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Gas and Humidity Sensing Properties of Pure and Ru-Doped TiO_2 Nanofibers

Mehtap Özdemir KÖKLÜ[1,2], Fevzi SÜMER[3], Ömer MERMER[3], Salih OKUR[4], Ümit CÖCEN[1] and Erdal ÇELIK[1, 5,6]

[1]*Dokuz Eylul University, Department of Metallurgical and Materials Engineering, Buca, Izmir, Turkey*
[2]*Gediz University, Department of Mechanical Engineering, Seyrek, Izmir, Turkey*
[3]*Ege University, Engineering Faculty, Department of Electrical and Electronics Engineering, Bornova, İzmir, Turkey*
[4]*Katip Çelebi University, Department of Materials Science and Engineering, Çiğli, Izmir, Turkey*
[5]*Dokuz Eylul University, Center for Fabrication and Application of Electronic Materials, Buca, Izmir, Turkey*
[6] *Dokuz Eylul University, Graduate School Natural and Applied Sciences, Nanoscience and Nanoengineering, Buca, Izmir, Turkey*
e-posta: omermermer@gmail.com

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Key words
Ru doping; TiO_2; Sol-gel; Humidity and Gas sensors

Abstract

TiO_2 and Ru-doped TiO_2 nanofibers were fabricated by calcining electrospun TiO_2-PVP hybrid fibers at 600 ^oC. Their humidity and O_2 sensing properties were investigated. The morphologies of nanofibers were characterized by scanning electron microscopy (SEM), which showed that the nanofibers with diameter of 260 nm formed a non-woven mat structure. Phase structures of the nanofibers were characterized by X-Ray difractometer (XRD) which showed that TiO_2 nanofibers are polycrystalline with a mixture of anatase and rutile structure at 600^oC. The effects of Ru doping in TiO_2 sensing properties were investigated. The results show that humidity and O_2 gas sensing properties of TiO_2 nanofibers are effectively enhanced by Ru doping.

Saf ve Ru-katkılı TiO_2 Nanofiberlerin Gaz ve Nemlilik Duyarlılık Özellikleri

Anahtar kelimeler
Ru katkı; TiO_2; Sol-jel; Nem ve Gaz sensörleri

Özet

TiO_2 ve Ru-katkılıTiO_2 nanofiberler 600 ^oC'de electrospin yapılmış TiO_2-PVP hibrid fiberler kalsine edilerek üretilmiştir. Bunların nemlilik ve O_2 duyarlılık özellikleri incelenmiştir. Nanofiberlerin morfolojileri taramalı elektron mikroskobu (SEM) kullanılarak karakterize edilmiştir. 260 nm boyutlu nanofiberler dokumasız mat yapıların oluştuğu bulunmuştur. Nanofiberlerin faz yapıları x-ışınları difraksiyonu (XRD) kullanılarak karakterize edilmiş ve TiO_2 nanofiberler 600 ^oC'de anataz ve rutil fazların karışımı olan polikristal yapıya sahip olmuştur. TiO_2'de Ru katkısının duyarlılık özelliklere etkisi araştırılmıştır. Sonuçlar TiO_2 nanofiberlerin nemlilik ve O_2 gaz duyarlılık özellikleri efektif olarak Ru katkısıyla desteklenmiştir.

1. Introduction

The measurement and control of environment humidity and gas leakage are very important for human comfort and environmental protection (Wang *et al.* 2011). Up to now, semiconducting metal oxides such as SnO_2, ZnO, TiO_2, In_2O_3, $BaTiO_3$ and WO_3 have been increasingly used for detection of gases and humidity (Park *et al.* 2010; Moon *et al.* 2010; Erol *et al.* 2010). Among the other semiconducting gas sensors TiO_2 has excellent sensing properties for various gases, such as CO, NO_x, CH_3CH_2OH, H_2 and O_2 (Zhang *et al.* 2010). There have been significant efforts to enhance the sensitivity of TiO_2 gas sensors. These efforts include doping of noble metal and changing of nanostructure to provide high surface to volume

ratio. Recently, Zhang et al. (2010) reported that the Pt doped TiO_2 film decreased the sensor response time. Cheng et al. (2011) showed Ag nanoparticle modified TiO_2 spherical structures enhanced the gas-sensing performance. Li et al. (2002) discussed Cr-doped TiO_2 thin films to improve gas sensibility. Moon et al. (2010) presented Pd-doped TiO_2 nanofibers are highly sensitive gas sensors because 1 D nanostructures are great interest in gas sensing applications due to their unique morphology and geometry.

