sensing properties of the material. Collectively, the reaction between Ni and Ce ions plausibly occurs at the interface of CeO<sub>2</sub> and the NiO NDs, as described by the following equation:

$$Ni^{2+} + Ce^{4+} \rightarrow Ni^{3+} + Ce^{3+}$$
 (4)

This type of redox reaction has been reported in previous studies of Ni decoration on a CeO<sub>2</sub> support [48,49]. The incorporation of Ni<sup>2+</sup> from the surface of NiO with Ce<sup>4+</sup> in CeO<sub>2</sub> at the interfaces generated Ni<sup>3+</sup> and Ce<sup>3+</sup> ions through a redox equilibrium. The increase in the content of Ce<sup>3+</sup> in CeO<sub>2</sub> signifies an oxygen-defective structure in CeO<sub>2</sub>. These oxygen defects on the CeO<sub>2</sub> surface behave as active sites for oxygen ion-binding, as described by the following equation:

$$O_{\nu} + O_{2(g)} \rightarrow O_2^- + O_{\nu}^{\bullet} \tag{5}$$

$$2O_{\nu} + O_{2(q)} \rightarrow O_{2}^{2-} + 2O_{\nu}^{\bullet} \rightarrow 2O_{2}^{-} + 2O_{\nu}^{\bullet}$$

wherein  $O_v^{\bullet}$  represents a single electropositive oxygen defect [52,53].

As a result, the interfacial redox reaction between NiO and CeO<sub>2</sub> promotes the formation of oxygen defects and increases the amount of surface-adsorbed oxygen ions, thereby enhancing surface reaction with target gases, especially for reducing gases such as  $CH_3COCH_3$  and  $C_2H_5OH$ .

Simultaneously, the Ni surface became oxygen-rich, showing the hydroxyl scavenging effect of CeO<sub>2</sub> with the adsorption of oxygen ions on the support metal oxide. The variation trends for the Ni and Ce ion ratios are consistent with the experimental results, reaching a maximum value when CeO<sub>2</sub> is deposited at a thickness of 5 nm, with the ratio reaching 0.48. Therefore, the 5 nm-CeO<sub>2</sub>-decorated NiO NDs exhibited the highest gas response due to the large amount of Ce<sup>3+</sup> on the surface of CeO<sub>2</sub>. In addition, the hydroxyl scavenging effect of CeO<sub>2</sub> reduces the surface hydroxyl groups, enabling humidity-resistant gas sensing, as confirmed by the data in Fig. 4h.

In summary, CeO<sub>2</sub> deposition initially formed a p–n heterojunction at the surface of the NiO NDs, making the NiO NDs sensitive to resistance changes. Upon increasing the thickness of CeO<sub>2</sub> to 5 nm, CeO<sub>2</sub> became oxygen-defective due to the incorporation of Ni<sup>2+</sup> into the NiO NDs. The oxygen defects enhanced the adsorption of oxygen ions on the surface, leading to an increase in the gas response. In addition, CeO<sub>2</sub> deposition removed surface hydroxyl groups, enabling humidity-resistant gas sensing.

#### 4. Conclusions

The development of CeO2-decorated NiO NDs was proven to be highly effective in enhancing the selectivity and response for acetone detection, which is critical for applications such as non-invasive diagnosis. Decoration of 5 nm CeO2 on the NiO NDs provided optimal gas sensing performance, significantly improving acetone detection even in high-humid environments. This enhancement in the gas-sensing performance is attributed to the reversible transition between the  $Ce^{3+}/$ Ce<sup>4+</sup> states in CeO<sub>2</sub> on the NiO NDs, which promoted the formation of oxygen vacancies on the NiO surface. The CeO2-decorated NiO NDs sensor achieved a low detection limit of 5.6 ppb at 400 °C under humid conditions (80 % RH), making it suitable for breath analysis for the diagnosis of diabetes. The developed strategy employing an unconventional n-type MOS decorated on a p-type MOS-based sensor demonstrates strong potential for next-generation breath analyzers, offering a low-cost, non-invasive solution for the real-time monitoring of diabetes biomarkers.

## CRediT authorship contribution statement

Jae Han Chung: Writing – original draft, Investigation, Data curation. Jinho Lee: Writing – review & editing, Supervision, Conceptualization. Hyeon Jae Kim: Investigation, Data curation. Jung Hwan Seo: Writing – review & editing, Supervision, Conceptualization. Junho Hwang: Writing – original draft, Investigation, Data curation. Young-Seok Shim: Writing – review & editing, Supervision, Conceptualization. Kwangjae Lee: Resources, Methodology. Donghwi Cho: Resources, Methodology. Seong-Jun Ro: Resources, Methodology. Hyojung Kim: Methodology, Investigation. Yun-Haeng Cho: Methodology, Investigation. Sungwoo Sohn: Methodology, Investigation. Wooyoung Lee: Writing – review & editing, Supervision, Conceptualization. See-Hyung Park: Investigation, Data curation.

## **Conflict of Interest**

The authors declare no competing interests.

## **Declaration of Competing Interest**

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jung Hwan Seo reports financial support was provided by Hongik University. Wooyoung Lee reports was provided by Yonsei University. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

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This research was supported by the National Research Foundation of Korea (NRF) grant, funded by the Korean Government (MIST) (NRF-2022M3H4A3053304, National Core Materials Research Center (Platform type)). This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2021M3H4A3A02099204). This research was supported by the Technology Innovation Program (20013621) under the Center for Super Critical Material Industrial Technology funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This research was supported by a grant of Research and Development Program under the National Fire Agency (RS-2024-00404040) funded by Ministry of the Interior and Safety of Korea (MOIS, Korea).

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2025.138070.

#### Data availability

Data will be made available on request.

