1. Introduction

Respiratory gas contains a range of volatile organic compounds (VOCs) and inorganic gases (e.g. hydrogen, nitric oxide, and hydrogen sulfide) that act as biomarker gases for the diagnosis of illnesses such as intestinal abnormalities [1], diabetes [2], lung cancer [3], asthma [4], and halitosis [5]. For example, an appropriate concentration of acetone gas in the breath can indicate diabetes [2], while hydrogen is a biomarker gas for intestinal abnormalities [1]. Thus, to accurately diagnose diabetes through breath analysis, a breath analyzer must be employed that exhibits a ppb-level of acetone detection in addition to a high selectivity for the various biomarker gases contained in the respiratory gas.

In this context, semiconductor-based gas sensors are effective for respiratory gas analysis from the standpoint of low cost, compactness, and low power consumption [6]. Indeed, we previously reported the responsiveness of semiconductor-based gas sensors based on p-type Co$_3$O$_4$, and noted a high selectivity toward hydrogen gas [7,8]. However, to accurately detect a specific gas within respiratory gas, an improved selectivity was required. In this context, it has been reported that the presence of nanoparticles in the cobalt oxide particles in addition to control over the particle shape will increase both the sensitivity and selectivity of such a system [9–11].

We recently reported the synthesis of a core-shell type cobalt oxide (core-shell type CoO; csCoO), which is comprised of a CoO core and a polymer shell [12]. Using the poloyol method, core-shell particles with particle sizes between 50 and 100 nm were prepared, where the polymer shells comprised 19 wt% of the total mass. These particles were easily dispersed in water and organic solvents without the use of dispersants. In addition, the core-shell particles were composed of an agglomeration of several tens of nanometer-sized core-shell primary particles, with sintering at 400°C generating the desired nanopore-containing core-shell type Co$_3$O$_4$ (csCo$_3$O$_4$). In this context, Kida et al. reported that in the SnO$_2$ system for H$_2$S sensing, nanopore manipulation in the sensor response layer leads to an increased response and selectivity toward H$_2$S compared to the smaller and more reactive hydrogen atoms [13]. We therefore expected that an increase in the specific surface area of sensing films through the formation of nanopores could result in additional reaction sites to lead to a higher gas responsiveness. Indeed, this was assumed to account for the high selectivities of high specific surface area cobalt nanofiber and nanosheet gas sensors toward acetone gas and ethanol gas [9,10]. Furthermore, to improve the gas reactivity at the reaction sites present in the nanopores, the inner areas of the nanopores must be loaded with noble metal catalysts. However, conventional methods such as the...
colloidal mixing method [14] are not suitable for the introduction of noble metal catalysts on the sensing film or within the nanoparticles. Thus, we herein report use of the polylol method for the synthesis of core-shell CoO particles containing noble metal catalysts in the nanoparticles (Figure 1). More specifically, polyvinylpyrrolidone (PVP)-coated Pt and/or Pd nanoparticles are mixed with the core-shell CoO particle synthetic solution to allow catalyst loading during syntheses of the cobalt oxide particles. Using such a PVP-coated metal colloid, metal nanoparticle synthesis and aggregation should be prevented. Subsequent sintering of the prepared particles leads to the formation of nanoparticles in the secondary particles. Finally, the gas sensor characteristics of the csCoO particles containing Pt or Pd on the surface are compared with those of CoO particles that do not contain nanoparticles, and the effectiveness of the noble metal catalyst-loaded 3D-nanostructure for gas sensing is considered.

