

Microstructures and CO gas sensing properties of Cu-TiO₂ powders prepared by the oxidation of mechanically synthesized Cu-TiN and Cu-TiH₂ composites

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Cu-TiH₂ and Cu-TiN powders were synthesized using a ball milling process under pressurized H₂ and N₂ atmospheres, respectively. Cu-TiO₂-h and Cu-TiO₂-n sensing materials were prepared by oxidizing the synthesized Cu-TiH₂ and Cu-TiN powders at 600 °C. The mean size of the Cu-TiN particles (34.5 nm) was much smaller than that of Cu-TiH₂ powder (106.1 nm). The TiH₂ phase of the Cu-TiH₂ powder entirely changed to a rutile phase while Cu-TiO₂-n powder consisted of both anatase and rutile phases. The Cu-TiO₂-n device had higher responses than the others at all CO concentrations and operating temperatures of 250-450 °C. The Cu-TiO₂-n powder exhibited an anatase phase and a larger surface area than the Cu-TiO₂-h powder. Additionally, the Cu-TiO₂-n powder had a microstructure with well dispersed CuO_x. Therefore, it is believed that the mechanical nitrifying process is more effective to enhance the sensing performance of Cu-TiO₂ to CO gas.

Key words: Nitrifying process, Oxidation of nitride and hydride, TiO₂ material, Metal oxide semiconductor.

Introduction

TiO₂ is a nontoxic, chemically stable, and low-cost n-type sensing material compared to other common metal oxides such as SnO₂ and ZnO. TiO₂ powder has been evaluated for gas sensing applications and exhibited good sensing characteristics [1]. However, TiO₂ materials have drawbacks including low response as well as poor selectivity and stability [2]. The principle of operation of semiconductor gas sensors is based on the interaction of gas molecules with the surface, which produces an interchange or trapping of free carriers. This sensing mechanism implies that the surface of the material is extremely important [3]. The high sensitivity for gases is supplied either by the surface of the grains or by a foreign material dispersed on them. Therefore, in order to obtain more sensitive surfaces, catalytic additives are incorporated into the base metal oxide [4-7]. Additive metals such as Cu, Co, and Au have been proven to be attractive for enhancing the gas sensing of TiO₂ [5, 8-10]. On the other hand, most TiO₂ sensing materials are prepared by wet chemical processes [5, 11]. However, the wet processes require multiple steps, which increases the handling requirements and generation of waste during the intermediate synthesis steps [12-13]. A mechanical alloying/milling technique can overcome the fabrication difficulties, achieve high solid solubility, effectively mix elements with a high vapor pressure

and/or large differences of melting points, and produce amorphous and nanocrystalline materials [14-16]. Furthermore, with this technique, it is possible to produce solid-solid, solid-liquid, and solid-gas chemical reactions that cannot be realized at room temperature. Among them, the gas-solid reaction can dissociate or reform phases using mechanical impact during the room-temperature mechanochemical process. In the case of pure Ti, compounds can be easily formed with hydrogen or oxygen as well as nitrogen because it is a highly reactive metal.

In this study, Cu-TiH₂ and Cu-TiN powders were synthesized using a ball milling process under pressurized H₂ and N₂ atmospheres, respectively. The Cu-TiO₂ sensing materials were prepared by oxidizing the synthesized Cu-TiH₂ and Cu-TiN powders. The oxidation behaviors of the synthesized Cu-TiH₂ and Cu-TiN powders and the CO sensing properties of the Cu-TiO₂ powders prepared by the oxidation of these powders were investigated.

Materials and Methods

Ti (purity 99.4%, -100 mesh) and Cu (purity 99.85%, -100 mesh) powders were used as the base materials. Mechanical alloying was carried out in a planetary high-energy ball mill under pressurized H₂ and N₂ atmospheres, respectively. The ball-to-powder weight ratio was 10 : 1. To prepare the powders for milling, approximately 20 g of the powder was placed into a stainless steel vial together with stainless balls (10 mm in diameter). The disc and vial rotating speeds were 600 and 320 rpm, respectively. The crystal structures of

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the synthesized and oxidized powders were analyzed by X-ray diffraction (XRD) using a CuK α source (Rigaku, D-Max 2500). The Brunauer-Emmett-Teller (BET) surface area was measured via nitrogen adsorption using a surface area analyzer (Micromeritics TRI-3000). The microstructures of the samples were observed using FE-SEM (Hitachi S-4800) and TEM (JEM-2010, JEOL).

