Semiconductor-type SnO₂-based NO₂ sensors operated at room temperature under UV-light irradiation

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Abstract

NO$_2$-sensing properties of typical oxide (SnO$_2$, In$_2$O$_3$, or WO$_3$)-based semiconductor gas sensors were measured at 30°C with and without UV-light irradiation (main wavelength: 365 nm), and effects of noble-metal (Pd or Pt) loading, UV-light intensity (0–134 mW cm^{-2}) and relative humidity in target gas (0–80%RH) on their NO$_2$-sensing properties were investigated in this study. The UV-light irradiation effectively reduced the resistances of all sensors, enhanced their NO$_2$ responses in some cases, and tended to accelerate their response and recovery speeds in dry air, because the UV-light irradiation promoted the adsorption and desorption of NO$_2$-species on the surface. The SnO$_2$ sensor showed the largest NO$_2$ response in dry air, among all the pristine oxide sensors, especially under weak UV-light irradiation ($\leq$ 35 mW cm^{-2}), together with relatively fast response and recovery speeds. The Pd or Pt loading onto SnO$_2$ enhanced the NO$_2$ response of the SnO$_2$ sensor and accelerated their response and recovery speeds in dry air, while XPS analysis indicated that most of the Pd and Pt nanoparticles loaded on the surface were oxidized after heat treatment at 500°C. Among all the sensors, the 0.05 wt% Pd-loaded SnO$_2$ sensor showed the largest NO$_2$ response under weak UV-light irradiation ($\leq$ 35 mW cm^{-2}), together with relatively fast response and recovery speeds. The addition of moisture to the target gas had adverse effects on the NO$_2$ responses and the response speeds of the SnO$_2$ and 0.05 wt% Pd-loaded SnO$_2$ sensors, but the weak UV-light irradiation (7 mW cm^{-2}) largely reduced the dependence of the NO$_2$ response of the *0.05*Pd/SnO$_2$ sensor on relative humidity while maintaining the large NO$_2$ response, probably because the weak UV-light irradiation promotes the desorption of physisorbed water molecules and then the effective adsorption of NO$_2$ on the *0.05*Pd/SnO$_2$ surface.

Keywords: NO$_2$ sensor; UV-light irradiation; tin dioxide; noble metal; room temperature

1. Introduction

Nitrogen dioxides (NO_2), one of gaseous air pollutants in modern society, are emitted in large amounts from various fossil-fuel combustion systems operated at elevated temperatures. Not only does NO_2 cause negative impacts on human health (e.g., an increase in respiratory symptoms and a reduction in pulmonic function) directly [1, 2], but also it reacts with water-based chemicals in the atmosphere to form acid rain causing severe environmental destruction [3]. In addition, NO_2 reacts also with various chemicals (e.g., volatile organic compounds) in the atmosphere under sunlight irradiation, to form other air pollutants such as suspended particulate matters and photochemical oxidants such as ozone, aldehydes, and peroxyacetyl nitrates, and these products also gave a serious risk to human health [4, 5]. Therefore, numerous efforts have been so far directed to developing various types of NO_2-sensing devices such as solid electrochemical [6–8], optical [9, 10], and acoustic sensors [11, 12]. Among them, it is well known that semiconductor gas sensors show relatively large sensitivity and excellent selectivity to NO_2 at elevated temperatures, and SnO_2 [13–16], In_2O_3 [17–19], WO_3 [20–23], and the related materials are especially promising candidates as the NO_2-sensing materials, among all the oxide semiconductors. However, the operation of these semiconductor gas sensors at elevated temperatures causes sintering among oxide particles and the grain growth involved, leading to reduction in the NO_2 sensitivity. The UV and/or visible-light irradiation to the semiconductor gas sensors is one of attractive approaches to solving such problems, because it can reduce the sensor resistance to allow the semiconductor gas sensors to operate even at room temperature (RT). Therefore, NO_2-sensing properties of the semiconductor gas sensors (e.g., SnO_2 [24–26], In_2O_3 [27, 28], WO_3 [29]) under UV and/or visible-light irradiation have been recently reported by many researchers, to improve the disadvantages of the operation at elevated temperatures. We also have already demonstrated that UV-light irradiation (main wavelength: 365 nm) enhanced NO_2-sensing properties of SnO_2-based sensors at RT and the

Pd loading onto SnO_2 which was prepared by a hydrothermal method improved their NO_2-sensing properties at RT under UV-light irradiation [30–32]. In this study, differences in NO_2-sensing properties between SnO_2, In_2O_3, and WO_3 sensors with and without UV-light irradiation and effects of the UV-light intensity on their NO_2-sensing properties were first examined at 30°C in air. In addition, impacts of the amount of Pd or Pt loading mainly onto the SnO_2 surface and the amount of moisture (i.e., humidity) in target gas on their NO_2-sensing properties were systematically investigated at 30°C in air.

2. Experimental

2.1 Preparation of SnO_2, In_2O_3, and WO_3 powders and loading of Pd or Pt onto their oxide surface

SnO_2 powder was prepared according to the following procedure. An appropriate amount of NH_4HCO_3 aqueous solution (1.0 mol dm^{-3}) was added into $SnCl_4$ aqueous solution (1.0 mol dm^{-3}). The obtained white precipitate was repeatedly centrifuged at a speed of 4500 rpm for 20 min and washed with pure water, and then dried at 100°C for 18 h in ambient air. The resultant powder was calcined at 600°C for 1 h in ambient air, to obtain SnO_2 powder. It was confirmed that the crystal structure of the prepared powder was tetragonal SnO_2 (JCPDS No. 41−1445) by X-ray diffraction (XRD) analysis (Rigaku Corp., RINT2200) using Cu Kα radiation (40 kV, 36 mA). In_2O_3 powder, of which crystal structure was assigned to cubic (JCPDS No. 6−416) by XRD analysis, was prepared by pyrolyzing $In(NO_3)_3$, which was dissolved in pure water, and followed by calcination at 600°C for 1 h in ambient air. WO_3 powder was prepared according to the following procedure. An appropriate amount of HNO_3 aqueous solution (0.8 mol dm^{-3}) was added into $NaWO_4$ aqueous solution (0.15 mol dm^{-3}). The yellow resultant precipitate was repeatedly centrifuged at a speed of 4500 rpm for 20 min and washed with pure water, and then dried at 100°C for 18 h in ambient air. The resultant powder was calcined at 500°C for 2 h in

ambient air, to obtain WO$_3$ powder. It was confirmed that the crystal structure of the prepared powder was monoclinic WO$_3$ (JCPDS No. 43−1035) by XRD analysis. Specific surface area of the SnO$_2$, In$_2$O$_3$, or WO$_3$ powder obtained, which was measured by the Brunauer–Emmett–Teller (BET) method using N$_2$ adsorption-desorption isotherms (Micromeritics Instrument Corp., Tristar3000), was 21.2, 23.7, or 12.0 m^2 g^{-1}, respectively.

In some cases, Pd or Pt nanoparticles were loaded onto the surface of these oxide powders. After an appropriate amount of oxide powders was added into Pd(NO$_3$)$_2$ or PtCl$_4$ aqueous solution (0.75 mol dm^{-3}) and then they were ultrasonicated at RT for 1 h, they were evaporated to dryness at 100°C for 2 h in air. The resultant solids were heat-treated at 200°C for 2 h in H$_2$ to obtain metallic nanoparticles on the oxide surface. The obtained oxide powders loaded with noble metal (N) were denoted as nN/MO [n: amount of noble metal (N: Pd or Pt), 0.03–0.10 (wt%)]. Specific surface area of the nN/MO powders obtained was hardly influenced by the loading of the noble-metal nanoparticles (e.g., specific surface area of 0.05Pd/SnO$_2$ powder: ca. 21.0 m^2 g^{-1}), because the amount of noble-metal loading onto the oxide surface was really small (≤ 0.10 wt%).

Chemical states of the noble metal (Pd or Pt) on the surface of representative nN/MO powders were characterized by X-ray photoelectron spectroscopy using Mg Kα radiation (XPS, Kratos, ACIS-TLATRA DLD), and the binding energy was calibrated using the C 1s level (285.0 eV) from usual contamination. Optical properties of representative oxide powders (SnO$_2$ and 0.05Pd/SnO$_2$) were investigated by ultraviolet (UV)–visible (Vis) spectrophotometer (JASCO Corp., V-650) with an integrated sphere (JASCO Corp., ISV-722).

2.2 Fabrication of thick film sensors and measurement of their gas-sensing properties

Thick film sensors were fabricated by screen printing employing the paste of each oxide powder on an alumina substrate equipped with a pair of interdigitated Pt electrodes (gap size:

ca. 500 μm), followed by calcination at 500°C for 1 h in ambient air. The top-view photograph of a representative sensor element, *0.05*Pd/SnO$_2$ sensor, is shown in Fig. 1(a). A thick film sensor was set in a test chamber with a temperature-controlled stage (Lincam Scientific Instr., LST420), which was connected with gas-flow system, and gas responses of these sensors were measured to 5 ppm NO$_2$ balanced with dry or wet (relative humidity (RH): 20–80%) air at 30°C at a flow rate of 100 cm^3 min^{-1} under UV-light irradiation by using light-emitting diode (UV-LED, Asahi Spectra Co., Ltd., POT-365, main wavelength: 365 nm, irradiation intensity: 0.8–134 mW cm^{-2}), after pre-heat treatment at 200°C for several tens of minutes in dry or wet air. The experimental setup for gas-sensing measurements under UV-light irradiation is shown in Fig. 1(b). The magnitude of response to NO$_2$ was defined as the ratio (R_{NO_2}/R_a) of sensor resistance in NO$_2$ balanced with air (R_{NO_2}) to that in air (R_a). The l% response time ($T_{RS}(l)$) were defined as a period necessary to reach l% value of the resistance change (log R_{NO_2} − log R_a) from the logarithm of sensor resistance in a base gas (log R_a) to that that in NO$_2$ balanced with air (log R_{NO_2}, generally after 15 min from the injection of NO$_2$ in air). The m% recovery time ($T_{RC}(m)$) were defined as a period necessary to reach $(100 − m)$% value of the resistance change (log R_{NO_2} − log R_a) after the injection of NO$_2$ in air was stopped. The response and recovery times contain a delay period from the gas-switching time to the response- and recovery-starting times, ca. 1.2 min, in this study, since the dead volume of the gas-flow pathway and the chamber in the measurement apparatus is ca. 106 cm^3.

3. Results and Discussion

3.1 NO$_2$-sensing properties of unloaded oxide sensors under UV-light irradiation

Figure 2 shows response transients of a SnO$_2$ sensor to 5 ppm NO$_2$ in dry air at 30°C under different UV-light irradiation intensities. Response transients of In$_2$O$_3$ and WO$_3$ sensors to 5 ppm NO$_2$ in dry air at 30°C under different UV-light irradiation intensities were also shown in

Fig. S1, and variations in their responses (R_{NO_2}/R_a) to 5 ppm NO_2, resistances in dry air (R_a), and 90% response and 10% recovery times ($T_{RS}(90)$ and $T_{RC}(10)$, respectively) with UV-light intensity were summarized in Fig. 3. In addition, typical sensing characteristics of these sensors were shown in Table 1. The resistance of the SnO_2 sensor under no UV-light irradiation was relatively large in dry air (R_a: ca. 2.5×10^5 Ω), since SnO_2 was a typical n-type semiconducting oxide and the density of electron carriers was relatively low at 30°C [13–15, 24, 25, 30–32]. In addition, the SnO_2 sensor showed a large positive NO_2 response (ca. 81) under no UV-light irradiation. The behavior indicates that a large amount of NO_2 molecules negatively chemisorbed as NO_2^- on the SnO_2 surface, trapping electron from the SnO_2 bulk [13–15]. However, the response speed was really slow ($T_{RS}(90)$: ca. 12 min) and the sensor showed little recovery behavior ($T_{RC}(10)$: ca. 30 min). Weak UV-light irradiation abruptly decreased the resistance of the SnO_2 sensor in dry air (e.g., R_a: ca. 1.2×10^4 Ω at 7 mW cm^{-2}) and the further increase in the UV-light intensity decreased the resistance gradually, because the UV-light irradiation excited electrons in the SnO_2 bulk to the conduction band and/or it reduced negatively oxygen adsorbates (mainly, O_2^-) on the SnO_2 surface [25, 33]. The NO_2 response of the SnO_2 sensor under weak UV-light irradiation (especially, ≤7 mW cm^{-2}) was much larger than that under no UV-light irradiation, but the further increase in the UV-light intensity (more than 35 mW cm^{-2}) decreased the NO_2 response, in comparison with that under no UV-light irradiation. The response speed was hardly improved by the weakest UV-light irradiation (0.8 mW cm^{-2}). The further increase in the UV-light intensity (≥7 mW cm^{-2}) was quite effective in reducing the response time, but the response time was less dependent on the UV-light intensity in the range between 7 mW cm^{-2} and 134 mW cm^{-2}. On the other hand, the recovery speed was relatively improved even by the weakest UV-light irradiation ($T_{RC}(10)$: ca. 5.1 min at 0.8 mW cm^{-2}), and the further increase in UV-light intensity tended to reduce the recovery time, probably because the UV-light irradiation promoted the desorption of NO_2^- on the SnO_2 surface.

