Hydrogen Gas Sensing Properties of AgNPs-Doped Titania Nanotubes by Electroless Deposition

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Abstract: Titania nanotubes thin films have been prepared by electrochemical anodization of Ti foil at room temperature (~25°C), in ethylene glycol base electrolyte with 0.5wt. % NH₄F and 4wt% deionized water at 30V at time 3hr and then AgNPs-doped TiO₂ nanotube arrays at different deposition ratios (0.3, 0.5, 0.7, 0.9 wt%) were carried out by electroless deposition. These tubes are well aligned and organized into high-density uniform arrays. The average tube diameter, ranging in size from 61 to 74 nm, the length of the tube 2.13 μ , and ranging in size of wall thickness from 21 to 29 nm. A possible growth mechanism is presented. The TiO₂ nanotubes were characterized by X-ray diffraction (XRD), scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDX(. Gas sensors based on AgNPs/TiO₂ nanotube arrays thin films were fabricated, and their sensing properties were investigated. The AgNPs/TiO₂ nanotube sensor demonstrated a good sensitivity at different concentration hydrogen atmospheres ranging from (15, 30, 45, 60, 75ppm) H₂. A temperature-dependent sensing from 25°C to 300°C was also found with an applied voltage was constant at 6V.

Keywords: TiO₂ nanotubes; anodization; ethylene glycol, electroless, gas sensor, H₂, AgNPs-doped TiO₂.

1. Introduction

Hydrogen has numerous applications in industry, such as chemical production, fuel cell technology, and rocket engines ^[1]. However, the flammable and explosive properties of hydrogen gas make its detection an important issue ^[2]. Therefore, today a wide range of investigations are being carried out toward the development of highly sensitive, compact, low cost, and reliable hydrogen sensors ^[3]. In order to overcome the disadvantages of commercially available hydrogen sensors ^[4], different detection principles, methods, and materials have been utilized to manufacture sensors during the last few decades. The basic categories of sensors include catalytic sensors, electrochemical sensors, resistive palladium and palladium alloy sensors, field effect transistors, Schottky diodes, and semiconductor metal oxide sensors ^[5]. Metal oxide films have been playing an increasingly important role in the last few years as sensing materials for various gases ^[5]. TiO₂ based gas sensors have been widely used because of their inert surface properties sensing abilities ^[6]. Recently, many and high nanotechnological approaches have been employed to enlarge the surface area of TiO₂ without increasing the device dimensions ^[7]. Highly ordered TiO₂ nanotubes were first synthesized using an anodization process by Grimes et al., using hydrofluoric acid (HF) electrolyte [8]. Thereafter, further studies succeeded in controlling and extending the nanotube morphology ^[9], the length and pore size ^[10], and the wall thickness ^[11]. The choice of electrolyte plays a critical role in determining the resultant nanotube array.

Titanium dioxide (TiO₂) is an important multifunctional material being used as photo-catalyst in solar cells, for the production of hydrogen, as a corrosion-protective coating, as an optical coating, as a gate insulator in MOSFETs, etc. ^[12,13]. In recent years a large number of contributions have reported the extraordinary sensitivity of TiO₂ towards H₂ ^[14]. TiO₂ also shows good sensing properties to CO ^[15], ethanol ^[16], methane ^[17], etc. and have an advantage of being chemically stable at high temperatures which makes it a good candidate for gas sensing applications ^[18]. However,

the main disadvantage of these gas sensors is the inability to distinguish between gases, but it has been reported that the selectivity could be improved by dopants ^[19]. Doped silver nitride-based TiO₂ nanotubes layer are relatively easy to obtain, to act as a host material for these applications ^[20]. The high ability of this material to form stable TiO₂ nanotubes layer, allied to the silver acting as a metallic nanostructure precursor, results in a promising new hybrid structure: self-growth metallic thin films over a TiO₂ nanotubes layer surface, obtained by electroless method. The electroless promotes the silver diffusion up to the TiO₂ nanotubes layer surface and then the reaction.

