Effect of annealing temperature on the characteristic of reduced highly ordered TiO$_2$ nanotube arrays and their CO gas-sensing performance

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Abstract

A study on the effect of temperature on the reduced highly ordered TiO$_2$ nanotube arrays (reduced-HOTNAs) and their CO gas-sensing performance is reported. The reduced-HOTNAs were prepared by anodizing method followed by annealing in the presence of urea at various temperatures (i.e. 450, 500, 550, 600, and 700 °C) under N$_2$ atmosphere. The reduced-HOTNAs were characterized by FTIR, FE-SEM, XRD, UV-Vis DRS, Raman spectroscopy and photoelectrochemical techniques. The sensing performance of the reduced-HOTNAs was assessed against CO gas in air mixture. The results show that the reduced-HOTNAs annealed at 450 °C (reduced-HOTNAs-450) is a material with the most significant improvement in sensitivity to detect CO compared with other reduced-HOTNAs. The reduced-HOTNAs-450 exhibits best sensing performance at a relatively low CO concentration in the range of 2–25 ppm at 300 °C. Findings of this study indicate that improvement of the reduced-HOTNAs-450 sensitivity might be attributed to the presence of Ti$^{3+}$/oxygen vacancy defect and the formation of more active sites on TiO$_2$ surface, making the reduced-HOTNAs-450 a promising active material for CO gas sensor application.

Keywords: titania, anodization, nanotube, calcination, carbon monoxide, gas sensor

I. Introduction

Incomplete combustion of wood, coal or fossil fuels is closely related to poisonous carbon monoxide (CO) emission [1,2]. Human exposure to moderate- or high-level of CO over a certain period may cause considerable health effects [3–5]. CO is a colourless, tasteless, flammable gas, and human senses cannot detect its presence. In this regard, a sensing device having sensitive and selective properties for early detection of the presence of poisonous CO gas is extremely important [1,2]. To date, a typical CO gas sensor has long been recognized as a common sensing device to detect CO gas and it is often part of a safety system at potential sites such as home, office, laboratories, factories and other poorly ventilated areas.

Several previous works have reported the construction of CO gas sensors. Currently, the development of CO gas sensors based on metal oxide semiconductors has received significant attention owing to its high sensitivity property, fast response, short recovery time, simplicity, long life span, good thermal and chemical stability [6–9]. Numerous metal oxide semiconductors have been used for CO reductive gas sensor applications, including ZnO, SnO$_2$, TiO$_2$, In$_2$O$_3$, ZrO$_2$, CeO$_2$, Fe$_2$O$_3$, WO$_3$, CdO, CuO, or their composite oxides [2,9–13]. Amongst them, titanium dioxide with nanotubular structure (TiO$_2$ nanotube) is by far the most widely studied metal oxide semiconductor for CO gas sensor applications. TiO$_2$ nanotube is one dimension (1D) structure having a high specific surface area [8], high mechanical strength [14], high electron mobility [12] and surface defects (oxygen vacancies) [2]. The latter plays a crucial
role in gas sensing [2,15]. Pan et al. [16] reported that surface defect as Ti$^{3+}$/oxygen vacancy is likely the most important factor affecting TiO$_2$ sensing performance, which may act as active surface site for the adsorption of oxygen molecules on the surface. A study by Zou et al. [17] indicated that the sensing response of reduced-TiO$_2$ nano rod-like structure was found to increase its linearity for CO gas in the range of 100–10000 ppm at an operating temperature of 300 °C. Furthermore Su et al. [18] reported that sensing properties of porous TiO$_2$ were affected by the Ti$^{3+}$/oxygen vacancy on the surface when detecting CO gas in the range of 100–10000 ppm at room temperature.

Recently, various methods for preparing TiO$_2$ nanotubes have been developed to obtain sensors with desired physicochemical and electronic properties, which improve sensing performance. Such preparation methods include sol-gel, template-assisted, hydrothermal, solvothermal and electrochemical anodization [14]. Among such feasible approaches, the electrochemical anodization method is important for obtaining a TiO$_2$ nanotube with a vertical self-organized nanotube layer with controllable nano geometry. In addition, the electrochemical anodization method is a relatively low-cost and straightforward process for large-scale production [14,19].

