

Gas-Sensing Properties of TiO₂ Nanoparticles Double Doped with Ag and Cu

OO Nubi¹ and TE Mosuang

Department of Physics, University of Limpopo, South Africa

E-mail: olatunbosun.nubi@ul.ac.za

Abstract. Nanometric powders of titanium dioxide TiO₂ were prepared by the sol-gel synthesis of titanium isopropoxide. With Ag and Cu as dopants, single and double-doped samples, at doping levels of 5% molar weight, were achieved. In addition, undoped samples were also prepared. The samples were dried in air at 100°C and post annealing was done at 300°C and 900°C, in order to obtain the anatase and rutile polymorphs respectively. The changes in the electrical conductivities of representative anatase and rutile TiO₂ nanopowders upon exposure to water-vapour, ammonia (NH₃) and hydrogen (H₂) were then investigated. Sensing measurements for water-vapour was done at room temperature for various humidity levels ranging from 5.4% RH to 88.4% RH. The detection of NH₃ and H₂ gases were carried out at temperatures extending from room temperature to 350°C and over concentration ranges of 25 sccm to 500 sccm and 15 sccm to 200 sccm respectively. The gas-sensing results show that the sol-gel fabricated TiO₂ nanoparticles (particularly in anatase form), has excellent fast and stable dynamic responses to humidity, NH₃ and H₂. They feature good sensitivities, even at low operating temperatures. However, acceptor behaviour, for which there was a conductivity switch from n-type to p-type, was recorded for the Ag-doped rutile powders at operating temperatures of 300°C and 350°C. Overall, the double-doped sample annealed at 300°C was deemed the most promising candidate for gas-sensing.

1. Introduction

The design and fabrication of gas sensors has become one of the most active research fields. Several crystallographic structures, including TiO₂, have been found to be useful as gas sensing materials. Extensive studies of the electric, magnetic, catalytic and electrochemical properties of Titanium dioxide (TiO₂ or Titania) have been conducted by various researchers [1-7].

Humidity and other gases present in a working environment can be highly variable in accordance with several factors. The ability to monitor and control these environments is therefore highly desirable – whether it is for human comfort, storage of various goods or industrial process control. [8]

The usual polymorphs of TiO₂ differ in crystallographic structure – tetragonal anatase and rutile, and orthorhombic brookite – and this difference can exert influences on the sensing properties of TiO₂ based devices [9].

This work attempts to demonstrate the advantage of single or double doping of TiO₂ nanoparticles with Ag and Cu, in gas sensing applications. The response of the TiO₂ species to NH₃ and H₂ presented here serves as a case study for reducing gases.

¹ To whom any correspondence should be addressed.

2. Experimental

2.1. Synthesis

Aldrich's reagent-grade precursors, namely $\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4$ (Titanium (IV) Isopropoxide), AgNO_3 and CuCl_2 , were used, via the sol-gel route, to prepare the anatase and rutile TiO_2 nanocrystalline samples. Dopant salts were first dissolved in water. This was followed by adding ethanol to the required amount of each dissolved precursor. The dopant solution was then added, in drops, to the Titanium Isopropoxide, while vigorously stirring for 1 hour. The precipitate (xerogel) formed was further diluted with 30 ml water, filtered and left to dry at room temperature for 16 hours. Further drying of the samples was done at 100°C for 1 hour before being ground to powders. At 5 wt% impurity levels, the undoped ($-\text{TiO}_2$), single-doped (Ag/TiO_2 , Cu/TiO_2) and double-doped ($\text{Ag}+\text{Cu}/\text{TiO}_2$) species were annealed at temperatures of 300°C (anatase) and 900°C (rutile) for one hour [10].

2.2. Characterisation

A dynamic computer-automated gas sensing system, KSGAS6S by Kenosistec, Italy, was used. The system is equipped with a 500 ml sensing chamber that accepts a total gas flow rate of 500 sccm. The gas sensing performances of the prepared TiO_2 nanoparticles were tested at various operating temperatures, namely Room ($20.8^\circ\text{C} \sim 28.0^\circ\text{C}$), 250°C , 300°C and 350°C , and toward ammonia (NH_3) and hydrogen (H_2) gases, as well as ten humidity levels (between 5.4% RH and 88.4% RH).

