Physical Science International Journal
4(3): 372-383, 2014

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Improvement in Gasochromic Properties of Tungsten Trioxide Using Optimized Pd Doping

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Authors' contributions

This work was carried out in collaboration between all authors. Author AN designed the study, managed the analyses of the study and wrote the protocol, Author MA wrote the first draft of the manuscript, performed the analysis and managed the literature searches. Author KAR also performed some analysis. All authors read and approved the final manuscript.

Original Research Article

Received 29th June 2013
Accepted 8th November 2013
Published 9th December 2013

ABSTRACT

Tungsten oxide layers are important structures in gasochromic and optical hydrogen sensing devices. In the present study, these layers were constructed using the sol-gel method and spin-coating deposition technique. WO_3 layers were coated with palladium using the same method to investigate the catalytic role of palladium on the surface of the layers. This catalyst was used to coat the WO_3 layers in the form palladium chloride using different concentrations of palladium. The layers were heated at different temperatures to study the gasochromic properties of the WO_3 layer in different crystalline and amorphous phases. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD) and spectrophotometer analysis were used to investigate the surface morphology, structure of layers and size of the nanoparticles. When the colored glass was exposed to air, the sensor returned to its initial transmission state. The results of XRD spectral analysis showed that the layers commenced crystallization at 300°C and were completely crystallized at 500°C. The effects of temperature and catalyst concentration are investigated simultaneously. Optimal conditions were achieved at 300°C and for the 0.05M concentration of palladium chloride solution. Under this condition, after applying 2.7% hydrogen gas, the transmission change of the sample ($\Delta T_1\%=T_a-T_b$, where T_a is initial

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transmission and T_b is coloring state of glass) was 47% and the response time was 3s. The transmission change ($\Delta T_2\% = T_c - T_b$, where T_c is bleaching and T_b is coloring state of glass) and recovery time were 22% and 25s, respectively, after exposure of the sensor to air.

Keywords: WO_3; thin film; Sol-gel; nanoparticles; Gasochrome; Palladium; Hydrogen sensor.

1. INTRODUCTION

Gasochromic film is an electrochromic layer such as WO_3 and a very thin coating of catalyst. On the surface of the catalyst, hydrogen gas is disaggregated into hydrogen atoms that colorize the gasochromic film [1]. This gasochromic device is applied for optical modulation of large-area windows [2]. Its simple layered structure [3] makes WO_3 a promising material of those showing gasochromic properties [4]. One aspect of the interesting using $WO_3$for gasochromic coloration is its response to H_2 gas [5,6].

Gasochromic specification depends mostly on the preparation method of the WO_3 film [7,8]. The sol-gel technique is the most promising method because it has advantages such as only requiring simple equipment and being low cost [9-11].

In the gasochromic process, electrons and ions enter and exit the gasochromic material in accordance with the gas density, so that the number of electric charges remains constant. This process results in formation of optical absorption bands in active gasochromic materials.

The thin layers of tungsten oxide show WO_{3-x} stoichiometry and oxygen vacancy before receiving hydrogen gas. Annealing them results in the absorption of oxygen and the filling of vacancies, which alters their structural patterns to WO_3. When hydrogen is applied and hydrogen atoms diffuse in the lattice, these atoms react with WO_3 and H_2O molecules to form a WO_2 lattice. The transmission of the layer decreases as theWO_3 converts to WO_2 [12, 13].

This is a reversible process; whenever the colored film is exposed to O_2 gas, a reverse reaction occurs and the sensor reverts to its initial transmission [14].

The characteristic of the Pd catalyst at the surface aids disintegration of the H_2/O_2 molecules to speed coloration/bleaching of the glass. The catalytic role of Pd and the mechanism of gasochromic coloration by H_2 having a columnar structure proceeds in the following steps [15]:

1. Adsorption and dissociation of H_2 on to the Pd catalyst.
2. Transfer of H from the Pd on to the WO_3 film surface.
3. Diffusion of H into the interior of WO_3 film pore surface.
4. Formation of an intermediate state having WO_3 and two H.
5. Formation of $WO_2 + H_2O$.
6. Diffusion of the oxygen vacancy.
7. Escape of the H_2O.

