

Carbon dioxide resistive sensor based on titanium oxide nanowires doped with potassium

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Potassium-doped titanium oxide (TiO₂) nanowires are fabricated by the moisture-assisted, direct oxidation of a thin film of titanium at 650°C. The influence of the fabrication conditions on the structure and morphology of the nanowires was investigated. It was shown that the presence of potassium (K) is necessary for the formation of the nanowires. The density of growth of the nanowires was high, and the lengths of the nanowires were tens of micrometres. The K-doped TiO₂ nanowires showed the possibility of use as a sensing material because of their significant and consistent response to responding to carbon dioxide (CO₂) gas. In addition, H₂ plasma treatment improved the sensitivity of the CO₂ gas sensor made of K-doped TiO₂ nanowires. Although the sensing mechanism is not clear, this development suggests opportunities for the fabrication of simple and inexpensive CO₂ microsensors with low power consumption.

1. Introduction: Gas sensors have been developed to monitor the presence of carbon dioxide (CO₂) in the environment because of its significant role in global warming. In addition, CO₂ gas significantly affects the corrosion rate of the industrial equipment used in chemical processing and combustion efficiencies in automotive applications. Because of the prevalence of CO₂ and its numerous negative effects, small, inexpensive and reliable solid-state CO₂ gas sensors with low power consumption have been in high demand for several years [1, 2].

Despite various approaches for monitoring CO₂ concentrations only a limited number of CO₂ sensing materials exist because of the stable chemical properties of CO₂ gas [3]. Currently, the most common type of CO₂ sensor is a potentiometric device that uses a combination of a solid electrolyte with an auxiliary phase of carbonates [4, 5]. Most existing CO₂ sensors are large, bulky devices that involve complicated fabrication processes.

Although we have been actively working on miniaturising CO₂ sensors based on solid electrolytes [6], we have also been aggressively exploring new CO₂ sensing materials. Thus, we report for the first time a novel CO₂ sensing material, that is, nanocrystalline titanium oxide (TiO₂) doped with potassium (K), which we have demonstrated successfully for the detection of CO₂ gas. In this reported work, we investigated the feasibility of using K-doped TiO₂ nanowires for the detection of CO₂ gas and the ability of H₂ plasma treatment of the nanowires to enhance their detection sensitivity.

2. Experimental: We fabricated TiO₂ nanowires by moisture-assisted, direct oxidation of titanium in the presence of KOH. Thin films of Ti were prepared using a DC magnetron sputtering system. Before deposition, the chamber was pumped down to a pressure of less than 1×10^{-7} Torr using a turbo molecular pump. A water-cooled Ti target with a diameter of 3 inches and a purity of 99.99% was mounted 13 cm away from the substrate holder. A pure, thin film of Ti was deposited at a constant operational pressure, that is, 5 mTorr, in Ar (99.999%) flowing at 45 sccm by heating the substrate to 400°C. A constant DC power of 120 W was maintained.

For the fabrication of the TiO₂ nanowires, one drop (2 ml, area of $\sim 1 \text{ cm}^2$) of a 1 wt% aqueous solution of KOH (Aldrich, 99⁺%) was placed at the centre of the Ti deposited on the substrate. Then, the substrate was inserted into a quartz tube and placed in a horizontal tube furnace (Lindberg, TF55035A) for heat treatments. First, the

tube was purged with 5% H₂ balanced with Ar gas flowing at a rate of 1000 ml/min for 10 min, and then it was heated to 150°C at a ramping rate of 5°C/min. After 30 min at 150°C, the temperature of the furnace was increased at the rate of 30°C/min to 650°C, at which it was maintained for 4 h in the humid Ar gas flow at the rate of 50 ml/min. The humid gas was prepared by bubbling the Ar gas through deionised (DI) water at room temperature. The humidity was also monitored by a humidity sensor (HMP234, Vaisala), and the relative humidity of the gas was maintained at approximately 60%. After heat treatment, the sample was cooled to room temperature rapidly by air quenching to minimise oxidation during cooling.

After the growth of the nanowires, the samples were washed with DI water for 24 h until the pH reached about 7 with stirring to remove any excess KOH. Then they were dried at 60°C for 24 h. X-ray diffraction (XRD) patterns of the products were recorded using a Scintag PAD-V diffractometer with Cu K α radiation at 45 kV and 20 mA in 2 θ , ranging from 20° to 60°. Field emission scanning electron microscopy (FESEM, Model XL-30, Philips) images were obtained.