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Junho Hwang received a Master's degree in the Department of Mechanical Design Engineering from Kookmin University in 2018. Since 2020, He is currently a Ph.D. candidate in the Department of Materials Science and Engineering at Yonsei University under the supervision of Prof. Wooyoung Lee. His research focuses on micro/nanostructured materials and their large-area synthesis methods for gas sensing applications.

Jae Han Chung is a combined bachelor-master's candidate under the supervision of Prof. Young-Seok Shim at School of Energy, Materials & Chemical Engineering at Korea University of Technology & Education (KOREATECH). His research interests are the fabrication of nanostructured metal oxide and their applications to various devices including sensor and electrochromic devices.

Hyeon Jae Kim received a Bachelor's degree in the advanced material engineering at Silla University in 2023. Since 2023, He is currently a M. S. candidate in the School of Energy, Materials & Chemistry Engineering at Korea University of Technology & Education (KOREATECH). under the supervision of Prof. Young-Seok Shim. His research focuses on micro/nanostructured materials and their large-area synthesis methods for gas sensing applications.

See-Hyung Park received a Bachelor's degree in the advanced material engineering at Silla University in 2023. Since 2023, He is currently a M. S. candidate in the School of Energy, Materials & Chemistry Engineering at Korea University of Technology & Education (KOREATECH). under the supervision of Prof. Young-Seok Shim. His research focuses on micro/nanostructured materials and their large-area synthesis methods for gas sensing applications.

Yun-Haeng Cho is currently a combined bachelor-master's candidate in the School of Energy, Materials & Chemical Engineering at Korea University of Technology & Education (KOREATECH) under the supervision of Prof. Young-Seok Shim. His research focuses on micro/nanostructured materials and their large-area synthesis methods for gas sensing applications.

**Sungwoo Sohn** received a bachelor's degree in the School of Energy, Materials & Chemical Engineering at Korea University of Technology & Education (KOREATECH) in 2023. Since 2023, He is currently a M. S. candidate in the Department of Materials Science and Engineering at Yonsei University under the supervision of Prof. Wooyoung Lee. His research focuses on micro/nanostructured materials and their large-area synthesis methods for gas sensing applications.

**Seong-Jun Ro** received a Bachelor's degree in the Department of Information Security Engineering in Sangmyung University. He is currently a M. S. candidate in the Department of Information Security Engineering in Sangmyung University. under the supervision of Prof. Kwangjae Lee.

**Hyojung Kim** received his Ph.D. degree from Department of Materials Science and Engineering at Seoul National University. Now she is a assistant professor of Department of Semiconductor Systems Engineering in Sejong University. **Kwangjae Lee** received his Ph.D. degree from Department of Electrical and Computer Engineering of Korea University in 2014. Now he is a professor of Department of Information Security Engineering in Sangmyung University, since 2017.

**Donghwi Cho** is a senior researcher of the Advanced Materials Division at the Korea Research Institute of Chemical Technology (KRICT) in Korea (2021~present). He is also the assistant professor of Advanced Materials and Chemical Engineering at the University of Science and Technology in Korea (2024~present). Before joining KRICT, He received his Ph.D. degree in Materials Science and Engineering at KAIST in 2020 and started to work at Querrey Simpson Institute for Bioelectronics of Northwestern University as a postdoctoral associate (2020–2021). His research topic spans various domains, including 3D nanopatterning, nanoarchitectonics of functional materials, and development of the advanced bioelectronic systems. He has published over 40 international publications.

Jung Hwan Seo received his B.S. from SNU, and M.S. and Ph.D from University of Michigan. He is currently an Associate Professor in the Hongik University. His research interests are gas phase micro-analytical system and MEMS devices for healthcare applications.

Young-Seok Shim is currently an Assistant Professor in the School of Energy, Materials & Chemical Engineering at Korea University of Technology & Education (KOREATECH), Korea since 2022. Before joining the KOREATECH, he was an Assistant Professor at Silla University (2020–2022). He received his Ph.D. (2016) degree in the Department of Materials Science & Engineering from Yonsei University, Korea. From 2016 to 2017, he was a postdoctoral research associate at the Electronic Materials Center at Korea Institute of

Science & Technology (KIST). From 2018–2020, he joined in the Department of Materials Science & Engineering at Korea Advanced Institute of Science and Technology (KAIST) as a postdoctoral researcher. His research interests are micro/nanostructured materials and their large-area synthesis methods for gas sensing applications. He has published more than 60 international journal articles (SCI indexed).

Jinho Lee received his Ph.D. degree from Department of Materials Science and Engineering at Korea Advanced Institute of Science and Technology (KAIST) in 2023. He is currently working as a post-doctoral fellow in Department of Materials Science and Engineering at Korea Advanced Institute of Science and Technology (KAIST).

**Wooyoung Lee** is the Underwood distinguished professor of the Department of Materials Science and Engineering at Yonsei University in Korea. He is also the Director of the Center for Super Critical Material Industrial Technology, National Core Materials Research Center and the institute of Korea Initiative for Fostering University of Research and Innovation. He is the President of The Korean Magnetics Society and a regular member of the National Academy of Engineering of Korea. In recent years, his research interests have centered on hydrogen sensors, various metal oxide semiconducting gas sensors, and breath analyzers. He is also studying rare-earth permanent magnets and thermoelectric materials and devices. He has received a number of awards in nano-related research areas including a Prime Minister Award (2023) in Nano Korea 2023, SeAH-Haiam Fellowship Award (2018) in The Korean Institute of Metals and Materials and a Service Merit Medal (2008) from the Government of Korea due to his contribution to the development of intellectual properties. He has authored and co-authored over 280 publications and has edited three special books on nanostructured materials and devices.