Steps 1 to 3 are quick; steps 4, 5 and 6 are slow; step 7 is slower than 4, 5 and 6.

The adsorbed H_2 molecules dissociate on the Pd layer and transfer to the WO_3 surface, forming W–OH groups. Diffusion models predict that two protons, instead of a single one, interact with W to form H_2O. Water formation generates vacancies for WO_2 and oxygen. Coloration proceeds from the diffusion of these oxygen vacancies in the surface into the interior of the film. Experimental results reveal that coloration is fast and exponential.

Bleaching is a reverse process where the O_2 dissociates on the Pd catalyst and diffuses into the interior of the film, recombining with the oxygen vacancies and reforming the WO_3.This process requires a film with a large surface area. The increased number of W=O bonds observed in colored films can be explained by the breakage of the W-O-W bonds by the formation of $H^+ \ldots {}^-OW$- bonds. This is similar to the formation of the x ($Li^{++} \ldots {}^-OW$-) and $W_{1-x}^{+6} W_x^{+5}$ O_3 species proposed for electrochemically colored WO_3films.

According to Faughman theory, the coloration of WO_3 thin films occurs because of the valence change in tungsten (W^{+6}-W^{+5}) that causes ray absorbance and the diffusion of electrons and positive ions into the WO_3 lattice that completes the coloration process.

Tungsten oxide is also used to make resistive hydrogen sensors. In these sensors, the contact of the gas with the surface of the samples allows electron transfer and band bending to change in the electrical resistance. These metal-oxide resistive sensors are made in the same way that the gasochromic sensor is made, but only act at working temperatures above 150°C. The present gasochromic sensor works at room temperature, reducing energy consumption and increasing the stability of this type of sensor. The lower working temperature is the greatest advantage of gasochromic devices.

2. MATERIALS AND METHODS

In this study, the sol-gel method was used to create the WO_3 solution. In the Kudo method [16], 5g tungsten metal powder (Merck) is poured into 20ml hydrogen peroxide and stirred for a few hours to produce a milky-colored peroxotungstic acid. This reaction is highly exothermic and the flask must be cooled to prevent the spurting of the reactants. The solution is heated at 60°C for 1 h to evaporate the extra H_2O_2. Then 10ml ethanol is added to the solution and it is heated at 80°C for 20 min. This process produces a light yellow transparent solution that can be deposited on to glass after 24h.

Pd can be added to distilled water in the form of $PdCl_2$ powder (Merck) to synthesize catalyst solutions having different concentrations. A few drops of HCl are added to the $H_2O + PdCl_2$ solution to facilitate dissolution and is stirred for 4-5 h to obtain a light brown solution with no palladium deposits. In this study, 3 molarities of the solution (0.01M, 0.05M, and 0.1M) were made.

Spin-coating was used for 25s at 2500 rpm to deposit the WO_3 and Pd solutions on to the glass in the form of thin films. Spin-coating produces layers with adjustable uniform thicknesses.

Primary annealing was done for each sample at 70°C for 10min after each deposition step using both WO_3 and Pd solutions so that the $PdCl_2$ chemical reduction occurred on the surface of the layer.

To study the effect of heating temperature and catalyst concentration, the samples were heated at different temperatures. When the optimum temperature was discerned, 3 concentrations of catalyst were tested at this temperature.

Response time (T90) can be defined as the time required for sensor output to change from the initial state (primary transmission of sensor) to 90% of the final value (after applying hydrogen and transmission reduction). Recovery time is defined as the time required for the transmission signal of the sensor, after flushing with air, to reach 90% of its initial transmission value.

The samples are exposed to 2.7% hydrogen gas and their transmission changes were measured. The colored films were then flushed at a rate of 10 lit/min with O_2 gas for 1 min to reach the initial transmission value to some extent. The rate and value of sample recovery to oxygen gas exposure was compared. Finally, the samples were exposed to the air to achieve 90% of the initial transmission.