Calculations for the performance indices (Sensitivity, Response Time and Recovery Time) of each powder, when exposed to various concentrations of the intervening gas, were carried out. The response and recovery times are respectively defined as the times the impedance takes to decline to 10% of its saturation value from the baseline, when the gas is introduced, and to recover 90% of its final value when the flux of air is restored. The sensor sensitivity S (%), was measured by comparing the impedance of the sensor in air R_{air} to that in the target gas R_{gas} using the equation S (%) = $\frac{R_{air}-R_{gas}}{R_{gas}} \times 100$. The calculations also include estimates of baseline drifts, which were calculated as the percentage increase or decrease of the resistance before the gas was introduced for the last time, as compared to the first "gas-out" resistance. Thus the Fractional Baseline Drift, D is given by $D = \frac{R_f-R_i}{R_i} \times 100\%$. This parameter serves as a rough indication of the ability of the sensor material to restore its initial properties (particularly the resistance) after being repeatedly exposed to pulses of increasing gas concentration. Positive values indicate resistances higher at the last "gas-out" than at the first.

3. Results and discussion

3.1. Sensor Response to Humidity (H_2O)

The dynamic response of the prepared undoped anatase $-\text{TiO}_2$ sensor to humidity levels ranging from 5% RH to 88% RH, and measured at room temperature, is presented in Figure 1. The corresponding performance indices are shown in Table 1. The profiles for the doped samples (Ag/TiO_2 , Cu/TiO_2 and $\text{Ag}+\text{Cu}/\text{TiO}_2$) are very similar but with much higher impedances than the undoped $-\text{TiO}_2$ (Figure 2). Consistent with other findings, the doping of TiO_2 improves its gas sensing capabilities [11]. In particular, faster responses were recorded for Ag and Cu doped materials [12].

All powders show reversible and reproducible response to all humidity levels with some short-term stability over several minutes of measurement. Generally, there is a systematic decrease in the measured resistances of sensor material as the intervening "gas" (humidity) is introduced ("gas-in"). Upon withdrawing the gas ("gas-out") 5 minutes later, an increase in the resistance is observed. However, it is apparent that more than 5 minutes is needed to obtain stabilised responses (constant resistance) in gas flow of constant humidity level. Adsorption or desorption processes on the surface of the sensor material can therefore not be fully accounted for with the available data.

Figure 3 displays TiO_2 nanopowder sensor characteristics, featuring the performance indices of Sensitivity, Response Times and Recovery Times. The sensitivity S is found to increase exponentially ($S = 0.62e^{0.06c}$ in the case of the undoped $-\text{TiO}_2$ powder) as the humidity level/concentration c increases (Figure 3 (a)). This implies that at low concentrations a change in concentration leads to a small response, whereas at higher concentrations, the same change yields a relatively larger response.

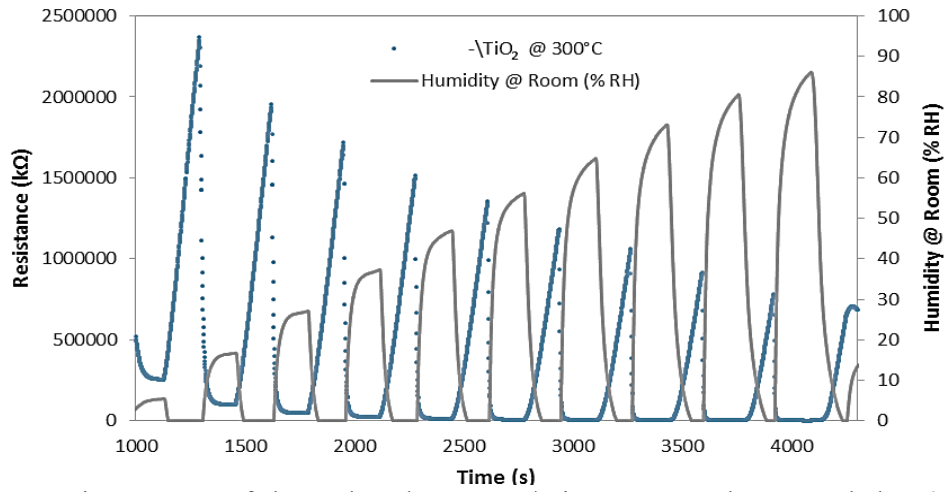


Figure 1. Dynamic response of the undoped anatase -TiO_2 nanopowders annealed at 300°C , when exposed to various room-temperature humidity levels (5.4% RH – 86.1% RH).