Although gas sensing performance of TiO$_2$-based materials prepared by electrochemical anodization method has been widely studied [20–22], there are only a few reports dealing with the effect of annealing temperature on physicochemical, electronic and sensing properties of TiO$_2$ nanotube. Thus, this remains a challenge in the gas sensor research field. From the perspective of regulation, National Air Quality Index (NAQI) sets that the concentration of CO posing an immediate danger to life and health (IDLH) is 35 ppm for 1 h exposure [23]. This set of concentration levels implies that a useful sensor should detect CO gas on that order of concentration level. Thus, the sensing performance development of TiO$_2$ nanotubes for better sensitivity in detecting CO gas below 100 ppm range is a great challenge. Herein, a study on the effect of annealing temperature on the characteristics of reduced highly ordered TiO$_2$ nanotube arrays (HOTNAs) and their CO gas-sensing performance is presented. The reduced-HOTNAs were prepared by the electrochemical anodization method and annealed at various temperatures. The morphology, crystal size and non-stoichiometric defects of the prepared TiO$_2$ nanotube were affected by the annealing temperature. The present study demonstrates the characteristics and sensing performance of the reduced-HOTNAs.

II. Experimental

2.1. Materials

Titanium foil (0.3 mm thick, an industrial grade with 99.6% purity) was purchased from Shanghai Chong Xin Electric Alloy Co. Ammonium fluoride (NH$_4$F, 95% purity), hydrofluoric acid (HF, 40% purity), nitric acid (HNO$_3$, 65% purity), hydrogen peroxide (H$_2$O$_2$, 30% purity), ethylene glycol (C$_2$H$_4$O$_2$, 99.5% purity), acetone (C$_3$H$_7$O, 99.8% purity) and ethanol (C$_2$H$_5$O, 99.9% purity) were purchased from Merck. Urea (CO(NH$_2$)$_2$, 99% purity) was purchased from Junsei Chemical Co. Ltd. All chemicals were pro-analysis grade and were used as received without any further purification. Deionized water with a resistivity of 0.055 µS/cm produced by a Millipore Milli-Q water purification system was used in all experiments.

2.2. Preparation

All HOTNAs samples were prepared from titanium (Ti) foils with 10 mm × 10 mm in dimensions each by adopting a method from the literature [24]. The method is briefly described as follows. The Ti foils were firstly treated by the chemical polishing method before being subjected to electrochemical anodizing to obtain as-prepared samples. The as-prepared samples were then annealed under atmospheric air, resulting in pristine-HOTNAs, while other as-prepared HOTNAs were used to prepare reduced-HOTNAs.

The reduced-HOTNAs were prepared from the as-prepared samples by adopting a method proposed by Su et al. [18] with slight modification. Briefly, the as-prepared HOTNAs were irradiated by using a UV-light (36 W with 365 nm wavelength as a light source) for 2 h. The irradiated samples were immersed in an ethanol solution containing 0.05 M urea at room temperature for 12 h. The treated HOTNAs samples were subjected to reduction by annealing under N$_2$ atmosphere at 450, 500, 550, 600 and 700 °C in a furnace for 2 h with 5 °C/min heating rate. The prepared samples are denoted as reduced-HOTNAs-T, where T is annealing temperature. All these reduced-HOTNAs were characterized and their CO sensing performances were evaluated.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu IR Prestige-21 spectrophotometer in the range of 400–4000 cm$^{-1}$ at a scanning rate of 4 cm$^{-1}$/min. The ultraviolet-visible diffuse reflectance (UV Vis-DR) spectra were obtained using a Shimadzu 2450 spectrophotometer at a wavelength ranging from 200 to 900 nm, and BaSO$_4$ powder was used as a reference. X-ray diffraction (XRD) patterns were recorded on an X’PERT Pro, PANalytical X-ray diffractometer using Cu Kα target ($λ = 1.5406$ Å) at 40 kV and 50 mA in the 2θ range of 10–90° at a speed of 0.25°/min. Anatase-rutile fractions were calculated by taking into account the diffraction peak intensities of anatase (101) and rutile (110) using the following formulas [25,26]:

$$F_A = \frac{0.79I_A}{0.79I_A + I_R}$$  \hspace{1cm} (1)
\[ F_R = \frac{1}{1 + 0.79 \frac{I_A}{I_R}} \] (2)

where \( F_A \) and \( F_R \) are the fraction of anatase and rutile in the sample, respectively, and \( I_A \) and \( I_R \) are the peak intensities of anatase (101) and rutile (110), respectively. The surface and cross-section images were recorded using FEI Inspect F50 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 15 kV. The Raman spectra were obtained using HORIBA Scientific LabSPec 6 Raman spectrometer with 532 nm line from Ar\(^+\) laser as an excitation source. Photo-electrochemical (PEC) properties of the HOTNAs samples were evaluated by using the linear sweep voltammetry (LSV) method under identical experimental conditions as reported in the literature [24].

The CO gas sensing measurement system has been designed in our laboratory (Fig. S1 in SI). Details about the sensing measurement system and its schematic illustration can be found in the Supporting Information (SI).

III. Results and discussion

3.1. FE-SEM study

Effect of the annealing temperature on morphological characteristics of the reduced-HOTNAs samples annealed at various temperatures was elucidated by observing the surface and cross-section of samples by FE-SEM and images are depicted in Figs. 1 and 2. The top view FE-SEM images of the reduced-HOTNAs at various annealing temperatures are shown in Fig. 1. As it can be seen, the nanotube structures on the surface of the reduced-HOTNAs-450 (Fig. 1a) are well-defined and well-ordered. Meanwhile, a well-ordered structure of TiO\(_2\) nanotubes partially covered by a thin layer of debris was observed at higher annealing temperatures of 500–600 °C (Figs. 1b-1d.). The formation of a thin layer of debris might be due to the accumulation of the anodization reaction products in the form of precipitated Ti(OH)\(_4\) on top of nanotube pores [27]. In addition, the annealing temperature induced a formation of a closing mouth structure on the nanotube. The closed mouth structure can be observed in the reduced-HOTNAs-550 (Fig. 1c) and reduced-HOTNAs-600 (Fig. 1d). The areas of closed mouth structure on the reduced-HOTNAs-600 are wider than that of the reduced-HOTNAs-550, implying that the formation of closed mouth structure is temperature-dependent. The closed mouth structure is linked to a wall thickening phenomenon due to the grain growth along the tube wall [28]. Generally, thermodynamically metastable nanostructured HOTNAs with a large surface area are susceptible to solid-state sintering at higher annealing temperatures [28]. The high temperature led to the growth of grain and crystallite, densification, as well as a thickening of the tube wall. The average tube diameter of the reduced-HOTNAs increases from 40.9 to 44.7 nm (Table S1 in SI) by increasing the annealing temperature from 450 to 600 °C. In addition to the formation of both thin layer of debris and closed mouth structure, the highest annealing temperature (700 °C in this study) led to the collapse of the nanotube structure of the reduced-HOTNAs. As it can be seen on the surface images of the reduced-HOTNAs-

Figure 1. Top view FE-SEM images of reduced-HOTNAs annealed at: a) 450, b) 500, c) 550, d) 600 and e) 700 °C
700 (Fig. 1e), some irregular structures from collapsing of the nanotube mostly cover the surface, which was probably a result of rutile protrusions over the titanium substrate (substrate effect) [29,30].

Figure 2 shows FE-SEM cross-sectional view of the reduced-HOTNAs at various annealing temperatures. From these cross-sectional views as well as tube length calculation data (Table S1 in SI) it was found that the annealing temperature influences the tube dimension with comparably length contrast. However, the decrease in the length of the nanotube is not directly associated with the increase in the annealing temperature. It is expected that the effect of annealing temperature may occur via rutile phase formation. From the calculated phase ratio of the rutile phase (Table S1 in SI), the length of the nanotube decreases from 1.1 to 0.61 µm by increasing the ratio of the rutile phase from 4 to 51%. A similar finding has been previously reported in the literature [31].

