Optical recognition of CO and H_2 by use of gas-sensitive Au–Co_3O_4 composite films

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Gold–cobalt oxide (Au–Co_3O_4) composite films have been prepared by the sputter-deposition of gold onto a glass plate substrate followed by pyrolysis of spin-coated cobalt 2-ethylhexanoate. The films comprise small Au particles and Co_3O_4 nanocrystals, and exhibit different and independent optical responses to CO and H_2 in air. Carbon monoxide caused only a decrease in absorbance, while H_2 caused both a decrease and an increase in absorbance at different wavelengths. Among solid-state gas sensor materials, this Au–Co_3O_4 composite film is probably the first example of an inorganic material which can be used for the recognition of CO and H_2 molecules through optical absorbance changes.

Optical gas sensors have been attracting attention owing to several advantages over conventional electricity-based gas sensors.[1,2] They show higher resistivity to electromagnetic noise, less danger of fire ignition, compatibility with optical fibers and the potential of multi-gas detection and recognition by using differences in the intensity, wavelength, phase and polarization of the output light signals.

We have already reported that in the presence of CO and H_2 thin films of p-type semiconductors, such as Co_3O_4, NiO and Mn_3O_4, show reversible changes in the VIS–near IR absorption band at 250–350 °C.[3] This phenomenon can be applied to the optical detection of reducing gases. Reversible absorbance changes can be ascribed to changes in positive hole density in the film during the catalytic reaction of surface-adsorbed oxygen anions with CO or H_2.[3–6] The deposition of small Au particles on NiO films with high dispersion is effective in enhancing both the absorbance change and response rate to CO and accordingly in lowering the operating temperature.[4–6] This enhancing effect relates to an increase in catalytic activity of the film for CO oxidation with decreasing size of Au particles.[4–8] We have also found that the plasmon absorption of Au particles at a specific wavelength region around 700 nm is sensitive to CO when small Au particles are combined with CuO.[6,9]

Multi-gas recognition can be realized if the optical absorption property of a material changes independently with the different gases present. As far as we know, this possibility has not yet been demonstrated for inorganic solid-state gas sensor materials until we preliminarily reported that the absorption spectrum of Au–Co_3O_4 composite films in air is changed differently by CO and by H_2 at a relatively high concentration of 1 vol.% (10 000 ppm).[10] Here, we show that the Au–Co_3O_4 composite film is sensitive to CO and H_2 at much lower concentrations and as a result, it is possible to recognize CO and H_2 over a concentration range from 50 to 10 000 ppm.

Experimental

Gold–cobalt oxide composite films were prepared in the following manner. Small Au particles were deposited directly on a glass plate substrate (18 mm × 18 mm × 0.1 mm) by the dc sputtering method.[6,9,10] The amount of Au deposited was estimated to correspond to a continuous Au film *ca.* 2 nm thick. A mixed solution of toluene and butan-1-ol containing cobalt 2-ethylhexanoate with a Co content of 1 mass% was then spin-coated at 2000 rpm, dried at room temperature and pyrolyzed at 380 °C in air.[3,6,9–12] X-Ray diffraction patterns showed that the obtained films consist of Au and Co_3O_4. Gold-free Co_3O_4 films were also prepared directly on the glass plate substrate for comparison. The thickness of the gold-free Co_3O_4 film and the Co_3O_4 layer in the Au–Co_3O_4 composite film, estimated using a Mizojiri DHA-XA2 ellipsometer, was 60 nm. The fine structure of the Au–Co_3O_4 composite film was observed using a TOPCON 002B transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV.

VIS–near IR absorption spectra of the thin films were measured in a quartz cell (200 ml) using a Shimadzu UV-3100PC spectrometer equipped with optical fibers. The spectrometer was operated with a resolution of <0.001 in absorbance, and could detect small absorbance changes with good reproducibility. The temperature of the quartz cell was controlled in the range 150–225 °C. Test gases were fresh air (dry atmospheric air without the addition of CO or H_2) and air containing CO or H_2, and either of the two gases was passed through the quartz cell at a constant flow rate of 100 ml min^{-1}. The concentration of CO or H_2 was varied from 50 to 10 000 ppm (1 vol.%). Gases tested were dried by passing through silica gel and molecular sieve columns at room temperature and a molecular sieve column at 0 °C prior to use. Film samples were pretreated at the operating temperature in fresh air for at least 1 h before the optical measurements. To investigate the effect of water vapor, air containing 0.6 vol.% water vapor (26% relative humidity at 20 °C) was introduced in the test cell.