Electrospinning technique has been proposed to be

an ideal route to design highly effective humidity and gas sensing material (Park *et al.* 2010; Wang *et al.* 2009; Li *et al.* 2009). Nanofibers produced by electrospinning technique have several advantages

such as high surface to volume ratio, high length to diameter ratio and uniform to diameter. Typically in this technique, a polymer solution or melt is ejected from a small opening or a nozzle under the influence of a strong electrostatic field. Electrostatic charges built upon the surface of a droplet induce the formation of a jet, which is subsequently stretched to form a continuous ultrathin fiber. During its flight to a collective target, the ejected and charged jet dries out, leaving ultrathin fibers on the target. The non-woven mat has a high surface area with relatively small pore size (Li *et al.* 2009; Watthanaaruna *et al.* 2006; Jun *et al.* 2003; Doshi *et al*. 1995; Herna´ndez-Ve´lez, 2006; Yuan *et al.* 2004).

The aim of this work improves the gas sensing properties of TiO_2 nanofibers with doping Ru. The electrospinning technique was used to produce sensing materials. The results show that Ru doping on TiO_2 improved the gas sensing properties.

2. Materials and Methods

The preparation of pure and Ru-doped TiO_2 precursor solutions was carried out under atmospheric conditions at room temperature. Titanium(IV)-isoproproxide (87560-Fluka), polyvinylpyrrolidone (PVP) (Mn = 1,300,000, Aldrich), acetic acid (BDH, 99,9%) and ethanol (BDH, 99,9%) and Ruthenium III chloride hydrate (%99.9, 011043-Alfa Aesar) were used as precursor materials.

In a typical procedure, the PVP/ethanol solution was prepared using a ratio of 0.45 g PVP to 7.5 ml ethanol. To obtain solution of TiO_2 and Ru-doped TiO_2, 2 ml titanium (IV) isopropoxide was dissolved in 3ml acetic acid and 3ml ethanol. 0,01 g $RuCl_3$ was added into the same volume TiO_2 precursor solution. Finally, the PVP/ethanol solution was added to the as-prepared solution and the mixture was constantly stirred at 25^{o}C for 2 hours to get a homogeneous polymer solution for electrospinning. In order to produce the nanofibers, Ti-based solutions were immediately loaded into a plastic syringe equipped with a 22-gauge needle made of stainless steel. The emitting electrode from a power supply was attached to the needle. The grounding electrode from the same power supply was attached to a piece of 316L stainless-steel which was used as the collector plate and was placed approximately 8 cm below the tip of the needle. The solution was fed at a rate of 0.5 ml/h using a syringe pump (TOP Syringe Pump TOP- 5300, Japan). 15 kV high voltage (Gamma, 0-30 kV) was applied to across the needle. Therefore the effect of the electric field was investigated. As the jet was accelerated towards the collector, the solvent was evaporated by leaving only ultrathin fibers on the collector. The obtained nanofibers were left exposed to moisture for approximately 2 hours to allow complete hydrolysis of titanium isopropoxide and consequently subjected to calcination at a high temperature 600^{o}C for 2 hours to remove residual organic chemicals. Because of the fact that the boiling temperature of PVP is approximately 400^{o}C, it can be completely decomposed after the calcination step (Moon *et al.* 2010).

In order to verify crystallinity of the coatings, X-ray diffraction (XRD) of TiO_2 nanofibers was performed on a Rigaku D/Max. 2200/RC Model diffractometer

with Cu-K_α radiation (1.5406 Å) using a 0.05° step size and a 2 s dwell time. The nanofiber morphologies were examined using a JEOL JJM 6060 scanning electron microscope (SEM).

In order to investigate the potential suitability of the Ru-doped TiO_2 nanofibers as a gas sensor their gas sensing properties were compared with pure TiO_2 nanofibers. The gas sensing properties were investigated by measuring the frequency change upon exposure to O_2, and humidity.

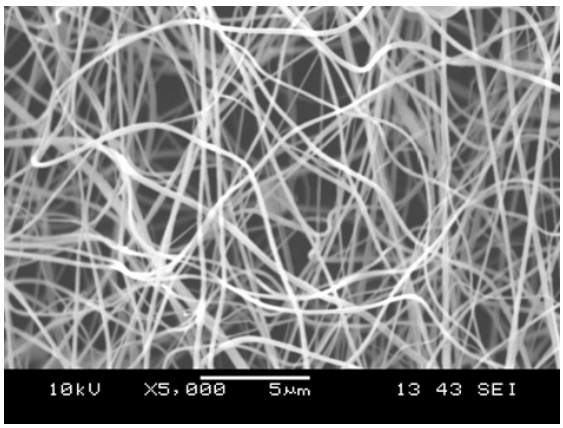
A Time-resolved Electrochemical Quartz Crystal Microbalance (EQCM) with the model of CHI400A Series from CH Instruments (Austin, USA) was used to measure the change in the resonance frequency of quartz crystals between gold electrodes via both serial and usb interface connected to a computer. The QCM works with oscillation frequencies between 7.995 and 7.950 MHz. The density (ρ) of the crystal is 2.684 g/cm^3, and the shear modulus (μ) of quartz is 2.947×1011 g/cm s^2. Around oscillation frequency of 7.995 MHz, a net change of 1Hz corresponds to 1.34 ng of materials adsorbed or desorbed onto the crystal surface of an area of 0.196 cm^2.