2. Experimental

Cobalt acetate tetrahydrate (1.5 g, Co(CH₃COO)₂·4H₂O; Wako Pure Chemical Industries, Ltd.), PVP (7.2 g, average molecular weight: 10,000; Sigma-Aldrich), and distilled water (10 mL) were added to diethylene glycol (60 mL, DEG; Wako Pure Chemical Industries, Ltd.). Subsequently, a 4 wt% Pt or 4 wt% Pd colloidal suspension (0.114 g) was added to the mixed DEG solution. The Pt and Pd contents were 1 wt% relative to the Co₃O₄ content in the mixed DEG solution. The Pt sizes of Pt and Pd in the colloidal suspension (Tanaka Kikinzoku Kogyo K. K.) were ~4 and 2 nm, respectively. The Pt present inside the csCoO and that outside the csCoO were denoted as Pt-in/csCoO and Pt-out/csCoO, respectively. The csCoO, Pt-in-out/csCoO, Pt-out/csCoO, and Pd-out/csCoO samples were baked at 400°C for 2 h under air to obtain csCo₃O₄, Pt-in-out/csCo₃O₄, Pt-out/csCo₃O₄, and Pd-out/csCo₃O₄, respectively. The Pd and Pt contents of the Pt-out/csCo₃O₄, Pd-out/csCo₃O₄, Pt-out/Co₃O₄ powder, and Pd-out/Co₃O₄ powder were 1 wt% relative to the Co₃O₄ content.

The obtained particles were then characterized using X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). XRD analysis was carried out using a Smartlab diffractometer (Rigaku Corporation) equipped with a copper source (CuKα) and a one-dimensional high-speed detector (D/teX Ultra 250). The X-ray generator was operated at 40 kV and 30 mA. TEM was performed using JEM-2100F/HK and JEM-1000K RS (JEOL Ltd.) instruments. XPS was performed by ESCA-3400 (Shimadzu Corporation) using MgKα radiation to investigate the chemical composition. The effect of charging on the binding energies was corrected with respect to the C 1s peak at 284.6 eV. The Brunauer-Emmett-Teller (BET) surface areas and...
Barrett-Joyner-Halenda (BJH) pore size distributions were obtained from nitrogen adsorption isotherms of the sample particles degassed at 200°C for 1 h and measured at 77 K in liquid nitrogen using a NOVA 4200e instrument (Quantachrome Instruments).

A ceramic paste of the sensing material powder was prepared by mixing an organic dispersant consisting of 10 wt% ethyl cellulose and 90 wt% terpineol. The weight ratio of the sensing material powder to the organic dispersant was 1:4. The paste was dispersed on an alumina substrate, which consisted of 3.4 × 4 mm² platinum interdigital electrodes with a line width of 100 μm and a space width of 200 μm. Subsequent baking to achieve evaporation of the organic dispersant produced a sensor composed of a sensing membrane on an alumina substrate.

The sensor element was then placed in a test chamber and heated to 200°C in an electrical tube furnace. Synthetic humid air was prepared by passing O₂ gas through ion-exchanged water at 25°C. The contents of O₂ in the synthetic humid air were 20 vol%. Synthetic humid air was introduced into the chamber for 20 min, and a gas mixture of acetone, isoprene, ammonia, nitric oxide, or hydrogen in synthetic humid air was then injected for 20 min. The gas mixture flow rate was 400 mL/min. The acetone, isoprene, ammonia, nitric oxide, and hydrogen gas concentrations in the synthetic humid air were controlled at 0.25, 1, 5, and 25 ppm. The sensor resistance in various gaseous atmospheres was measured via a two-probe method at 5 s intervals using a K2700 digital multimeter (Keithley). The sensor response value (S) was defined using the following equation: \( S = \frac{R_g}{R_a} \), where \( R_g \) denotes the resistance after exposure to acetone, isoprene, ammonia, nitric oxide, or hydrogen in synthetic humid air for 20 min, and \( R_a \) denotes the resistance in synthetic humid air prior to exposure to the gas mixture of acetone, isoprene, ammonia, nitric oxide, or hydrogen in synthetic humid air for 20 min.

