Electrospun TiO₂ nanofibre-based gas sensors fabricated by AC electrophoresis deposition

E Z KARIMI^{1,*}, J ESMAEILZADEH² and E MARZBANRAD³

¹Department of Metallurgy and Ceramics, Islamic Azad University, Mashhad Branch, Mashhad 9187147578, Iran

²Department of Ceramics, Materials and Energy Research Center, Tehran 14155-4777, Iran

³Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

MS received 26 November 2013; revised 14 March 2014

Abstract. In this paper, gas sensing properties of the sensor based on titanium dioxide (TiO₂) nanofibres are reported. These nanofibres were synthesized through electrospinning of polyvinyl pyrrolidone (PVP) / titanium tetra isopropoxide. Calcination of the obtained amorphous PVP/TiO₂ nanofibres resulted in nanofibres of TiO₂ with the same morphology. In this step, scanning electron microscopy and X-ray diffraction were applied in order to analyse these nanofibres. Then, nanofibres of TiO₂ were deposited selectively by AC electrophoretic deposition on interdigitated electrodes and exposed to different concentrations of NO₂ (8–50 p.p.m.) at 450–550°C. Gas sensing measurements illustrated that this sensor had adequate response to target gas at 450°C. The maximum response of gas sensors, S (the ratio of sensor resistances $S = R_{\text{gas}}/R_{\text{N}_2}$), achieved was around 30 for 50 p.p.m. NO₂ at 450°C.

Keywords. TiO₂ nanofibres; electrospinning process; AC electrophoretic deposition; NO₂ gas sensor.

1. Introduction

Semiconductor metal oxide-based gas sensors with different working temperatures have enabled us to detect low levels of gases in a wide range of temperatures. Depending on the application of interest and availability of fabrication methods, different surface morphology and configurations of the metal oxides have been achieved.^{1–3} Of these, one-dimensional (1D) nanostructures are particularly suited to this application because of their high surface-to-volume ratio as well as good chemical and thermal stabilities under different operating conditions.^{4,5} Among different strategies for producing 1D nanostructures, electrospinning (ES) offers several advantages including ease of fabrication and versatility.^{6,7}

ES is a top to bottom approach to produce continuous nanofibre of polymers. Synthesis of metal oxide nanostructures by ES process recently gained increasing attention due to the prospect of its application in producing 1D nanostructure on a commercial scale. A large number of metal oxides are synthesized as nanofibre by ES.⁸ In a typical ES process, under the effect of high voltage, the jet of precursor ejects from the tip of the needle towards the collector. As a result, the jet whips rapidly and the solvent evaporates forming a nonwoven fibrous mat on the collector.⁹ If the polymeric solution contains metal ions required for forming an inorganic solid, then appropriate post-annealing produces continuous nanofibre of reduced diameters than the parent polymeric fibre.

The metal oxide selected in this research is titanium dioxide (TiO₂). The reason of this choice is the applicability of this metal oxide as a high temperature gas sensor and its chemical and thermal stability at elevated temperatures. These characteristics have stimulated intense research on this material.^{10–14} Some of these researches address issues like poor conductivity and addition of doping agents,^{9,12,13} others focus on synthesizing 1D TiO₂ nanostructures.¹⁵ Recent reports show that nanocrystalline TiO₂ gas sensors produced by ES demonstrate excellent performance in terms of gas sensitivity, reversibility and response time. For instance, Dan *et al*¹⁶ and Maensiri *et al*¹⁷ have fabricated electrospun TiO₂ nanofibres by carefully controlling the ES parameters and the composition of the precursor solution. Furthermore, Kim *et al*^{18,19} and Landau *et al*²⁰ have reported ultra high sensitivity of TiO₂ nanofibres towards CO and NO₂ gases.