However, even strong UV-light irradiation was not able to turn the resistance in dry air back to the original level before the NO_2 injection, during the measurement period. These facts indicate that the injection of photon energy into the SnO_2 was effective in enhancing chemical adsorption/desorption of NO_2 on the SnO_2 surface and the balance between adsorption and desorption of NO_2 probably determined not only the magnitude of NO_2 response but also the response and recovery speeds.

The effects of UV-light irradiation on the NO_2-sensing properties of In_2O_3 and WO_3 sensors are fundamentally similar to those of the SnO_2 sensor, but some important behavior was different among them. The resistance of both the sensors decreased with an increase in UV-light intensity, as is the case with that of the SnO_2 sensor. The resistance of the In_2O_3 sensor was smaller than that of the SnO_2 sensor, while the resistance of the WO_3 sensor was larger that of the SnO_2 sensor, with or without UV-light irradiation. The In_2O_3 sensor showed the largest NO_2 response among all the pristine oxide sensors when UV light was not irradiated. However, even weak UV-light irradiation largely reduced the NO_2 response of the In_2O_3 sensor and the NO_2 response decreased with an increase in UV-light intensity. Thus, the NO_2 response of the In_2O_3 sensor under UV-light irradiation was much smaller than that of the SnO_2 sensor. The dependence of response and recovery speeds of the In_2O_3 sensor on UV-light intensity was also quite similar to those of the SnO_2 sensor, and the UV-light irradiation was effective in reducing the response and recovery times. On the other hand, the NO_2 response of the WO_3 sensor was not able to be confirmed under no UV-light irradiation, because the resistance in 5 ppm NO_2 balanced with dry air was too high to be measured with the measurement apparatus used in this study. However, the magnitude of NO_2 response of the WO_3 sensor under no UV-light irradiation was over 900, which was larger than that of the SnO_2 sensor. The large NO_2 response of the WO_3 sensor under no UV-light irradiation in comparison with other oxide sensors has already been reported by several researchers [19–22]. The UV-light irradiation drastically

reduced the NO_2 response, and the NO_2 response of the WO_3 sensor under UV-light irradiation was the smallest among all the sensors under all the UV-light irradiation range. The response and recovery speeds under no UV-light irradiation were not also be calculated because of too high resistance in 5 ppm NO_2 balanced with dry air beyond the range of measurement, and thus the effect of the UV-light irradiation on the response and recovery speeds was not able to be discussed in this study. However, the response and recovery speeds of the WO_3 sensor even under UV-light irradiation were much slower than those of the SnO_2 and In_2O_3 sensors. These results indicate that the WO_3 sensor, which generally shows large NO_2 response at elevated temperatures, is not suitable for detecting NO_2 at RT under UV-light irradiation. Considering the above results based on the impacts of the UV-light intensity on the magnitude of their NO_2 responses, we should investigate the NO_2-sensing properties of these sensors under much weaker UV-light irradiation, but such weak UV-light irradiation (< 0.8 mW cm^{-2}) is out of control for our experimental setup. In addition, the too slow response and recovery speeds of the WO_3 sensor under weak UV-light irradiation presently make our interests go away from the investigation in this study, especially from the aspect of the practice use. As mentioned above, the WO_3 sensor as well as the In_2O_3 sensor showed smaller NO_2 responses under UV-light irradiation at ca. 365 nm in this study, than that of the SnO_2 sensor. However, the In_2O_3 and WO_3 sensors may be able to detect NO_2 and other gases more sensitively under visible-light irradiation in comparison with the SnO_2 sensor, because the band gaps of In_2O_3 [28] and WO_3 [29] were generally lower than that of SnO_2. The impacts of wavelength of irradiated light on the gas-sensing properties of these sensors will be investigated in the near future.

3.2 Effects of Pd loading onto SnO_2 and In_2O_3 sensors on their NO_2-sensing properties

Effects of Pd loading onto both the SnO_2 and In_2O_3 sensors, which showed much excellent NO_2-sensing properties and relatively lower resistance in dry air under UV-light irradiation than

the WO$_3$ sensor, on the NO$_2$-sensing properties were investigated in this study. Figure 4 shows response transients of representative nPd/SnO$_2$ sensors (n: *0.05* and *0.07*) to 5 ppm NO$_2$ at 30°C in dry air under different UV-light irradiation intensities. In addition, Fig. 5 shows variations in response to 5 ppm NO$_2$ and resistance of all nPd/SnO$_2$ sensors in dry air with the amount of Pd loaded, and Fig. S2 shows variations in 90% response and 60% recovery times of all nPd/SnO$_2$ sensors with UV-light intensity, together with those of the SnO$_2$ sensor. Typical sensing characteristics of the *0.05*Pd/SnO$_2$ sensor were shown also in Table 1. Here, the resistance of most of nPd/SnO$_2$ sensors under no UV-light irradiation was instable in 5 ppm NO$_2$ balanced with dry air, and the NO$_2$-sensing property of only the *0.05*Pd/SnO$_2$ sensor was able to be measured under no UV-light irradiation. The Pd loading onto the SnO$_2$ surface increased the resistance in dry air with or without UV-light irradiation. It is well known that Pd nanoparticles are oxidized by heat treatment at elevated temperatures in air [34–36]. Therefore, XPS spectra of Pd on the surface of representative nPd/SnO$_2$ powders (n: *0.05* and *0.10*) after the heat treatment at 500°C for 1 h in ambient air, which is the same heat-treatment condition as the sensor fabrication, were investigated as shown in Fig. 6. The obtained XPS spectra of Pd 3d$_{5/2}$ and 3d$_{3/2}$ obviously exhibited that the heat treatment at 500°C oxidized almost all Pd nanoparticles on the surface of *0.05*Pd/SnO$_2$ and *0.10*Pd/SnO$_2$ powders, to form PdO [36]. The electron affinity of PdO (ca. 5.5 eV) [34] are larger than that of SnO$_2$ (ca. 4.5 eV) [37, 38], and therefore electrons of SnO$_2$ are likely transferred into the PdO nanoparticles. This is the reason why the resistance of nPd/SnO$_2$ sensors in dry air increased with an increase in the amount of Pd loading, as shown in Fig. 5(b). In addition, the resistance of all the nPd/SnO$_2$ sensors monotonically decreased with an increase in UV-light intensity, as is the case with the SnO$_2$ sensor. The Pd loading effectively enhanced the NO$_2$ response of the SnO$_2$ sensor, probably because the large amount of NO$_2$ molecules directly adsorbed on the surface of PdO nanoparticles and SnO$_2$ and/or the NO$_2$ species adsorbed on the PdO surface spilt over onto the

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SnO$_2$ surface. The UV-light irradiation drastically changed their response behavior to 5 ppm NO$_2$ at 30°C in dry air. Namely, all the nPd/SnO$_2$ sensors showed the largest NO$_2$ response under UV-light irradiation of 7 mW cm^{-2} (ca. 3.4×10^3 for *0.05*Pd/SnO$_2$), their NO$_2$ responses decreased with an increase in the UV-light intensity, regardless of the amount of Pd loaded onto the SnO$_2$ surface, and thus the NO$_2$ responses of SnO$_2$ and *0.05*Pd/SnO$_2$ sensors under strong UV-light irradiation of 75 and 134 mW cm^{-2} was lower than those under no UV-light irradiation. Then, the *0.05*Pd/SnO$_2$ sensor showed the largest NO$_2$ response among all the sensors at every UV-light intensity. The *0.05*Pd/SnO$_2$ sensor, which only had relatively stable NO$_2$ response among all the nPd/SnO$_2$ sensors under no UV-light irradiation, showed quite slow response speed without recovery behavior under no UV-light irradiation, as is the case with the SnO$_2$ sensor. The weak UV-light irradiation stabilized the NO$_2$-response behavior of the nPd/SnO$_2$ sensors and drastically accelerated the response speeds of all the nPd/SnO$_2$ sensors to NO$_2$ (e.g., $T_{RS}(90)$: ca. 2.8 min for the *0.05*Pd/SnO$_2$ sensor at 7 mW cm^{-2}), but the further increase in UV-light irradiation tended to slow down the response speeds (e.g., $T_{RS}(90)$: ca. 6.7 min for the *0.05*Pd/SnO$_2$ sensor at 134 mW cm^{-2}). On the other hand, an increase in UV-light irradiation tended to improve the recovery speeds of all the nPd/SnO$_2$ sensors to NO$_2$ (e.g., $T_{RC}(60)$: ca. 5.5 min, for the *0.05*Pd/SnO$_2$ sensor at 134 mW cm^{-2}).

The resistance change of SnO$_2$ and *0.05*Pd/SnO$_2$ sensors with O$_2$ injection into dry N$_2$ was investigated at 30°C with and without UV-light irradiation, to clarify the effects of adsorption and desorption of oxygen species on their resistances. Figure 7 shows representative response transients of the SnO$_2$ and *0.05*Pd/SnO$_2$ sensors to 30% O$_2$ in dry N$_2$ at 30°C and variations in response of these sensors to 30% O$_2$ in dry N$_2$ at 30°C with UV-light intensity. The magnitude of response to 30% O$_2$ in dry N$_2$ was defined as the ratio of sensor resistance in 30% O$_2$ balanced with dry N$_2$ (after 70 min upon exposure to O$_2$) to that in dry N$_2$. These sensors were heat-treated in dry N$_2$ at 200°C for 2 h, prior to the measurement, to remove oxygen species (O$_2^-$)

which are adsorbed on the SnO_2 surface. The resistance of the SnO_2 sensor was smaller than that of the *0.05*Pd/SnO_2 sensor even in dry N_2 with or without UV-light irradiation, and the UV-light irradiation reduced these resistances in dry N_2, as is the cases in dry air. These facts under the O_2-free atmosphere strongly supports that electrons in SnO_2 and *0.05*Pd/SnO_2 bulk excited from valence band and/or some defect levels to the conduction band by the UV-light irradiation, because most of oxygen species (O_2^-) on their surface should be desorbed by the pre-heat treatment in N_2 at 200°C. Figure 8 shows diffuse reflectance UV−Vis spectra (normalized Kubelka–Munk function ($F(r)/F(r)_{MAX}$) *vs*. wavelength, where r stands for reflectance and $F(r)_{MAX}$ is the maximum of Kubelka−Munk function ($F(r)$)) of SnO_2 and *0.05*Pd/SnO_2 powders, together with their Tarc plots (($hvF(r))^2$ *vs*. photon energy, where h and v stand for Plank constant and frequency, respectively [39]). Band gaps (E_g) of SnO_2 and *0.05*Pd/SnO_2, which was determined from the Tarc plots, were ca. 3.5 eV and ca. 3.7 eV, respectively, which were closely correspondent with those of typical SnO_2, 3.4–3.8 eV [38, 40, 41]. The difference in E_g between SnO_2 and *0.05*Pd/SnO_2 probably depends on whether or not PdO nanoparticles were loaded onto their surfaces and/or they were heat-treated at 200°C under H_2 atmosphere. Since the band-gap energies of SnO_2 and *0.05*Pd/SnO_2 powders are slightly larger than main photon energy of UV light emitted from the UV-LED (ca. 3.40 eV, which was calculated from the main wavelength, 365 nm), electrons in valence band cannot easily excite to the conduction band. However, the optical absorption edge up to the range of visible light (i.e., >400 nm) was observed for the SnO_2 and *0.05*Pd/SnO_2 powders, which are pale yellow and pale brown, respectively, in Fig. 8. The absorption probably arises from some energy levels of various defects such as oxygen vacancies [40], since these powders were prepared under relatively moderate condition (at 600°C for 1 h in ambient air). These optical properties are one of the reasons why the UV-light irradiation reduced even the resistance of both the sensors in dry N_2 (see Fig. 7). The injection of 30% O_2 in dry N_2 increased the resistance of both the sensors with

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or without UV-light irradiation, because oxygen species negatively adsorbed on the oxide surface, according to the forward reaction of the following equation [25, 33].