3.2. XRD study

Structural characteristics dependence of the reduced-HOTNAs-T on the annealing temperature was studied. Figure 3a presents XRD patterns of the pristine-HOTNAs and reduced-HOTNAs at different annealing temperatures. As it can be seen from Fig. 3a, both the pristine-HOTNAs and reduced-HOTNAs-T show diffraction peaks at 35.29°, 40.37°, 53.16° and 70.78°. These peaks are in agreement with the diffraction peaks of Ti metal substrate (JCPDS card No. 21-1294) [32] as a result of penetrating X-ray into the substrate [33]. In addition to Ti metal peaks, the existence of TiO₂ peaks is also clearly observed (Fig. 3a). For anatase phase, the peaks can be observed at 25.5°, 48.2°, 54.1°, 55.2° and 62.8°, which correspond to (101), (200), (105), (211) and (204) crystal planes (JCPDS card No. 21-1272), respectively [32]. These anatase peaks are found to be temperature-dependent. The peaks’ intensity of anatase phase sharply increases when annealing temperature changes from 450 °C (the reduced-HOTNAs-450) to 550 °C (the reduced-HOTNAs-550), then decreases by increasing annealing temperature. In general, XRD intensity closely relates to the crystallinity of the phase and crystallite size of the studied material and annealing temperature dependence [34]. Increased peak intensity indicates the increase of crystallinity and crystallite size [35,36]. The formation of a rutile phase also indicates such dependence. The peaks of rutile TiO₂ phase at 27.6°, 36.2°, 41.4° and 56.8° (Fig. 3a) correspond to the (110) (101), (111) and (220) crystal planes (JCPDS card No. 21-1276), respectively [32]. Rutile phase begins to appear in the reduced-HOTNAs-550. The result shows that the peak intensity of rutile (27.6°) increased with increasing annealing temperature of the reduced-HOTNAs to 700 °C. Thus, the TiO₂ crystal phase transformation from anatase to rutile is effectively affected by annealing temperatures [35–37]. In addition, the anatase peak of (101) plane of the reduced-HOTNAs-T (Fig. 3b) shifted to a lower 2θ in comparison to that of the pristine-HOTNAs. This plane shifting phenomenon was probably due to the existence of oxygen vacancy resulting from the reduction event in the presence of urea as a reduction agent. Sarkar and Khan [38] reported that reducing agents might lead to the formation of oxygen vacancy in the TiO₂ matrix, resulting in shifting
of XRD peak of TiO$_2$. The average crystallite sizes of the HOTNAs samples (Table S1 in SI) were determined from the width of the anatase (101) diffraction peak using the Debye-Scherer equation [39]. It can be seen that the crystallite sizes of anatase reduced-HOTNAs (Table S1 in SI) are temperature-dependent [36] and thus increase by increasing annealing temperature from 450 to 700 °C.

3.3. FTIR study
The FTIR spectra of HOTNAs samples (the pristine-HOTNAs and reduced-HOTNAs-T) are presented in Fig. 4. As shown in Fig. 4a, the vibration band at a lower energy region (400–800 cm$^{-1}$) may be attributed to the formation of anatase Ti–O–Ti lattice. Two characteristic bands at 2050 and 2200 cm$^{-1}$ found in the reduced-HOTNAs-T are assigned to stretching vibration of –OCN from cyanate as a decomposition product of urea at 450 °C [40]. The intensity of these two peaks decreased by increasing the annealing temperature from 450 to 700 °C. In addition, local magnified FTIR spectra region (Fig. 4b) shows that Ti–O–Ti– vibration mode of the reduced-HOTNAs-T at around 848 cm$^{-1}$ slightly shifted to a higher wavenumber in comparison to the pristine-HOTNAs. The shifting of the vibration band is due to the formation of oxygen vacancy [38,41] during the reduction of HOTNAs. This finding is in agreement with XRD data as mentioned earlier.