In this research, in addition to applying ES for obtaining TiO₂ nanofibres, another electric field-based technique was also used. Named ‘alternative current electrophoretic deposition (AC EPD)’, the technique was used to transfer the nanofibres, once suspended in an organic medium, on to a substrate. The AC EPD technique, which is well established for polymer and biomaterial film deposition can also be used, in principle, for the deposition of metal oxide nanoparticles. In fact, in this method, sensing material is deposited from a liquid media and morphology of the layer can be engineered by controlling different process parameters such as voltage, frequency and time of the deposition.²¹ AC EPD is a technique based on movement of particles in the presence of electric field, which guarantees a gentle mechanism to transfer particles suspended in the alcoholic media on to the

*Author for correspondence (ebrahimzk888@gmail.com)

substrate. The material of interest is suspended in a volatile and interaction-free solvent with a low concentration. These suspended particles are forced to follow a specific path by properly designed electric field and cover the desired region of the substrate.²² This technique has already been employed for fabrication of the sensors based on mesoporous WO_3 ,²³ ZnO nanowires and nanoparticles,^{24,25} TiO_2 nanoparticles^{26,27} and In_2O_3 nanoparticles and nanoribbons.^{28,29}

In our previous work regarding TiO_2 nanoparticles, stable sensors with high responses in the temperature range of 450–550°C using AC EPD were obtained.²⁶ In this new research, after deposition of electrospun TiO_2 nanofibres by AC EPD on interdigitated substrates, their gas sensing properties towards NO_2 were investigated by electrical measurements in controlled environment and working temperature.

2. Experimental

2.1 Synthesis of electrospun TiO_2 nanofibres

The electrospun solution comprised 0.225 g polyvinyl pyrrolidone (PVP, $M_w = 1300000 \text{ g mol}^{-1}$, Aldrich) dissolved in 5 ml of ethanol (Merck), onto which 0.75 ml of titanium(IV) isopropoxide (TTIP, Aldrich) and 1.5 ml of acetic acid (AA, Merck) were added dropwise. The resulting solution was stirred for 60 min and then loaded into a 50-ml plastic syringe with stainless steel needle (inner diameter of 0.495 mm, 21G and length of 0.5 inch) connected to a high-voltage supply (Glassman High Voltage Inc.), which is capable of generating high direct currents (DCs). An electric field of 15 kV cm^{-1} was applied between the stainless steel orifice and the collector. An aluminium plate was used as a collector and the distance between the capillary and the collector was set at 15 cm. The precursor solution was electrospun at room temperature on aluminium plate and the feed rate was controlled by an electrical syringe pump (Top 5300) fixed at 1.0 ml h^{-1} to produce nanofibres. The as-electrospun nanofibres were placed under vacuum at room temperature for 12 h in order to remove the solvent residuals, and then calcined at three different temperatures of 450, 500 and 600°C for 3 h with a heating rate of 5°C min^{-1} .

X-ray diffraction (XRD) patterns of the TiO_2 nanostructures, after calcination, were recorded by Unisantix-XMD300 system with $\text{CuK}\alpha_1$ ($\lambda = 0.154056 \text{ nm}$) radiation with 2θ ranging between 10 and 90° with step size of 0.02° . The microstructure of the obtained deposit was analysed using scanning electron (Cambridge, S360) and optical (Olympus DP72) microscopes. The average diameter of the fibres was obtained by measuring 50 fibres on SEM images, using ImageJ software.

2.2 Sensor fabrication and sensor response measurement

AC EPD was carried out in the deposition setup that consisted of a signal generator (Rigol, DG1022) and a

voltage amplifier (HP, 6826A Signal Amplifier). TiO_2 (0.003 g) nanofibres were suspended in 10 ml pure acetone by ultrasonic and then deposited by AC EPD on interdigitated electrode in frequency of 1 Hz, voltage of 35 V and by a symmetric sinusoid wave. Interdigitated platinum electrodes with a gap of 200 μm designed on an alumina sheet were used for sensor fabrication. In order to reach the desired working temperature, this alumina-based sensor was equipped with a micro heater. The response of sensor towards various concentrations of NO_2 gas at different temperatures was measured and recorded in a fully automated dynamic gas sensor testing setup. Sensor was stabilized by exposing to N_2 gas for 1 h before each sensing test. NO_2 was diluted by mixing the gas with N_2 (base gas) to reach pre-designed concentrations using digital flow controller. Then, the gaseous mixture was made to pass through a chamber equipped with sensor.