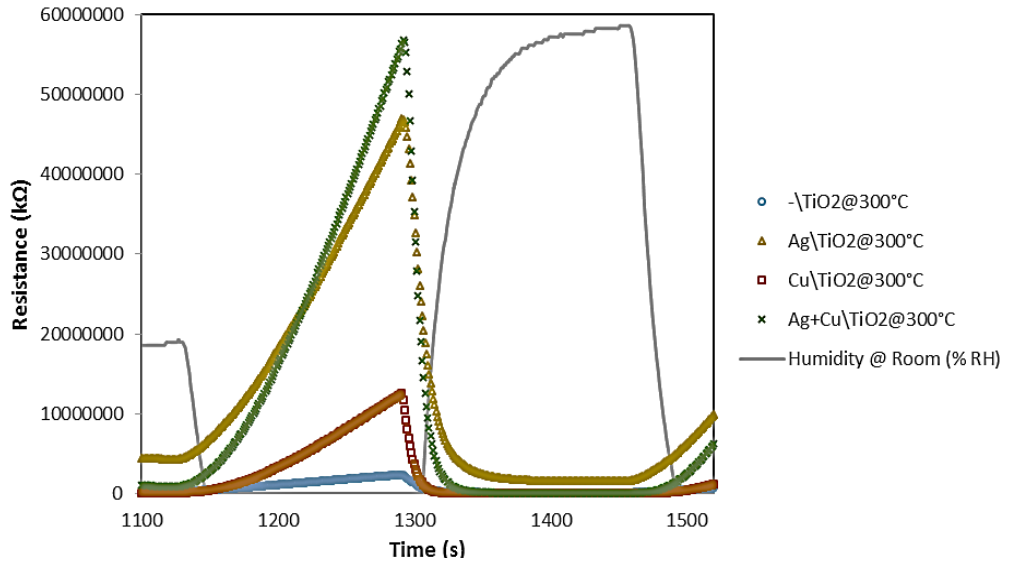


Figure 2. Response-recovery profiles for anatase samples of -TiO_2 , $\text{Ag}\text{-TiO}_2$, $\text{Cu}\text{-TiO}_2$ and $\text{Ag+Cu}\text{-TiO}_2$, annealed at 300°C and exposed to room-temperature humidity of 16.7% RH.

Table 1. Performance indices of the undoped anatase -TiO_2 sample (annealed at 300°C) that was exposed to various levels of humidity at room temperature.

Humidity (% RH)	Sensitivity	Response Time (s)	Recovery Time (s)	Baseline Drift (%)
5.5	8.38	440.22	530.21	
16.7	18.62	74.71	526.61	
27.1	35.74	62.12	540.09	
37.3	68.39	52.23	548.22	
46.9	129.09	47.73	553.61	
56.2	227.35	44.10	555.43	-66.91
64.8	371.60	40.51	562.62	
73.1	560.25	35.11	566.25	
80.6	795.81	32.41	570.73	
86.1	1105.21	28.81	592.33	