3.4. Raman study
More information regarding the role of annealing temperature in the formation of oxygen vacancy in the HOTNAs samples (both pristine-HOTNAs and reduced-HOTNAs-T) was obtained by using Raman spectroscopy technique and the results are depicted in Fig. 5. As it can be seen in Fig. 5, there are five Raman peaks at 144 cm$^{-1}$ ($E_g$), 196 cm$^{-1}$ ($E_g$), 395 cm$^{-1}$ ($B_{1g}$), 517 cm$^{-1}$ ($B_{1g}$) and 639 cm$^{-1}$ ($E_g$), which correspond to TiO$_2$ anatase phase [38]. The $E_g$ and $B_{1g}$ peaks are mainly related to the symmetric stretching vibration and symmetric bending vibration of O–Ti–O bonds in TiO$_2$, respectively [38]. In addition, Fig. 5 shows that the intensities of those five typical Raman peaks of anatase in the reduced-HOTNAs-T were lower than that of the pristine-HOTNAs, implying that the reduction process could induce a broadening effect in TiO$_2$ Raman peaks. Moreover, two dominant Raman peaks for $E_g$ mode at around 144 cm$^{-1}$ and 146 cm$^{-1}$.
of the reduced-HOTNAs-T (inset of Fig. 5) are slightly shifted its wave number. This shift in $E_g$ wave number and peak broadening are attributed to the lattice disorder or non-stoichiometric defect associated with the existence of oxygen vacancy [42,43]. In addition, the Raman peak (144 and 146 cm$^{-1}$) intensity of the reduced-HOTNAs-T increases by increasing the annealing temperature in the following order: reduced-HOTNAs-450 $<$ reduced-HOTNAs-500 $<$ reduced-HOTNAs-550 $<$ reduced-HOTNAs-600, implying an increase in crystallinity followed by the provision of more active Raman facets [43]. However, a higher annealing temperature of 700 °C resulted in low-intensity Raman peaks (144 and 146 cm$^{-1}$) of the reduced-HOTNAs-700, which is lower than those of the reduced-HOTNAs-450, reduced-HOTNAs-500, reduced-HOTNAs-550 and reduced-HOTNAs-600. This phenomenon was probably due to the peel off of the TiO$_2$ film which resulted in the lower amount of TiO$_2$ analysed by Raman.

3.5. Photo-electrochemical study

The linear sweep voltammetry analysis of the reduced-HOTNAs at different annealing temperatures under visible light irradiation revealed that the photocurrent density (at 0.5 V potential) of the reduced-HOTNAs gradually decreases with increasing annealing temperatures (Fig. S2 in SI). The photocurrent density follows the order: reduced-HOTNAs-450 $>$ reduced-HOTNAs-500 $>$ reduced-HOTNAs-550 $>$ reduced-HOTNAs-600, and the values are listed in Table S1 in SI. A higher photocurrent density of the reduced-HOTNAs-450 implies the formation of the highly ordered nanotubes with open mouths tubes and large surface area and the generation of an excessive amount of Ti$^{3+}$/oxygen vacancies in the lattice of TiO$_2$ [44].

3.6. UV-Vis DRS study

Compared with the pristine-HOTNAs, the UV-Vis DRS analysis of the reduced-HOTNAs at various annealing temperatures shows a significantly stronger absorption intensity in the visible light region (400–800 nm) (Fig. S3a in SI), ascribed to the additional transitions between the different energy levels of the Ti$^{3+}$ species, oxygen vacancy, conduction band, and valence band [44,45]. The Ti$^{3+}$ species are formed with energies 0.27–0.87 eV below the conduction band of TiO$_2$ [45], leading to the bandgap narrowing for the reduced-HOTNAs-T. The corresponding Tauc plots of the HOTNAs samples for bandgap determination are generated (Fig. S3b in SI), and the calculated bandgaps are listed in Table S1 in SI. As it can be seen, the bandgap energies (2.82–3.05 eV) of the reduced-HOTNAs-T (Table S1 in SI) were lower than that of the pristine-HOTNAs (3.19 eV). The lower bandgap energies of the reduced-HOTNAs-T are probably attributed to the presence of more significant amounts of Ti$^{3+}$/oxygen vacancy defects in the bulk phase of the TiO$_2$ lattice [43]. These results are consistent with other previous studies [43–45].

