A General Solution to Mitigate Water Poisoning of Oxide Chemiresistors: Bilayer Sensors with Tb$_4$O$_7$ Overlayer

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Water poisoning, the dependence of gas-sensing characteristics on moisture, in oxide chemiresistors remains a long-standing challenge. Various approaches are explored to mitigate water poisoning but they are often accompanied by significant deterioration of sensing capabilities such as gas response deterioration, gas selectivity alteration, and sensor resistance increase up to unmeasurable levels. Herein, a novel sensor design with a moisture-blocking Tb$_4$O$_7$ overlayer is suggested as a facile and universal strategy to remove moisture poisoning without sacrificing intrinsic sensing properties. A submicrometer-thick coating of Tb$_4$O$_7$ overlayer on In$_2$O$_3$ sensors effectively eliminates the humidity dependence of the gas-sensing characteristics without significantly altering the gas response, selectivity, and sensor resistance. Furthermore, the general validity of the water-blocking effect using the Tb$_4$O$_7$ overlayer is confirmed in diverse gas sensors using SnO$_2$, ZnO, and Pd/SnO$_2$. The negligible moisture interference of the bilayer sensor is explained in terms of the hydrophobic nature of the Tb$_4$O$_7$ overlayer and the prevention of formation of the —OH radical by the interaction between Tb$_4$O$_7$ and In$_2$O$_3$. A universal solution to design diverse humidity-independent gas sensors with different gas selectivities can open up new pathways toward building accurate and robust gas sensors with new functionalities and high-performance artificial olfaction.

1. Introduction

Water vapor is an inevitable and strong interfering gas for oxide semiconductor gas sensors. Thus the water poisoning of sensors has been a major impediment to reliable gas sensing during the past six decades.[1–6] There are three key reasons why the mitigation of moisture interference on gas-sensing behaviors remains challenging. First, the typical water vapor concentration in the atmosphere is extremely high (e.g., 1207–62604 ppm for relative humidity [RH] 20% at 0 °C to RH 80% at 38 °C), whereas oxide chemiresistors usually detect several tens of ppm or sub-ppm-levels of toxic, harmful, and explosive gases (Figure 1a). Second, the ambient moisture dynamically changes according to the climate, weather, season, day/night, temperature, and location (Figure 1b). Third, the water vapor consumes the active sensing sites (O$^-$$_{ads}$ or O$_2^-$$_{ads}$) on the surface of the oxide chemiresistors by the following reaction (Figure 1c).[1,2,7–9]

\[
\text{H}_2\text{O}(g) + \text{O}_{ads}(or \text{O}_2^-_{ads}) \rightarrow \text{M} - \text{2OH}^- + e^- (or 2e^-) \quad (1)
\]

The consumption of active sites and the generation of electrons are responsible for the decrease in the gas response and sensor resistance in n-type oxide semiconductor gas sensors, respectively (Figure 1d, left).

To date, various additives and dopants such as Pd,[10,11] Rh,[12] Sb,[13] NiO,[14,15] CuO,[16,17] Tb,[18] Pr,[19] and CeO$_2$[20] have been explored to solve this long-standing problem of water poisoning. Although the additives/dopants were effective in suppressing the humidity dependence of the gas-sensing characteristics, their use was usually accompanied by unintended side effects (Figure 1d, right). For example, additives such as Pd, Rh, Sb, NiO, and CuO with high catalytic activity can significantly alter the gas selectivity of sensors.[21–28] On the other hand, the additives of Tb, Pr, and CeO$_2$ with moderate catalytic activity are known to increase sensor resistance excessively, while being able to maintain gas selectivity.[18–20,29–31] The former set of additives impedes the tailored design of selective gas sensors and the latter hampers the facile measurement of sensor resistance using a cost-effective electric circuit. Furthermore, the role of each additive is not general, but varies depending on the sensing material. That is, the additives can be incorporated into the lattice of the sensing materials or may exist as a second phase. The catalytic and electronic interactions between the sensing materials and additives make the rational design of on-demand gas sensors a difficult one. Therefore, it is highly necessary to establish a general strategy to mitigate water poisoning without sacrificing gas response, selectivity, and measurable sensor resistance.
Herein, for the first time, we propose a novel, universal, and facile solution to design humidity-independent oxide semiconductor gas sensors using a moisture-blocking Tb₄O₇ overlayer (Figure 1e, left). In order to facilitate the water blocking without changing the gas selectivity, hydrophobic Tb₄O₇ with moderate catalytic activity has been utilized as the overlayer material. Unlike conventional sensors uniformly loaded with additives, the gas-sensing reaction at the lower part of the sensing film is separated from the moisture-blocking reaction at the upper Tb₄O₇ overlayer, enabling the removal of humidity dependence on gas-sensing characteristics without significant alteration of the gas response, selectivity, and sensor resistance. Furthermore, the general validity of this humidity-independent bilayer sensor concept was confirmed using diverse sensing materials including highly porous In₂O₃ spheres, hollow In₂O₃ spheres, SnO₂, ZnO, and Pd/SnO₂ spheres. The unique bilayer sensor design with the Tb₄O₇ overlayer in the present study significantly enhances the precision and reliability of most oxide semiconductor gas sensors. The universal design of diverse gas sensors without water poisoning can open a new pathway toward constructing high-performance gas alarms, enhanced food quality control, effective environmental monitoring, exhaled breath analysis using gas sensors, and powerful electronic noses (Figure 1e, right).