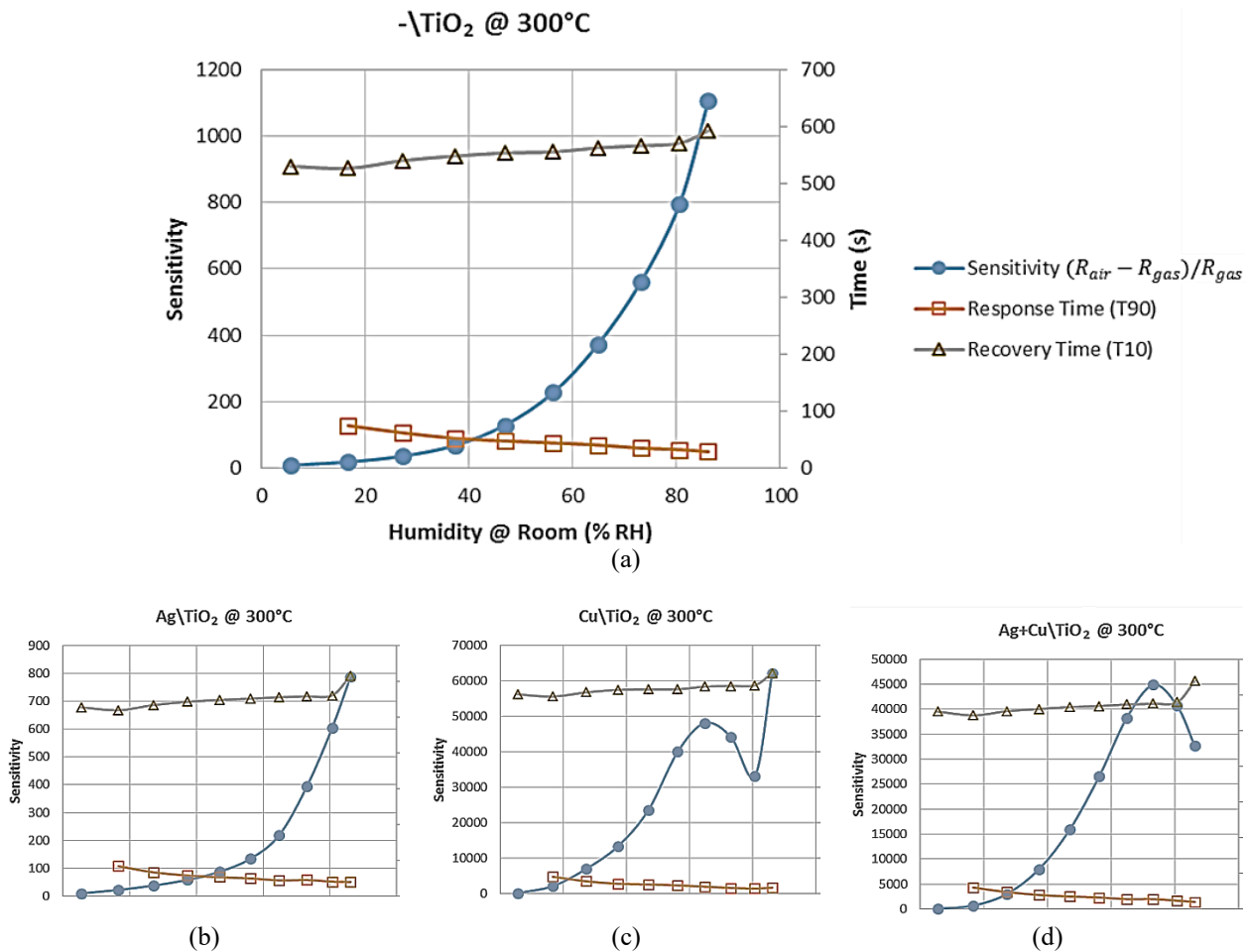


Figure 3. Sensor characteristics of the prepared gas sensors based on (a) the undoped $-\text{TiO}_2$, (b) AgTiO_2 , (c) CuTiO_2 and (d) $\text{Ag+Cu}\text{TiO}_2$. The anatase nanopowders (annealed at 300°C) were exposed to various humidity levels (5.4% RH – 86.1% RH) and measured at room temperature.

In spite of the inflexion in the trend, the Cu-doped sample shows the highest sensitivity levels. AgTiO_2 , on the other hand, was not as sensitive as $-\text{TiO}_2$. The combined influence of Ag and Cu impurities can be observed for the double-doped $\text{Ag+Cu}\text{TiO}_2$. Here, the sensitivity levels are above those of AgTiO_2 , but not as high as those of CuTiO_2 . Where the response time is following a decreasing trend in the concentration evolution, the recovery tends to increase, and vice versa.

The dynamic responses of the rutile powders (Figure 4) are not as well-defined as those of the anatase samples, particularly in cases where Cu impurities are present. The impedances, as well as the sensitivities, of the rutile samples are also higher by several orders of magnitude. However, the sensitivities of the undoped and Ag-doped (whether anatase or rutile) still remained fairly exponential. Further, the Ag impurities appear to reduce the sensitivity to humidity, in the case of anatase TiO_2 , but improved the parameter in the rutile counterpart. It turns out that the anatase samples are generally better suited for detecting humidity, in terms of reliability, repeatability and stability, but the undoped and Ag-doped rutile TiO_2 have superior performance indices (higher sensitivities, shorter response and recovery times).