To measure the sensor response of the pure and 4 at% Cu-added TiO₂ powders, sensor devices were fabricated as follows. Unmodified and 4 at% Cu-added TiO₂ powders were mixed with alpha-terpineol (C₁₀H₁₈O, 96%) and ground in an agate mortar for 30 min. The prepared pure and Cu-added TiO₂ pastes were applied to 15 mm $\times$ 15 mm alumina circuit boards, each with an interdigitated Pt electrode area of 10 mm $\times$ 10 mm. These boards were then sintered at 600 $^{\circ}$ C in an electric furnace for 3 hrs. The resistance changes of these devices in response to the presence of the test gas were measured using a high-resistance meter (Agilent 34970A). These tests were carried out at temperatures ranging from 200 to 550 $^{\circ}$ C under various concentrations of CO (200–1,000 ppm) in a temperature-controlled environment. The balance gas was N₂ and the air was mixed to contain 10.5% oxygen. The total gas flow rate was 100 mL/min. The sensor response (R_s) of the n-type sensors to CO gas was determined as R_a/R_g , where R_a is the resistance in air with 10.5% O₂ and R_g is the resistance in the test and mixed gases.

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the Cu-TiH₂ and Cu-TiN powders synthesized by ball milling under pressurized H₂ and N₂ atmospheres for 25 hrs, respectively. Both powders were observed to contain only peaks of conducting TiH₂ and TiN phases, respectively.

Fig. 2 shows the SEM images and particle distributions of (a) Cu-TiH₂ and (b) Cu-TiN synthesized by the mechanical gas-solid reaction. The Cu-TiN powder had smaller particles and a more narrow distribution than the Cu-TiH₂ powder. The mean size of the Cu-TiN particles was 34.5 nm, which is much smaller than that of the Cu-TiH₂ powder (106.1 nm). It was found that the mechanically nitrifying process is more effective at reducing the particle size than the hydrogenating process. In order to investigate the oxidation behavior of both powders, DTA and DSC were carried out in air and Ar atmospheres, respectively, at a heating rate of 40 $^{\circ}$ C/min, and the phases produced by the reactions were investigated by employing an X-ray diffractometer, as shown in Fig. 3. The first exothermic reaction (DTA) of the Cu-TiH₂ sample started at about 250 $^{\circ}$ C and ended at about 350 $^{\circ}$ C, which is the onset temperature of the endothermic reaction of DSC, as shown in Fig. 3(a). The TiH₂ phase must have been dissociated to Ti and H₂ via the endothermic reaction of DSC. As shown in Fig. 3(b), it could be confirmed that the TiH₂ phase was partially

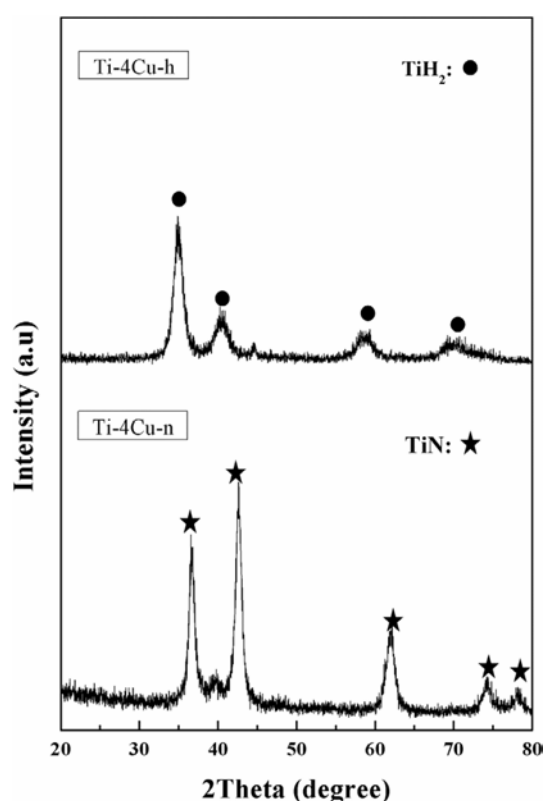


Fig. 1. XRD patterns of the powders milled under H₂ and N₂ atmospheres.