$$O_2 + e^- \rightleftarrows O_2^-(ad) \tag{1}$$

However, the resistances of both the sensors even after 70 min upon exposure to 30% O_2 in dry N_2 (ca. 1.2×10^3 Ω and ca. 3.0×10^4 Ω for SnO_2 and 0.05Pd/SnO_2 sensors, respectively) were much smaller than those in dry air (21% O_2) (ca. 2.3×10^5 Ω and ca. 4.0×10^5 Ω for SnO_2 and 0.05Pd/SnO_2 sensors, respectively, cf. Figs. 2–5) under no UV-light irradiation. On the other hand, the UV-light irradiation improved the rate of resistance change of both the sensors. Namely, the resistance of the SnO_2 sensor after 70 min upon exposure to 30% O_2 in dry N_2 under UV-light irradiation (e.g., ca. 7.9×10^2 Ω at 134 mW cm^{-2}) was slightly smaller than those in dry air (21% O_2) (e.g., ca. 3.2×10^3 Ω at 134 mW cm^{-2}) and the resistance of the 0.05Pd/SnO_2 sensor after 70 min upon exposure to 30% O_2 in dry N_2 under UV-light irradiation (e.g., ca. 4.5×10^3 Ω at 134 mW cm^{-2}) was already larger than those in dry air (21% O_2) (e.g., ca. 4.0×10^3 Ω at 134 mW cm^{-2}). These results obviously show that the UV-light irradiation enhanced the rate of the forward reaction of the eq. (1), producing the large amount of negatively adsorbed oxygen species (O_2^-). In addition, the behavioral difference between these sensors indicates that PdO nanoparticles on the SnO_2 surface accelerated the adsorption of O_2^- onto the surface and the adsorption rate of oxygen species on the PdO surface (and/or the amounts) was larger than that on the SnO_2 surface. Furthermore, the UV-light irradiation drastically accelerated also the desorption rate of negatively adsorbed oxygen species (i.e., the reverse reaction of eq. (1)), on the basis that the resistances of both the sensors smoothly decreased after the injection of O_2 in dry N_2 was stopped. However, large NO_2 responses of the SnO_2 and 0.05Pd/SnO_2 sensors with their fast response speed and slow recovery speed in dry air (see Figs. 2–4 and S2) shows that NO_2 molecules promptly adsorbed even onto the oxide surface which was covered with O_2^- adsorbed, according to the forward reaction of the following equation [24, 42].

$$NO_2 + e^- \rightleftarrows NO_2^-(ad) \qquad\qquad (2)$$

In summary, the forward reaction of the following equation promptly proceeds even in a low concentration (5 ppm) of NO_2 balanced with dry air (21% O_2), probably because the adsorption energy of NO_2 onto the surface (eq. (2)) is much larger than that of O_2 (eq. (1)).

$$NO_2 + O_2^-(ad) \rightleftarrows NO_2^-(ad) + O_2 \qquad\qquad (3)$$
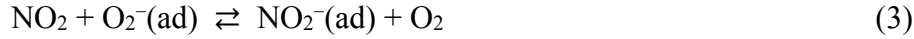
In addition, Ruhland et al. reported that physisorbed NO_2 molecules form deeper acceptor levels on the SnO_2 surface than negatively adsorbed oxygen species (O_2^-), and thus bound electrons are transferred from the O_2^- to physisorbed NO_2 molecules forming NO_2^- species [43]. The deep acceptor levels which are formed by NO_2^- species on the oxide surface is the main reason of large resistances of the sensors in NO_2 balanced with dry air. Furthermore, Fig. 7 shows the response of the *0.05*Pd/SnO_2 sensor to 30% O_2 was larger than that of the SnO_2 sensor in dry N_2 and the recovery speed of the *0.05*Pd/SnO_2 sensor was faster than that of the SnO_2 sensor. This is probably because PdO nanoparticles on the SnO_2 surface accelerated the adsorption and desorption of O_2, which is one of important factors in determining faster response and recovery speeds of the *0.05*Pd/SnO_2 sensor to NO_2 than that of the SnO_2 sensor.

On the other hand, an increase in UV-light intensity reduced the magnitude of NO_2 response of these sensors. It is well known that NO_2 was converted to NO and atomic oxygen under UV-light irradiation, according to the following reaction [44].

$$NO_2 + h\nu \rightarrow NO + O \qquad\qquad (4)$$

In addition, an increase in UV-light intensity reduces the amount of adsorbed NO_2^- on the oxide surface, and thus accelerates the reverse reaction of eq. (2). It is expected that these reactions were promoted with increasing UV-light intensity to decrease the NO_2 response of these sensors. Furthermore, an increase in UV-light intensity improved the response and recovery speeds of both the sensors, because the rates of adsorption and desorption of O_2 and NO_2 increased with increasing UV-light intensity.

Figure S3 shows response transients of 0.05Pd/In$_2$O$_3$ and 0.07Pd/In$_2$O$_3$ sensors to 5 ppm NO$_2$ at 30°C in dry air under different UV-light irradiation intensities, and Fig. S4 shows variations in response of these sensors to 5 ppm NO$_2$ and resistance in dry air with the amount of Pd loaded and UV-light intensity, respectively. In addition, an XPS spectrum of Pd 3d$_{5/2}$ and 3d$_{3/2}$ on the surface of representative nPd/In$_2$O$_3$ powder (n: 0.07) after heat treatment at 500°C for 1 h in ambient air is shown in Fig. S5. The XPS spectrum of Pd was quite similar to those of 0.05Pd/SnO$_2$ and 0.10Pd/SnO$_2$ powders (Fig. 6), which indicates that most of the Pd nanoparticles loaded on the 0.07Pd/In$_2$O$_3$ powder were also oxidized to form PdO [36]. The resistance in dry air increased with an increase in the amount of Pd loaded onto In$_2$O$_3$, because of smaller electron affinity of In$_2$O$_3$ (ca. 3.7 eV) [45] than the electron affinity of PdO, and it decreased with an increase in UV-light intensity, as is the case with the nPd/SnO$_2$ sensors. However, even the response of the 0.05Pd/In$_2$O$_3$ sensor to 5 ppm NO$_2$ under UV-light irradiation of 7 mW cm^{-2} (ca. 38), which was the largest among those of the nPd/In$_2$O$_3$ sensors, was much smaller than that of the 0.05Pd/SnO$_2$ sensor (R_{NO_2}/R_a: ca. 3.4×10^3). The response times of the nPd/In$_2$O$_3$ sensors (e.g., $T_{RS}(90)$: ca. 3.2 min and ca. 3.0 min for the 0.05Pd/In$_2$O$_3$ sensor at 7 and 134 mW cm^{-2}, respectively) were comparable to (or faster than, in some cases) those of the nPd/SnO$_2$ sensors (e.g., $T_{RS}(90)$: ca. 2.8 min and ca. 6.8 min for the 0.05Pd/SnO$_2$ sensor at 7 and 134 mW cm^{-2}, respectively), while the recovery times of the nPd/In$_2$O$_3$ sensors (e.g., $T_{RC}(60)$: ca. 37 min and ca. 30 min for the 0.05Pd/In$_2$O$_3$ and 0.07Pd/In$_2$O$_3$ sensors at 7 mW cm^{-2}, respectively) were much longer to those of the nPd/SnO$_2$ sensors (e.g., $T_{RC}(60)$: ca. 16 min and ca. 17 min for the 0.05Pd/SnO$_2$ and 0.07Pd/SnO$_2$ sensors at 7 mW cm^{-2}, respectively). These results show that the Pd loading was not effective in improving the NO$_2$-sensing properties of the In$_2$O$_3$ sensor under UV-light irradiation at least, in comparison with those of the SnO$_2$ sensor. Hereafter, the gas-sensing properties of the nPd/In$_2$O$_3$ sensors should be measured under visible-light irradiation, together with those of both the In$_2$O$_3$ and WO$_3$

sensors as shown in Section 3.1, to clarify the potential as a light-driven gas sensor which can be operated in the vicinity of room temperature.

3.3 Effects of Pt loading onto SnO$_2$ sensor on the NO$_2$-sensing properties

Effects of Pt loading on the NO$_2$-sensing properties of the SnO$_2$ sensor were also investigated in this study. XPS spectra of Pt 4f$_{7/2}$ and 4f$_{5/2}$ on the surface of prepared nPt/SnO$_2$ powders (n: *0.05* and *0.10*) after heat treatment at 500°C for 1 h in ambient air, which is the same heat-treatment condition as the sensor fabrication, are shown in Fig. 9. A major majority of the Pt nanoparticles loaded on both the powders (~90%) was oxidized after the heat treatment, to turn into PtO$_2$ and PtO (Pt^{4+}:Pt^{2+}:Pt (metal) = 50.9:38.6:10.5 for *0.05*Pt/SnO$_2$ and 57.5:33.3:9.2 for *0.10*Pt/SnO$_2$) [46]. Figure S6 shows response transients of *0.05*Pt/SnO$_2$ and *0.10*Pt/SnO$_2$ sensors to 5 ppm NO$_2$ at 30°C in dry air under UV-light irradiation, and Fig. 10 shows variations in response of these sensors to 5 ppm NO$_2$ with UV-light intensity, together with those of the SnO$_2$, *0.05*Pd/SnO$_2$ and *0.10*Pd/SnO$_2$ sensors. In addition, typical sensing characteristics of the *0.05*Pt/SnO$_2$ sensor were shown in Table 1. The resistance of these sensors in dry air, which increased with an increase in the amount of Pt loaded onto SnO$_2$, also decreased with an increase in UV-light intensity. The 0.05 wt% Pt loading improved the NO$_2$ response and the response speed of the SnO$_2$ sensor under every UV-light irradiation intensity (e.g., R_{NO_2}/R_a: ca. 1.5×10^3 and $T_{RS}(90)$: ca. 3.2 min for the *0.05*Pt/SnO$_2$ sensor at 7 mW cm^{-2}), but the effectiveness was smaller than that of the 0.05 wt% Pd loading, especially under higher UV-light irradiation. On the other hand, the 0.05 wt% Pt loading was effective in improving only the recovery speed under every UV-light irradiation intensity (e.g., $T_{RC}(60)$: ca. 13 and ca. 3.5 min for the *0.05*Pt/SnO$_2$ sensor at 7 and 134 mW cm^{-2}, respectively). However, an increase in the amount of Pt loading (i.e., 1.0 wt% Pt loading) tended to slow down the response and recovery speeds as well as to reduce the NO$_2$ response. These results indicate that the Pd loading

onto the SnO_2 surface was more effective in improving the NO_2-sensing properties of the SnO_2 sensor at 30°C in dry air under UV-light irradiation, than the Pt loading.

3.4 Effects of humidity in gaseous atmosphere on the NO_2-sensing properties of SnO_2 and *0.05*Pd/SnO_2 sensors

Figure S7 shows representative response transients of SnO_2 and *0.05*Pd/SnO_2 sensors to 5 ppm NO_2 in wet air (80%RH), and Fig. 11 shows variations in response (R_{NO_2}/R_a) of these sensors to 5 ppm NO_2 in air at 30°C under different UV-light irradiation intensities with relative humidity. The addition of moisture into air drastically had great impacts on the NO_2-sensing properties of both the sensors. The resistances of both the sensors in wet air (80%RH) decreased with an increase in UV-light intensity, as is the case with those in dry air. The resistance of the SnO_2 sensor in wet air (80%RH) under no UV-light intensity (ca. $2.2×10^5$ Ω) was slightly smaller than that in dry air (ca. $2.5×10^5$ Ω, see Figs. 2 and 3), and the addition of moisture did not have a considerable influence on the resistance in air, even under UV-light irradiation. These results imply that adsorbed water molecules have only a little influence on the adsorption state of oxygen adsorbates (O_2^-) on the SnO_2 surface. The loading of 0.05 wt% Pd largely increased the resistance of the SnO_2 sensor, also in wet air (80%RH) and the addition of moisture into air largely decreased the resistance of the *0.05*Pd/SnO_2 sensor, with or without UV irradiation (e.g., ca. $6.3×10^5$ Ω in dry air (see Figs. 4 and 5) and ca. $2.8×10^5$ Ω in wet air (80%RH) under no UV irradiation, and ca. $2.5×10^4$ Ω in dry air (see Figs. 4 and 5) and ca. $2.5×10^3$ Ω in wet air (80%RH) under UV irradiation at 75 mW cm^{-2}). These facts indicate that the loaded PdO nanoparticles enhanced the adsorption of water molecules on the SnO_2 surface and then the adsorbed water molecules reduced the resistance of the *0.05*Pd/SnO_2 sensor at 30°C [31]. These effects of the Pd loading on the resistance of a SnO_2 sensor at 30°C under UV-light irradiation seem to be different from those at elevated temperatures [47]. The injection of NO_2 in wet air