Results

Fig. 1 shows high-resolution TEM photographs of the Au–Co_3O_4 composite film. Spherical gold particles (black circles) with diameters in the range 10–30 nm are well dispersed in the light coloured Co_3O_4 matrix consisting of a number of ultrafine crystals with sizes of 5–10 nm in which a lattice pattern is seen. The spacing observed most frequently is 0.467 nm, which corresponds to the (111) planes in the spinel-type Co_3O_4. (220) planes with a spacing of 0.287 nm and the (311) planes with a spacing of 0.246 nm are also seen.

Fig. 2(*a*)–(*c*) and 3(*a*)–(*c*) show the absorption spectra of the Au-free Co_3O_4 film and the Au–Co_3O_4 composite film, respectively, in air with and without 1 vol.% CO or H_2. Difference spectra shown in Fig. 2(*d*), (*e*) and 3(*d*), (*e*) were obtained by subtracting the absorption spectra in fresh air from those in air containing the reducing gases.

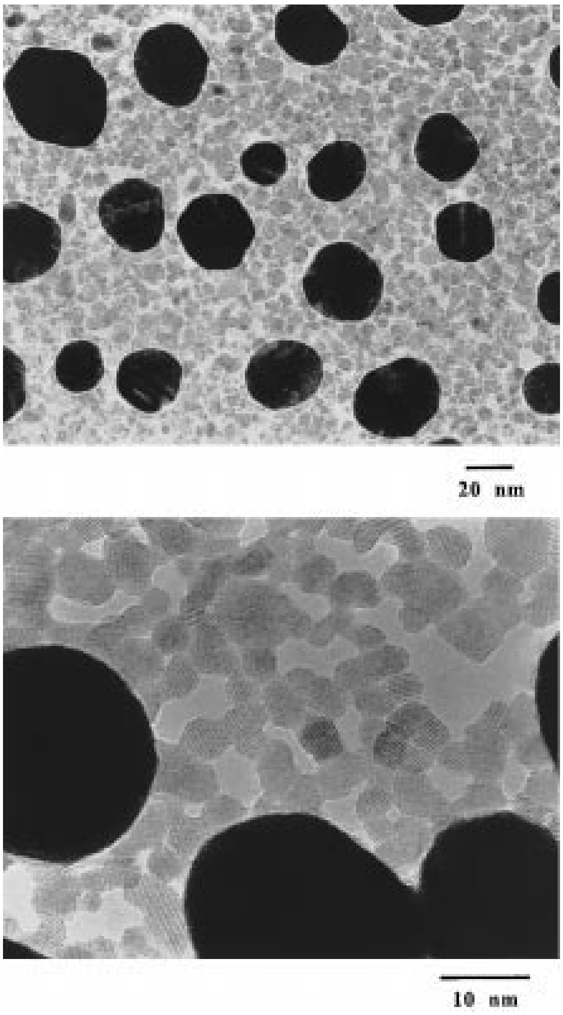

Fig. 1 Transmission electron micrographs of the Au–Co_3O_4 composite film

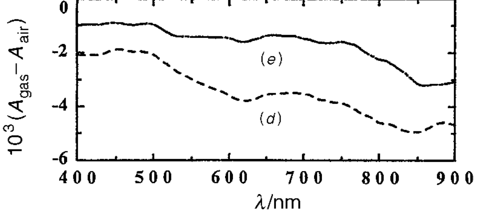

Fig. 2 Absorption spectrum of the Co_3O_4 film in air and its changes by CO and by H_2. (*a*) Absorption spectrum in air. (*b*) Absorption spectrum in air containing 1 vol.% CO. (*c*) Absorption spectrum in air containing 1 vol.% H_2. (*d*) Difference absorption spectrum in air with and without 1 vol.% CO. (*e*) Difference absorption spectrum in air with and without 1 vol.% H_2. Temperature 200 °C.