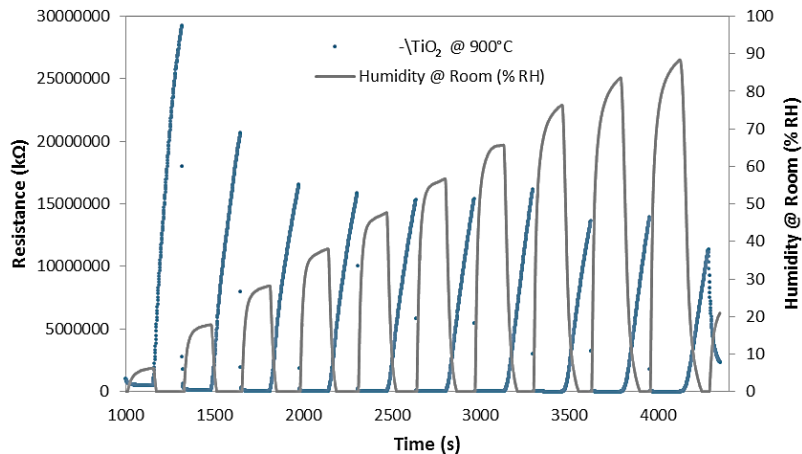


Figure 4: Dynamic response of prepared gas sensors based on undoped rutile -TiO_2 (annealed at 900°C), when exposed to various room-temperature humidity levels (5.4% RH – 86.1% RH).

3.2. Sensor Response to Ammonia Gas (NH_3)

As it was in the case of humidity, the rutile samples registered higher impedances (over the anatase counterpart) but failed to exhibit discernible dynamic response profiles at certain operating temperatures. Notable are, Ag/TiO_2 and Cu/TiO_2 at room temperature and at 250°C , as well as Ag+Cu/TiO_2 at 350°C . In operating environments where temperatures may range between room temperature and 300°C , the anatase powders will be suitable as sensor material for detecting NH_3 , the optimal being the Cu/TiO_2 . For higher temperatures (at least up to 350°C) the undoped -TiO_2 , in its rutile form, will suffice. The rutile samples not only feature higher impedances over the anatase counterparts, but also higher sensitivities.

3.3. Sensor Response to Hydrogen Gas (H_2)

In mixed phase TiO_2 nanomaterials, the predominance of rutile in anatase-rutile mixture has been found to result in increased sensitivity towards hydrogen [13]. In this investigation however, the rutile samples continue to display responses that, collectively, are below par when compared with those of their anatase counterpart. If the temperature limitation of 300°C is not an inhibiting factor, then the undoped -TiO_2 rutile powder will be suitable as a sensor material for H_2 . The next best performance is observed for the single-doped Cu-impregnated sample (Cu/TiO_2). (It has been shown elsewhere [14] that Cu promoted rutile formation.) To cover the entire range from “Room” to 350°C , the only sample that can be utilised for sensing hydrogen gas is the undoped -TiO_2 .

Ag-doped TiO_2 sensors have shown good sensitivities at different concentration hydrogen atmospheres. [15]. The nanomaterial however falls short, when compared with the Cu counterparts in this study.

3.4. Discussion

Over three-quarters of the gas-sensing cases investigated here (particularly the anatase species) show excellent fast and stable dynamic responses to humidity, NH_3 and H_2 . They feature good sensitivities, even at a low operating temperatures. To deduce the best overall performance for each intervening gas, and at the four operating temperatures, the performance indices of samples were combined. The anatase TiO_2 display more pronounced gas sensing abilities over the rutile. This can be ascribed to the morphological characteristics of the two material categories. Anatase TiO_2 is characterised by a smaller crystallite sizes relative to the rutile powders [10]. This implies higher surface area to volume ratio for anatase and consequently, a greater surface activity over rutile [16].