increased the resistance of both the sensors with or without UV-light irradiation, but the impacts of the moisture addition on the NO_2-response behavior were dependent on the relative humidity and the UV-light intensity. The NO_2 response of the SnO_2 sensor drastically decreased with an increase in the relative humidity under no UV-light irradiation, and the SnO_2 sensor showed only a small NO_2 response (R_{NO_2}/R_a at 80%RH: ca. 1.4) in air containing a large amount of moisture under no UV-light irradiation. The UV-light irradiation enhanced the NO_2 response of the SnO_2 sensor in wet air, and the NO_2 response of the SnO_2 sensor in wet air under UV-light irradiation tended to increase with a decrease in UV-light intensity. However, the NO_2 responses of the SnO_2 sensor in wet air ($\geq$40%RH) even under weak UV-light irradiation (7 and 35 mW cm^{-2}) were much smaller than those in dry air (see Figs. 2 and 3). On the other hand, the further increase in UV-light intensity (namely, at 75 and 134 mW cm^{-2}) seems to decrease the dependency of relative humidity on the NO_2 response of the SnO_2 sensor, probably because the UV-light irradiation reduced the adsorption of water molecules on the SnO_2 surface. The addition of moisture in air also led to slow down the response speed under UV-light irradiation (especially at 7 mW cm^{-2}, $T_{RES}(90)$: ca. 27.5 min in wet air (80%RH) in comparison with ca. 4.6 min in dry air (see Figs. 2 and 3)). These NO_2-sensing properties of the SnO_2 sensor show that a large amount of physisorbed water molecules, which do not contribute to a reduction in the sensor resistance, exist on the SnO_2 surface in wet air with or without UV-light irradiation and they interfered the negatively charged adsorption of NO_2 onto the SnO_2 surface. However, the injection of a large amount of photon energy to the SnO_2 sensor (i.e., strong UV-light irradiation at 75 and 134 mW cm^{-2}) is likely to promote the desorption of the physisorbed water molecules on the SnO_2 surface in wet air, to reduce the RH dependence of the NO_2 response.

On the other hand, the injection of NO_2 unstabilized the resistance of the *0.05*Pd/SnO_2 sensor in wet air (80%RH) under no UV-light irradiation even though the resistance in wet air (80%RH) was able to be somehow measured (R_a at 80%RH: ca. 2.5×10^5 Ω), and thus the

response transient of the *0.05*Pd/SnO$_2$ sensor in wet air (80%RH) under no UV-light irradiation

is not shown in Figs. S7 and 11. The NO$_2$ response of the *0.05*Pd/SnO$_2$ sensor was much larger

than that of the SnO$_2$ sensor, also in wet air under each UV-light irradiation intensity, and the

NO$_2$ response also tended to decrease with an increase in the relative humidity and UV-light

intensity. In addition, the NO$_2$ response at stronger UV-light irradiation ($\geq$35 mW cm^{-2}) was

largely dependent on the relative humidity (especially in the range of 0–40%RH (a small

amount of relative humidity)). The stronger UV-light irradiation probably promoted the

production of hydroxyl groups from physisorbed water molecules on the *0.05*Pd/SnO$_2$ surface,

to inhibit the adsorption of NO$_2$. On the other hand, the NO$_2$ response under the weakest UV-

light irradiation (namely, at 7 mW cm^{-2}) was the largest among all conditions, and it showed

the smallest dependency of the NO$_2$ response of the *0.05*Pd/SnO$_2$ sensor on the relative

humidity (R_{NO_2}/R_a: ca. 1.9×10^3 in wet air (80%RH) at 7 mW cm^{-2}). These results probably

indicate that a small amount of photon energy (i.e., $\leq$7 mW cm^{-2}) promotes the desorption of

physisorbed water molecules and then the effective adsorption of NO$_2$ on the *0.05*Pd/SnO$_2$

surface. The response speed of the *0.05*Pd/SnO$_2$ sensor in wet air (80%RH) was quite slower

than that in dry air. In addition, the *0.05*Pd/SnO$_2$ sensor showed the fastest response speed in

wet air (80%RH) under the weakest UV-light irradiation ($T_{RS}(90)$: ca. 8.4 min at 7 mW cm^{-2}),

and the response speed tended to slow down with an increase in UV-light intensity in spite of

the small NO$_2$ response (e.g., $T_{RS}(90)$: ca. 11.8 min at 134 mW cm^{-2}). On the other hand, the

recovery speed of the *0.05*Pd/SnO$_2$ sensor was hardly dependent on relative humidity (e.g.,

$T_{RC}(60)$ in wet air (80%RH): ca. 18.9 min and 5.3 min at 7 mW cm^{-2} and 134 mW cm^{-2},

respectively, and $T_{RC}(60)$ in dry air (cf. Figs. 2 and 3): ca. 16.1 min and 5.5 min at 7 mW cm^{-2}

and 134 mW cm^{-2}, respectively), and the recovery speed in wet air also increased with an

increase in UV-light intensity, as is the case in dry air. The behavior probably indicates that the

desorption rate of NO$_2^-$ accelerated with an increase in UV-light intensity, but physisorbed

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water molecules and hydroxyl groups on the *0.05*Pd/SnO$_2$ surface have little influence on the desorption rate of NO$_2^-$ under UV-light irradiation.

Conclusion

Effects of noble-metal loading onto typical semiconducting oxides (SnO_2, In_2O_3, and WO_3), intensity of UV-light irradiation to these sensors and addition of moisture in target gas on the NO_2-sensing properties of the oxides-based semiconductor gas sensors were investigated in air at 30°C in this study. The UV-light irradiation effectively reduced the resistances of all the pristine oxide sensors and accelerated the response and recovery speeds of the SnO_2 and In_2O_3 sensors in dry air, while the magnitude of response of all the sensors to 5 ppm NO_2 tended to decrease with an increase in UV-light intensity. However, only the SnO_2 sensor showed larger NO_2 response in dry air under weak UV-light irradiation ($\leq$ 35 mW cm^{-2}) than that under no UV-light irradiation. The Pd loading increased the sensor resistance and enhanced the NO_2 response of the SnO_2 sensor in dry air under every UV-light irradiation intensity. In addition, the Pd loading accelerated the response speeds of the SnO_2 sensor mainly under weak UV-light irradiation ($\leq$ 35 mW cm^{-2}), while the recovery speeds of the nPd/SnO_2 sensors were faster than that of the SnO_2 sensors under every UV-light irradiation intensity. The difference in these NO_2-sensing properties of SnO_2 and nPd/SnO_2 sensors in dry air with and without UV-light irradiation seems to arise from adsorption-desorption rates of NO_2 and O_2 on each oxide surface under each UV-light irradiation intensity. In addition, the Pd loading onto the SnO_2 sensor was more effective in improving the NO_2-sensing properties than the Pt loading onto the SnO_2 sensor as well as the Pd loading onto the In_2O_3 sensor. On the other hand, the addition of moisture in target gas tended to reduce the magnitude of NO_2 responses of both the SnO_2 and *0.05*Pd/SnO_2 sensors and slowed down their response speeds, but the *0.05*Pd/SnO_2 sensor maintained relatively large NO_2 response and fast response speed even in wet air, only under weak UV-light irradiation (7 mW cm^{-2}).

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Figure Captions

Fig. 1. Schematic drawing of *0.05*Pd/SnO$_2$ sensor and experimental setup for gas-sensing measurements.

Fig. 2. Response transients of SnO$_2$ sensor to 5 ppm NO$_2$ at 30°C in dry air under different UV-light irradiation intensities.

Fig. 3. Variations in (a) responses to 5 ppm NO$_2$ (R_{NO_2}/R_a), (b) resistances in dry air (R_a), and (c) 90% response ($T_{RS}(90)$, open symbols) and 10% recovery times ($T_{RC}(10)$, filled symbols) of SnO$_2$ sensor with UV-light intensity, together with those of In$_2$O$_3$, and WO$_3$ sensors.

Fig. 4. Response transients of *0.05*Pd/SnO$_2$ and *0.07*Pd/SnO$_2$ sensors to 5 ppm NO$_2$ at 30°C in dry air under different UV-light irradiation intensities.

Fig. 5. Variations in response to 5 ppm NO$_2$ (R_{NO_2}/R_a) and resistance of all *n*Pd/SnO$_2$ sensors in dry air (R_a) with the amount of Pd loaded, together with those of SnO$_2$ sensor.

Fig. 6. XPS spectra of Pd on the surface of *0.05*Pd/SnO$_2$ and *0.10*Pd/SnO$_2$ powders after heat treatment at 500°C for 1 h in ambient air.

Fig. 7. (a) Representative response transients of SnO$_2$ and *0.05*Pd/SnO$_2$ sensors to 30% O$_2$ at 30°C in dry N$_2$ and (b) variations in response of these sensors to 30% O$_2$ at 30°C in dry N$_2$ with UV-light intensity.

Fig. 8. Diffuse reflectance UV−Vis spectra of (a) SnO$_2$ and (b) *0.05*Pd/SnO$_2$ powders, together with their Tarc plots.

Fig. 9. XPS spectra of Pt on the surface of *0.05*Pt/SnO$_2$ and *0.10*Pt/SnO$_2$ powder after heat treatment at 500°C for 1 h in ambient air.

Fig. 10. Variations in response of *0.05*Pt/SnO$_2$ and *0.10*Pt/SnO$_2$ sensors to 5 ppm NO$_2$ (R_{NO_2}/R_a) with UV-light intensity, together with those of SnO$_2$, *0.05*Pd/SnO$_2$ and *0.10*Pd/SnO$_2$ sensors.

Fig. 11. Variations in response of SnO_2 and *0.05*Pd/SnO_2 sensors to 5 ppm NO_2 (R_{NO_2}/R_a) at 30°C in air under UV-light irradiation intensities with relative humidity.

(b) Experimental setup

UV-LED (POT-365, Asahi Spectra)

To control module

Quartz glass
(17 mmφ)

UV light (365 nm)

(a) Sensor element*

7 mm

Oxide film

9 mm

Alumina
substrate

Interdigitated Pt electrodes
(gap size: ca. 500 μm)

Test chamber (LST420, Lincam Sci.)

(i) Cross-section

23 mm

*Sensor element

Temperature-controlled stage

Gas in

(ii) Top view
(with top cover)

(iii) Top view
(without top cover)

166 mm

Quartz glass
(17 mmφ)

90 mm

Pt wires

To external
circuit

Gas out

*Sensor element

To external circuit

Fig. 1. Hyodo et al.

Fig. 2. Hyodo et al.
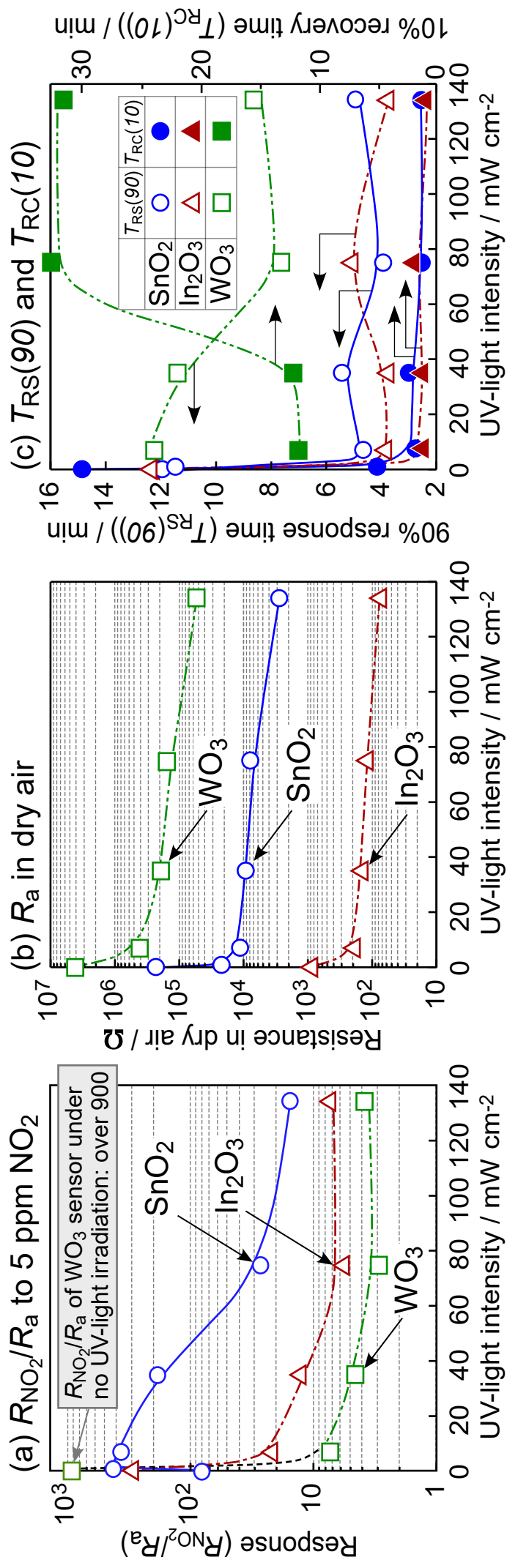
Fig. 3. Hyodo et al.