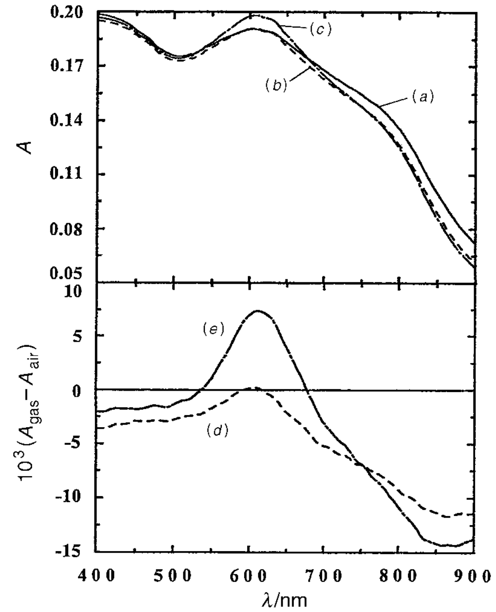

Fig. 3 Absorption spectrum of the Au–Co_3O_4 composite film in air and its changes by CO and by H_2. (*a*) Absorption spectrum in air. (*b*) Absorption spectrum in air containing 1 vol.% CO. (*c*) Absorption spectrum in air containing 1 vol.% H_2. (*d*) Difference absorption spectrum in air with and without 1 vol.% CO. (*e*) Difference absorption spectrum in air with and without 1 vol.% H_2. Temperature 200 °C.

As shown in Fig. 2, both CO and H_2 reduced the absorbance of the Au-free Co_3O_4 film in the whole VIS–near IR region ($\lambda = 400$–900 nm). The decrease of absorbance can be ascribed to a decrease in positive hole density of Co_3O_4[3,6] during the catalytic oxidation of reducing gases. Although the absorbance change (ΔA) by CO was about twice that of H_2, the shape of the difference spectra was similar in both cases and so does not allow the Au-free Co_3O_4 film to distinguish between CO and H_2 in air.

As shown in Fig. 3, the absorption spectrum of the Au–Co_3O_4 composite film is changed differently by CO and H_2 in air. The dipolar plasmon excitation of small Au particles[13] was observed with a maximum at a wavelength of *ca.* 600 nm as well as broad absorption bands due to spinel-type Co_3O_4[14,15] in the whole VIS–near IR region. In the plasmon excitation region, the absorbance changes by CO and by H_2 clearly differ. This implies that the Au–Co_3O_4 film can recognize CO and H_2. In the wavelength region outside the plasmon band of small Au particles, for example, at $\lambda = 900$ nm, the absorbance was decreased both by CO and H_2. As is obvious from comparison of Fig. 3 and 2, such a CO- or H_2-sensitive decrease in absorbance is enhanced by the presence of small Au particles. This indicates that the decrease in the positive hole density of Co_3O_4 during the catalytic oxidation of reducing gases was accelerated by the combination of Co_3O_4 with Au particles.

Fig. 4 shows the correlation between absorbance change (ΔA) for the Au–Co_3O_4 film and the concentration of CO and H_2 at a wavelength of 900 nm. Values of ΔA decrease with a decrease in CO or H_2 concentration, showing sensitivity to CO and H_2 down to 50 ppm.

Fig. 5 shows that the absorbance of the Au–Co_3O_4 film at *ca.* 600 nm is increased by H_2 at concentrations over a wide range, while it is not affected by CO. Thus, monitoring the absorbance change at the plasmon band leads to the selective detection of H_2 over a wide range of concentration from 50 ppm to 1 vol.%. Small Au particles deposited on a glass plate substrate without Co_3O_4 did not show any detectable change of absorbance by CO or H_2 in air, therefore, the unique

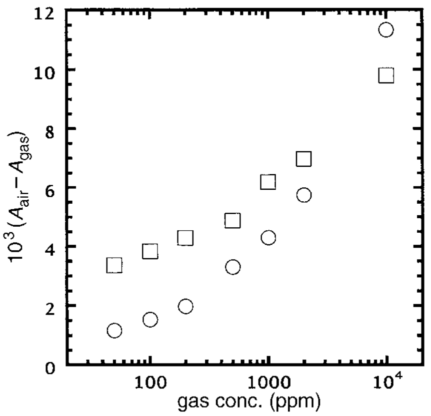

Fig. 4 Correlation between the gas-sensitive absorbance change of the Au–Co_3O_4 composite film and the concentration of CO or H_2 at a wavelength of 900 nm. ○, absorbance change by H_2; □, absorbance change by CO. Temperature 200 °C.