2. Results and Discussion

A bilayer sensor with a porous In₂O₃ sensing film and a Tb₄O₇ overlayer was prepared. For this, indium-containing precursor spheres were prepared by ultrasonic spray pyrolysis of an aqueous suspension consisting of indium(III) nitrate, polystyrene (PS) spheres (diameter ≈100 nm), multi-walled carbon nanotubes (MWCNTs, diameter ≈15 nm), and citric acid (Figures S1 and S2, Supporting Information). The PS spheres and MWCNTs remained within the In-precursor spheres (see Figure S2, Supporting Information) even after spray pyrolysis at 700 °C due to the short retention time of droplets (≈4.3 s) in
the reaction zone, which were completely removed by subsequent heat treatment at 600 °C for 3 h in air.

The In2O3 spheres contained hierarchical porosity: PS-derived spherical macropores and MWCNT-derived elongated mesopores. The mean diameter of ≈100 In2O3 spheres was 0.77 ± 0.29 μm (Figure S3a, Supporting Information). Spherical pores developed by the decomposition of the PS spheres were observed on the surface of the microspheres (inset in Figure S3a, Supporting Information). In the transmission electron microscopy (TEM) images, contour of the inner part confirms that the In2O3 spheres are extremely porous and that the pores are highly interconnected (Figure S3b,c, Supporting Information). The porosity and highly interconnected morphology was further confirmed by the high-angle annular dark field image (Figure S3d, Supporting Information) and scanning electron microscopy (SEM) observation of the cross-section of In2O3 spheres prepared by a focused ion beam treatment (Figure S3e, Supporting Information). A lattice-resolved TEM image exhibited a lattice pattern with an interplanar distance of 2.92 Å, which corresponded to the (222) plane of the In2O3 cubic structures (Figure S3f, Supporting Information). The N2 adsorption and desorption isotherms of the In2O3 spheres showed type IV isotherms with H3 hysteresis loops, and the Barrett–Joyner–Halenda surface area was 27.2 m² g⁻¹. The pore size distribution suggests the presence of mesopores by the decomposition of PS and MWCNT templates as well as outgassing.[12,13] Furthermore, macropores (>100 nm) were observed in the TEM image. The results of the SEM, TEM, and BET analyses indicate that porous In2O3 spheres with high surface area-to-volume ratios as well as highly gas-accessible structures are advantageous for gas sensing.[12]

The In2O3 sensing film was fabricated by screen-printing a slurry on an Al₂O₃ substrate with two Au electrodes (Figure 2a1), followed by heat treatment at 500 °C for 3 h (Figure 2a2). Then, the Tb₂O₇ layer was coated on the top of the In₂O₃ sensing film via electron beam (e-beam) deposition (Figure 2b1) and subsequent annealing at 500 °C for 2 h (Figure 2b2). The thickness of the Tb₂O₇ overlayer was controlled by the e-beam deposition time. For simplicity, the In₂O₃ sensors with 0.2-, 0.3-, 0.4-, and 0.6-μm-thick Tb₂O₇ overlayers will be referred to as 0.2Tb₂O₇–In₂O₃, 0.3Tb₂O₇–In₂O₃, 0.4Tb₂O₇–In₂O₃, and 0.6Tb₂O₇–In₂O₃, respectively.