The nanowires were attached to the interdigitated electrode area (1.10 mm $\times$ 0.99 mm) by mixing them with α -terpineol organic binder (Fisher Chemicals). Finally, the sensors were heated at 500°C for 2 h to remove the organic binder. For sensing tests, the sensor was held in a tube furnace and heated to 450°C at different CO₂ levels, ranging from 500 to 2500 ppm. To improve their sensitivity, the K-doped TiO₂ nanowires were H₂ plasma treated. During the H₂ plasma treatment, the chamber pressure was 5 mTorr in 40 sccm of H₂ gas. The radio frequency power was 400 W and the substrate temperature was maintained at 350°C.

3. Results and discussion: The scanning electron microscopy (SEM) images of the nanowires obtained by the oxidation of the thin film of Ti with KOH are shown in Fig. 1a. The diameters of the nanowires were about 10 nm or less, and their lengths were up to tens of micrometres. The density of the nanowires was so high and uniform on the entire area of the substrate that many of the nanowires were made into large bundles. However, some of the nanostructures had a different morphology, which looked like nanowhiskers about 1 μm wide and 10 μm long. Higher K concentration in a small localised area might result in wider nanostructures [7]. Fig. 1b shows that there was no growth of the nanowires unless KOH was used, so we concluded that KOH

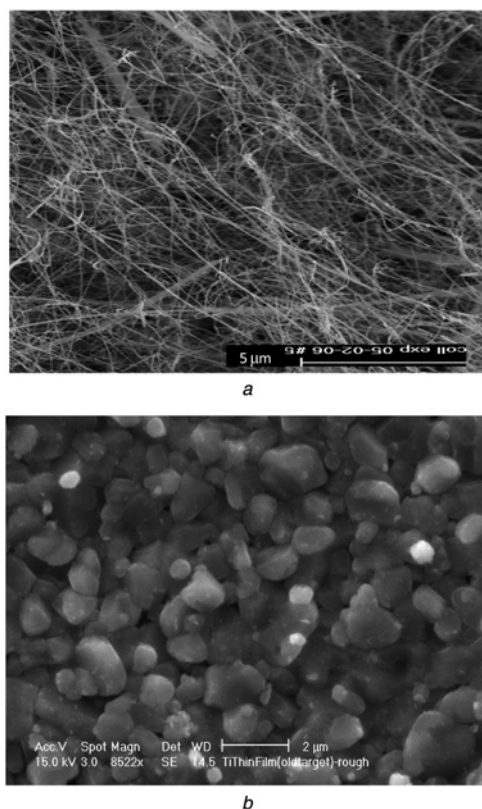


Figure 1 SEM images
a Nanowires fabricated on thin Ti film with KOH
b Surface heat-treated thin Ti film without KOH

played an important role in the formation of the nanowires. The Figure also shows the surface morphology, which indicated that most of the thin film of Ti was oxidised uniformly after the heat treatment. In related previous work, potassium iodide was used as a catalyst for the growth of tungsten oxide nanoribbons, and it was proposed that the nanoribbons grew by a vapour–liquid–solid (VLS) mechanism from a liquid K–W–O alloy [8]. The results of this earlier work may indicate that the likely mechanism for the growth of the K-doped TiO₂ nanowires from K–Ti–O alloy droplets was similar to that of the tungsten oxide nanoribbons from a K–W–O alloy. However, there were no caps of the catalyst at the end of the nanowires, which is a well-known characteristic of the VLS mechanism [9, 10]. Thus, there also is the possibility of growth by the VSS mechanism. On the surface of Ti thin film, potassium can easily adsorb oxygen at the limited oxygen atmosphere, so the oxidation of Ti thin film is more pronounced on potassium. Finally, one-dimensional TiO₂ can grow because of the role of potassium [11].

Fig. 2*a* shows the XRD patterns of the K-doped TiO₂ nanowires. The XRD pattern indicated that the rutile phase was stable (JCPDS Card No 21-1276). The dominant peaks at 26.9°, 53.7° and 55.8° can be assigned to rutile-TiO₂ (110), (211) and (220), respectively [12]. Energy dispersive X-ray spectroscopy (EDX) was performed in the SEM mode and an EDX examination of the nanowires indicated that they consisted of titanium, oxygen and potassium, as shown in Fig. 2*b*.

Fig. 3*a* shows the resistance changes to CO₂ concentration from 500 to 2500 ppm at 450°C on as-grown K-doped TiO₂ nanowires. Since the as-grown K-doped TiO₂ nanowires were a p-type semiconductor and CO₂ was categorised as reducing species, the resistance of the nanowires increases when they are exposed to CO₂ gas [13]. The baseline of the sensors drifted slightly in air. These observations are being investigated further. Sensitivity (*S*) was defined as