3. Results and discussion

Figure 2 shows the XRD patterns of (a) Pt-in-out/csCoO, (b) Pd-in-out/csCoO, (c) csCoO, (d) Pt-in-out/csCo₃O₄, (e) Pd-in-out/csCo₃O₄, and (f) csCo₃O₄, where samples (a)–(c) had undergone pre-sintering at 400°C, and samples (d)–(f) were subjected to post-sintering at 400°C. A CoO peak was verified using the pre-400°C sintered Pt-in-out/csCoO, Pd-in-out/csCoO, and csCoO samples, while a Co₃O₄ peak was verified using the post-400°C sintered Pt-in-out/csCo₃O₄, Pd-in-out/csCo₃O₄, and csCo₃O₄ samples. Since during the creation of gas sensor elements the paste-printed elements are baked at 400°C for 2 h, all samples should exhibit the gas responsiveness of Co₃O₄.

Using the Scherrer equation, \( D = \frac{k\lambda}{\beta\cos\theta} \), to determine the sizes of the crystallites, it was determined that the crystallite size prior to baking at 400°C bake was ~10 nm (see Table 1), while after baking, it was ~15 nm. Peaks that were attributable to Pt and Pd could not be verified, but

| Structural characteristics of the CoO and Co₃O₄ particles. | XRD | SEM |
|----------------------------------------------------------|-----|-----|
| Crystallite size (nm) | Average secondary particle size (nm) | BET surface area (m²/g) |
| Pt-in-out/csCoO | 9.4 | 36.8 | — |
| Pd-in-out/csCoO | 10.7 | 52.8 | — |
| csCoO | 10.6 | 97.6 | — |
| Pt-in-out/csCo₃O₄ | 14.5 | 38.3 | 39.4 |
| Pd-in-out/csCo₃O₄ | 17.6 | 56.9 | 24.3 |
| csCo₃O₄ | 15.6 | 109.7 | 20.5 |

Figure 2. XRD patterns of (a) Pt-in-out/csCoO, (b) Pd-in-out/csCoO, (c) csCoO, (d) Pt-in-out/csCo₃O₄, (e) Pd-in-out/csCo₃O₄, and (f) csCo₃O₄.
this is likely due to the particularly low contents of these noble metals within the mixture. In our previous report, we found CoOOH in the XRD pattern of csCoO; however, in this case, only a single phase of CoO was observed [12] likely due to the removal of CoOOH through washing.

Figure 3 shows the SEM images of Pt-in-out/csCoO, Pd-in-out/csCoO, csCoO, Pt-in-out/csCo₃O₄, Pd-in-out/csCo₃O₄, and csCo₃O₄. As indicated, the pre-400°C baked Pt-in-out/csCoO, Pd-in-out/csCoO, and csCoO samples contained primary particles of ~10 nm in diameter, which converted into secondary particles measuring ~20–150 nm. The sizes of these primary particles are comparable to those of the crystallites, and the particulate shapes are similar to those of our previously reported core-shell cobalt oxide particles [12], core-shell cerium oxide particles [15], and core-shell zinc oxide particles [16]. Table 1 shows the secondary particle sizes calculated from the SEM images, where it is apparent that the secondary particle sizes of Pt-in-out/csCoO and Pd-in-out/csCoO are smaller than that of csCoO. It was therefore assumed that since the core-shell oxide particle sizes are influenced by the formation of the PVP polymer shell layer, the secondary particle size is smaller due to acceleration of PVP shell layer formation through Pt and Pd catalysis [15]. In addition, comparison of the post-400°C baked Pt-in-out/csCo₃O₄, Pd-in-out/csCo₃O₄, and csCo₃O₄ samples with the pre-400°C baked equivalents showed that the secondary particle surface was somewhat smoother, likely due to fusion between the primary particles upon baking. Since no major changes were observed in the secondary particle size before and after baking, we assumed that the PVP shell layer suppressed fusion of the secondary particles. We then examined the effect of the noble metal loading on the csCoO secondary particle shape, and the findings are presented in Figure 4. As indicated, smaller CoO secondary particle sizes were observed for 2 wt% Pt compared to 1 wt% Pt, likely due to more rapid PVP shell layer formation. However, in the presence of 5 wt% Pt, uneven secondary particles were observed at ~300 nm, likely due to secondary particle aggregation catalyzed by Pt. As we wished to examine the gas selectivity in the presence of nanopores created on evenly formed secondary particles, a noble metal loading of 1 wt% was selected.