The In₂O₃ film was ≈5 μm thick, and a continuous Tb₂O₇ overlayer with a thickness of 0.4 μm was observed in the uppermost region of the 0.4Tb₂O₇–In₂O₃ film (Figure 2b2). The thickness and phase of the Tb₂O₇ overlayer were confirmed by the cross-sectional image and X-ray diffraction (XRD) pattern of the film deposited on a planar Si substrate (Figure S5, Supporting Information). A high-magnification SEM image further revealed that the upper half of the porous In₂O₃ spheres at the uppermost part of the sensing film was uniformly covered with the Tb₂O₇ nanoparticles (Figure 2c). In the EPMA analysis (Figure 2d), the In element was uniformly distributed throughout the film, whereas the Tb element was observed only in the uppermost thin region of the film. This is consistent with the SEM observation shown in Figure 2b2. In order to understand the role of the Tb₂O₇ overlayer in gas sensing, 0.2Tb₂O₇–In₂O₃, 0.3Tb₂O₇–In₂O₃, and 0.6Tb₂O₇–In₂O₃ films were also prepared and their gas-sensing characteristics were compared. The thickness of the In₂O₃ sensing film was fixed at ≈5 μm, and the coating thickness of Tb₂O₇ overlayer was confirmed by SEM analysis of Tb₂O₇ film coated on the Si substrate (Figure S6, Supporting Information).

The phase and crystallinity of the pure and Tb₂O₇-coated In₂O₃ films were characterized using XRD (Figure S7, Supporting Information). All the samples exhibited only cubic In₂O₃ (ICDD #06-0416) and cubic Tb₂O₇ (ICDD #13-0387) phases, and no other phases were found. The crystallite sizes of In₂O₃ and Tb₂O₇, calculated from the XRD patterns of pure In₂O₃ and 0.4Tb₂O₇–In₂O₃ samples using Scherrer’s equation, were 9.3 ± 0.2 and 10.0 ± 0.9 nm, respectively. No peak shift was observed, indicating that Tb was not incorporated into the In₂O₃ lattice. The pure and Tb₂O₇-coated In₂O₃ samples were further analyzed using X-ray photoelectron spectroscopy (XPS) (Figure S8, Supporting Information). The measured spectra were modified by the C 1s reference at a binding energy of 284.6 eV. In the Tb₂O₇-coated In₂O₃ samples, Tb 3d₅/₂ and Tb 3d₃/₂ were observed at 1240.98 and 1275.86 eV, respectively, revealing the coexistence of Tb³⁺ and Tb⁴⁺ as well as the formation of the Tb₂O₇ phase in the In₂O₃ sensing film.[34,35]

The dynamic sensing transients of pure and Tb₂O₇-coated In₂O₃ sensors toward 10 ppm acetone at 400 °C under different RH conditions (RH 0%, red; RH 20%: cyan; RH 50%: blue; RH 80%: navy) were measured (Figure 3a1–e1). All of the sensors (with and without the Tb₂O₇ overlayer) displayed n-type gas-sensing characteristics with decreased resistance in the reducing atmosphere. Accordingly, the gas response (S) was defined as Rₐ/Rₚ where Rₛ is the sensor resistance in air and Rₚ is the sensor resistance in the analyte gas. In the pure In₂O₃ sensor, the Rₛ value was 121.1 kΩ and the Sₐceton value was 44.9 in a dry atmosphere (Figure 3a1). Both Rₛ and Sₐceton values significantly decreased with increasing humidity (e.g., Rₛ = 675, 52.9, and 476 kΩ in RH 20%, 50%, and 80%, respectively, which are the typical water poisoning effects of n-type oxide semiconductor chemiresistors in the literature.[16,19,20,36,37] It is interesting that the humidity dependence of Rₛ and Sₐceton gradually diminishes with the coating of the Tb₂O₇ overlayer (Figure 3b1–c1) and nearly vanishes when a 0.4-μm-thick Tb₂O₇ overlayer was coated on the In₂O₃ sensing film (Figure 3d1). This indicates that the Tb₂O₇ overlayer plays a key role in mitigating water poisoning in gas sensors.

For a quantitative analysis, we calculated the resistance and response ratios (Rₛ/ₐceton/Rₛ/ₚ and Sₐceton/ₐceton/Sₐceton/ₚ) under dry and humid atmospheres (Figure 3f). The Rₛ/ₐceton/Rₛ/ₚ and Sₐceton/ₐceton/Sₐceton/ₚ values are close to unity, indicating that the sensor shows negligible dependence on ambient moisture, whereas those significantly lower than unity indicate a decrease in the gas response and resistance due to water poisoning. The pure In₂O₃ sensor showed significantly low Rₛ/ₐceton/Rₛ/ₚ and Sₐceton/ₐceton/Sₐceton/ₚ values (0.26 and 0.39 at 350 °C, 0.18 and 0.29 at 400 °C) (Figure 3a,f). In general, water molecules are known to form inactive hydroxyl groups (–OH) on the metal oxide surface by reacting with gas-sensing adsorbates (oxygen ions, O⁻_ads or O²⁻_ads), which
generate electrons.\cite{8,14} This explains the significant decrease in gas response and sensor resistance in pure In$_2$O$_3$ sensor with increasing humidity. The water poisoning of the metal oxide surface can be gradually and partly alleviated by increasing the temperature because dehydration becomes more favorable at high temperatures.\cite{38} Indeed, the $R_a$-RH80%/R$_a$-dry and $S_{acetone}$-RH80%/S$_{acetone}$-dry values of pure In$_2$O$_3$ sensor increases to 0.62 and 0.46, respectively, with an increase in the sensing temperature to 450 °C (Figure 3f). Nevertheless, these values are still insufficient for sensors with high endurance against humidity.