3. RESULTS AND DISCUSSION

A TEM image of the WO_3 solution taken using a Philips EM208 microscope at 100 kV is shown in Fig. 1.

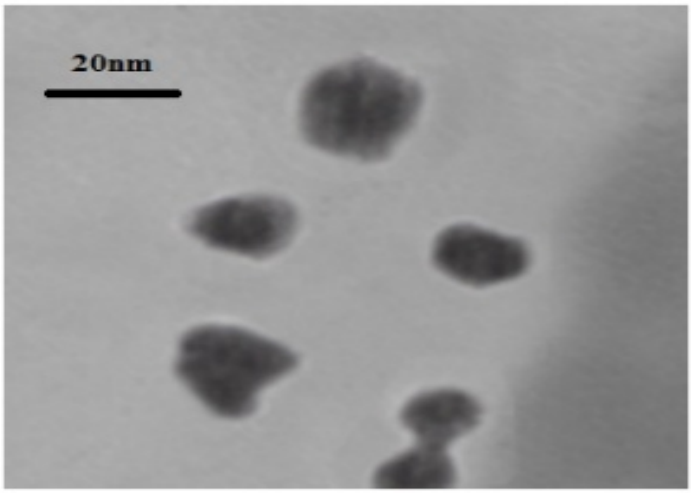
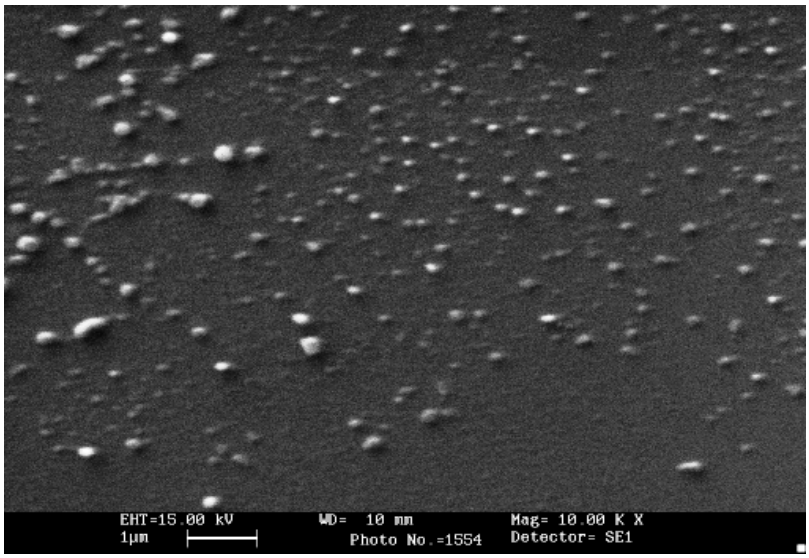


Fig. 1. TEM image of WO_3 solution

The TEM results indicate that the size of the WO_3 nanoparticles are about 10-20 nm**.** The diffusion rate of gas in to the layer depends on the diffusion coefficient and the surface morphology, thus, the surface morphology should be studied first. The samples were doped with Pd at different annealing temperatures and their images recorded using SEM (Leo440i electron microscope). The results for the 0.05M catalyst solution and their respective SEM images at 20 kV are summarized as follows: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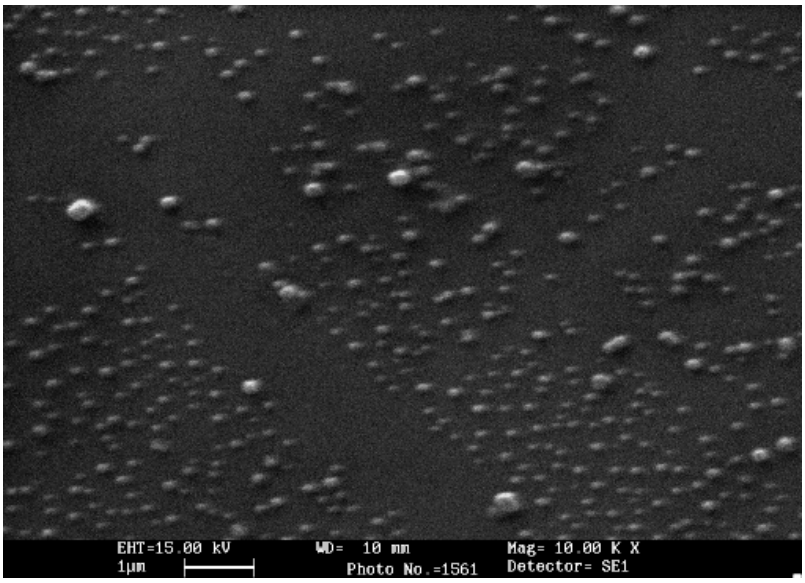
WD= 10 mm
Mag= 10.00 K X
1µm
Photo No.=1554
Detector= SE1