In this study, we synthesize highly-ordered TiO_2 nanotubes by anodic oxidation of titanium foil in an aqueous solution containing (0.5wt %) of NH₄F in ethylene glycol (95.5wt%) with (4wt %) DI water at (3hours) room temperature, 30 Vdc. Then silver nanoparticles doped on titania nanotubes sample at different deposition rations by electroless method, and investigate their hydrogen sensing properties in terms of the temperature and the hydrogen concentration. The hydrogen sensing mechanism of the TiO₂ nanotubes will be explained in detail.

2. Experimental

2.1 Preparation of titania nanotubes TiO₂

Pure titanium foil (99.7% purity, 0.25mm in thickness) purchased from Sigma Aldrich and cut into the desired size (20×20 mm). A direct current power supply (Agilent E3612A) was used as the voltage source for the anodization. The anodization process was carried out in a homemade plexi glass cell with two electrode configuration; titanium foil as the working electrode and 0.1 mm thick. Platinum mesh (20×30 mm) as the counter electrode under constant potential at room temperature (~ 25° C). The titanium sheets were sonicated in acetone and ethanol each for (15) minutes, followed by rinsing with de-ionized (DI) water to remove the impurities and then drying in (N₂) gas. The anodization set-up is shown in Figure (1). The anodization was carried

out at 30 Vdc, the cell electrolyte was (0.5wt %) of NH₄F in ethylene glycol (95.5wt%) with (4wt %) DI water at (3hours). The prepared samples were rinsed immediately

with (DI) water for several minutes and dried with high pressure (N_2) gas.



Figure 1: Apparatus set-up of titanium anodization experiment

2.2 Preparation of AgNPs/TiO₂ catalysts

After anodizing of titanium, the samples were ultrasonically cleaned in distilled water for 10-20 min to remove surface debris. Then the TiO_2 nanotubes sample were immerged into the bath for electroless deposition.

This technique was composed of two steps. The first step was the titania nanotubes sample was immersed into AgNPs solution, which was prepared by dissolving the silver nitrate (2g) in the water (50mL), at room temperature and different time deposition (5, 10, 15, 20 and 25sec), the solution was sonicated for 20 min until silver nitrate is fully dissolved (water color), adding several drops of the aqueous ammonia to form brownish fine precipitate of silver oxide, and then adding aqueous ammonia further to make the solution transparent due to formation of $Ag(NH_3)_2^+$ complex.

The second step was the sample of $AgNPs/TiO_2$ immersed into a reducing agent solution, which was Formaldehyde, then obtained $AgNPs/TiO_2$ sample was washed also washed with immersion in water.

In order to reach rates fixed by weight of doping noble metal (silver) on the layer of titania nanotubes i.e. values that we adopt in this paper, namely, (0.3, 0.5, 0.7, 0.9 and 1.1 wt. %), we did more experience and solutions to the way deposition electroless metal (silver) and examined by (EDX) to determine the proportion of metal doping, and we got the conditions that lead to get these percentages of doping metals.

2.3 Physical characterization

For the structural and morphological characterization of the anodized samples, top views were recorded by scanning electron microscopy (FESEM) using JEOL JSM-6510LVF FEG-SEM, (USA), and (AFM) study carried out by (AA3000, Angstrom Advanced Inc. USA). The crystallographic structures of the samples were determined using Ultima IV X-ray diffractometer of 1.5406 Å from Cu-k α (supplied by Rigaku Co.), USA.

Then the hydrogen sensing measurements were carried out using aluminum as electrodes in the temperature range of 25-150°C. The sensing element was placed in a flow type homemade chamber. A Keithley 6517A Electrometer/High Resistance Meter was used to test the resistance variation of the nanotube sensor in alternating atmospheres of air and dilute H_2 (50, 100, 500, 1000 ppm). During the measurements, the temperature of the sensor was controlled with a Lakeshore 340 temperature controller.