The moisture dependence of the gas-sensing characteristics significantly decreased with the coating of the Tb$_4$O$_7$ overlayer on the In$_2$O$_3$ sensing film. Overall, the 0.2Tb$_4$O$_7$–In$_2$O$_3$ sensor showed higher $R_a$-RH80%/R$_a$-dry and $S_{acetone}$-RH80%/S$_{acetone}$-dry values than those of the pure In$_2$O$_3$ sensor, and became nearly humidity independent at 450 °C ($R_a$-RH80%/R$_a$-dry = 0.78 and $S_{acetone}$-RH80%/S$_{acetone}$-dry = 0.86) (blue-shaded regions in Figure 3b2,b3). The increase in the Tb$_4$O$_7$ overlayer thickness to 0.3, 0.4, and 0.6 µm further suppressed the humidity dependence of the gas-sensing characteristics and interestingly decreased the minimum temperature to show negligible humidity dependence of the gas-sensing characteristics down to 425, 375, and 350 °C, respectively (blue-shaded regions in Figure 3c2–e2,c3–e3). It is worth noting that the 0.4Tb$_4$O$_7$–In$_2$O$_3$ and 0.6Tb$_4$O$_7$–In$_2$O$_3$ sensors showed a high gas response (0.4Tb$_4$O$_7$–In$_2$O$_3$: $S = 11.2$–$11.8$ at 400 °C; 0.6Tb$_4$O$_7$–In$_2$O$_3$: $S = 12.4$–$12.6$ at 350 °C) to 10 ppm acetone regardless of the humidity level (Figure 3d3,e3). These results confirm that the Tb$_4$O$_7$ overlayer coating is effective for detecting trace...
concentrations of gas without water poisoning at relatively low sensing temperatures. The water poisoning effect was also substantially suppressed by the coating of Tb$_4$O$_7$ on In$_2$O$_3$ even at the lower sensing temperature (200 °C) (Figure S9, Supporting Information), demonstrating that the bilayer sensor design can decrease the humidity dependence of gas-sensing characteristics at the wide range of sensing temperature. The low operating temperature is advantageous for reducing heater power consumption, improving long-term stability of the sensor, and facilitating CMOS-compatible sensor packaging. Moreover, humidity-independent gas-sensing properties over a wide temperature range make the sensor more reliable against fluctuations in the temperature.

For sensor applications, the response and recovery kinetics are also important factors. Thus, the 90% response and recovery times ($\tau_{\text{res}}$ and $\tau_{\text{recov}}$) the times taken to reach 90% resistance variation upon exposure to 10 ppm acetone and air, respectively) of the pure In$_2$O$_3$ and Tb$_4$O$_7$–In$_2$O$_3$ sensors were calculated from the sensing transients at 400 °C (Figure S10, Supporting Information). The $\tau_{\text{res}}$ and $\tau_{\text{recov}}$ values of the Tb$_4$O$_7$–In$_2$O$_3$ sensors ($\tau_{\text{res}} = 8–23$ s and $\tau_{\text{recov}} = 388–3419$ s) were similar to those of the pure In$_2$O$_3$ sensor ($\tau_{\text{res}} = 10–18$ s and $\tau_{\text{recov}} = 383–4543$ s). Similar $\tau_{\text{res}}$ and $\tau_{\text{recov}}$ values, despite the Tb$_4$O$_7$ overlayer coating, indicate that the mass transport of gas toward the lower regions of the sensing film close to the electrodes is not significantly limited by a thin Tb$_4$O$_7$ overlayer.