(a)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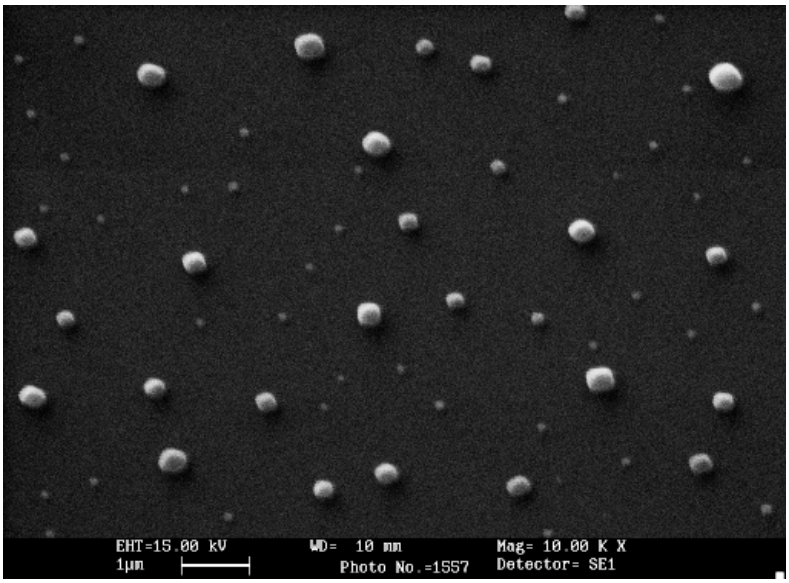
WD= 10 mm
Mag= 10.00 K X
1µm
Photo No.=1561
Detector= SE1

(b)



(c)

Fig. 2. SEM images of Pd/WO_3, annealed at a) 200ºC,b) 300ºC and c)400ºC

As the SEM images show, as temperature increased, the grains joined and the grain size increased and the structure being more regular. SEM image of the sample annealed at 400°C shows that these layers, like the previous templates, have uniform distribution. It is clear that as the particles joined, their size increased more than in previous templates.

Also XRD was used to study the layers at $2\theta = 20° \text{ to } 80°$. In order to determine the structure of the layers, the spectra were taken using a STADI MP microscope at 40 V and 30mA before and after doping the layers with Pd at different temperatures. Annealing the layer resulted in the rearrangement of atoms. Re-crystallization of the layer began at 300ºC and completed at 500ºC. This fact is effective for characterization of the layer.

The XRD spectra of the WO_3 layers where prepared at 200, 300 and 400ºC and after depositing the $PdCl_2$ solution on the layer at 500°C, are shown in Fig. 3.