Figure 5 shows the TEM images of Pt-in-out/csCo₃O₄ and Pd-in-out/csCo₃O₄. In the Pt-in-out/csCo₃O₄ TEM image, CoO particles with diameters of 50 nm can be seen in addition to black phases of ~4 nm in diameter, which were attributed to Pt particles. As the Pt and Pd particles present in the colloidal solutions contain a covering of PVP, we assumed that grain growth and aggregation were suppressed during synthesis. In contrast, in the TEM image of the Pd-in-out/csCo₃O₄ sample, CoO particles of 50 nm diameter were observed, but no black phases were detected. As it has been previously reported that PdO is formed upon baking Pd at 400°C, the contrast is reduced [8,17], therefore preventing the Pd particles being observed by TEM. Figure 6 shows the XPS spectra of Pt-in-out/csCo₃O₄ and Pd-in-out/csCo₃O₄. For the Co 2p spectra, the binding energies assigned to Co 2p₁/₂ and Co 2p₃/₂ were observed at 795.5 and 780.0 eV for Pt-in-out/csCo₃O₄ and 795.5 and 780.1 eV for Pd-in-out/csCo₃O₄, which were generated from CoO [18]. For the O 1s spectra, the binding energies assigned to

![Figure 3. SEM images of (a) Pt-in-out/csCoO, (b) Pd-in-out/csCoO, (c) csCoO, (d) Pt-in-out/csCo₃O₄, (e) Pd-in-out/csCo₃O₄, and (f) csCo₃O₄.](image-url)
two chemical states of oxygen were observed. The peaks with binding energies of 531.4 eV for Pt-in-out/csCo$_3$O$_4$ and 531.5 eV for Pd-in-out/csCo$_3$O$_4$ assigned to surface-absorbed oxygen. The peaks with binding energies of 529.4 eV for Pt-in-out/csCo$_3$O$_4$ and 529.5 eV for Pd-in-out/csCo$_3$O$_4$ assigned to lattice oxygen of Co$_3$O$_4$ [18]. In Figure 6(c), the binding energies assigned to Pt 4f$_{5/2}$ and Pt 4f$_{7/2}$ were observed at 74.1 and 70.8 eV, respectively. These peaks corresponded to metallic Pt [19]. For Figure 6(f), the binding energies assigned to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ were observed at 341.6 and 336.4 eV, respectively. According to the literature, the binding energies of metallic Pd and PdO in the Pd 3d$_{5/2}$ showed 335.1 and 336.3 eV, respectively [20]. Therefore, the dominant binding state of Pd in Pd-in-out/csCo$_3$O$_4$ was PdO. The results of TEM and XPS demonstrate the presence of PdO rather than metallic Pd. The contents of Pt in Pt-in-out/csCo$_3$O$_4$ and Pd in Pd-in-out/csCo$_3$O$_4$ by the XPS measured were 1.41 and 1.19 wt%, respectively.

To verify whether Pt particles are present in the Co$_3$O$_4$ secondary particles for the Pt-in-out/csCo$_3$O$_4$ sample, stereoscopic TEM observations were carried out [21,22]. Thus, Figure 7 shows the stereoscopic pairs of TEM images for Pt-in-out/csCo$_3$O$_4$, where in Figure 7 (a), the sample stage is in the horizontal position, while in Figure 7(b), a tilt angle of 15° is employed.
Interestingly, the distance between Pt particles A and B changed from 8.2 mm in Figure 7(a) to 3.3 nm in Figure 7(b). As the position of Pt particle A remains relatively constant in relation to the center of the cobalt oxide particles at different tilt angles, this particle was assumed to be present within the cobalt oxide particle. Furthermore, since Pt particle B shifts greatly in the horizontal direction when the tilt angle is changed, it was assumed to be present at the surface of the cobalt oxide particle. If we hypothesize that Pt particle A is within the CoO particle, then the distance between Pt particle A and Pt particle B would be the equivalent of the radius of the CoO particle. The calculated distance between A and B was 24.5 nm, which is comparable to the particle radius 23.8 nm calculated using the TEM image. Based on these results, it was apparent that Pt-in-out/csCo$_3$O$_4$ contains Pt particles within the Co$_3$O$_4$ secondary particles. We were also able to identify an approximately 10–20 nm-sized round phase on the cobalt oxide particles, indicating the presence of