To investigate the effect of the Tb$_4$O$_7$ configuration, Tb-loaded In$_2$O$_3$ sensors were prepared and their gas-sensing characteristics were investigated (Figure 4 and Figure S11, Supporting Information). For this, 5.0 and 10.0 at% Tb$_4$O$_7$ ([Tb]/([Tb] + [In]) = 0.05 and 0.10) were uniformly loaded on the
Figure 4. Dynamic acetone sensing transients of a1) 5Tb-loaded In$_2$O$_3$ and a2) 10Tb-loaded In$_2$O$_3$ sensors at 400 °C (concentration of the acetone: 10 ppm). b) Sensor resistances of pure In$_2$O$_3$, Tb$_4$O$_7$-coated In$_2$O$_3$, and Tb-loaded In$_2$O$_3$ sensors in air at 400 °C.

entire sensing surface of the In$_2$O$_3$ spheres and sensing films were formed using the Tb-loaded powders (5Tb-loaded and 10Tb-loaded In$_2$O$_3$ sensors) (Figure S11a-d, Supporting Information). The $R_{\text{wet}}/R_{\text{dry}}$ and $S_{\text{acetone-wet}}/S_{\text{acetone-dry}}$ values of Tb-loaded In$_2$O$_3$ sensors (Figure S11e,f, Supporting Information) were higher than those of pure In$_2$O$_3$ sensor (Figure 3f). These results suggest that Tb$_4$O$_7$ additives can suppress water poisoning, which is consistent with our previous results.[18]

However, the gas responses of the 10Tb-loaded In$_2$O$_3$ sensor to acetone (3.3 in RH 80%) were significantly lower than that of the 0.4 and 0.6Tb$_4$O$_7$–In$_2$O$_3$ sensors (11.8 and 12.4 in RH 80%, respectively). Because Tb$_4$O$_7$ is uniformly loaded on the entire In$_2$O$_3$ surface in Tb-loaded In$_2$O$_3$ sensors, the decrease in the gas response may be associated with the interaction between In$_2$O$_3$ and Tb$_4$O$_7$ on the gas-sensing reaction (e.g., the decrease of sensing surface by a large number of Tb$_4$O$_7$ nanoclusters), although detailed studies are necessary to confirm this presumption.

More importantly, the uniform loading of Tb$_4$O$_7$ dramatically increased the sensor resistance in air. Note that the $R_s$ values of the four bilayer sensors (0.035–0.067 MΩ) at 400 °C are similar to those of the pure In$_2$O$_3$ sensor (0.121 MΩ), whereas those of two Tb-loaded sensors (120–140 MΩ) are nearly three orders of magnitude higher (red bars in Figure 4b). This remarkable increase in the baseline resistances of the In$_2$O$_3$ sensors by uniform Tb loading can be explained by the decrease of conducting area due to the presence of the insulating Tb$_4$O$_7$ phase, the variation of chemisorbed-oxygen/carrier concentration by ionic-doping, or charge transfer from In$_2$O$_3$ to Tb$_4$O$_7$.[39] In stark contrast, the conduction at the lower part of the In$_2$O$_3$ sensing film near the electrodes is hardly affected by the Tb$_4$O$_7$ overlayer coating because the catalytic overlayer is located at the outlying region, which is supported by the similar $R_s$ values of pure and Tb$_4$O$_7$-coated In$_2$O$_3$ sensors (blue bars in Figure 4b). This has an important meaning for real applications. In general, the sensor resistance should not exceed Ω because excessively high sensor resistance cannot be measured using a cost-effective electric circuit. Negligible changes in sensor resistance in spite of mitigating humidity dependence emanated from the distinctive bilayer design to separate humidity-blocking and gas-sensing reactions.

In oxide semiconductors, humidity-independent gas sensing is extraordinary. In order to understand this unprecedented endurance against moisture, the surface states of pure In$_2$O$_3$ and 0.4Tb$_4$O$_7$–In$_2$O$_3$ films stored under different humidity conditions for 100 h were investigated by Fourier-transform infrared (FTIR) spectroscopy (Figure S12, Supporting Information). The pure In$_2$O$_3$ film stored in air under moderate humidity (RH 30–50%) exhibited substantial absorption from 3200 to 3800 cm$^{-1}$ due to OH stretching.[40,41] which indicates the adsorption of H$_2$O (dotted blue line). The amplitude of this band becomes significantly high in the In$_2$O$_3$ sample stored at RH 80% (solid blue line). However, the water-related peaks nearly disappeared with the coating of the Tb$_4$O$_7$ overlayer (solid red and dotted amber lines), which suggests that the interaction between water and the In$_2$O$_3$ sensor surface can be blocked by the Tb$_4$O$_7$ overlayer. This can be attributed to the hydrophobic nature of lanthanide terbium due to its unique electronic structure which inhibits hydrogen bonding with interfacial water molecules.[42] Furthermore, this is experimentally confirmed by the observation that the contact angles of water droplets on the Tb$_4$O$_7$ thin film and 0.4Tb$_4$O$_7$–In$_2$O$_3$ film (87.9° ± 0.97° and 117.2° ± 1.18°) are higher than that on In$_2$O$_3$ thin film (47.0° ± 0.26°). The contact angle test was conducted on five different samples (Figure S13, Supporting Information). The different contact angles on the Tb$_4$O$_7$ thin film and 0.4Tb$_4$O$_7$–In$_2$O$_3$ film can be attributed to the effect of surface roughness.[43,44] Accordingly, the moisture-blocking effect by the hydrophobic Tb$_4$O$_7$ overlayer can be considered as a probable and primary reason for suppressing the humidity dependence of the gas-sensing characteristics. In addition, the interaction at the interface between the Tb$_4$O$_7$ overlayer and In$_2$O$_3$ sensing layer might be considered as a minor reason. We previously suggested that the uniform loading of multivalent lanthanide-based elements such as Ce, Tb, and Pr over the entire sensing material significantly reduced water poisoning via the regenerative self-refreshing of the sensing sites (O$_{ads}$) by the interaction between the Ln$^{3+}$/Ln$^{4+}$ redox pair and surface OH groups although the sensor resistance increased to a great extent.[18–20] In the present study, the interface between Tb$_4$O$_7$ and In$_2$O$_3$ is
not ubiquitous. However, as only a trace amount of moisture penetrated through the hydrophobic Tb₄O₇ overlayer, the In₂O₃ sensing surface near the interface (i.e., the uppermost part of the sensing film) can be refreshed in a regenerative manner by the assistance of the adjacent Tb₂O₇ overlayer. This might block the further migration of moisture to the lower sensing regions.