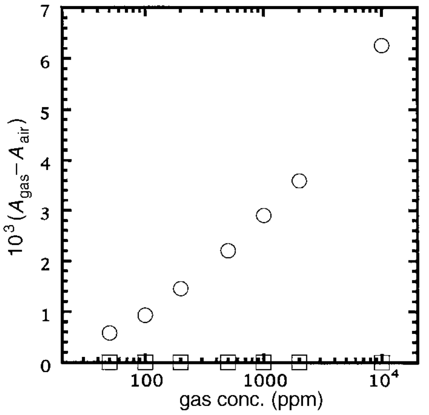

Fig. 5 Correlation between the gas-sensitive absorbance change of the Au–Co_3O_4 composite film and the concentration of CO or H_2 at a wavelength of 600 nm. ○, absorbance change by H_2; □, absorbance change by CO. Temperature 200 °C.

behavior observed at *ca.* 600 nm can not be explained by a simple superposition of the spectra of Co_3O_4 and small Au particles and must be a synergistic effect between Co_3O_4 and Au.

Fig. 6 shows the time response of the absorbance of the Co_3O_4 and Au–Co_3O_4 films to H_2 at 900 nm. The H_2-sensitive decrease in the absorbance of the Au–Co_3O_4 composite film was reversible and was faster than that of the Au-free Co_3O_4 film. The time response curve of the Au–Co_3O_4 film to 1 vol.% CO (Fig. 7) at this wavelength was similar to that to 1 vol.% H_2. As shown in Fig. 8, the H_2-selective increase in the absorbance of the Au–Co_3O_4 film at a wavelength of 595 nm is also reversible. Under the experimental conditions used in this study, the response time required to reach 90% of the steady-state signal intensity was 2–3 min after the addition of CO or H_2 in air. Even when the Au–Co_3O_4 film was exposed to $\geqslant$1 vol.% CO or $\geqslant$1 vol.% H_2 for more than 30 min, the recovery ratio of the CO- or H_2-sensitive absorbance decrease outside the plasmon band region was unity, while the recovery ratio of the H_2-sensitive absorbance increase near the plasmon absorption peak (around 600 nm) was sometimes somewhat lower than unity. At concentrations $\leqslant$0.5 vol.%, the recovery ratio of the absorbance changes was always unity.

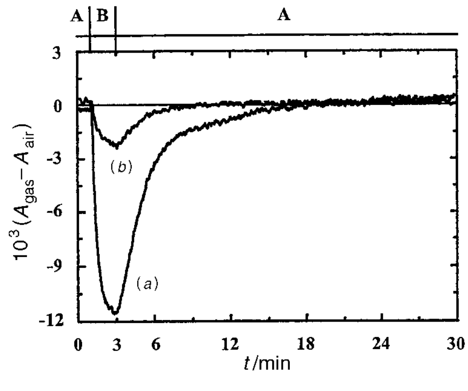

Fig. 6 Time response of the absorbance of films to 1 vol.% H_2 in air at a wavelength of 900 nm. (*a*) Au–Co_3O_4 composite film. (*b*) Co_3O_4 film. A, in air; B, in air containing 1 vol.% H_2. Temperature 200 °C.

Fig. 9 shows the reversible absorbance changes of the Au–Co_3O_4 film in response to a much lower concentration (500 ppm) of CO and H_2. The response rate to CO was larger than that towards H_2 at 900 nm, which suggests that the positive hole density decreases faster with CO than with H_2 owing to the higher reaction rate of CO over supported gold catalysts.[7]

Fig. 10 shows the temperature dependence of the gas-sensitive absorbance change of the Au–Co_3O_4 film at wavelengths of 600 and 900 nm. The CO- and H_2-sensitive absorbance change increased linearly with increasing operating temperature. However, reversible absorbance change by H_2 was not detected at 600 nm for temperatures below 175 °C. On the other hand, at 900 nm, reversible absorbance changes for CO and H_2 both occurred at and above 150 °C.