3. Results and discussion

Crystallographic information obtained from XRD analyses of the ES products calcined at 450, 500 and 600°C is presented in figure 1. These reflections can be indexed to (004), (200), (105) and (204) planes of the TiO_2 anatase form with JCPDS No. 00-004-0472. Also, the strong and sharp peak in $2\theta=25^\circ$ is assigned to (101) crystal plane. As reported by, Landau *et al*²⁰ the minimum temperature necessary to remove the organic compounds in the ES layer is 450°C. However, it can be clearly seen that, enhancing the calcining temperature increased the characteristic peak intensity, which indicates higher degree of crystallinity at 600°C. Moreover, XRD measurements illustrated that calcination of TiO_2 nanofibres in the temperature range of 450–600°C made TiO_2 anatase remain stable and not transform to rutile phase up to 800°C. TiO_2 is used in anatase form because of its lower resistance and higher response to the gas specimen compared to that of the rutile phase, which is stable at higher temperatures.³⁰ Figure 2a and b show

Figure 1. X-ray diffraction patterns of TiO_2 nanofibres obtained after calcination in 450, 500 and 600°C, respectively.

the SEM images of as-prepared nanofibres with different magnifications. Figure 2c depicts their related diameter size distributions, which were acquired by measuring of fibre diameters on SEM images using ImageJ software. As exhibited, uniform, smooth, long and continuous composite fibres were formed. The region of distribution of TiO_2/PVP nanofibre (figure 2c) was broadly distributed in the range of 40–300 nm, but the majority of the fibres were in the range of 120–200 nm. The average diameter of TiO_2/PVP nanofibres was 245 nm.

Figure 2. (a and b) Different magnifications of SEM images and (c) diameter size distribution of as-electrospun TiO_2/PVP nanofibres.

TiO_2 fibre mats were calcinated at 600°C in air for 3 h to remove the PVP. As it can be seen from figure 3a, the nanofibres have shrunk and remained single with diameters in the range of 40–320 nm. Distribution graph (figure 3b) supports this claim and indicates that after calcination, the average diameter of TiO_2 nanofibres was 165 nm. As shown in figure 3a, nevertheless, the removal of PVP from hybrid fibres during calcination, the network and continues structure of nanofibres were well maintained. Besides, there was a dimensional change percentage of about 20–30 in fibre diameters after calcination, caused by burning-out of PVP from composite fibres (as shown in figure 3b).

The optical image of deposition pattern of TiO_2 nanofibres on interdigitated platinum electrode is presented in figure 4. As it is seen, the sensing materials have filled the gap between electrodes leaving almost no material on the surface of electrodes. In fact, the left over material on the electrode surface does not participate in the sensing process. SEM photographs of the obtained deposition pattern with different magnifications are shown in figure 5a–c. It seems that these nanofibres have filled the inter-electrode region randomly and the 1D morphology of these nanofibres leads to a porous layer. This morphology can provide the high-diffusivity path for target gas—especially for gas

Figure 3. (a) SEM image and (b) related diameter size distribution graph of TiO_2 nanofibres obtained after calcination in 600°C for 3 h.

Figure 4. Optical microscopy image of electrophoretically deposited TiO_2 nanofibres in the frequency of 1 Hz and voltage of 35 V on interdigitated platinum electrodes.

with large molecular size such as NO_2 —in order to maximize surface reactions. Sensor response to different NO_2 concentrations operating in the temperature range of 450–550°C is plotted in figure 6. Here, and according to the literature,^{28,29} the response towards NO_2 is defined as ($S = R_g/R_0$), where R_g and R_0 are resistance in the presence of NO_2 and in N_2 (carrier gas), respectively. As the conductance of these sensors seemed to be too low for practical temperature, less than 450°C, the sensor working temperature have been varied between 450 and 550°C in order to find the optimal operating temperature to detect NO_2 gas. At each operating temperature, TiO_2 nanofibres are sensitive to NO_2 and follow an increment trend by increasing gas concentration. The optimum operating temperature for this sensor is 450°C and further increase in temperature decreases the variation in primary resistance for all concentrations. By extrapolating the results to lower gas concentrations, one can estimate the detection limit to be ~500 p.p.b. for NO_2 . The other feature of these results which is desirable for NO_2 gas sensors is the linear behaviour of sensor for the concentration range.