In addition, the presence of a localized Ti$^{3+}$/oxygen vacancy defect in the HOTNAs band gap resulted in the absorption tail extending to the forbidden gap. This absorption tail is called the Urbach tail and is related to the Urbach energy [46,47]. Thus, another key parameter that may be obtained from the UV-Vis DRS is the Urbach energy or Urbach tail (Fig. S4 in SI) [48]. The Urbach energy is calculated using the following formula:

$$\alpha = \alpha_0 + \exp \left( \frac{E}{E_u} \right)$$

where $\alpha$ is the absorption coefficient, $E$ is the photon energy, and $E_u$ is the Urbach energy. Urbach energy is determined by plotting $\ln(\alpha)$ against $E$. Since the absorption coefficient $\alpha$ is directly proportional to the absorbance $F(R)$, a plot of $\ln(F(R))$ against the photon energy ($E$) can be made instead (Fig. S5 in SI). The reciprocal slope of the linear curve, formed under the optical band gap, produces the Urbach energy value [46,47]. At lower annealing temperatures, the decrease in the bandgap is accompanied by the increase in the Urbach energy of the reduced-HOTNAs (Fig. 6). The increase in the Urbach energy is due to the higher number of oxygen vacancies in the reduced-HOTNAs [46,47]. This result is consistent with the findings
Figure 7. Response characteristics of reduced-HOTNAs annealed at different temperatures: a) 450, b) 500, c) 550, d) 600 and e) 700 °C toward CO gas at operating temperature of 300 °C.

reported elsewhere [46–48]. The highest Urbach energy value can be achieved in the reduced-HOTNAs-450. This result agrees with the highest photo-absorption activity of the reduced-HOTNAs-450 in the visible light region (Fig. 6).

3.7. Gas sensing study

Figure 7 shows response characteristics of the reduced-HOTNAs annealed at different temperatures toward CO gas at an operating temperature of 300 °C. From Fig. 7, it was found that the response values of the reduced-HOTNAs-T increase by increasing the concentration of CO gas, and the response-recovery curves obtained Figs. 7a-d show a typical curve for metal oxide semiconductor n-type against the response to CO and air. The baseline resistance values of the reduced-HOTNAs under air exposure increase and follow the order of reduced-HOTNAs-450 (56 kΩ) (Fig. 7a), reduced-HOTNAs-500 (165 kΩ) (Fig. 7b), reduced-HOTNAs-550 (241 kΩ) (Fig. 7c) and reduced-HOTNAs-600 (627 kΩ) (Fig. 7d). Under this condition, the reduced-HOTNAs become more conductive with lower annealing temperatures due to the higher Ti³⁺/oxygen vacancies in the reduced-HOTNAs. The Ti³⁺/oxygen vacancy level of the various reduced-HOTNAs-T can be estimated using these resis-
tance properties [49]. In addition, the typical response-recovery curve of the reduced-HOTNAs can be explained by the reaction pathway given by Eqs. 4–9, and it can be described as follows. The $O_2$ molecules from the air are first adsorbed onto the surface of the $TiO_2$ and then converted into adsorbed oxygen species ($O_2^-$, $O^-$, $O_2^-$) as a result of the electron attraction from the $TiO_2$ conduction band (Eqs. 4–6). Furthermore, electron depletion layers were formed, which led to the increase in the electrical resistance of $TiO_2$. Upon exposure to CO gas, the CO reacts with the adsorbed oxygen species to form $CO_2$, and correspondingly the electron returns to the conduction band of $TiO_2$ (Eqs. 7–9). As a result, the width of the depletion layer of the $TiO_2$ surface is narrowed, which leads to the decrease of the resistance of the whole sensing layer of $TiO_2$ [2,5,50]. It is worth noting that the resistance response of the reduced-HOTNAs-700 (Fig. 7e) was remarkably low upon exposure to air because the $TiO_2$ nanotube film was damaged and peeled off from the Ti metal substrate.