The absorbance change caused by water vapor was compared with that of H_2, as water is produced during the catalytic oxidation of H_2. Fig. 11(*a*) shows that the addition of 0.6 vol.%

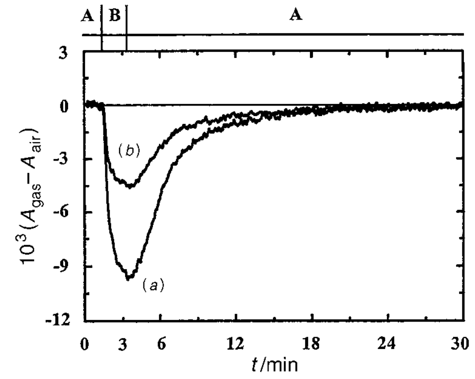

Fig. 7 Time response of the absorbance of films to 1 vol.% CO in air at a wavelength of 900 nm. (*a*) Au–Co_3O_4 composite film. (*b*) Co_3O_4 film. A, in air; B, in air containing 1 vol.% CO. Temperature 200 °C.

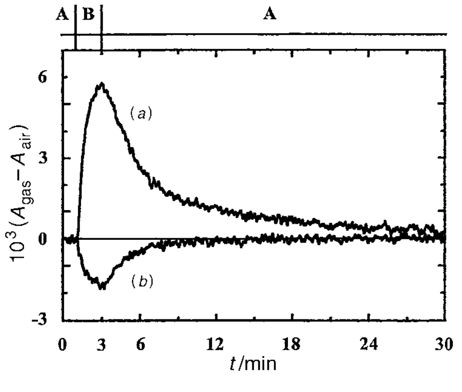

Fig. 8 Time response of (*a*) Au–Co_3O_4 composite film and (*b*) Co_3O_4 film to 1 vol.% H_2 in air at a wavelength of 595 nm. A, in air; B, in air containing 1 vol.% H_2. Temperature 200 °C.

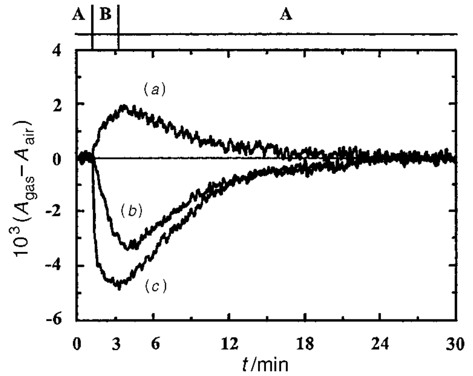

Fig. 9 Time response of the absorbance of the Au–Co_3O_4 composite film to 500 ppm CO and to 500 ppm H_2 at wavelengths of 600 and 900 nm. (*a*) 500 ppm H_2 at 600 nm. (*b*) 500 ppm H_2 at 900 nm. (*c*) 500 ppm CO at 900 nm. A, in air; B, in air containing 500 ppm CO or 500 ppm H_2. Temperature 200 °C.

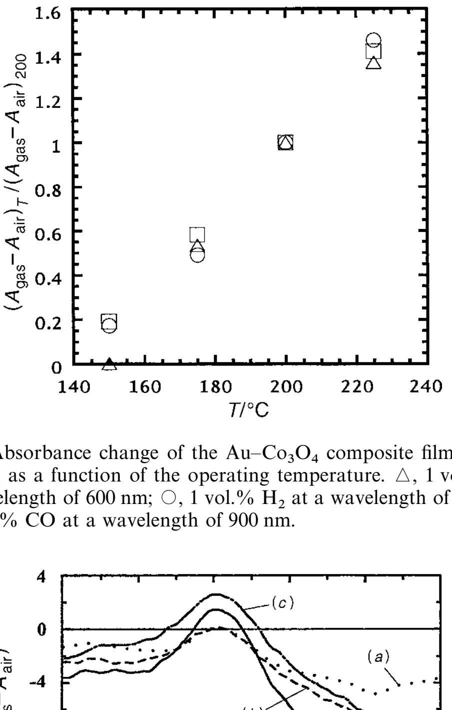

Fig. 10 Absorbance change of the Au–Co_3O_4 composite film by CO or by H_2 as a function of the operating temperature. △, 1 vol.% H_2 at a wavelength of 600 nm; ○, 1 vol.% H_2 at a wavelength of 900 nm; □, 1 vol.% CO at a wavelength of 900 nm.