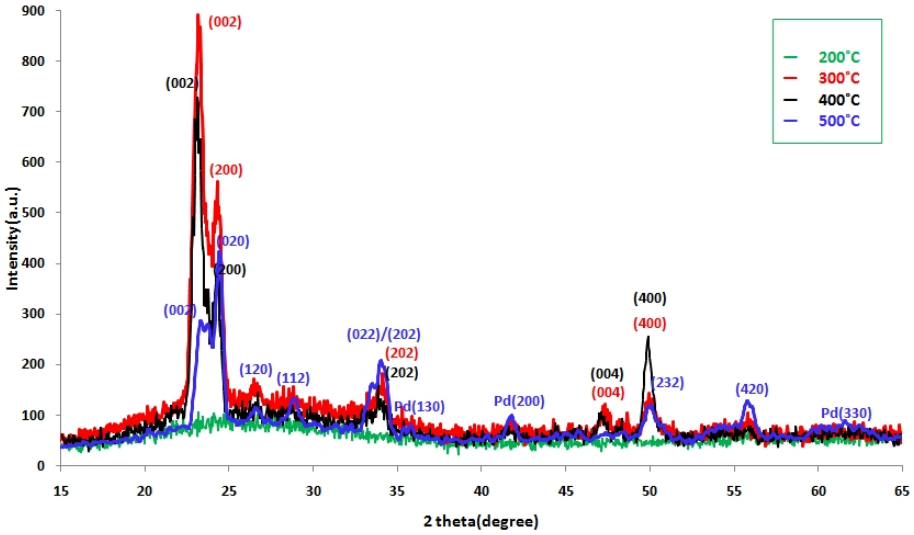


Fig. 3. XRD spectra of pure WO_3 thin film annealed at 200, 300 and 400ºC and Pd/ WO_3 thin film annealed at 500ºC

Fig. 3 shows that the thin WO_3 film annealed at 200°C are totally amorphous and no refractive peak is observed. Only one broad peak is seen in the range of 20° to 40°, indicating very little ordering and large amorphous shapes within the layers.

The XRD image of the sample annealed at 300°C shows the presence of a few refractive peaks; indicate that increasing the temperature improved the crystalline structure of the WO_3 layers. The structure is still amorphous with no perfect crystalline order. In this sample, 5 peaks are observed at $2\theta = 23.16^{\circ}, 24.28^{\circ}, 34.12^{\circ}, 47.24^{\circ}, \text{and } 49.92^{\circ}$ that represent the crystalline directions of (002),(200),(202),(004), and (400), respectively. The crystallized parts of the sample annealed at 300°C show triclinic symmetry.

In Fig.3, the sample annealed at 400°C shows more crystalline peaks than the sample annealed at 300°C. As Figure shows, increasing the annealing temperature results in the crystallization of the WO_3 layers. These samples were annealed at 400°C and represent 5 main peaks at $2\theta = 23.12^{\circ}, 24.36^{\circ}, 33.84^{\circ}, 47.08^{\circ}, \text{ and } 49.88^{\circ}$ that indicate the crystalline directions of (002), (200), (202), (004), and (400), respectively. The crystallized parts of the sample annealed at 400°C have monoclinic symmetry.

The WO_3 peaks increase as temperature increase. They are observed in almost all directions at 500ºC, indicating complete crystallization of the sample. The crystal structure has lost nearly all water at 500ºC. The peaks for Pd are evident in the figure.

The amorphous layers are formed by tungsten trioxide and used for gasochromic devices. Increasing the temperature increased crystallization. The regularity of the layers resulted in a longer time required for entrance and exit of the ions and electrons to and from the layers. This resulted in decreased transmission variation and reduced the reverse reaction for the layers.

The transmission and absorption spectrum was measured using a high-resolution miniature fiber optic spectrometer (HR 4000/HR 4000 CG-UV-NIR, Ocean Optics). The optical transmission graphs were plotted versus wavelength before and after exposure to 2.7% hydrogen gas and application of 10liter/min O_2 for 1 min. Figure 4 shows the transmittance spectrum of Pd/WO_3 thin film at optimum temperature.