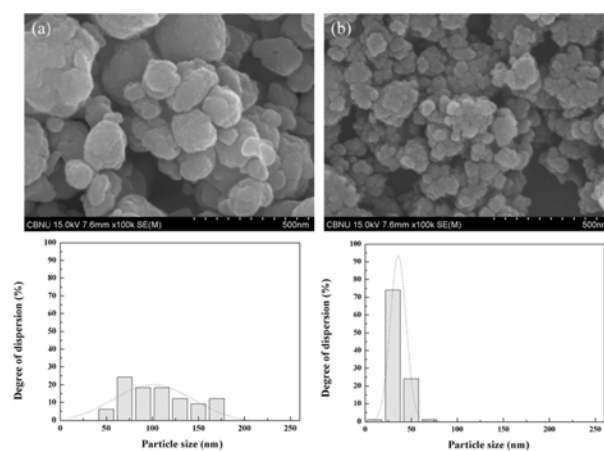


Fig. 2. FE-SEM images and particle distributions of the as-milled (a) Cu-TiH₂ and (b) Cu-TiN.

changed to a rutile phase via the exothermic reaction below 350 $^{\circ}$ C. It seems that the oxidation reaction (DTA) offsets the amount of heat consumed by the endothermic reaction of DSC. Therefore, it is considered that the oxidation of Cu-TiH₂ consisted of two steps.

In the case of Cu-TiN, it had two exothermic peaks where the first exothermic reaction occurred in the temperature range of 320–400 $^{\circ}$ C, as shown in Fig. 3(c). The oxidizing temperature of Cu-TiN was higher than that of Cu-TiH₂. This demonstrates that Cu-TiN is more

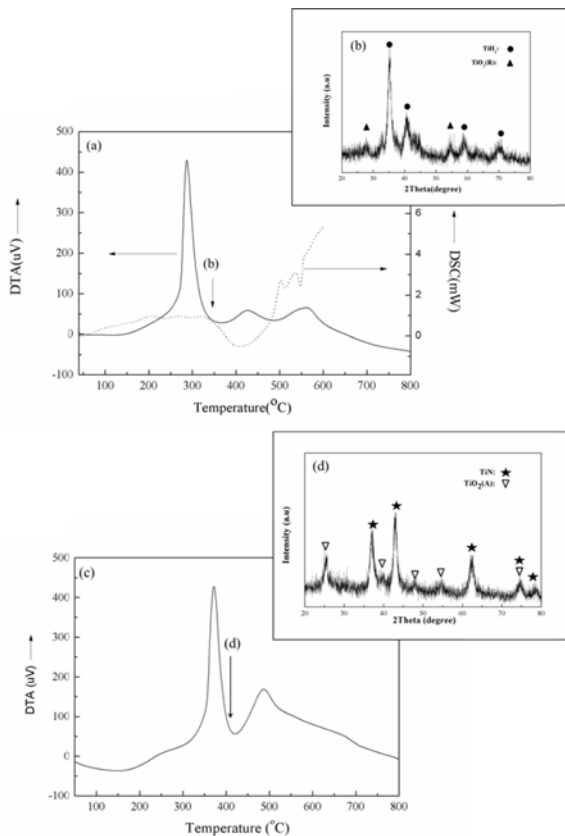


Fig. 3. DTA results of the (a) Cu-TiH₂ powder and (b) reaction products at 350 $^{\circ}\text{C}$ and the (c) Cu-TiN powder and (b) reaction products at 400 $^{\circ}\text{C}$.

thermally stable and the oxidizing rate is slower than that of Cu-TiH₂. As shown in Fig. 3(d), in this exothermic reaction, the TiN phase was partially changed to an anatase phase. It is known that a rutile phase is thermodynamically more stable than an anatase phase under ambient conditions. However, the thermodynamic stability is particle-size dependent and when the particle size is decreased, an anatase phase is more stable than a rutile phase [17-20]. Practically, Cu-TiN with a smaller mean size of 34.5 nm was partially changed to an anatase phase at 400 $^{\circ}\text{C}$ while the Cu-TiH₂ with a mean size of 106.1 nm changed to a rutile phase at even a lower temperature of 350 $^{\circ}\text{C}$.