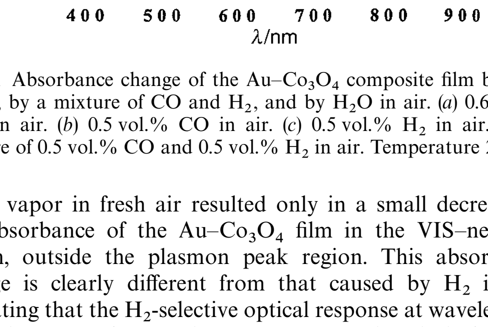

Fig. 11 Absorbance change of the Au–Co_3O_4 composite film by CO, by H_2, by a mixture of CO and H_2, and by H_2O in air. (*a*) 0.6 vol.% H_2O in air. (*b*) 0.5 vol.% CO in air. (*c*) 0.5 vol.% H_2 in air. (*d*) A mixture of 0.5 vol.% CO and 0.5 vol.% H_2 in air. Temperature 200 °C.

water vapor in fresh air resulted only in a small decrease of the absorbance of the Au–Co_3O_4 film in the VIS–near IR region, outside the plasmon peak region. This absorbance change is clearly different from that caused by H_2 in air, indicating that the H_2-selective optical response at wavelengths around 600 nm is not due to water produced during the catalytic oxidation of H_2.

Fig. 11(*b*)–(*d*) shows the effect of the presence of both CO and H_2 on the optical absorption of the Au–Co_3O_4 film. For the plasmon band of Au ($\lambda = 600$ nm), the presence of 0.5 vol.% CO reduced the absorbance increase (ΔA) due to 0.5 vol.% H_2 by *ca.* 40%. However, the decrease in absorbance (ΔA) at $\lambda = 900$ nm, obtained from a mixture of 0.5 vol.% of CO and 0.5 vol.% H_2, coincided reasonably well with that obtained by 1 vol.% CO or 1 vol.% H_2. There is, therefore, little mutual retardation between the optical response to CO and that to H_2 at $\lambda = 900$ nm.

Discussion

At wavelengths outside the Au plasmon band, $\lambda = 900$ nm, the large ΔA of the Au–Co_3O_4 film can be explained by the enhanced catalytic activity for the oxidation of CO and H_2.[3,5,6,10] Surprisingly, Au–Co_3O_4 films require a much higher operating temperature for optical CO sensing, compared with the operating temperature of Au–Co_3O_4 powdered catalyst [d(Au) = 6–7 nm] for catalytic oxidation of CO to CO_2, for example, −70 °C.[6–8] This difference in the operating temperature is thought to reflect differences in the reaction pathways for CO sensing and catalytic CO oxidation. Study on Au–ZnO and Au–TiO_2 catalysts[16–18] indicates that the reaction pathways for CO sensing, that is the CO-sensitive charge carrier density change, depend on the formation and decomposition of carbonate-like species such as CO_3^{2-} at the oxide surface. During CO_3^{2-} formation, the positive hole density decreases in the following manner:[17]

$$CO + 2O^{2-} + 2V_O^{2+} \rightarrow CO_3^{2-} + 2V_O^{+}$$

where V_O^{2+} is a divalent oxygen vacancy and V_O^{+} is a monovalent oxygen vacancy. This reaction is relatively slow and is accelerated only at temperatures above 100 °C. On the other hand, the reaction pathways for the catalytic oxidation of CO to CO_2, which take place even at −70 °C, mainly consist of the formation and decomposition of intermediate species like $O{\equiv}C{-}Au{=}O$ on the Au surface and the Au sites at the Au–oxide perimeter interface.[17]

The temperature of Au–Co_3O_4 films is assumed to increase due to the exothermic catalytic oxidation of CO or H_2 on the surface of the films. However, the increase of temperature of the Au–Co_3O_4 film upon exposure to CO or H_2 (up to 1 vol.% in air) is considered to be marginally small to contribute to the observed gas-sensitive absorbance changes.[19]