\[
\begin{align*}
O_2 + e^- & \rightleftharpoons O_2^- \quad (4) \\
O_2^- + e^- & \rightleftharpoons 2O^- \quad (5) \\
O^- + e^- & \rightleftharpoons O_2^- \quad (6) \\
2CO + O_2^- & \rightarrow 2CO_2 + e^- \quad (7) \\
CO + O^- & \rightarrow CO_2 + e^- \quad (8) \\
CO + O_2^- & \rightarrow CO_2 + 2e^- \quad (9)
\end{align*}
\]

Figure 8 shows the calibration curves for CO gas sensing of the reduced-HOTNAs. From Fig. 8, it can be observed that the linear dependence covers a higher CO concentration range with the increase of calcination temperature of the reduced-HOTNAs. The linear range for reduced-HOTNAs-450 (Fig. 8a), reduced-HOTNAs-500 (Fig. 8b), reduced-HOTNAs-550 (Fig. 8c) and reduced-HOTNAs-600 (Fig. 8d) are 2–25 ppm, 50–150 ppm, 500–10000 ppm and 1000–20000 ppm, respectively. The reduced-HOTNAs-450, (Fig. 8a) reduced-HOTNAs-500 (Fig. 8b) and reduced-HOTNAs-550 (Fig. 8c) can be exposed to CO gas higher than 25, 150 and 10000 ppm, respectively. The response was found to be non-linear, at high concentration, due to the saturation of $TiO_2$ surface of the sensor probe, which is indicated by the plateau curve (Fig. S6 in SI). Moreover, on the basis of slope examination of each calibration curve, the sensitivity of CO sensors follows the order of reduced-HOTNAs-450 > reduced-HOTNAs-500 > reduced-HOTNAs-550 > reduced-HOTNAs-600. A significant improvement in sensitivity of the reduced-HOTNAs-450 can be ascribed to the formation of well-ordered nanotubes on the surface (Fig. 1a) with open mouths of nanotubes that provide a higher surface area for gas molecules adsorption. This finding is in agreement with the available literature report [51]. In addition, the sensitivity of the sensors is remarkably affected by the crystallite size of HOTNAs. The smallest crystallite size (28.5 nm) in the reduced-HOTNAs-450 also leads to a higher surface area, providing more active surface sites to interact with CO molecules. As reported by Yamazoe et al. [52] the sensitivity of gas sensors was enhanced with the decrease of crystallite size. In addition, from the XRD results, the reduced-HOTNAs-450 comprises a pure anatase phase that is more reactive and conductive than rutile phase [14,53]. As anatase is transformed to rutile phase, the sensor sensitivity is significantly decreased [8]. The highest sensitivity of the

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**Figure 8.** Calibration curves of CO for the reduced-HOTNAs-T annealed at: a) 450, b) 500, c) 550 and d) 600 °C in a chamber at 30 °C with 30% RH
reduced-HOTNAs-450 might be also caused by a larger amount of Ti$^{3+}$/oxygen vacancy defects on the surface. This phenomenon was verified by the lower bandgap, the higher Urbach energy, the higher photocurrent densities, and the lower baseline resistance of the reduced-HOTNAs-450. Analysis of X-ray photoelectron spectroscopy (XPS) will be intensively investigated in our future works for direct confirmation of the presence of Ti$^{3+}$/oxygen vacancy defect in the reduced-HOTNAs. According to Su et al. [18] the Ti$^{3+}$/oxygen vacancy defect on the titania surface was responsible for decreasing the resistance of TiO$_2$, and increasing the chemisorbed oxygen species, leading to a higher sensitivity of the CO gas sensor.