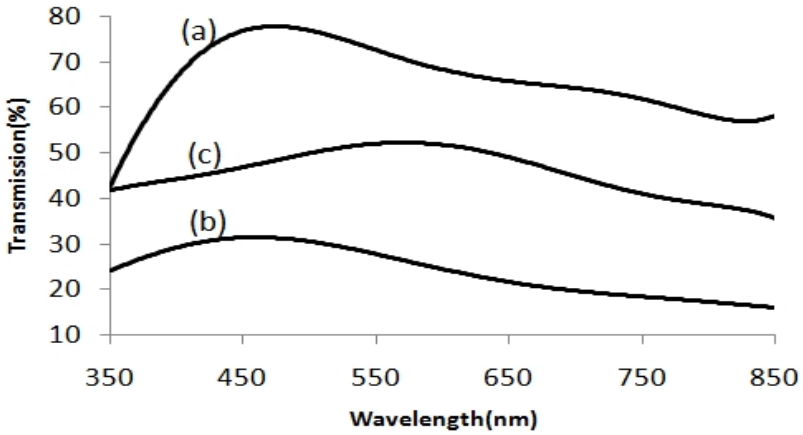


Fig. 4. Transmission spectrum versus wavelength at 300˚C annealing temperature a) before and b) after exposure of hydrogen gas, respectively and c) after applying oxygen gas flow for 1 min

ΔT_1%and ΔT_2% data for the Pd/WO_3 thin films at 450nm wavelengths are presented in Table1 at different temperatures after flushing with 2.7% H_2 and 10 liter/min O_2 for 1min.

Table 1. Transmission change for Pd/WO3 layers at 450nm and different temperature

Film specification	ΔT % at 200˚C	ΔT % at 300˚C	ΔT % at 400˚C	ΔT % at 500˚C
After 2.7% H_2 ($\Delta T_1\%=T_a-T_b$)	13%	47%	30%	22%
After 10 lit/min O_2 ($\Delta T_2\%= T_c - T_b$)	5%	22%	3%	1%

The table shows that maximum transmission variation occurs at 300°C after application of hydrogen (ΔT_1%) and oxygen (ΔT_2%) gases.

At temperatures over 300°C, the samples gradually crystallize up to 400°C and above, creating a nearly complete crystalline lattice. Increased crystallization at higher temperatures means more regularity in the gasochromic material. This is a barrier to transforming the crystal lattice to WO_2 after hydrogen gas application. Consequently, the transmission modulation changes (ΔT_1%and ΔT_2%) decreased comparing to those at 300°C. As the annealing temperature increased, the size of the nanoparticles also increased. Because of the reduction in the surface-to-volume ratio, the unique properties of nanoparticles and the sensing performance decreased.

The recorded response times (T90) of the samples were 2, 3, 5 and 7s at 200, 300, 400 and 500°C, respectively. These results indicate that the samples responded to hydrogen later at higher temperatures. This means that, at higher temperatures, the change in structure was

more difficult and took longer because of the increased crystallization level. On the other hand, after exposure to oxygen gas for 1min, the samples annealed at higher temperatures, respond to oxygen later and return to their initial transparency later than the amorphous templates. Table1 shows that the samples heated at 400 and 500°C return slightly to their initial transmissions. No significant return was observed for samples annealed at 500°C.

The long recovery times for the crystalline samples are caused by the order of the atoms, which acts as a barrier for conversion after exposure to oxygen. This caused the transparency of these samples to change with more difficultly and later.

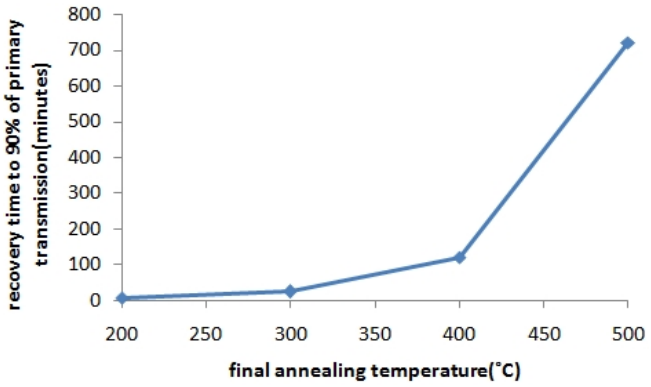


Fig. 5. Graph of recovery time of samples with different final annealing temperatures, in the air

Samples with different concentrations of $PdCl_2$ solution (0.01M, 0.05M, and 0.1M) were also tested at 300ºC. Other conditions were kept the same. The spectrophotometer graphs of the samples were plotted and $\Delta T_1\%$ and $\Delta T_2\%$ data for the Pd-doped WO_3 thin film at 450nm wavelength are shown in Figs. 6 and 7. Table 2 shows that the optimum concentration of catalyst solution in the gasochromic device is 0.05M.