Fig. 4. Hyodo et al.

(a) R_{NO_2}/R_a to 5 ppm NO_2

(b) R_a in dry air
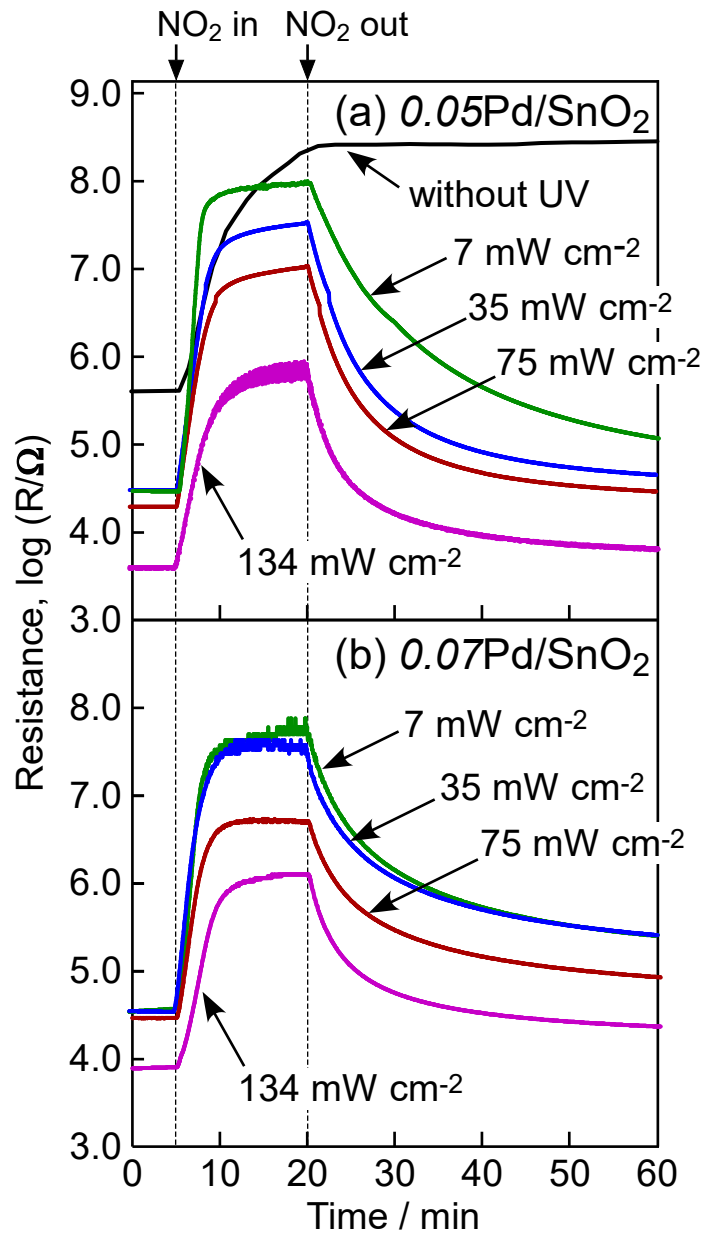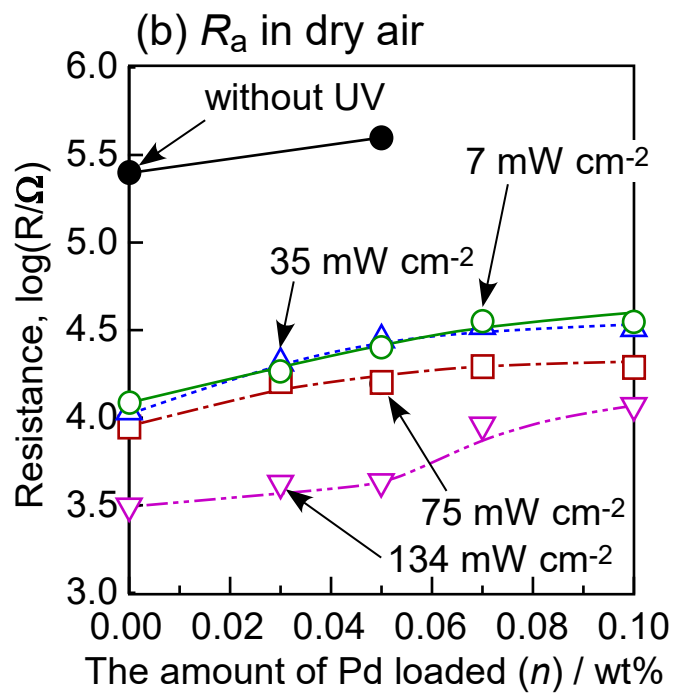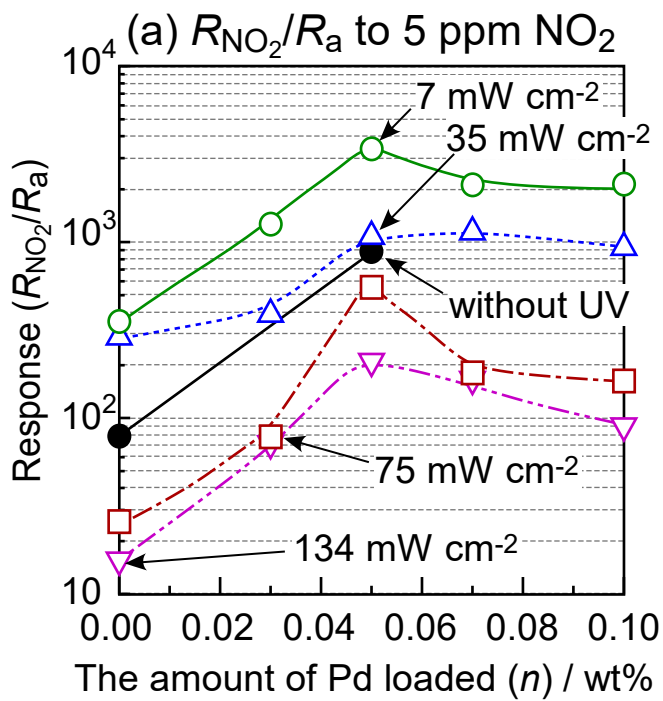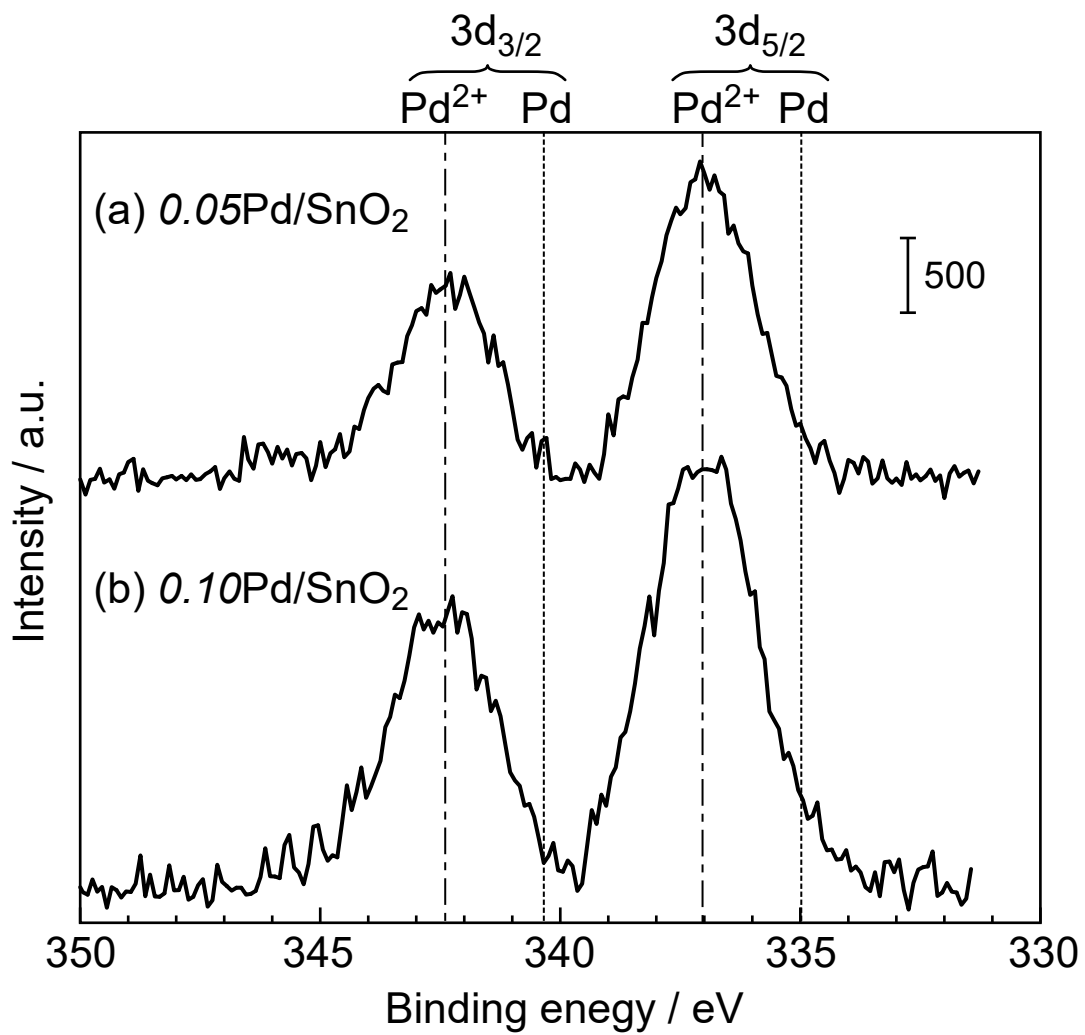
Fig. 5. Hyodo et al.

Fig. 6. Hyodo et al.

(a) Response transients

O$_2$ in   O$_2$ out
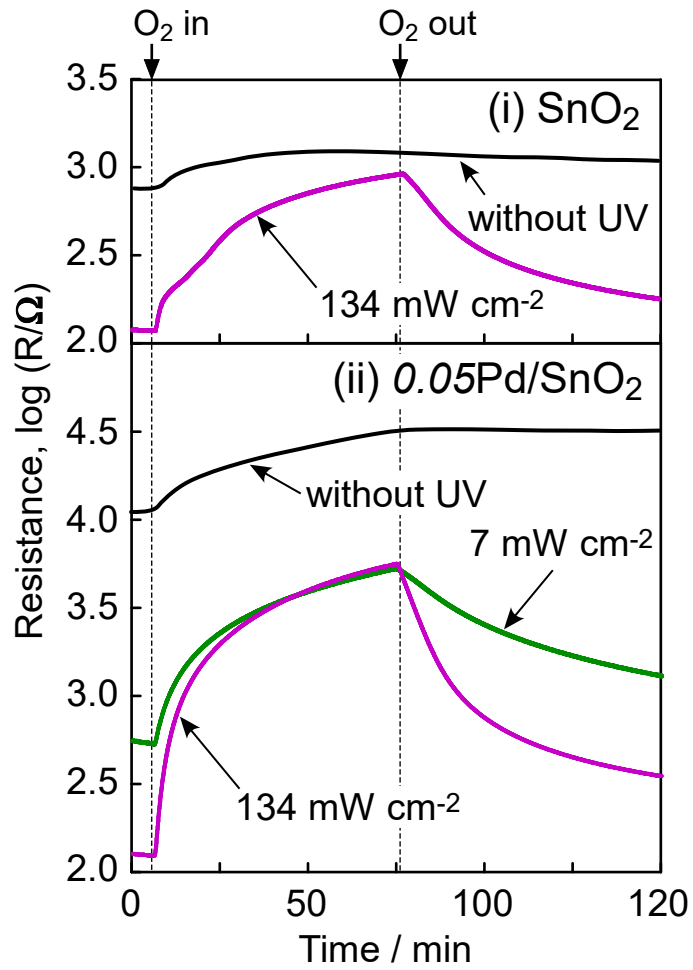
(b) Response to 30% O$_2$ in N$_2$

Fig. 7. Hyodo et al.