3. Results and Discussions

3.1Synthesis of titania nanotubes

The mechanism of TiO₂ nanotube formation in fluorine-ion based electrolytes is said to occur as a result of three simultaneous processes: the field assisted oxidation of Ti metal to form titanium dioxide (Eqn.1) ^[21,22], the field assisted dissolution of Ti metal ions in the electrolyte (Eqn.2)^[21,22], and the chemical dissolution of Ti and TiO₂ due to etching by fluoride ions (Eqn.3) ^[21,22], which is enhanced by the presence of H⁺ ions ^[22]. TiO₂ nanotubes are not formed on the pure Ti surface but on the thin TiO₂ oxide layer naturally present on the Ti surface. Therefore, the

mechanism of TiO_2 nanotubes formation is related to oxidation and dissolution kinetics. Schematic diagram of the formation of TiO_2 nanotubes by anodization process is shown in figure (2) ^[21]. For a description of the process displayed in figure (2), the anodization mechanism for creating the nanotube structure is as follows:

- a) Before anodization, a nano scale TiO_2 passivation layer is on the Ti surface.
- b) When constant voltage is applied, a pit is formed on the TiO_2 layer.
- c) As anodization time increases, the pit grows longer and larger, and then it becomes a nanopore.
- d) Nanopores and small pits undergo continuous barrier layer formation. (e) After specific anodization time, completely developed nanotubes are formed on the Ti surface.

$$Ti + 2H_2 \rightarrow TiO_2 + 2H_2 \qquad \dots \qquad \dots \qquad \dots \qquad (1)$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2 \qquad \dots \qquad (2)$$

$$Ti^{4+} + 6F^- \rightarrow TiF_6^{2-} \qquad \dots \qquad \dots \qquad (3)$$

In general the current density starts at a high magnitude then it reduces gradually with time then became nearly constant (steady state).



Figure 2: Schematic illustration of TiO₂ nanotube formation^[21]

FESEM examinations revealed that the nanotubes, with an average diameter of \approx 74 nm and a height of \approx 3.2 μ m, figures (3a-f) shows FESEM images with different magnifications of typical TiO2 nanotube layers covered with Ag nanoparticles at different doping ratios (0.0, 0.3, 0.5, 0.7, 0.9 and 1.1 wt.%), respectively. The electroless-deposited Ag formed nanoparticles, the nucleation of the Ag takes place randomly on the surface of the nanotubes which diameter varies from 17 to 34 nm, which changes with the doping ratios, also we observed of the silver nanoparticles are located at the top edges of the nanotubes, on their side walls and on the exterior mouth of the TiO₂ nanotubes. TiO₂ nanotubes covered with Ag nanoparticles with increasing of doping ratios exhibit quite a different morphology. The Ag particles are agglomerated and in the form of rings at the top of the nanotubes. The amount of Ag is here so high, that it results in a visible reduction of their internal diameter of titania nanotubes, as shown Table (1).

Table 1: The average diameter, inner diameter, wall thickness and grain size of un-doped TiO₂ nanotubes and AgNPs/TiO₂ nanotubes at different doping ratios

Sample	Diameter	Inner	Wall	G. Size of
	(nm)	diameter	thickness	Ag (nm)
Sumple	(nm)	(nm)	(nm)	Ag (nm)

Un-doped	74	63	11	==
AgNPs/TiO ₂ at 0.3 wt.%	78	60	18	17
AgNPs/TiO ₂ at 0.5 wt.%	84	56	28	21
AgNPs/TiO ₂ at 0.7 wt.%	87	48	39	23
AgNPs/TiO ₂ at 0.9 wt.%	91	46	45	29
AgNPs/TiO ₂ at 1.1 wt.%	95	32	63	34

At the doping ratios (0.9 and 1.1 wt.%), Ag nanoparticles are formed due to a further merge of the nanoparticles until having diameters as big as 150 nm. We can be explained the following growth mechanism to explain the difference between the AgNPs diameter at the tube inner surface and those (AgNPs) at the top of the substrate. At the beginning of the electrodeposition process, the solution containing Ag⁺ species can reach all the surfaces exposed by the titania nanotubes sample. Once the Ag nanoparticles are formed and decorate the inner surface of the nanotubes, they grow inwards the nanotubes center, thus blocking at a certain point the further access for the Ag precursor solution into the nanotubes lumen. Thus, only the top of the sample is further accessible for the precursor solution resulting in a covering of Ag nanoparticles, this result is in agreement with the previous work [24].