Figure 7 shows the dynamic response curves for this sensor during gas sensing measurement at different temperatures. The sensor exhibits reversible and reasonably fast responses, with NO_2 gases switching on and off. The response time (t_{res}) and recovery time (t_{rec}) are two significant parameters identifying rate of sensors to gas specimen. t_{res} and t_{rec} are calculated based on the time period during which the resistance of film reaches 90% of the saturated resistance (when switching to the target gas) and 10% of the saturated resistance (after switching back to N_2 as the base gas), respectively. As it can be seen in figure 7, the response time is about 2–4 min and recovery time is less than 20 s. These values are comparable with those doped TiO_2 gas sensor reported in literature. For instance, Li and Xia³¹ reported a response time of about 85 s and recovery

Figure 5. (a–c) SEM image of deposited layer of TiO_2 nanofibres in the frequency of 1 Hz and voltage of 35 V on platinum electrodes with different magnifications.

Figure 6. Response values of sensor towards different NO_2 concentrations at the temperature range of 450–550°C.

Figure 7. Dynamic response curves of gas sensor towards different NO_2 concentrations at the operating temperature range of 450–550°C.

Figure 8. Comparison of response values of TiO_2 nanofibre-based gas sensor and TiO_2 nanoparticle-based gas sensor at their optimal temperature.

time of 160 s for Cr-doped TiO_2 gas sensor exposed to NO_2 gas. Response and recovery times of gas sensors are affected by (i) physical adsorption of gas specimen on sensing material surface, (ii) chemical reaction of gas molecules and surface of sensing material and (iii) the desorption.³² SEM image of sensing electrode (figure 5c) reveals the fact that layer deposited through AC EPD is highly porous. Moreover, high surface-to-volume ratio of nanofibres as sensing materials provides the maximum physisorption and surface reaction. So, this sensor has a high sensitivity as well as fast response and recovery times. Here, we observed an increase in resistivity of our sensor, which is typical in n -type semiconductor gas sensors during exposure to oxidizing chemical species such as NO_2 . Moreover, it is obvious that responses are more for higher concentrations, while they are acceptable for low concentrations. These sensors demonstrate the ability to detect traces of NO_2 gas well below the environmental standards, suggesting potential applications in environmental monitoring.

However, as we had reported before,²⁶ the story is quite different for sensors based on TiO_2 nanoparticles deposited by AC EPD in similar conditions. Increasing the working temperature from 450 to 500°C increased the response of the TiO_2 nanoparticle-based sensor, while further increasing the temperature diminished the responses towards NO_2 gas. Figure 8 compares the responses of the TiO_2 nanofibre- and nanoparticle-based gas sensors, at their optimum working temperatures. As shown in the figure, responses of the nanofibre-based sensor are less than those of nanoparticle-based sensors at concentrations lower than 25 p.p.m. NO_2 , while for responses higher than 25 p.p.m., values related to nanofibre-based sensors surpass those of nanoparticle-based sensors.

Furthermore, in nanoparticle-based sensor the primary resistance changes considerably due to temperature, whereas this change is not noticeable for nanofibre-based sensor. This indicates that connections of nanofibres to each other and to the electrodes are stronger in comparison to nanoparticles and, therefore, they have much better resistance towards thermal variations. However, it is interesting that the two sensors show nearly equal responses and recovery times, indicating identical mechanisms for the adsorption and desorption of gas molecules on the TiO_2 surface in both.

On the other hand, electrospun TiO_2 nanofibres reported by Kim *et al.*^{18,19} had similar responses towards H_2 and NO_2 gas in the working temperature range of 300–350°C. Moreover, Landau *et al.*²⁰ reported that hot pressing the electrospun nanofibre TiO_2 improved its sensing towards NO_2 and CO gas with concentration as low as 50 p.p.b. Therefore, considering reports regarding gas sensing properties of nanofibre TiO_2 and our research, it seems that the AC EPD method have been successful in improving the sensitivity of this metal oxide.

4. Conclusion

TiO_2 nanofibres were made of an ethanol solution containing PVP and titanium tetraisopropoxide. These nanofibres could be subsequently converted to anatase without changing their morphology *via* optimum calcination in air. TiO_2 nanofibre-based gas sensor was fabricated *via* low frequency AC EPD method and its gas sensing characteristics were investigated. Response measurements were performed in the temperature range of 450–550°C. The results showed that sensor had a good stability and repeatability performance and the highest sensitivity. The response of TiO_2 nanofibres deposited by AC EPD on interdigitated electrodes was around 30 towards 50 p.p.m. NO_2 at 450°C.