(a) SnO$_2$

(b) 0.05Pd/SnO$_2$

E_g: ca. 3.5 eV

E_g: ca. 3.7 eV

Fig. 8. Hyodo et al.

(a) *0.05*Pt/SnO$_2$

Pt^{4+} (ca. 50.9%)

Pt^{2+} (ca. 38.6%)

500

Pt metal (ca. 10.5%)

(b) *0.10*Pt/SnO$_2$

Pt^{4+} (ca. 57.5%)

Pt^{2+} (ca. 33.3%)

Pt metal (ca. 9.2%)

82   80   78   76   74   72   70   68

Binding enegy / eV
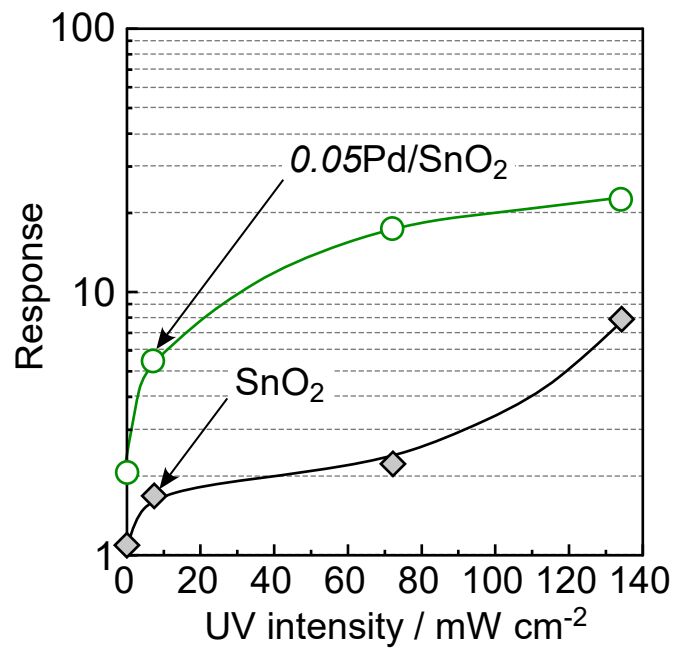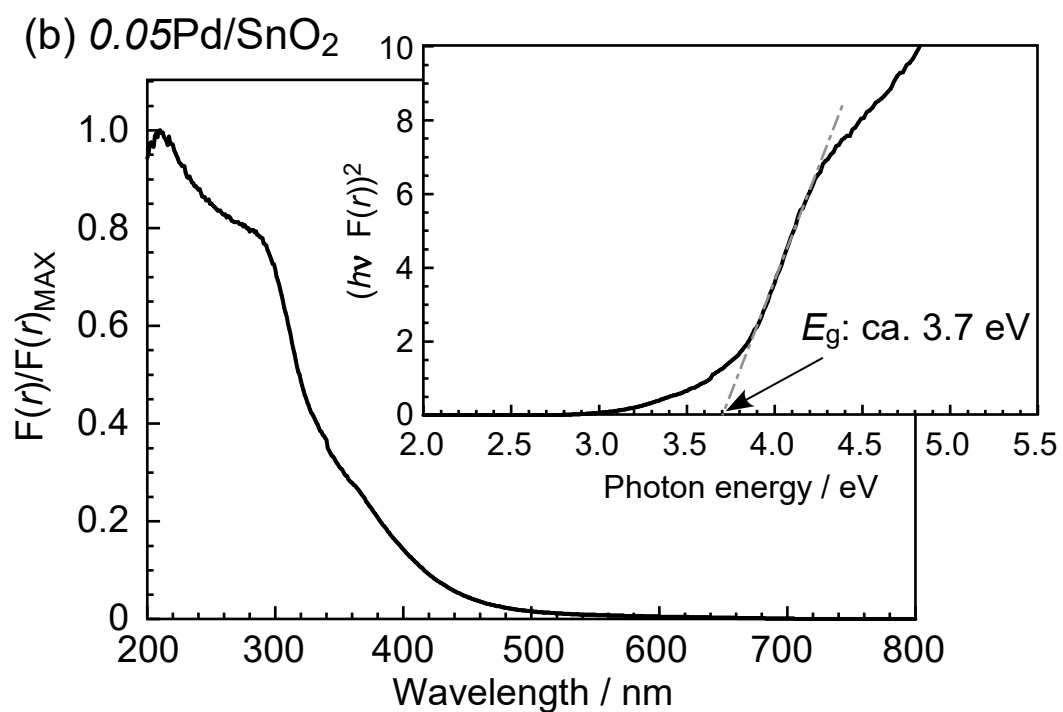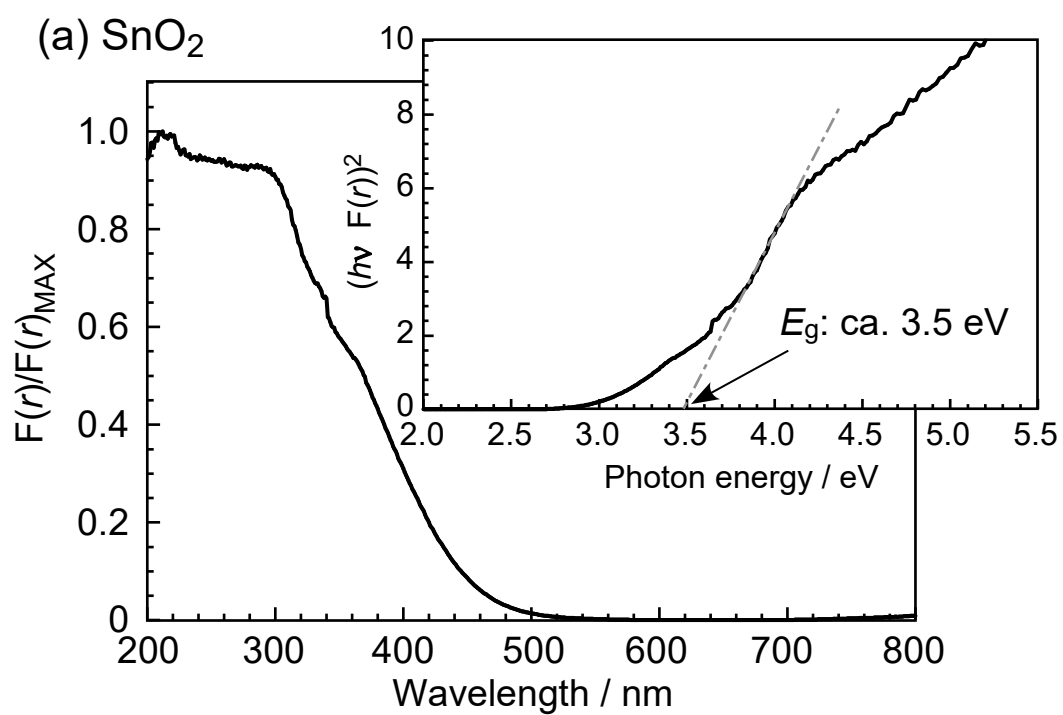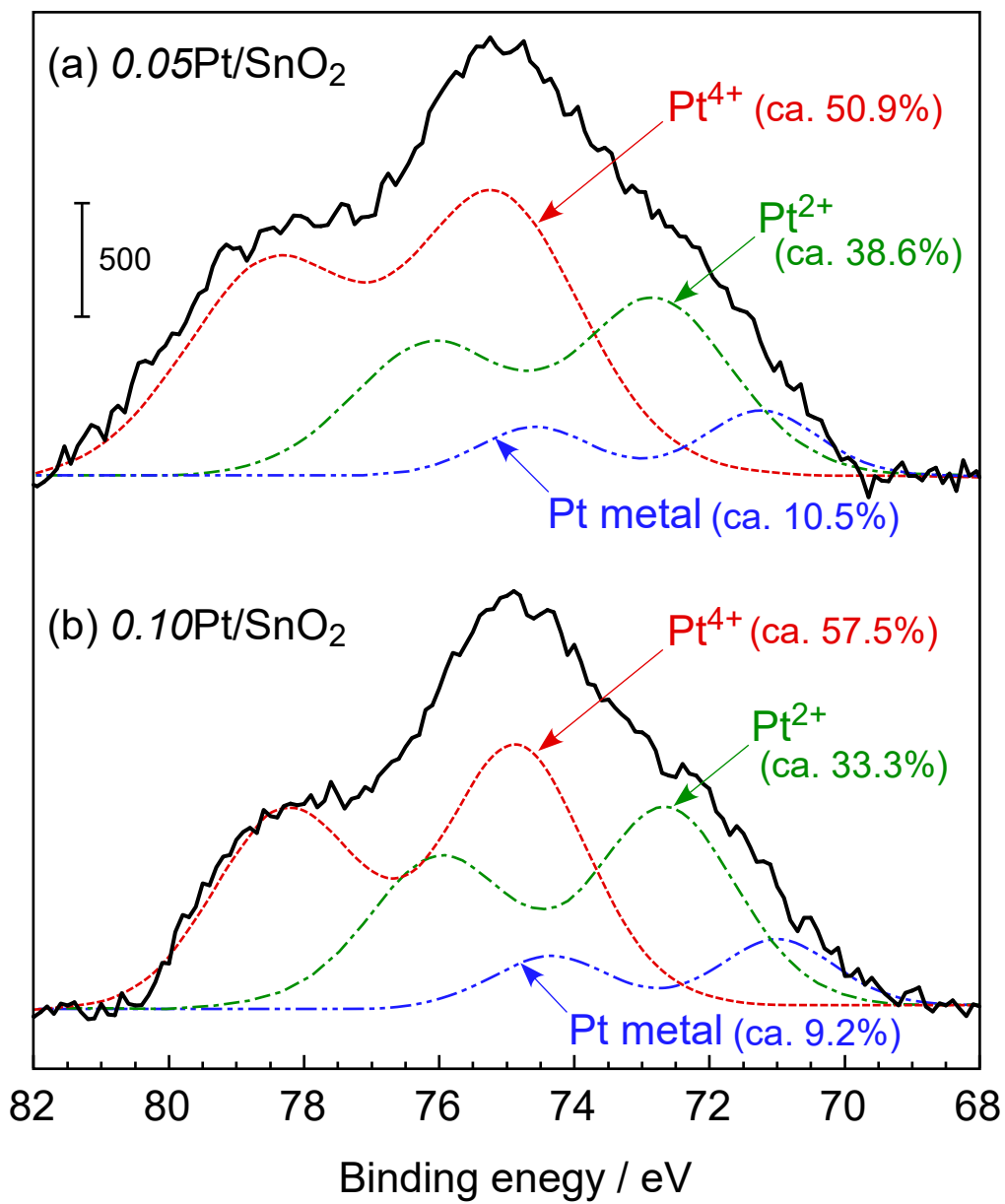
Fig. 9. Hyodo et al.

Fig. 10. Hyodo et al.