Figure 3: FESEM images of (a) un-doped TiO₂ nanotubes, (b) AgNPs/TiO₂ nanotubes (top view) and (Insert of cross section) at 0.3 wt.%, (c) AgNPs/TiO₂ nanotubes at 0.5 wt.%, (d) AgNPs/TiO₂ nanotubes at 0.7 wt.%, (e) AgNPs/TiO₂ nanotubes (top view) and (Insert of cross section) at 0.9 wt.%, (f) AgNPs/TiO₂ nanotubes (top view) and (Insert of cross section) at 1.1 wt.%.

AFM analysis of the un-doped TiO₂ nanotubes and doped AgNPs/TiO₂ nanotubes at different doping ratios (0.0, 0.3, 0.5, 0.7, 0.9 and 1.1 wt.%), are shown in figure (4a-f) respectively in 2D and 3D dimensional AFM images. The surface morphology of the TiO₂ nanotubes and doped AgNPs/TiO₂ nanotubes changes with the different doping ratios, as observed from the AFM micrographs figures (4) left pictures proves that the grains are semiuniformly distributed within the scanning areas, with individual columnar grains extending upwards. The bright yellow color represents the wall of tubes with palladium nanoparticles while darker yellow represents pores. The tilted image reveals doped grains heights of a few tens of nanometers.

Despite the fact that the layers were deposited from the aggregation of nanoparticles, the morphologies of obtained films are rather satisfactory. All the deposited layers are quite uniform and their root mean square roughnesses vary. Film from un-doped TiO_2 exhibits a slightly higher roughness, which can be due to stronger aggregation of the nanoparticles comparing to the doped ones.

The roughness of the doped surface is an important parameter, where the surface roughness not only describes the light scattering but also gives an idea about the quality of the surface under investigation, in addition to providing some insight on the growth morphology and the increase in

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surface roughness of the films leads to a increase in the efficiency for sensing properties, therefore, it is very important to investigate the surface morphology of the films.

The values of the root mean square (RMS), surface roughness of TiO_2 nanotubes and grain size of doped AgNPs/TiO₂ nanotubes are shown in the Table (2), i.e. the root mean square (RMS) and surface roughness increased with increasing the doping ratios of Ag nanoparticles due the presence of the fine dispersed phase, this result is in agreement with the previous work ^[25].

In general, as the doping ratios of Ag nanoparticles increases on titania layer, the RMS and roughness of the AgNPs/ TiO_2 nanotubes and the grain size increase.

Table 3: Morphological characteristics from AFM images for TiO₂ nanotubes and doped AgNPs/TiO₂ nanotubes

	1	0 2	
	Grain size	Roughness	Root mean
Sample	of Ag	average	square
	(nm)	(nm)	(RMS) (nm)
Un-doped TiO ₂	==	2.3	3.03
AgNPs/TiO2 at 0.3 wt.%	23.83	3.7	4.84
AgNPs/ TiO ₂ at 0.5 wt.%	31.31	4.13	6.85
AgNPs/TiO2 at 0.7 wt.%	38.48	5.89	2.13
AgNPs/TiO2 at 0.9 wt.%	43.97	7.81	9.92
AgNPs/TiO2 at 1.1 wt.%	34.78	13.1	15





Figure 4: 2D and 3D AFM images of (a) TiO₂ nanotubes, (b) AgNPs/TiO₂ nanotubes at 0.3 wt.%, (c) AgNPs/TiO₂ nanotubes at 0.5 wt.%, (d) AgNPs/TiO₂ nanotubes at 0.7 wt.%, (e) AgNPs/TiO₂ nanotubes at 0.9 wt.%, (f) AgNPs/TiO₂ nanotubes at 1.1 wt.%.

EDX analysis for elemental composition of un-doped titania and silver doped titania was done, as shown in figure (5) and Table (3). The high weight % of titanium and oxygen shows that they are the main components. The weight % loading of the dopant in Ag-TiO₂ at 0.3 wt.% was much higher compared to that of Ag-TiO₂ at 0.5 wt.% and this can be suggested to be due to silver dopant attaching onto the surface of titania and not incorporated into the crystal lattice in which case it would be shadowed from detection, this result is in agreement with the previous work ^[26,27,28].