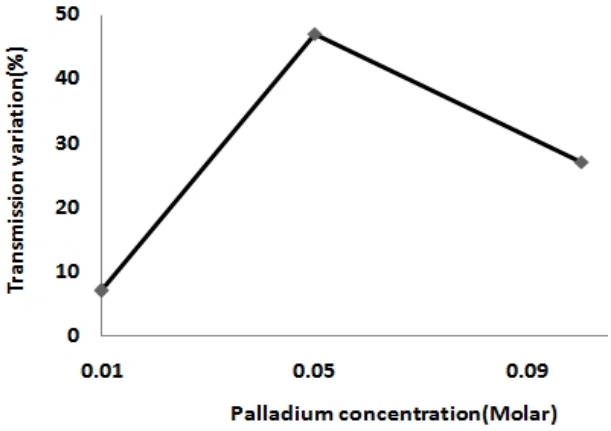


Fig. 6. Graph of transmission variation versus catalyst concentration ($\Delta T_1\%=T_a-T_b$) with 0.01M, 0.05M and 0.1M of Pd catalyst after applying 2.7% hydrogen. (Annealing temperature was 300ºC)

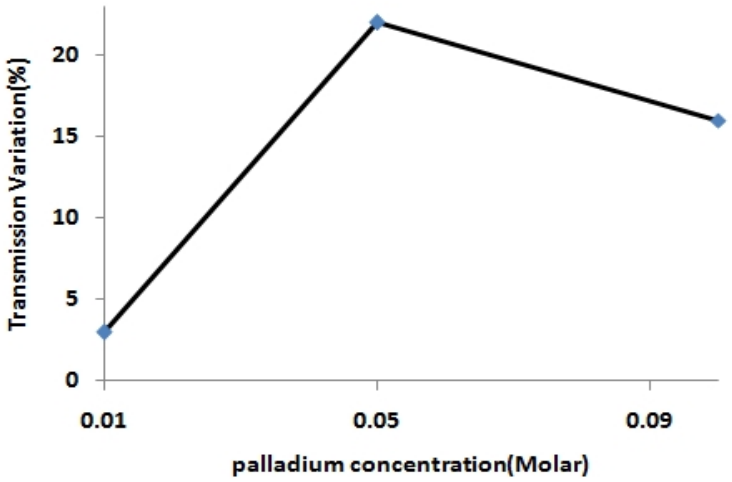


Fig. 7. Graph of transmission variation versus catalyst concentration in returning to initial transmission($\Delta T_2\% = T_c - T_b$) with 0.01M, 0.05M and 0.1M of Pd catalyst after applying 1 minute oxygen. (Annealing temperature was 300ºC)

Table 2. Transmission modulation change for Pd/WO3 layers annealed at 300ºC, measured at 450nm, at different concentration of Pd catalyst

Film specification	ΔT% at 0.01M	ΔT% at 0.05M	ΔT% at 0.1M
After 2.7% H_2 ($\Delta T_1\% = T_a - T_b$)	14%	47%	30%
After 10 liter/min O_2 ($\Delta T_2\% = T_c - T_b$)	3%	22%	17%

To demonstrate the long time stability of the device, the optimum sample was switched 1000 times over 3 months without a significant change in performance. The characteristics of transmission for long time stability of coloration were obtained and are shown in Fig. 8