For the majority of samples tested, the measured resistances decrease upon interacting with the reducing gases – a typical behaviour for n -type semiconductors. This is because, the gases act as a reducing agent for the metal-oxide. The process involves the extraction of electrons from its conduction

band by the adsorbed oxygen species at the surface of the semiconductor. In other words, the chemisorbed oxygen species trap free electrons on the surface of the grains which results in a build-up of a negative surface charge. This in turn creates an energetic barrier in the conduction band which electrons must overcome in order to cross to the next grain. When the desired concentration of the target gas is introduced, the gas then reacts with the adsorbed oxygen. This leads to the freeing of previously trapped electrons (i.e. a reduction in the amount of bound surface charge), thereby decreasing the *n*-type carrier content and lowering the barrier potential. Thus, the resistivity decreases in the presence of a reducing gas, owing to electron transfer into the conduction band [17].

However, acceptor behaviour, for which there was a conductivity switch from *n*-type to *p*-type [10], was recorded for the Ag-doped rutile samples (Ag/TiO₂) at operating temperatures of 300°C and 350°C. In these cases, it is believed that the Ag dopant impurities modify the electronic structure of TiO₂ and form localised acceptor levels in the forbidden band gap. This leads to the increase in the electron concentration and the decrease in the electrical resistance over a low-to-medium temperature range [16]. The discussion here is only qualitative since generally, the energetic barrier is not constant but changes with varying temperature [17], thereby rendering the temperature dependencies more complicated.

4. Conclusions

According to the estimates provided, to sense water vapour (at room temperature) the anatase Cu/TiO₂ comes out on top. NH₃ and H₂ are best detected using undoped rutile –TiO₂, for temperatures ranging from “Room” to 350°C and probably beyond. Where specific operating temperatures (except at temperatures exceeding 300°C) are required in applications, the anatase powders remains generally preferred. Otherwise, the rutile samples may come into play. It is also important to note that the double-doped Ag+Cu/TiO₂ sample that was annealed at 300°C, showed better promise in detecting water-vapour, NH₃ and H₂ at various temperatures, over other powders.

Acknowledgements

Gratitude is hereby extended to NRF, IBSA and the University of Limpopo for financial support, and CSIR’s Centre for Nanostructured Materials for experimental resources.

References

- [1] Mo S-D and Ching W Y 1995 *Phys. Rev. B* **51** 19
- [2] Yu J-G, Yu J C, Cheng B, Hark S K and Iu K 2003 *J Solid State Chem.* **174**, 372–380
- [3] Shimizu Y 2002 *Chem. Sens.* **18**, no. 2, 42–54
- [4] Carney C M, Yoo S and Akbar S A 2005 *Sens. Act. B* **108**, no. 1 29–33
- [5] Benkstein K D and Semancik S 2006 *Sens. Act. B*, **113**, no. 1, 445–453
- [6] Yadav B C, Shukla R K and Bali L M 2005 *Indian J. Pure Appl. Phys.* **43**, 51
- [7] Barsan N, Koziej D and Weimar U 2007 *Sens. Act. B* **121**, 18–35
- [8] Fine G F, Cavanagh L M, Afonja and Binions R 2010 *Sensors* **10**, 5469–5502
- [9] Alivisatos A P 1996 *J. Phys. Chem.* **100**, no. 31, 13226–13239
- [10] Nubi O O, Rammutla K E, Mosuang T E 2016 *Adv. Sci. Lett.* **22**, no. 4, 889–895
- [11] Su P G, and Huang L N 2007 *Sens. Act. B*, **123**, 501–507
- [12] Zare A H and Mohammadi S 2011 *Mater. Sci. Eng.* **17**, 012015
- [13] Zakrzewska K and Radecka M 2017 *Nanoscale Res. Lett.* **12**, no. 1, 89
- [14] Teleki A, Bjelobrck N and Pratsinis S E 2008 *Sens. Act. B* **130**, 449–457
- [15] Hamdan H H, Mohammed G H 2016 *Int. J. Sci. Res.* **5** no. 2, 2224–2233
- [16] Garzella C, Comini E, Tempesti E, Frigeri C and Sberveglieri G 2000 *Sens. Act. B* **68**, 189–196
- [17] Haidry A A, Schlosser P, Durina P, Mikula M, Tomasek M, Plecenik T, Roch T, Pidik A, Stefecka M, Noskovic J, Zahoran M, Kus P and Plecenik A 2011 *Cent. Eur. J. Phys.* **9**, 1351–1356