For convenience, the Cu-TiO₂ powders prepared by the oxidation of Cu-TiH₂ and Cu-TiN in air at 600 $^{\circ}\text{C}$ for 3 hrs are named Cu-TiO₂-h and Cu-TiO₂-n, respectively. The TiH₂ phase of the Cu-TiH₂ powder was entirely changed to the rutile phase while the Cu-TiO₂-n powder coexisted with anatase and rutile phases, as shown in Fig. 4. This means that anatase-rutile transformation of Cu-TiO₂-h was completed at temperatures below 600 $^{\circ}\text{C}$, whereas that of Cu-TiO₂-n was in progress at the same temperature. The diffractions that can be attributed to CuO were not detected in the Cu-TiO₂-n powder, whereas the Cu-TiO₂-h powder exhibited small CuO peaks. As mentioned, the oxidation process of the two samples

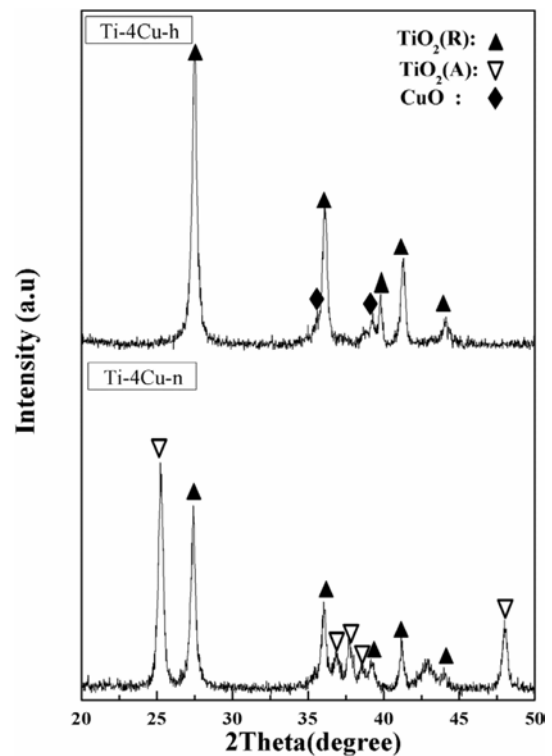


Fig. 4. XRD patterns of the powders oxidized at 600 $^{\circ}\text{C}$ for 3 hrs.

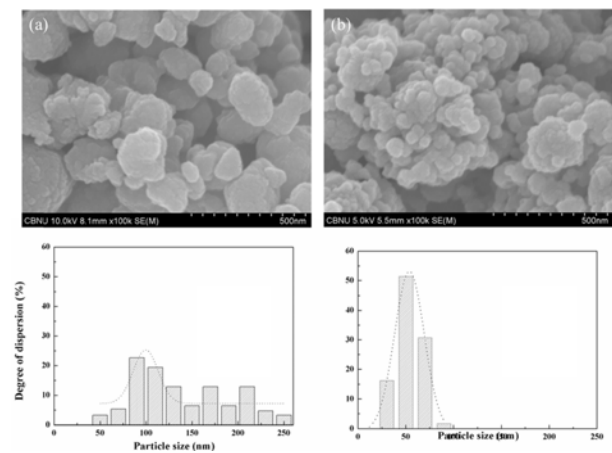


Fig. 5. FE-SEM images and particle distributions of the (a) Cu-TiO₂-h and (b) Cu-TiO₂-n powders.

consisted of two steps. It can be interpreted that the first step is the oxidizing process of an amorphous or supersaturated solid solution with hydrogen or nitrogen near the surface of particles, which would be activated by mechanical collision, and the other is an oxidizing reaction occurring with dissociation of the TiH₂ and TiN phases.