Table 3: Energy dispersive X-ray spectroscopy results of
un-doped TiO ₂ nanotubes and AgNPs/TiO ₂ doped at
different doping ratios

1					
		Titanium	Oxygen	Dopant	
	Sample	(Ti)	<i>(O)</i>	(Ag)	
		w%	w%	wt%	
-	Un-doped TiO ₂	74.4	25.6	0	
	AgNPs/TiO2 at 0.3 wt.%	73.8	25.9	0.3	
	AgNPs/TiO2 at 0.5 wt.%	75.4	24.1	0.5	
	AgNPs/TiO2 at 0.7 wt.%	73.7	25.6	0.7	
	AgNPs/TiO ₂ at 0.9 wt.%	74.6	24.5	0.9	
	AgNPs/TiO2 at 1.1 wt.%	73.4	24.7	0.11	



Figure 5: EDX analysis of (a) un-doped TiO₂ nanotubes, (b) AgNPs/TiO₂ nanotubes at 0.9 wt. %

Throughout studying the X-ray diffraction spectrum, we can understand the crystalline growth nature of TiO_2 nanotubes prepared by anodization method and Ag nanoparticles deposition on TiO_2 nanotubes layers by electroless method at different doping ratios (0.0, 0.3, 0.5, 0.7, 0.9 and 1.1 wt.%).

The phase composition and crystallite sizes of the synthesized titania nanotubes were determined by XRD analysis. The XRD patterns of TiO_2 nanotubes and AgNPs/TiO₂ nanotubes are shown in figure (6). The wide-angles XRD pattern showed anatase-phase TiO_2 with characteristic diffraction peaks of 2θ values. Thus the prepared TiO_2 nanotubes (pattern a) and AgNPs/TiO₂ nanotubes (pattern b-f) nanotubes were well-crystallized

pure anatase form, this means predominating the anatase phase.

This can be seen when increasing the doping ratio leads to increased (FWHM) of anatase peaks.

From the peaks it can be concluded that change in the doping ratio lead to increased concentration of Ag nanoparticles on the surface layer of titania nanotubes and thus increase the fill of titania nanotubes with Ag nanoparticles. The increased doping ratio might have to the increased potential energy of atomic diffusion barrier and grain growth, this result is in agreement with the previous work ^[26,29,30].

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Figure 6: XRD patterns of (a) un-doped TiO₂ nanotubes, (b) AgNPs/TiO₂ nanotubes at 0.3 wt.%, (c) AgNPs/TiO₂ nanotubes at 0.5 wt.%, (d) AgNPs/TiO₂ nanotubes at 0.7 wt.%, (e) AgNPs/TiO₂ nanotubes at 0.9 wt.%, (f) AgNPs/TiO₂ nanotubes at 1.1 wt.%

3.2 Hydrogen sensing properties

Fabricated AgNPs-doped TiO_2 nanotubes were converted into the gas sensor device. Finally, these devices were placed to gas sensor testing cell.

The gas sensing measurements of AgNPs/TiO₂ samples were carried out by measuring the resistance across two electrodes for different temperatures and H_2 concentrations. The sensor response was calculated by following equation^[31]:

$$=\frac{R_a}{R_g} \qquad \dots \ \dots \ \dots \ \dots \ (4)$$

where Ra is the resistance in dry air, and Rg is the resistance under a reducing gas. The response time, Tres is defined as the time required to reach 90% of the steady response signal. The recovery times, Trec denotes the time needed to recover 90% of the original baseline resistance ^[32].

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The hydrogen sensing measurements are carried out using aluminum as electrodes in a temperature range 25-300 °C. The sensing element was placed in a flow type homemade chamber. A constant bias voltage of 6V is applied to the AgNPs/TiO₂ nanotube sensor device, and the change in the

DC resistivity is measured upon exposure to (15, 30, 45, 60, 75ppm) H₂ in atmosphere at different temperatures. The resistivity values versus time for the AgNPs/TiO₂ nanotube sensor at various temperatures. To establish the baseline, the resistivity is measured under atmosphere flow. Then the AgNPs/TiO₂ nanotube sensor is exposed to the desired concentration of H₂ for 100 sec at room temperature. The exposing and purging times are 43sec at 100°C.