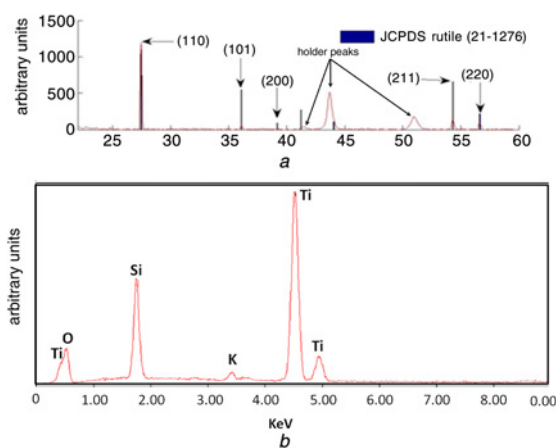


Figure 2 XRD patterns of the nanowires, and representative EDX spectrum
a XRD patterns of the nanowires
b Representative EDX spectrum

the ratio of $[(R_{\text{CO}_2} - R_a)/R_a] \times 100$, where R_{CO_2} is the resistance of the nanowires when they are exposed to specific concentrations of CO₂, and R_a was measured as the resistance in air. Fig. 3*b* shows the sensitivity at post-H₂ plasma treatment with different times. The sensitivity of the as-grown nanowires was 3.9% at 500 ppm CO₂ concentration. After treatment with the H₂ plasma for 5 min, the sensitivity increased from 3.9 to 6.1% at 500 ppm CO₂

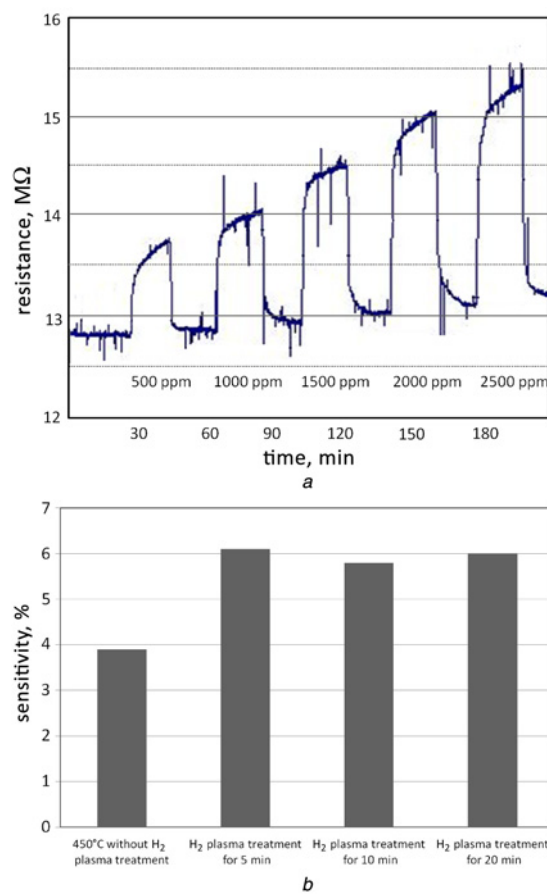


Figure 3 Resistance changes of the K-doped TiO₂ nanowires sensor from CO₂ concentration at 450°C, and sensitivity changes of the sensors at post-H₂ plasma treatment with different times
a Resistance changes
b Sensitivity changes

concentration. The improvement of sensitivity was not dependent on the time of the plasma treatment. After H₂ plasma treatment for times ranging from 5 to 20 min, the improvements were similar. This improvement might be because of physical and chemical effects from ion bombardment, surface charges and etching by the H₂ plasma [14]. Hydrogen ion bombardment might modify the surfaces of the nanowires and create dangling bonds that can easily react with CO₂ and produce hydrocarbonates on the nanowires [15].

The K-doped TiO₂ nanowire-based CO₂ microsensor is a resistor-type sensor, which can be easily integrated into a sensor array to detect various gases and to provide signals for automatic control systems. To the best of our knowledge, this is the first time it has been demonstrated that K-doped TiO₂ nanowire sensing material can respond to various concentrations of CO₂ gas in a significant and consistent way. This development creates opportunities for the fabrication of simple and inexpensive CO₂ microsensors with low power consumption because of their small sizes. Although there is some scientific speculation about the sensing mechanism, we are still uncertain exactly how it works. Further exploration will include expanding the detection range of the sensor, improving the baseline stability of the sensor, and understanding the sensing mechanism.

4. Conclusion: K-doped TiO₂ nanowires were prepared by the moisture-assisted, direct oxidation of titanium in the presence of KOH. The K-doped TiO₂ nanowires had a rutile structure and contained potassium. K-doped TiO₂ nanowires are promising as potential CO₂ gas sensors. After treatment with H₂ plasma, the sensor showed improved sensitivity to CO₂ gas. Although the sensing mechanism is still not clear and further research is needed to define the variable range of CO₂ detection and to stabilise the baseline, the results of this study indicate that K-doped TiO₂ nanowires provide a promising opportunity for the development and use of simple, inexpensive CO₂ microsensors.

5 References

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