Fig. 5 shows the SEM images and particle distributions of the (c) Cu-TiO₂-h and (d) Cu-TiO₂-n powders that were oxidized at 600 $^{\circ}\text{C}$. The mean sizes of Cu-TiO₂-h and Cu-TiO₂-n increased to 138.4 and 53.5 nm compared to 106.1 and 34.5 nm of the as-milled state, respectively. The microstructures of the (a) Cu-TiO₂-h and (b) Cu-

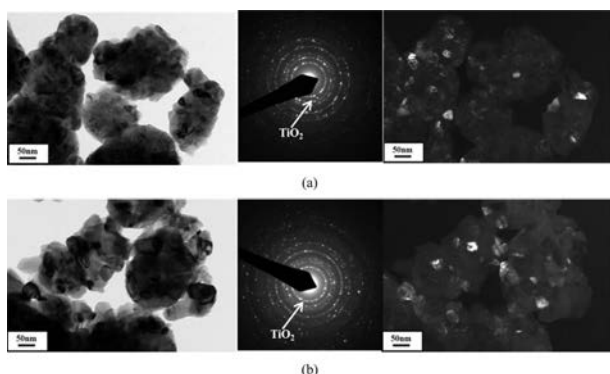


Fig. 6. TEM images of the (a) Cu-TiO₂-h and (b) Cu-TiO₂-n powders oxidized at 600 °C for 3 hrs.

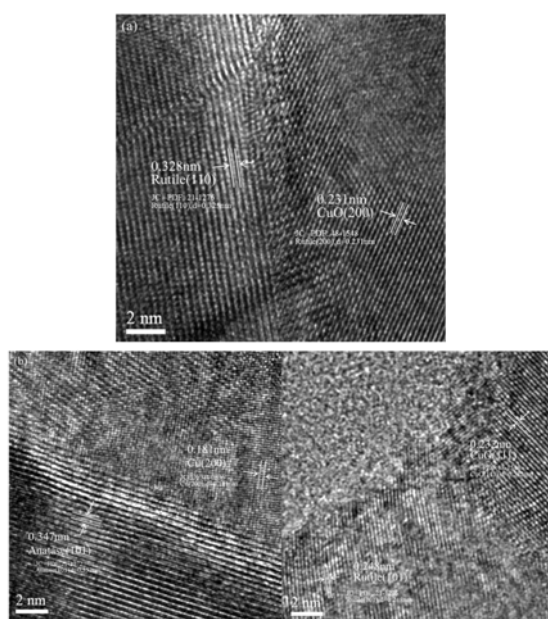


Fig. 7. HR-TEM images of the (a) Cu-TiO₂-h and (b) Cu-TiO₂-n powders oxidized at 600 °C for 3 hrs.

TiO₂-n powders were investigated using TEM, including light field image diffraction-mode images and dark field images corresponding to the TiO₂ planes. As shown in Fig. 6, the grains of TiO₂ crystals in the (a) Cu-TiO₂-h and (b) Cu-TiO₂-n powders had similar sizes with ranges of 15 to 41 nm and 15 to 46 nm, respectively.

Fig. 7 shows the HRTEM images of the (a) Cu-TiO₂-h and (b) Cu-TiO₂-n powders. As shown in Fig. 5(b), clearly resolved crystal lattice fringes of 0.347, 0.181, 0.248, and 0.232 nm were observed in the Cu-TiO₂-n powder, which coincide with the anatase (101), Cu (200), CuO (111), and rutile (101) planes, respectively. It was observed that Cu-TiO₂-n powder consisted of Cu, CuO, and TiO₂ crystallites. However, metallic Cu was not observed in the Cu-TiO₂-h powder, as shown in Fig. 5(a).

Table 1 summarizes the anatase fractions, crystallite sizes, and specific surface areas (SSA) of the Cu-TiO₂-h and Cu-TiO₂-n powders that were oxidized at 600 °C. The

Table 1. Crystallite sizes of the anatase (D_a) and rutile (D_r) phases, anatase content, and specific surface areas (SSA) of the Cu-TiO₂ powders oxidized at 600 °C.