The H₂ sensing mechanism of TiO₂ nanotubes is explained by a variety of factors. The primary factor in the interaction between the nanotubes and hydrogen is the chemisorption of the dissociated hydrogen on the TiO_2 surface ^[32]. The electrical conductivity of TiO2 nanotubes is enhanced when the chemisorbed hydrogen acts in the surface states of the nanotubes. The chemisorption of hydrogen onto the walls and intertubular connecting points could cause easy charge transfer with less resistance in tube to tube transfers. Another factor is that the platinum electrode pads may play a role in the hydrogen absorption. It is well known that platinum is a catalyst for hydrogen. Thus, hydrogen can dissociate on platinum surfaces. These dissociated hydrogen atoms may spill onto the nanotube surface, where they diffuse into the nanotube surface ^[33]. Another factor is that anatase, the polymorph of TiO₂, has been reported to be of high sensitivity toward reducing gases like hydrogen and carbon monoxide [34]. The hydrogen diffused to the interstitial sites of TiO₂.

In this study, the gas sensing properties of un-doped TiO_2 and AgNPs-doped TiO_2 sensing films are characterized in terms of response, response time and recovery time as a function of operating temperature, gas concentration and Ag loading.

The sensitivity and response time of the thin films of undoped TiO₂ and AgNPs-doped TiO₂ nanoparticles at different concentrations (0.3, 0.5, 0.7, 0.9 wt.%) of Ag nanoparticles as a function of H₂ concentration between (15, 30, 45, 60, 85ppm) of concentration at temperature range (25-350°C) are shown in Figure (5). The sensitivity increased considerably by AgNPs-doped TiO₂ nanotubes [show in Figures (5a-f)]. Therefore, doping the TiO₂ nanoparticles with 0.9 Wt.% Ag sensor at 300°C had better sensitivity. In Figure (5) it can be seen that the sensitivity increased considerably by AgNPs-doped TiO₂ nanotubes with 0.9 wt.% Ag. The sensitivity of 79 and response time of 45sec were obtained at 75ppm of H₂ concentration for the AgNPs-doped TiO₂ nanotubes with 0.9 wt.% Ag.

Thus, in this study 0.9 wt.% AgNPs/TiO₂ showed good sensitivity for H₂ gas as compared to the other literatures. The gas-sensing sensitivity, S is defined as the ratio Ra/Rg, where Ra is the resistance in dry air, and Rg is the resistance in test gas. The response time, Tres is defined as the time required until 90% of the response signal is reached. The recovery times, Trec denotes the time needed until 90% of the original baseline signal is recovered.









Figure 8: Response time of the AgNPs/TiO₂ with concentration (0.9wt.%) at different working temperatures





4. Conclusions

Titania nanotubes films were successfully prepared by a electrochemical anodization process. Special efforts were made to enhance the porosity of TiO_2 nanotubes films. In addition silver deposition on titania nanotubes layer using

electroless process at different concentrations of silver. The structural, morphological and sensing properties of prepared films were investigated as a function of film fabrication conditions, testing temperature and H₂ concentration. The gas sensor sensitivity was temperature dependent and the highest sensitivity was observed at temperature (250°C) of H₂ gas at (0.9wt.%) of AgNPs doped on TiO₂ nanotubes layer. It was found that the AgNPs/TiO₂ nanotubes films have several important sensor characteristics such as repeatability, high response, and fast response/recovery times to H₂ gas. The overall recovery times of the sample were decreased by increasing the operating temperatures. It was also found that the doping of AgNPs and porosity of the film were two important parameters, which affect the main gas sensing characteristics of TiO2 based H2 sensors. The measurements revealed that the sensor response decreased by increasing the film thickness. The maximum sensitivity of 79% was measured at 250°C.

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