The general validity of the Tb₄O₇ overlayer to prevent water poisoning has been investigated using sensing materials with different morphology and composition. First, in order to investigate the effect of morphology of sensing materials, a 0.4-µm-thick Tb₄O₇ overlayer was coated on the sensing films of In₂O₃ hollow spheres (In₂O₃ HSs) (Figure 5a,b and Figure S14, Supporting Information). The pure In₂O₃ HS sensor at 350 °C showed significant humidity dependences on the sensor resistance and acetone response (Figure 5a and Figure S14e, Supporting Information), whereas these variations substantially diminish with the coating of the 0.4-µm-thick Tb₂O₇ overlayer (Figure 5b and Figure S14f, Supporting Information). Second, different sensing materials such as SnO₂ and ZnO were used (Figure 5c–f and Figures S15 and S16, Supporting Information). For the pure SnO₂ and ZnO sensors, both the gas response and baseline resistance significantly decreased with increasing the humidity level to 80%, which are consistent with those reported in the literature.[5,14,20,45] The SnO₂ sensor became nearly moisture independent over a wide range of sensing temperatures (350–450 °C) when a 0.1-µm-thick Tb₂O₇ overlayer was applied (Figure 5c,d and Figure S15f, Supporting Information). Similarly, the 0.1Tb₂O₇–ZnO sensor also exhibited humidity-independent sensing characteristics at 400 °C (Figure 5e,f and Figure S16f, Supporting Information). Finally, to examine the effect of the overlayer on gas selectivity, a toluene-selective Pd/SnO₂ sensor[46] was coated with the Tb₄O₇ overlayer. Neither the gas response nor the toluene selectivity was changed by the overlayer coating (Figure S17, Supporting Information). These results clearly confirm that the Tb₂O₇ overlayer can be applied to diverse sensing materials in order to mitigate the water poisoning effect without significantly altering the gas response and selectivity, providing a universal and powerful solution for getting rid of long-lasting moisture-dependent problems in oxide semiconductor gas sensors.

The potential of the present bilayer sensor for exhaled breath analysis was examined. For this purpose, breath acetone, a...
biomarker gas to diagnose type I diabetes\cite{47} and monitor the ketogenic diet,\cite{48} has been measured. The pure In$_2$O$_3$ sensor showed selectivity toward acetone over other possible interfering biomarker gases (ammonia, toluene, CO, and hydrogen) and an indoor pollutant (HCHO) in a dry atmosphere. However, under wet conditions (RH 80%), the selectivity and gas response decreased significantly, which made the quantitative detection of breath acetone difficult (Figure 6a). In contrast, the 0.4Tb$_4$O$_7$–In$_2$O$_3$ sensor exhibited similar gas response and selectivity in both dry and wet conditions (Figure 6b). The selective detection of acetone using oxide chemiresistors is frequently reported in the literature,\cite{49–52} which is explained either by the specific interaction between polar acetone and ferroelectric sensing materials (e.g., Si- or Cr-doped $\varepsilon$-WO$_3$)\cite{49,50} or by the high reactivity of acetone. Furthermore, if the gases with the similar reactivity are detected by the reaction with O$_{{\text{ads}}}$ on the surface, a gas molecule composed of the more C, H, and N atoms will lead to the higher chemiresistive variation. In the present study, since neither Tb$_4$O$_7$ nor In$_2$O$_3$ is ferroelectric material, the acetone selectivity can be attributed to the high reactivity of acetone with relatively high number of C and H atoms for the reaction with O$_{{\text{ads}}}$. The dynamic sensing transients of 1–20 ppm acetone at 400 °C under both dry and humid (RH 80%) conditions were nearly the same (Figure 6c), confirming the humidity-independent gas-sensing characteristics regardless of concentration variations. The detection limit of acetone estimated by linear regression line fitting of the gas responses was 18 ppb when $R_{\text{acetone}} > 1.2$ was used as the criterion for gas sensing (Figure 6d). Moreover, the sensor showed highly stable sensing characteristics upon repetitive exposure to 10 ppm acetone (Figure 6e). The breath acetone concentration is known to be higher than 1.8 ppm in diabetic patients and lower than 0.8 ppm in healthy people,\cite{53} and it can increase to 2.5 ppm after 12 h on a ketogenic diet.\cite{48,54} From this perspective, the present bilayer sensor is capable of detecting breath acetone in a highly selective, sensitive, and reliable manner.