(i) SnO$_2$

0.8 mW cm^{-2}

7 mW cm^{-2}

35 mW cm^{-2}

75 mW cm^{-2}

134 mW cm^{-2}

without UV

Response (R_{NO_2}/R_a)

Relative humidity (RH%)

(ii) *0.05*Pd/SnO$_2$

without UV

7 mW cm^{-2}

35 mW cm^{-2}

75 mW cm^{-2}

134 mW cm^{-2}

Response (R_{NO_2}/R_a)

Relative humidity (RH%)
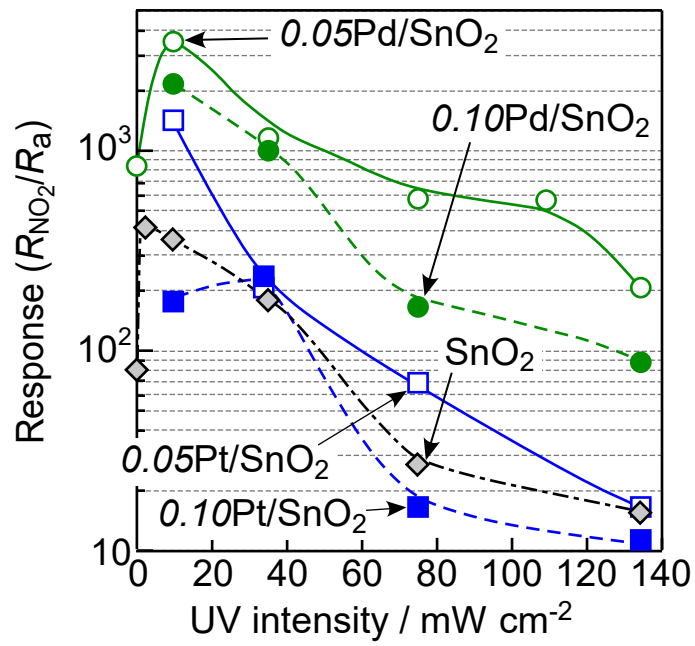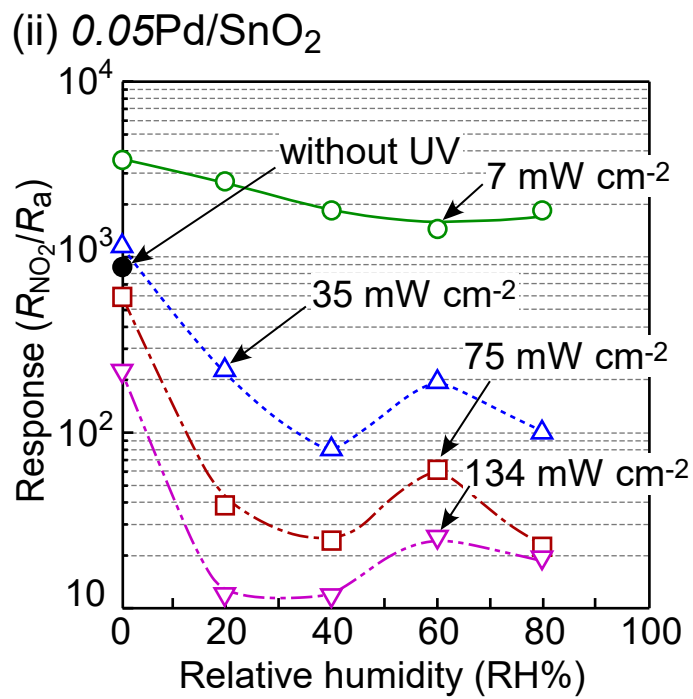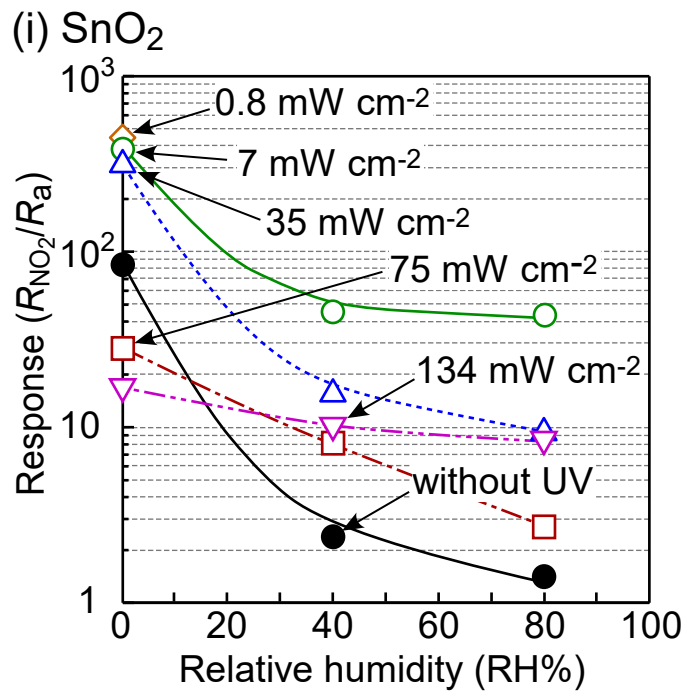
Fig. 11. Hyodo et al.

Supporting Information

Semiconductor-type SnO$_2$-based NO$_2$ sensors operated at room temperature under UV-light irradiation