At wavelengths around 900 nm, the Au–Co_3O_4 film showed absorbance changes at the same temperature region (> 150 °C) for both CO and H_2, while the temperature for the catalytic oxidation of CO to CO_2 is much lower than the temperature for the catalytic oxidation of H_2 to H_2O over Au–Co_3O_4 powdered catalyst. For powdered catalyst, the temperatures for 50% oxidation of CO and of H_2 at a space velocity of 2×10^4 h^{-1} ml (g cat.)$^{-1}$ are < −70 °C and 55 °C, respectively.[7] As the difference in the operating temperature between H_2 sensing and catalytic oxidation of H_2 to H_2O is smaller than that for CO, we speculate that the optical CO sensitivity of Au–Co_3O_4 films may be related to the formation and decomposition of carbonate-like species on the oxide surface. The optical H_2 sensitivity, on the other hand, may relate to the overall catalytic oxidation of H_2 to H_2O.

The mechanism for the selective absorbance increase at $\lambda = 600$ nm in the Au–Co_3O_4 film by H_2 in the Au plasmon band is, however, much more complex and, at present, the reason for the observed increase is still not clear. The plasmon absorption of Au particles depends on the size, shape, electrical conductivity and relative permittivity of Au particles (as well as the relative permittivity of the medium in which the Au particles exist), and the dipole–dipole interactions between Au particles.[20–26] These changes can be caused by changes in the chemical atmosphere. For example, a TEM study of small Au particles ($d = 4$ nm) deposited on MgO suggests that the Au particles sink into MgO during catalytic reaction.[27] Reversible changes in the plasmon absorbance of the Au–V_2O_5 system at wavelengths near 600 nm [d(Au) = 7 nm] by electrochemical redox[26] and the Ag–SiO_2 system at wavelengths near 400 nm [d(Ag) = 9 nm] by atmospheric gases[28,29] are considered to be due to changes in relative permittivity and morphology of the small Au or Ag particles, respectively. Electromagnetic theory predicts that the peak wavelength and width of the plasmon band of Au particles increase with increasing relative permittivity of the surrounding medium.[21] For the Au–Co_3O_4 film, any increase of the peak wavelength and width of the plasmon band could not be detected upon exposure to H_2. We speculate that the H_2-sensitive plasmon absorbance change at $\lambda = 600$ nm in the Au–Co_3O_4 film may be caused by morphological changes at the Au–Co_3O_4 interface, as smaller H_2 molecules may penetrate into the inner part of the Au–Co_3O_4 interface region more deeply than the larger CO molecules.

Although both Co_3O_4 and NiO films, containing no Au, show similar absorbance changes and catalytic properties to CO and H_2, the Au–Co_3O_4 film alone shows an H_2-sensitive absorbance change at the plasmon band of Au ($\lambda = 600$ nm). The only difference observed by electron microscopy is that while the average diameter of Au particles was nearly in the same range (20–40 nm) in the Au–Co_3O_4 film and Au–NiO film, the size of Co_3O_4 crystallites (5–10 nm) was smaller than the size of NiO crystallites by a factor of 2–4. This suggests that the size of oxide crystallites may be important in creating the peculiar gas sensing selectivity of the Au–Co_3O_4 film.

The fact that the Au plasmon absorbance at 600 nm for the Au–Co_3O_4 film is CO-insensitive implies that the CO-sensitive absorbance change of the Co_3O_4 is suppressed by the Au particles. Similar suppressing effects have also been observed in Au–NiO films.[4,5] For a thin metal film deposited on a transparent metal oxide, the evanescent wave from the metal oxide was effectively absorbed by the surface plasmon of the thin metal film at the interface.[30] This suggests that the absorbance decrease of Co_3O_4 at around 600 nm by CO might be compensated by the plasmon band absorption of small Au particles.

Conclusion

Composite films consisting of ultrafine Co_3O_4 crystals (d = 5–10 nm) and small Au particles (d = 20–40 nm) can optically recognize CO and H_2 in air over a wide range of concentration. In the VIS–near IR absorption spectrum, at wavelengths near 600 nm, in the plasmon absorption band of small Au particles, the absorption is not changed by CO but is selectively increased by H_2. Outside the plasmon band, near 900 nm, both CO and H_2 reduce the light absorption ability of the Co_3O_4 moiety in the film. Therefore, absorption measurements at both 600 and 900 nm make it possible to distinguish H_2 from CO in air.

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