The surface-to-volume ratio ($S/V$) of the prepared reduced-HOTNAs was calculated by using an adopted formula (Eq. 10) from the literature reported elsewhere [54], and the results are summarized (Table S1 in SI). The calculation was conducted considering that the outer wall surface is neglected because there is no wall separation between nanotubes, as shown in FE-SEM images (Fig. 1).

$$S/V = \frac{\pi \cdot r}{2(r + D + \frac{3}{4})^2} \quad (10)$$

where $r$ is the inner radius, $D$ is wall thickness, and $S$ is wall separation between nanotube. The surface-to-volume ratio of the reduced-HOTNAs-450 was higher than reduced-HOTNAs at higher annealing temperatures (500–600 °C) (Table S1 in SI). The high surface-to-volume ratio of the reduced-HOTNAs-450 may lead to its better sensitivity. In addition, the higher sensitivity of the reduced-HOTNAs-450 is attributed to the presence of a large amount of Ti$^{3+}$/oxygen vacancies as active sites on the surface for the adsorption of CO. Its high photocurrent activity also confirms this phenomenon under visible light irradiation (Fig. S2 in SI). Thus, the reduced-HOTNAs-450 has shown an interesting sensing property.

The sensing performance of the reduced-HOTNAs sensors toward CO gas prepared in this study in comparison to other published reports of nanostructured TiO$_2$ sensors is shown in Fig. 9. It can be observed that some of the nanostructured TiO$_2$ sensors demonstrated relatively low sensitivity to CO (Fig. 9). For instance, Su et al. [18] and Chesler et al. [55] reported that lower sensitivity of porous TiO$_2$ nanostructures sensor toward CO was obtained having values of 0.0013 and 0.0052, respectively. Perillo et al. [56] reported that the sensitivity of TiO$_2$ nanotubes on Si wafer-based sensor towards CO gas is 0.016. Such relatively low sensitivities may not meet the requirement of practical application [57] since a high working range of CO concentrations (>100 ppm) is obtained by those previous studies. A quiet higher sensitivity and a lower working range of concentrations (<100 ppm) were obtained by other TiO$_2$ nanotube-based CO gas sensors, as reported by Gönülülü et al. [58] and Kim et al. [59]. In our current study, the sensitivity of the reduced-HOTNAs-450 (2.23) toward CO was found to be higher than in other published reports (Fig. 9). Consequently, a lower working range of CO concentrations of 2–25 ppm can be achieved by using reduced-HOTNAs-450. This result suggests that the reduced-HOTNAs-450 has a high potential to be applied as a CO gas sensor.

IV. Conclusions

Preparation of reduced highly ordered TiO$_2$ nanotube arrays (reduced-HOTNAs) was successfully carried out by anodization method followed by annealing in the presence of urea at various temperatures 450, 500, 550, 600 and 700 °C under N$_2$ atmosphere. Characterization results showed that the reduced-HOTNAs annealed at 450 °C (reduced-HOTNAs-450) were found to be pure anatase with smaller crystallite size, lower bandgap, the higher surface to volume ratio, and higher photocurrent density under visible light in comparison to other prepared reduced-HOTNAs. Furthermore, the experimental application of the reduced-HOTNAs-450 as a CO gas sensor showed better sensing performances with a high response at concentrations of 2 to 25 ppm at 300 °C. Such great sensitivity might be attributed to the following factors, namely: i) the high number of chemisorbed oxygen on the surface of the reduced-HOTNAs-450 due to the formation of Ti$^{3+}$/oxygen vacancy defect (non-stoichiometric defect), ii) anatase phase of the reduced-HOTNAs-450 crystal, and the presence of Ti$^{3+}$ species led to the lowering of its resistance and iii) well-ordered nanotube structure on the surface and a smaller crystallite size of the reduced-HOTNAs-450 contributed to a high surface area, providing more active sites on the surface. Thus, improvement in its sensitivity implies that the reduced-HOTNAs-450 is a promising active material for CO gas sensors.

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§ Supporting Information can be downloaded using following link: https://bit.ly/32OdXLO

References