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**Figure 6.** XPS spectra of Pt-in-out/csCo$_3$O$_4$: (a) Co 2p, (b) O 1s, and (c) Pt 4f. XPS spectra of Pd-in-out/csCo$_3$O$_4$: (d) Co 2p, (e) O 1s, and (f) Pd 3d.

**Figure 7.** Stereoscopic pairs of TEM images of Pt-in-out/csCo$_3$O$_4$. The tilt angles of the sample stages are (a) 0° and (b) 15°.
a void. It also appeared that one CoO particle was comprised of multiple grains. While it was not possible to verify this for the Pd-in-out/csCo$_3$O$_4$ sample due to the influence of the low contrasting effect of PdO, use of the same synthetic method as for the preparation of Pt-in-out/csCo$_3$O$_4$ allowed us to speculate that it is present within the CoO particle.

Figure 8 shows the pore distributions of Pt-in-out/csCo$_3$O$_4$, Pd-in-out/csCo$_3$O$_4$, csCo$_3$O$_4$, and Co$_3$O$_4$ powder samples, where it is apparent that Pt-in-out/csCo$_3$O$_4$, Pd-in-out/csCo$_3$O$_4$, and csCo$_3$O$_4$ contained greater numbers of nanopores measuring 2–6 nm. It was therefore assumed that a nanopore-containing Co$_3$O$_4$ nanostructure was formed, as in the case reported by Choi et al [9]. In addition, the BET specific surface areas of the various samples are summarized in Table 1. Although Pt-in-out/csCo$_3$O$_4$ had a slightly larger specific surface area compared to Pd-in-out/csCo$_3$O$_4$ and csCo$_3$O$_4$, this was assumed to be due to the effect of the smaller cobalt oxide secondary particle size. Indeed, the nanopores of the cobalt oxide secondary particles are not only related to the voids inside the particles, but also to the noble metal catalysts.

We then moved on to examine the gas sensing properties of the prepared materials. Thus, Figure 9 shows the response curves of the Pd-in-out/csCo$_3$O$_4$, Pd-out/csCo$_3$O$_4$, and Pd-out/Co$_3$O$_4$ gas sensors to 0.25, 1, 5, and 25 ppm acetone gas exposure at 200°C, in addition to their gas responses to 5 ppm acetone, 5 ppm isoprene, 5 ppm ammonia, 5 ppm NO, and 5 ppm hydrogen. All three sensors exhibited an increased sensor resistance when exposed to 0.25–25 ppm acetone gas, and in the presence of synthetic air, the sensor resistance decreased until it recovered its original resistance value. Similar responses were observed for isoprene, ammonia, NO, and hydrogen gas. A correlation between the gas concentration and the sensor response.
resistance was also observed, and we verified that all sensors demonstrated the typical p-type semiconductor gas sensor response. In addition, Pd-in-out/csCo$_3$O$_4$ and Pd-out/csCo$_3$O$_4$ exhibited excellent responses to acetone gas, while the gas responses for ammonia, NO, and hydrogen gas were less sensitive. Indeed, this trend was previously reported for nanosheet and nanofiber cobalt oxide sensors [9,10]. We also found that the acetone and isoprene gas responses of Pd-out/csCo$_3$O$_4$ were approximately one third that of the gas response of Pd-in-out/csCo$_3$O$_4$. In addition, the responses of Pd-out/CsCo$_3$O$_4$ powder to acetone and isoprene gas were comparable to those for ammonia, NO, and hydrogen gas. These observations indicate that Pd loading into the csCo$_3$O$_4$ secondary particle nanopores effectively improved the responses toward acetone and isoprene.