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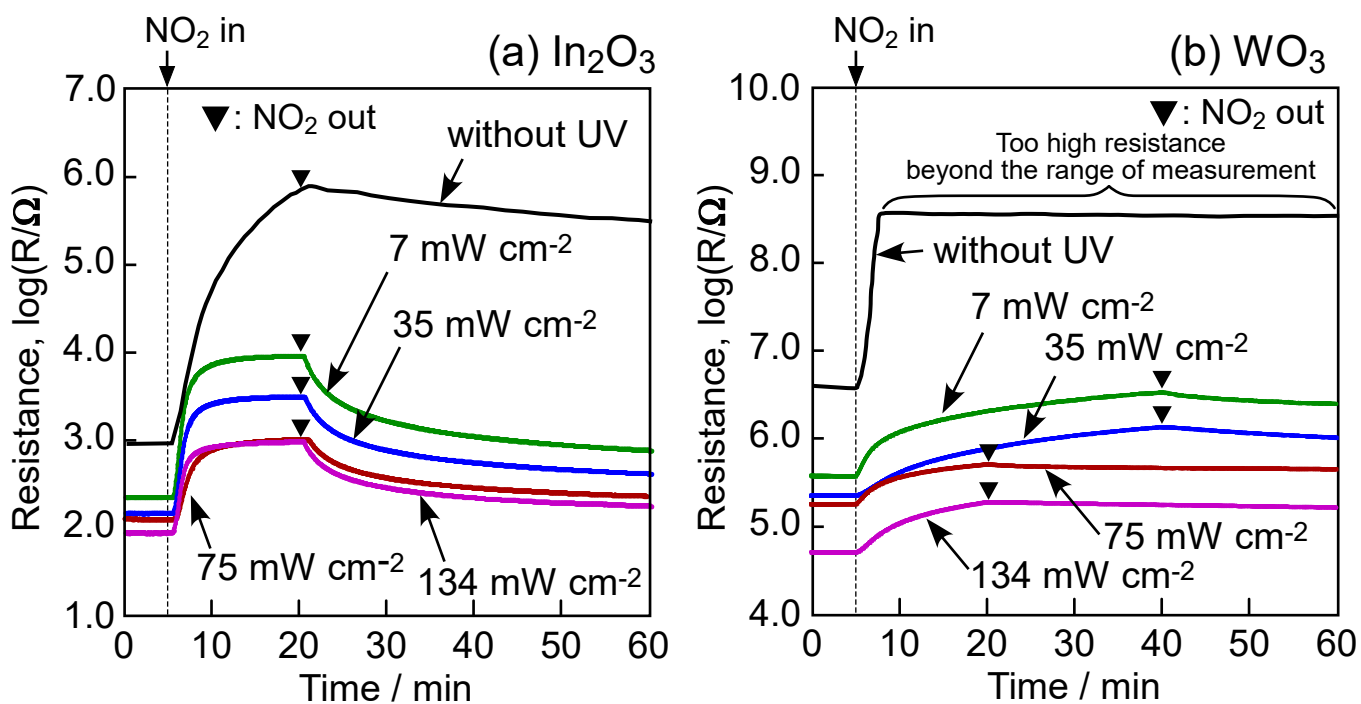
Fig. S1. Response transients of In_2O_3 and WO_3 sensors to 5 ppm NO_2 at 30°C in dry air under different UV-light irradiation intensities.
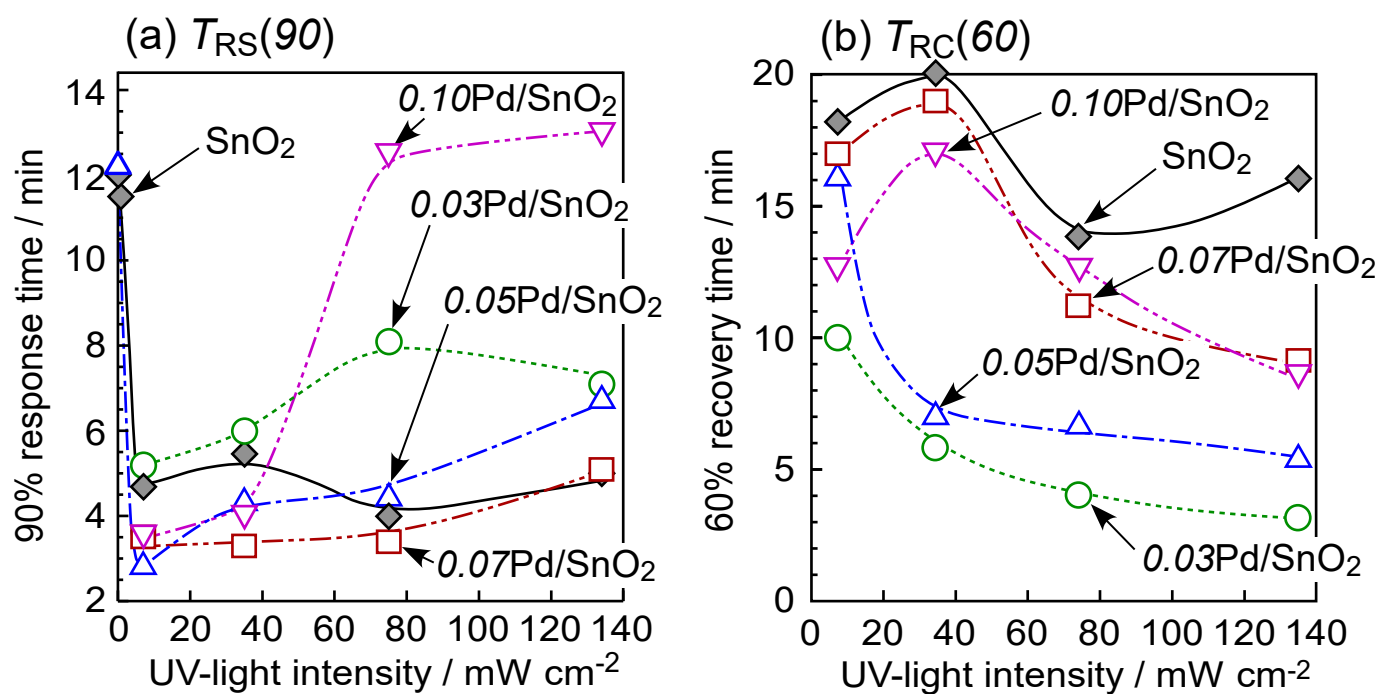
Fig. S2. Variations in 90% response and 60% recovery times ($T_{RS}(90)$ and $T_{RC}(60)$, respectively) of all nPd/SnO$_2$ sensors with UV-light intensity, together with those of SnO$_2$ sensor.
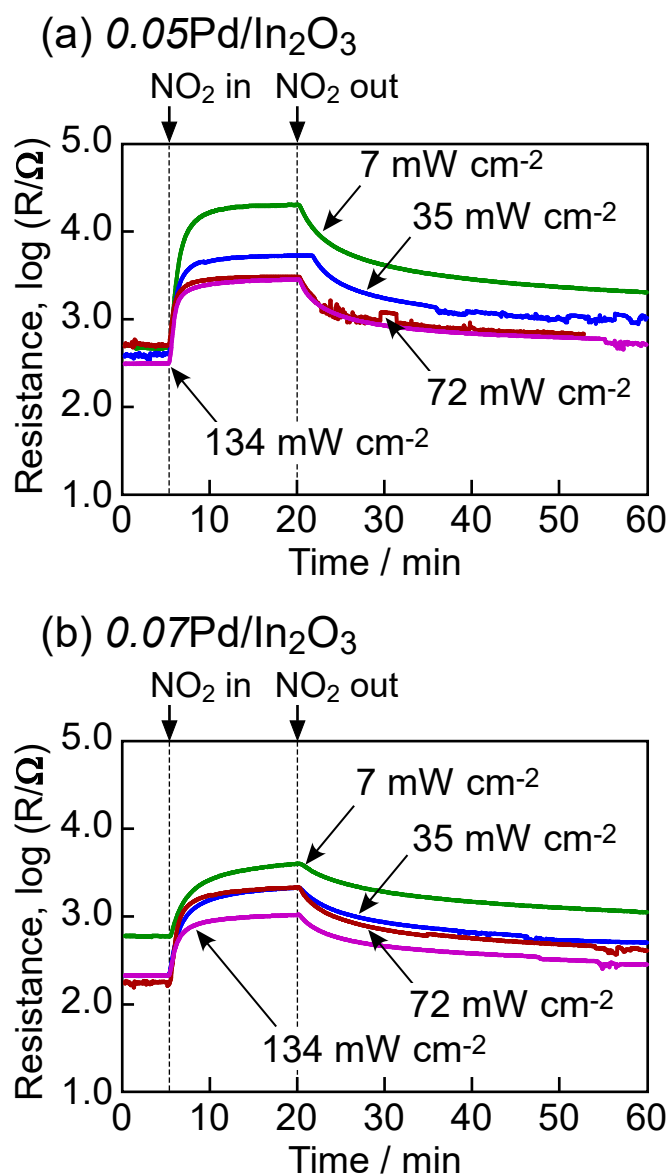
Fig. S3. Response transients of *0.05*Pd/In$_2$O$_3$ and *0.07*Pd/In$_2$O$_3$ sensors to 5 ppm NO$_2$ at 30°C in dry air under different UV-light irradiation intensities.
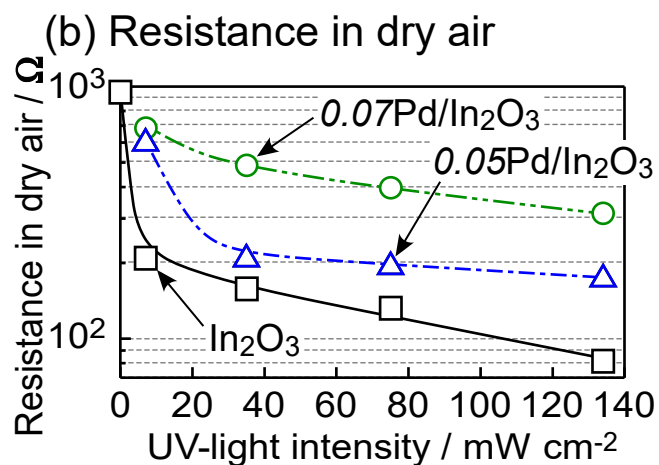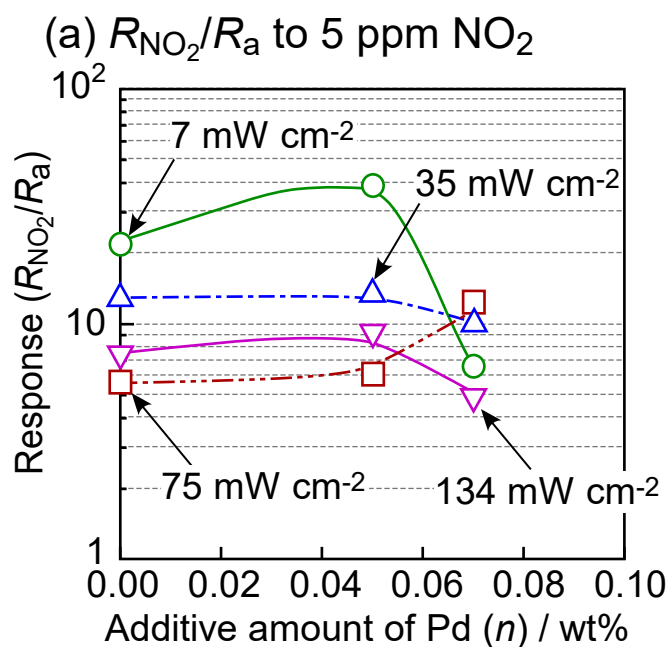
Fig. S4. Variations in response of *0.05*Pd/In_2O_3 and *0.07*Pd/In_2O_3 sensors to 5 ppm NO_2 (R_{NO_2}/R_a) and resistance in dry air (R_a) with the amount of Pd loaded and UV-light intensity, respectively, together with those of In_2O_3 sensor.
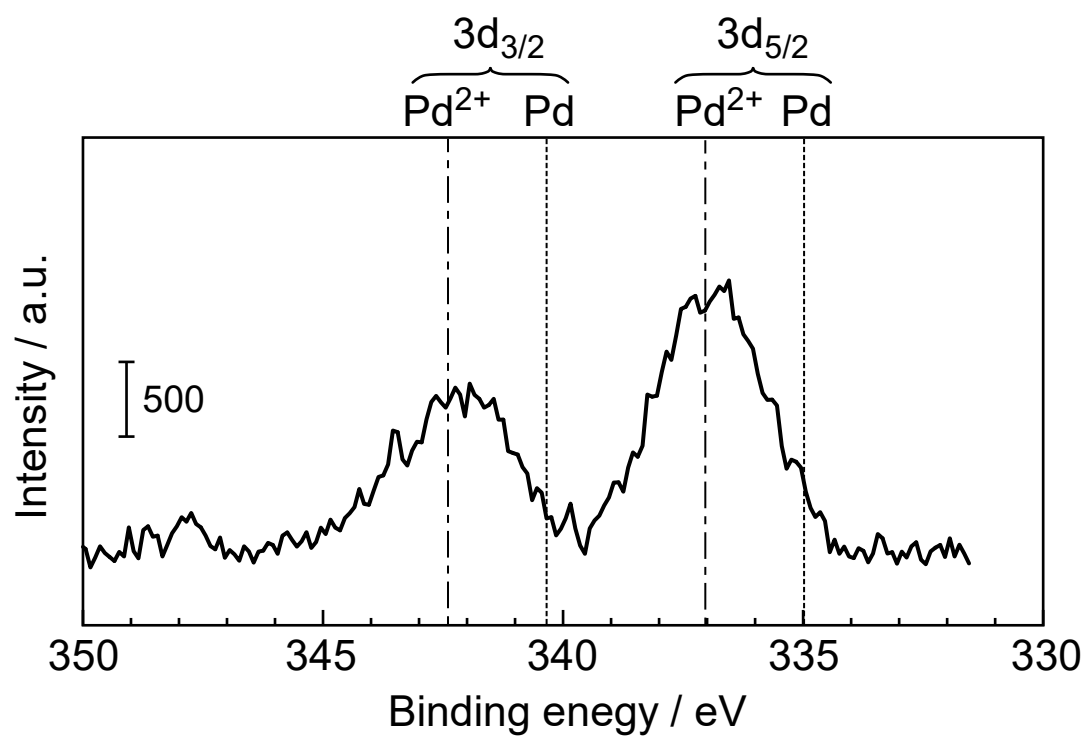
Fig. S5.   XPS spectrum of Pd on the surface of *0.07*Pd/In$_2$O$_3$ powder after heat treatment at 500°C for 1 h in ambient air.
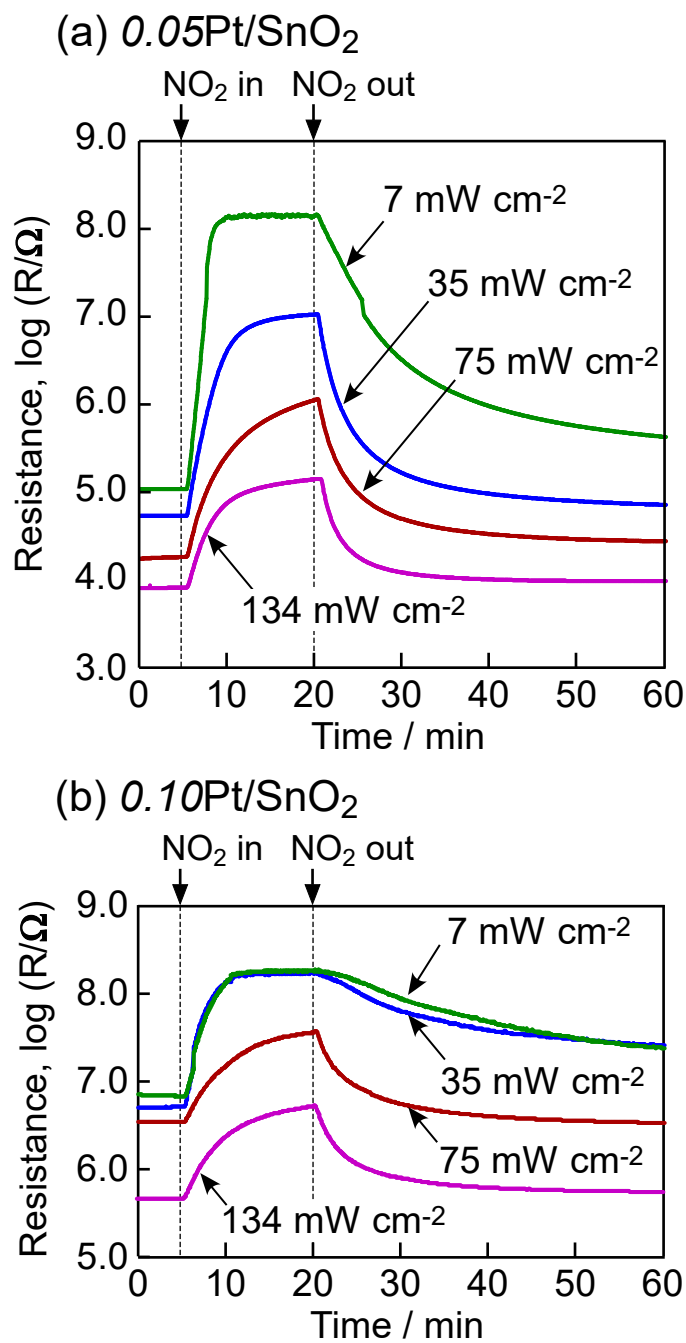
Fig. S6. Response transients of *0.05*Pt/SnO$_2$ and *0.10*Pt/SnO$_2$ sensors to 5 ppm NO$_2$ at 30°C in dry air under UV-light irradiation.
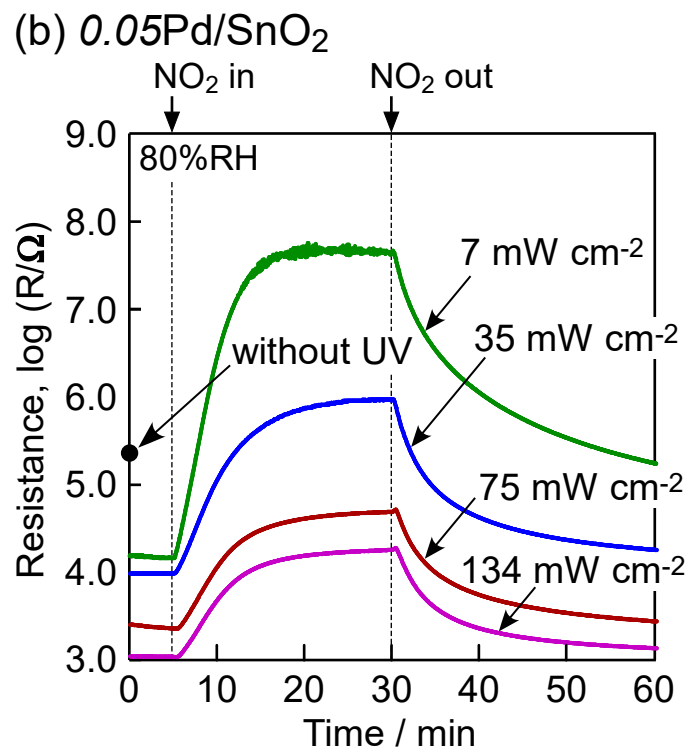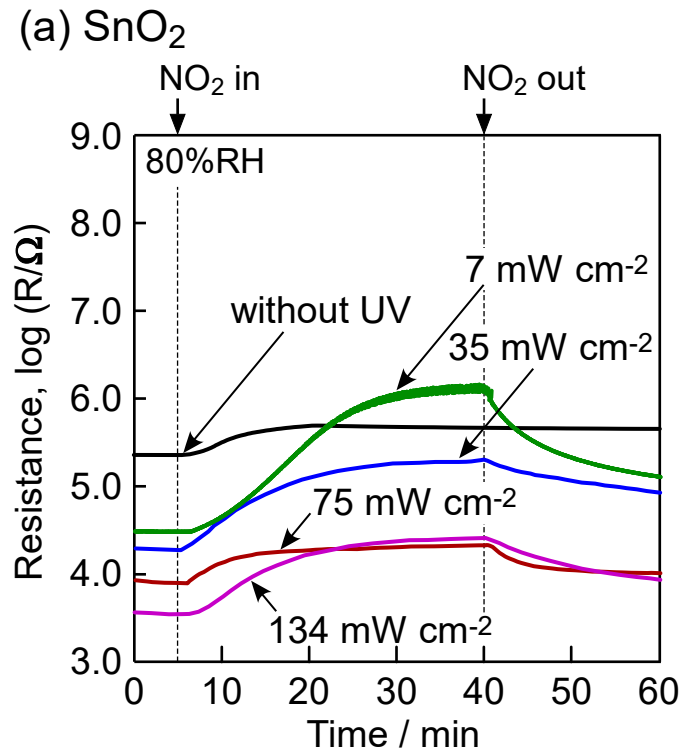
Fig. S7. Response transients of SnO_2 and *0.05*Pd/SnO_2 sensors to 5 ppm NO_2 at 30°C in wet air (80%RH) under different UV-light irradiation intensities.