References

1. Huang J and Wan Q 2009 *Sensors* **9** 9903
2. Shimizu Y, Hyodo T and Egashira M 2004 *J. Eur. Ceram. Soc.* **24** 1389

3. Kiriakidis G, Moschovis K, Kortidis I and Binas V 2011 *Vacuum* **1** 12
4. Comini E, Baratto C, Faglia G, Ferroni M, Vomiero A and Sberveglieri G 2009 *Prog. Mater. Sci.* **54** 1
5. Arafat M M, Dinan B, Akbar S A and Haseeb A S 2012 *Sensors* **12** 7207
6. Ding B, Wang M, Yu J and Sun G 2009 *Mater. Today* **9** 1624
7. Ding B, Wang M, Wang X, Yu J and Sun G 2010 *Mater. Today* **13** 16
8. Archana P S, Jose R, Jin T M, Vijila C, Yusoff M M and Ramakrishna M 2010 *J. Am. Ceram. Soc.* **93** 4096
9. Rutledge G C and Fridrikh S V 2007 *Adv. Drug Deliv. Rev.* **59** 1384
10. Dutta P K, Frank M, Hunter G W and George M 2005 *Sens. Actuators B* **106** 810
11. Al-Homoudi I A, Thakur J S, Naik R, Auner G W and Newaz G 2007 *Appl. Surf. Sci.* **253** 8607.
12. Moon H G, Jang H W, Kim J S, Park H H and Yoon S J 2010a *Electron Mater. Lett.* **6** 135
13. Moon J, Park J A, Lee S J, Zyung T and Kim I D 2010b *Sens. Actuators B* **149** 305
14. Seeley Z M, Bandyopadhyay A and Bose S 2010 *Thin Solid Films* **519** 434
15. Wang C, Tong Y, Sun Z, Xin Y, Yan E and Huang Z 2007 *Mater. Lett.* **61** 5125
16. Dan L and Younan X 2003 *Nano Lett.* **3** 555
17. Maensiri S, Nuansing W, Ninmuang S, Jarernboon W and Seraphin S 2006 *Mater. Sci. Eng. B* **131** 147
18. Kim I D, Rothschild A, Tuller H L, Kim D Y and Jo S M 2006a *NSTI-Nanotech.* **3** 483
19. Kim I D, Rothschild A, Lee B H, Kim D Y and Jo S M 2006b *Nano Lett.* **6** 2009
20. Landau O, Rothschild A and Zussman E 2009 *Chem. Mater.* **21** 9
21. Riahifar R, Raissi B, Marzbanrad E and Zamani C 2011 *J. Mater. Sci. Mater. Electron.* **22** 40
22. Besra L and Liu M 2007 *Prog. Mater. Sci.* **52** 1
23. Heidari E K, Zamani C, Marzbanrad E, Raissi B and Nazarpour S 2010 *Sens. Actuators B* **146** 170
24. Mahmoodi S R, Raissi B, Marzbanrad E, Shojayi N, Aghaei A and Zamani C 2009 *Procedia Chem.* **1** 947
25. Ghashghaie S, Marzbanrad E, Raissi B, Zamani C and Riahifar R 2012 *Am. Ceram. Soc.* **95** 1843
26. Esmaeilzadeh J, Marzbanrad E, Zamani C and Raissi B 2011 *Sens. Actuators B* **161** 401
27. Esmaeilzadeh J, Ghashghaie S, Raissi B, Marzbanrad E, Zamani C and Riahifar R 2012 *Ceram. Int.* **38** 5613
28. Khiabani S, Marzbanrad E, Zamani C, Riahifar R and Raissi B 2012a *Sens. Actuators B* **166** 128
29. Khiabani S, Hosseinmardi A, Marzbanrad E, Ghashghaie S, Zamani C, Kianpour-Rad M and Raissi B 2012b *Sens. Actuators B* **162** 102
30. Wisitsoraat A, Tuantranont A, Comini E, Sberveglieri G and Wlodarski W 2009 *Thin Solid Films* **517** 2775
31. Li D and Xia Y 2003 *Nano Lett.* **3** 555
32. Esmaeilzadeh J, Ghashghaie S, Khiabani S, Hosseinmardi A, Marzbanrad E, Raissi B and Zamani C 2014 *J. Eur. Ceram. Soc.* **34** 1201