Figure 10 shows the response curves of the Pt-in-out/csCo$_3$O$_4$, Pt-out/csCo$_3$O$_4$, and Pt-out/Co$_3$O$_4$ gas sensors at 200°C against 0.25, 1, 5, and 25 ppm acetone gas, in addition to the gas responses to 5 ppm acetone, 5 ppm isoprene, 5 ppm ammonia, 5 ppm NO, and 5 ppm hydrogen. As indicated, the csCo$_3$O$_4$ gas sensor showed lower gas responses than the Pt- or Pd-loaded csCo$_3$O$_4$ gas sensor.

Figure 11 shows the gas response curves of the Pt-in-out/csCo$_3$O$_4$, Pd-in-out/csCo$_3$O$_4$, Pd-out/csCo$_3$O$_4$, Pt-out/csCo$_3$O$_4$, Pt-out/Co$_3$O$_4$ powder, and Pd-out/Co$_3$O$_4$ powder gas sensors toward 5 ppm acetone gas and 5 ppm hydrogen gas at 200°C. Interestingly, all six gas sensors responded to acetone gas but showed little response to hydrogen gas. The sensing properties toward acetone gas ($S_{acetone}$) and hydrogen gas ($S_{hydrogen}$) are presented in Table 2 along with the corresponding selectivity ($S_{acetone}/S_{hydrogen}$) results. Upon comparison between Pd-in-out/csCo$_3$O$_4$ and Pd-out/csCo$_3$O$_4$, it was found that Pd-in-out/csCo$_3$O$_4$ exhibited an approximately four times greater acetone gas responsiveness and selectivity. Pd-in-out/csCo$_3$O$_4$ is presumed to contain Pd catalysts within the cobalt oxide secondary particles, and this was thought to enhance the acetone gas response in the nanopores. Furthermore, Pt-out/Co$_3$O$_4$ powder and Pd-out/Co$_3$O$_4$ powder exhibited low gas responses to

Figure 10. Sensor responses during exposure to 0, 0.25, 1, 5, and 25 ppm acetone, and gas responses ($R_g/R_a$) toward 5 ppm acetone, 5 ppm isoprene, 5 ppm ammonia, 5 ppm nitric oxide, and 5 ppm hydrogen: (a, d) Pt-in-out/csCo$_3$O$_4$, (b, e) Pt-out/csCo$_3$O$_4$, and (c, f) Pt-out/Co$_3$O$_4$ powder.
both acetone gas and hydrogen gas, in addition to a low acetone gas selectivity. Following the inflow of acetone gas, the sensor resistance gradually increased to reach an equilibrium; however, in the case of hydrogen gas, the sensor resistance initially increased rapidly prior to reducing to reach an equilibrium. Such behavior has been reported to occur for small molecular weight gases, and has been attributed to the difference in the gas diffusivity and its adsorption on the surface of an oxide semiconductor [9].

Also of interest is the report by Choi et al., who examined the ethanol/hydrogen selectivity of secondary particle shapes of cobalt oxide possessing nanopores when the secondary particles were in the form of sheets, rods, cubes, and spheres [9]. According to their report, the sheet-shaped particles had both a high specific surface area (43.6 m²/g) and a high ethanol/hydrogen selectivity (56.0), while the spherical-shaped particles had a low specific surface area (19.3 m²/g) and a poor ethanol/hydrogen selectivity (5.1). Although our Pd-in-out/csCo₃O₄ particles were spherical in shape with a relatively low specific surface area (24.3 m²/g), they exhibited an acetone/hydrogen selectivity of 26.3, thereby indicating that the higher-order structural control of Pd-loaded nanopores in cobalt oxide secondary particles is effective in improving the acetone gas selectivity. Although the csCo₃O₄ sample had some nanopores, the Pd-out/csCo₃O₄ and Pt-out/csCo₃O₄ sensors showed lower acetone response than the Pd-in-out/csCo₃O₄ and Pt-in-out/csCo₃O₄ sensors. It can be suggested that the inner Pd or Pt particles enhances the gas response toward acetone. As a result, the acetone/hydrogen selectivity was enhanced. We therefore predict that increasing the specific surface areas of cobalt oxide secondary particles in addition to increasing the number of nanopores, and optimizing the loading of the noble metal catalyst, could further improve the gas sensing performances of such materials.