Sample	Anatase (%)	D_a (nm)	D_r (nm)	SSA (m ² /g)
Cu-TiO ₂ -h	—	—	27.9	2.73
Cu-TiO ₂ -n	64.9	23.0	31.6	4.24

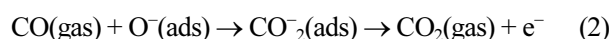
crystallite sizes of anatase (D_a) and rutile (D_r) were determined from the diffraction peak broadening obtained using the Debye-Scherrer equation, and the anatase percentages were determined using the following equation [10]:

$$\left(\frac{\text{Anatase}}{\text{TiO}_2}\right) = 1.369 \frac{I_a}{I_a + I_r} - 0.369 \left[\frac{I_a}{I_a + I_r} \right]^2 \quad (1)$$

where I_a and I_r are the intensities of the anatase (1 0 1) and rutile (1 1 0) reflections, respectively. The Cu-TiO₂-n powder exhibited an anatase phase. The grain size of the rutile phase was larger than that of the anatase phase, and the specific surface area (SSA) of Cu-TiO₂-n was larger than that of the Cu-TiO₂-h powder.

To evaluate the gas sensing properties of the TiO₂ samples, the electrical resistances of the Cu-TiO₂-h and Cu-TiO₂-n samples were measured under exposure to various CO concentrations. Regarding the response to CO, it was observed that both samples exhibited n-type behavior, where the resistance of the sample decreased after exposure to CO, as shown in Fig. 8(a). Fig. 8(b) shows the CO gas responses as a function of the CO concentration (200–1,000 ppm) at a working temperature of 400 °C. The responses of both samples increased with increasing CO concentration and the response of Cu-TiO₂-n was greater than that of Cu-TiO₂-h at all CO concentrations.

Fig. 9 shows the sensor responses to 1,000 ppm CO gas as a function of the operating temperature for the Cu-TiO₂-h and Cu-TiO₂-n samples as well as unmodified TiO₂ for comparison. The TiO₂ powders show an enhanced gas response with the addition of Cu. The responses of Cu-TiO₂-h and Cu-TiO₂-n increased with increasing temperature up to 400 °C and subsequently decreased beyond 450 °C. The Cu-TiO₂-n device had higher responses than the others at operating temperatures of 250–450 °C. It is well known that dispersed Cu in TiO₂ acts as a catalyst for the oxidation of CO gas [21]. Based on the literature [22], the following oxidation reaction of CO can be written.



In this scheme, CO reacts with oxygen species that are adsorbed on the oxide surface. The CO sensitivity can increase with the addition of Cu because of the promotion of reaction sites for CO oxidation when the amount of adsorbed oxygen on the surface increases