We previously reported that the coating of nanoscale overlayers with high catalytic activity such as Au, Co$_3$O$_4$, Cr$_2$O$_3$, TiO$_2$, and SnO$_2$ on oxide semiconductor sensing film can be used to change gas selectivity by reforming and oxidation of the analyte gases.\cite{55–58} However, a general solution to suppress water poisoning without altering gas selectivity, as demonstrated in the present study, is also of crucial importance to make the gas sensor as well as an electronic nose both reliable and precise. First, the precision of the gas sensors becomes substantially higher by removing the humidity interference on the sensing signal. Second, researchers can remove the humidity dependence of selective gas-sensing materials, which facilitates the on-demand design of sensing materials. Last but not the least, this issue is highly important in electronic nose using sensor arrays. When the gas-sensing characteristics of multiple sensors in the electronic nose fluctuate significantly depending on humidity, the pattern recognition of the sensing signal becomes less reliable, which deteriorates the performance of the electronic nose to a great extent.\cite{59} This is well supported by the report that the dehumidification of exhaled breath significantly enhances the precision of the electronic nose for medical diagnosis.\cite{6,60} That is, highly precise and reproducible electronic noses and gas sensors can be fabricated simply by coating a humidity-blocking overlayer via facile e-beam evaporation and sputtering. From this perspective, a universal strategy to mitigate the water poisoning effect in the present study can open up various pathways for medical diagnosis using exhaled
3. Conclusion

A novel bilayer sensor with a moisture-blocking Tb4O7 overlayer was suggested as a universal and facile solution for eliminating the humidity interference on the performance of oxide chemiresistors. In2O3 sensors coated with submicrometer-thick Tb4O7 exhibited robust humidity-independent sensing characteristics, whereas the pure In2O3 sensor showed typical moisture poisoning behaviors. The humidity-independent sensing properties of bilayer sensors are attributed to a moisture-blocking effect by the hydrophobic Tb4O7 overlayer and the prevention of -OH radical formation by the interaction between Tb4O7 and In2O3 at the interface. Moreover, the proposed bilayer sensor can separate gas-sensing and moisture-blocking reactions into independent processes, thereby enabling the effective removal of moisture interference without sacrificing the intrinsic sensing properties such as gas response, selectivity, and measurable sensor resistance.

The general validity of the proposed bilayer sensor design with extreme endurance against moisture was further confirmed by applying the Tb4O7 overlayer on diverse sensing films using In2O3 hollow spheres, SnO2, ZnO, and Pd/SnO2 spheres. These results demonstrate that bilayer sensors with a Tb4O7 overlayer are a universal solution for moisture poisoning. This novel strategy can be used to enhance the precision of gas sensors and to design on-demand artificial olfaction with high reliability, which will eventually open up various new applications in the fields of medical diagnosis, environmental monitoring, and food quality assessment.

4. Experimental Section

Preparation of Pore Templates (Polystyrene Spheres and MWCNTs): A colloidal solution of PS nanospheres was prepared using an emulsion polymerization method. Briefly, the emulsion was prepared by dissolving styrene (30.0 mL) (Sigma-Aldrich, USA), sodium 4-styrenesulfonic acid (0.25 g) (Sigma-Aldrich, USA), and sodium bicarbonate (0.15 g) (NaHCO3, 99.995%, Sigma-Aldrich, USA) in distilled water (300 mL).