4. Conclusions

We herein reported the successful formation of nanopores within core-shell Co₃O₄ (csCo₃O₄) particles using the shell layer as a template. More specifically, during synthesis of the cobalt oxide particles, polyvinylpyrrolidone was used to cover Pt and Pd particles and suppress particle growth and aggregation. The crystallite size of the csCo₃O₄ containing Pt and Pd particles loaded both in the nanopores and on the particle surface was ~15 nm, while the particle diameter was ~50 nm, and the nanopores measured between 2 and 6 nm. Upon the loading of Pt or Pd particles on csCo₃O₄, the response and selectively to acetone gas were both improved. In addition, upon comparison with csCo₃O₄ containing Pt and Pd particles on the surface alone (and also commercially available cobalt oxide containing no nanopores), the csCo₃O₄ particles loaded with Pt or Pd particles within the nanopores exhibited a more than 4-fold increase in selectivity toward acetone gas over hydrogen gas. These results are of importance as they would be expected to contribute to the development of a diagnostic breath analyzer that exhibits a ppb-level of acetone detection in addition to a high selectivity for the various biomarker gases contained in respiratory gas.
Acknowledgments
This work was partly supported by the Nagoya University microstructural characterization platform as a “Nanotechnology Platform” program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The authors are grateful to Professor S. Arai of Nagoya University for TEM observations. We would like to thank Editage (www.editage.com) for English language editing.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
This work was supported by the Nagoya University microstructural characterization platform as a “Nanotechnology Platform” program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Table 2. Sensing properties toward 5 ppm acetone and 5 ppm hydrogen.

|                  | 5 ppm Acetone response \( S_{\text{acetone}} \) \( (R_g/R_a) \) | 5 ppm Hydrogen response \( S_{\text{hydrogen}} \) \( (R_g/R_a) \) | Selectivity \( (S_{\text{acetone}}/S_{\text{hydrogen}}) \) |
|------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Pt-in-out/csCo\(_3\)O\(_4\) | 18.7                                           | 1.4                                            | 13.4                                            |
| Pd-in-out/csCo\(_3\)O\(_4\) | 31.5                                           | 1.2                                            | 26.3                                            |
| Pt-out/csCo\(_3\)O\(_4\)  | 4.8                                            | 1.5                                            | 3.2                                             |
| Pd-out/csCo\(_3\)O\(_4\)  | 8.4                                            | 1.4                                            | 6.0                                             |
| Pt-out/Co\(_3\)O\(_4\)   | 3.1                                            | 1.4                                            | 2.2                                             |
| Pd-out/Co\(_3\)O\(_4\)   | 2.2                                            | 1.2                                            | 1.8                                             |
| csCo\(_3\)O\(_4\)        | 2.6                                            | 1.3                                            | 2.0                                             |

Figure 12. Gas sensing transients of (a) Pt-in-out/csCo\(_3\)O\(_4\), (b) Pd-in-out/csCo\(_3\)O\(_4\), (c) Pt-out/csCo\(_3\)O\(_4\), (d) Pd-out/csCo\(_3\)O\(_4\), (e) Pt-out/Co\(_3\)O\(_4\) powder, and (f) Pd-out/Co\(_3\)O\(_4\) powder to 5 ppm acetone and 5 ppm hydrogen at 200°C.
Platform* program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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