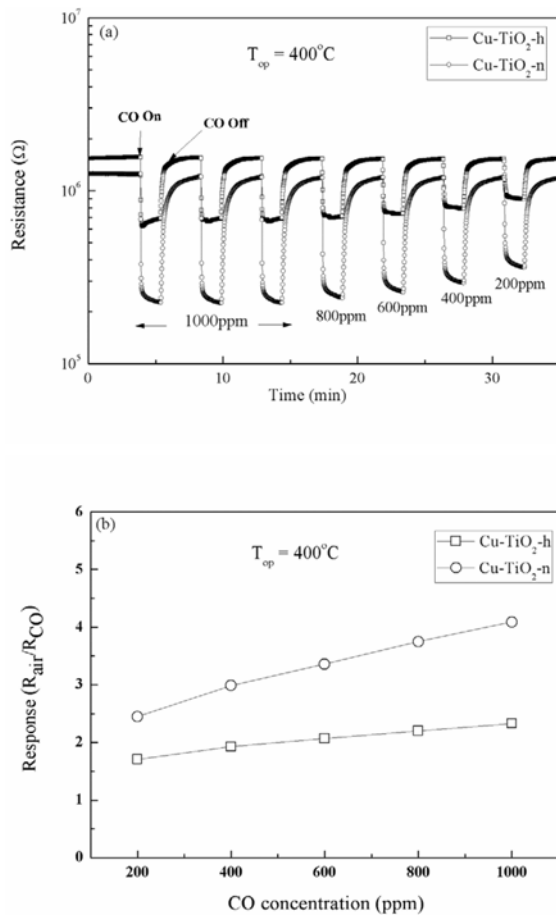


Fig. 8. (a) The variation of the resistance upon exposure to CO gas and (b) response changes of Cu-TiO₂-h and Cu-TiO₂-n powders oxidized at 600 °C for 3 hrs as a function of the CO concentration.

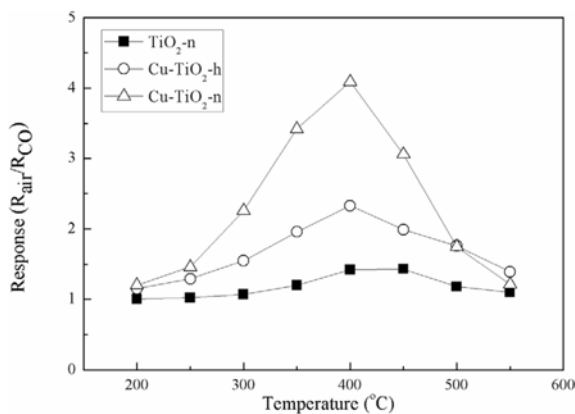


Fig. 9. CO gas responses of the TiO₂-n, Cu-TiO₂-h, and Cu-TiO₂-n powders.

[21]. Indeed, the donor-type behavior of Cu may favor the dissociation of molecular oxygen into adsorbed O⁻ atoms. In this reaction, the Cu valence has been proposed to cycle between Cu (II) and Cu (0) [23]. The dispersed CuO_x species have a high catalytic activity for the oxidation of CO gas, and Cu²⁺ is a scavenger of electrons after the reaction of CO with surface oxygen (O²⁻) and the desorption of CO₂. In this study, both

metallic Cu and CuO crystallites were observed in the Cu-TiO₂-n powder, which indicates that the CO catalytic reaction was promoted more by the cycling of the Cu valence, as shown in Fig. 7(b).

The Cu-TiO₂-n powder exhibited an anatase phase and a larger surface area than the Cu-TiO₂-h powder (Table 1). Additionally, the Cu-TiO₂-n powder had a microstructure with well dispersed CuO_x species, whereas the Cu added to the Cu-TiO₂-h powder was precipitated as CuO crystallites at 600 °C (Fig. 4). Therefore, regarding the aforementioned difference, it was demonstrated that compared to the hydrogenating process, the mechanically nitrifying process is more effective at enhancing the sensing performance of TiO₂ to CO gas.

Conclusions

Cu-TiH₂ and Cu-TiN powders were synthesized using a ball milling process under pressurized H₂ and N₂ atmospheres, respectively. Cu-TiO₂-h and Cu-TiO₂-n sensing materials were prepared by oxidizing the synthesized Cu-TiH₂ and Cu-TiN powders at 600 °C. The mean size of the Cu-TiN particles (34.5 nm) was much smaller than that of the Cu-TiH₂ powder (106.1 nm). The TiH₂ phase of the Cu-TiH₂ powder was entirely changed to a rutile phase while the Cu-TiO₂-n powder coexisted with anatase and rutile phases. The Cu-TiO₂-n powder consisted of Cu, CuO, and TiO₂ crystallites, while metallic Cu was not observed in the Cu-TiO₂-h powder. The Cu-TiO₂-n device had higher responses than the others at all CO concentrations and operating temperatures of 250–450 °C. Both metallic Cu and CuO crystallites were observed in the Cu-TiO₂-n powder. It was demonstrated that the CO catalytic reaction of Cu-TiO₂-n powder was promoted more by the cycling of the Cu valence. Therefore, it was found that the mechanically nitrifying process is more effective than the hydrogenating process at enhancing the sensing performance of TiO₂ to CO gas.

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