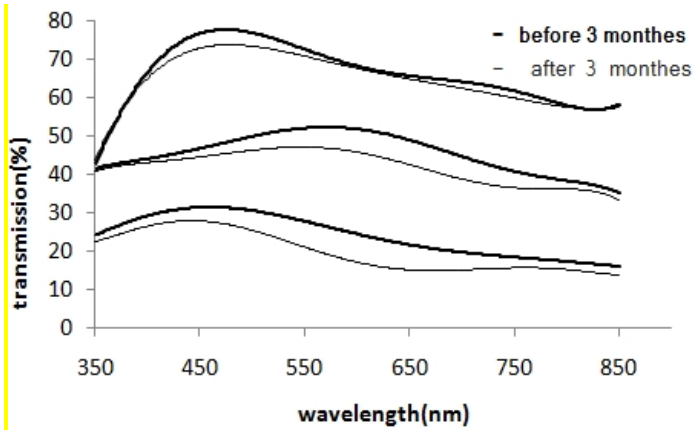


Fig. 8. The long time stability of coloration in Pd/WO3 thin film

The figure shows that the difference between transmission graphs of the sample is negligible after 3 months.

Lin et al. [9] conducted a similar test by adding $PdCl_2$ to WO_3 solution and dip coated the glass to apply the layer. They calculated the size of grains to be 50-60nm. They applied 5% H_2/Ar to the samples and reported response and recovery times lower than 60s for the optimum condition.

Ranjbar et al. [14] used pulsed laser deposition (PLD) for WO_3 and electro less plating for Pd. The rate of maximum coloring/bleaching was obtained as ΔOD in 820s with the application of 10% H_2/Ar.

The proposed method used a simpler and cost-effective method (sol-gel and spin coating) to achieve 47% ΔT, compared to 35% ΔT in the optimum condition for Lin et al. [9], in only 3s by applying 2.7% H_2 and 10-20nm nanoparticles.

The sol-gel method makes the WO_3 film more porous than those obtained in other methods. Its porous structure increased the surface area and the dissociation sites.

The properties of WO_3 thin film were influenced by the annealing temperature and catalyst concentration. Samples were tested under different annealing temperatures and catalyst solutions. The results showed that the optimum Pd/WO_3 sample was obtained at an annealing temperature of 300°C and the catalyst concentration of 0.05M. The Pd/WO_3 response time (T90) for the 2.4% H_2 was 3s and the recovery time was 25 s, which is a significant reduction from the results (60 s) of Lin et al. [9].

A comparison of the present study with Lin et al. [9] indicates that the size of the grains decreased and the surface-to-volume ratio increased, which improved the efficiency of the gasochromic sensor. In addition, the transmission change (ΔT_1%) increased 12% and the concentration of H_2 decreased about 2%.

4. CONCLUSION

In this study, the nanostructure of WO_3 and the catalyst solution was prepared using the sol-gel method. Several thin film samples from WO_3 and the Pd solution were also constructed using spin-coating technique. The size of WO_3 (10-20nm) was measured using TEM images. XRD patterns of the samples indicate that the WO_3 thin film annealed at 200°C was amorphous. Increasing the annealing temperature resulted in crystallization of the tungsten oxide layer so that it completely crystallized at 500°C and the water disappeared. The thin film annealed at 300°C and coated with 0.05M catalyst solution showed the most appropriate gasochromic properties. Based on these results, the transmission spectra of WO_3 film under these conditions showed the highest transmission change (ΔT_1%and ΔT_2%), the best coloration, and an appropriate response and recovery times.

At temperatures higher than 300°C, the increase in lattice crystallization results in a regular increment that acts as a barrier to transformation of the crystal lattice to WO_2 after application of hydrogen gas. Therefore, both ΔT_1% and ΔT_2% of the samples decrease compared to those at 300°C. This regularity is also the main reason to increase recovery time.

In the optimal condition, ΔT_1% increased 47% after exposure to 2.7% hydrogen gas and ΔT_2% increased 22% after flushing with 10 liter/min oxygen gas for 1 min. The response and recovery times obtained in this study were 3s and 25s, respectively.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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