The signals coming from a QCM electrode and a commercial RH humidity sensor were simultaneously measured during the adsorption and desorption process. Both the relative humidity and temperature were also recorded during measurements while maintaining the temperature around 23 ◦C. For this purpose, a EI-1050 selectable digital relative humidity and temperature probe with a response time of 4 s and a resolution of 0.03% RH was used with a USB controlled LabJack U12 ADC system combined with a single chip sensor module (SHT11) manufactured by Sensirion (Staefa, Switzerland).

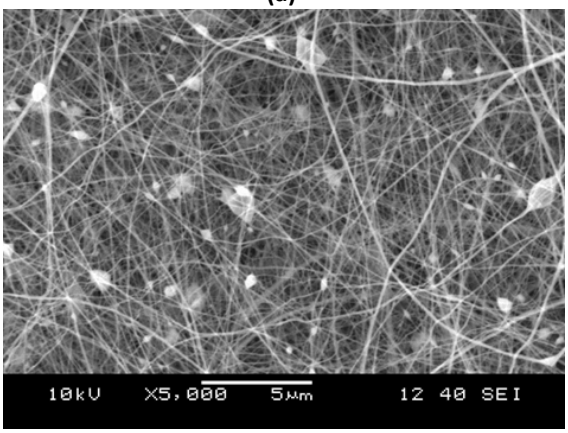
3. Results and Discussions

3.1. Structure Characteristics

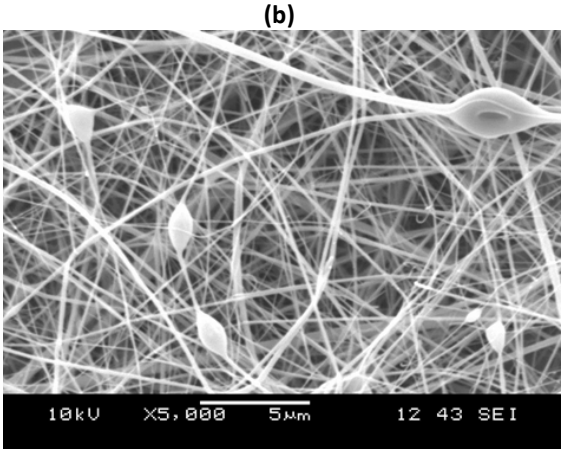
Scanning electron microscopy (SEM) has been used to characterize the size and morphologies of pure and Ru-doped TiO_2 nanofibers before and after calcination. The fibers are deposited as multi-layered random network structure.



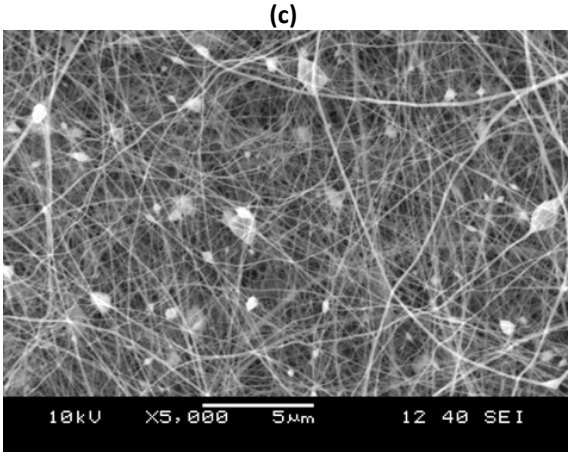
(a)



(b)



(c)



(d)

Figure 1. SEM images of produced nanofibers (a) as-spun TiO_2, (b) calcined TiO_2 at 600^{o}C, (c) as-spun Ru doped TiO_2 and (d) calcined Ru doped TiO_2 at 600^{o}C.

The randomness is due to the instability of the spinning jet (Park *et al.* 2010). Figure 1.a shows the as-spun TiO_2 nanofibers with diameter 260 nm and smooth surface. After calcination at 600°C for 2 hours crystalized TiO_2 nanofibers are shown in Figure 1.b. In spite of the decomposition of the PVP from the nanofibers the network structure and structural continuity were well maintained. Because of shrinkage space in the nanofibers network is more open. From the SEM images (Figures 1.c and 1.d), it can be clearly seen that in contrast to pure TiO_2 nanofibers, diameter of Ru-doped TiO_2 nanofibers become thinner because of Ru addition during the electrospining process (Li *et al.* 2009).