After stirring for 1 h at 70 °C, potassium persulfate (0.15 g) (K2S2O8, 99.99%, Sigma-Aldrich, USA) was added to the solution and refluxed at 70 °C for 18 h under an N2 atmosphere. MWCNTs (2.0 g) (diameter ~15 nm, Carbon Nano-material Technology, Korea) were surface-modified using the mixed solution of nitric acid (HNO3, 70%, Samchun, Korea) and sulfuric acid (H2SO4, 95%, Samchun, Korea) (1:3 vol%) at 70 °C for 4 h. The acid-treated MWCNTs were washed with distilled water and ethanol solution and redispersed in distilled water (200 mL) for future use.

Synthesis of Sensing Materials: Highly porous In2O3 spheres were prepared by one-pot ultrasonic spray pyrolysis. The experimental setup is shown in Figure S18, Supporting Information, and the detailed procedures are shown in refs. [32,33]. The solution for spray pyrolysis was prepared by adding indium(III) nitrate hydrate (3.76 g) (In(NO3)3·6H2O, 99.999%, Sigma-Aldrich, USA) in an aqueous suspension (500 mL) containing PS nanospheres (6.0 g), citric acid monohydrate (2.5 g) (C6H8O7·H2O, 99.5%, Samchun, Korea), and the above-prepared MWCNTs colloidal solution (30 mL). The resulting solution was sonicated for 1 h. The droplets were nebulized by ultrasonic transducers and directly conveyed into a high-temperature (700 °C) quartz reactor by N2 gas at a flow rate of 10 L min⁻¹. The In-containing precursor spheres were collected by a Teflon bag filter and annealed at 600 °C for 3 h under air to remove residual carbon components and to convert them into In2O3 spheres. The experimental procedures to prepare In2O3 hollow spheres, SnO2, and ZnO spheres are provided in the Supporting Information.

Fabrication of Bilayer Sensors: The porous In2O3 spheres were mixed with a terpineol-based ink vehicle (FCM, USA) (In2O3/binder = 1:3 by weight), and the slurry was screen-printed onto an alumina substrate (size: 1.5 mm × 1.5 mm, thickness: 0.25 mm), which had two Au electrodes on the upper surface and a Ru micro-heater on the lower surface. After the screen-printing process, the sensing film was heated at 500 °C for 3 h to remove the organic components. Tb4O7 overlayers were coated on In2O3 films by e-beam evaporation of Tb grains (99.9%, Kojundo Chemical Laboratory, Japan) in a vacuum environment (base pressure = 2 × 10⁻⁶ Torr). The bilayer films were annealed at 500 °C for 2 h in air.

Characterization: FE-SEM (SU-70, Hitachi Co. Ltd., Japan) and HR-TEM (JEM-ARM200F, JEOL Co. Ltd., Japan) were used to investigate the morphologies and microstructures of the materials and sensing films. The compositional variation of the In2O3 film coated with a Tb4O7 overlayer was observed via FE-EPMA (JXA-8530F, JEOL Co. Ltd., Japan). The pore-size distribution and surface area of the porous In2O3 spheres were analyzed by BET (TriStar 3000, Micromeritics, USA) method. The crystal structure was characterized by XRD (D/MAX-2500 V/PC, Rigaku, Japan) with an CuKα radiation source (λ = 1.5418 Å). The chemical bonding states of the bilayer films were determined using XPS (PHI X-tool, ULVAC-PHI, Japan). To ascertain the surface states of the pure In2O3 and 0.4Tb4O7–In2O3 films (RH 30–50% or RH 80% conditions), FTIR spectroscopy was performed using a Vertex 80v (Bruker Optics, Germany). To investigate the hydrophobic/hydrophilic properties, contact angle measurements were conducted by injecting ~3 μL droplets of distilled water using a Drop Shape Analyzer (Phoenix 300 Touch, SEO, Korea).

Gas-Sensing Characteristics: Prior to measuring the gas-sensing characteristics, the sensors were heated at 500 °C for 2 h for stabilization. The sensor was placed in a specially designed quartz tube (inner volume: 1.5 cm³), and the atmosphere was controlled via an automatic four-way valve. The flow rate of the gas was fixed at 200 cm³ min⁻¹. RH (0%, 20%, 50%, and 80%) at 25 °C and gas concentrations (10 ppm of acetone, ammonia, toluene, carbon monoxide, hydrogen, and formaldehyde) were controlled by changing the mixing ratios between dry air and humid air or that between synthetic gases and dry/humid air (Figure S19, Supporting Information). To ensure a constant humidity concentration, the humidity level (RH) was measured using a SHT75 sensor (Sensirion AG, Switzerland) at 25 °C within the sensing chamber. An electrometer (Picoammeter 6487, Keithley, Tektronix Inc., USA) interfaced with a computer was used to measure the direct-current two-probe resistance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