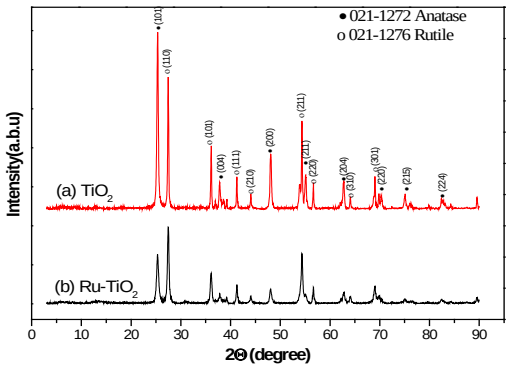


Figure 2. Diffraction peaks of (a) TiO_2 and (b) Ru doped TiO_2 nanofiber after calcinations process

According to XRD patterns as shown in Figure 2, it was found that the obtained TiO_2 nanofibers contain pure anatase and rutile phases even when the annealing temperature was 600 °C for 2 h in air. Especially, anatase phase of pure TiO_2 having tetragonal structure was strongly observed at 600°C as explained in literature. It has been well known that anatase phase of TiO_2, which is less stable than rutile phase thermally and transfer into rutile phase at higher temperature, has an important role in photocatalysis. It can be seen that the peaks at 2θ of 25.28, 38.08, 47.92, 56.32 and 62.66 are assigned to (101), (004), (200), (211) and (214) lattice planes of TiO_2. We have no peak which belongs to Ru because of the fact that a small amount of Ru was added into the precursor.

3.2.Gas Sensing Properties

Figures 3.a and 3.b shows the frequency response of undoped and Ru doped TiO_2 films covered QCM during adsorption process at fixed point relative humidity conditions between 20% and 70% RH. In this figure, QCM frequency shifts after adsorption and desorption cycles between relative humidity values recovers back to the initial value. All measurements show no hysteresis after the moist adsorption and desorption process. Figure 4 also shows the frequency response of these films covered QCM adsorption-desorption process at fixed oxygen concentration. All measurements show no hysteresis after the O_2 adsorption and desorption process (not shown in the figure).

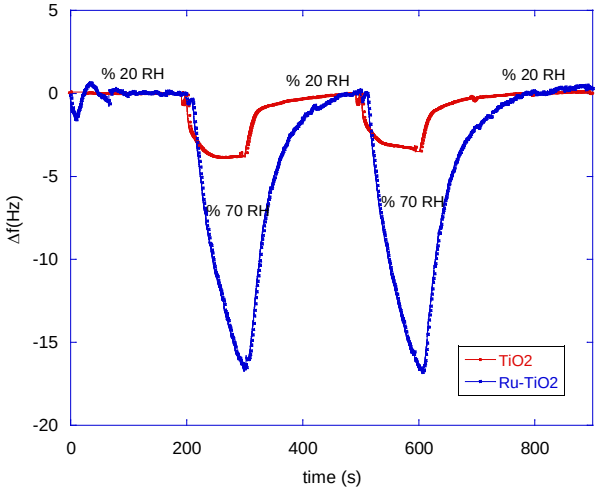


Figure 3. QCM frequency shifts for adsorption and desorption cycle between 20% RH and %70 RH values

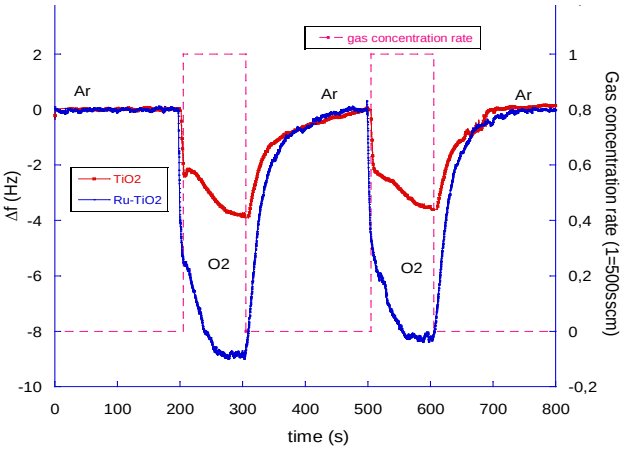


Figure 4. QCM frequency shifts for adsorption and desorption cycles under O_2.

4. Conclusions

Undoped and Ru doped TiO_2 nanofibers were obtained by electrospinning technique. Humidity and O_2 sensors based on the undoped/Ru-doped TiO_2-coated QCM have been fabricated. In order to enhance sensitivity of these sensor effectively, the TiO_2 nanofiber structure are doped by Ru molecules. Ru doped TiO_2 nanofibers show a favored kinetic reaction against humidity and O_2 molecules and have potential application for QCM based gas sensors at room temperature operation.

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