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Journal Name:	Physical Review & Research International
Manuscript Number:	2013_PRRI_5663
Title of the Manuscript:	Improvement in Gasochromic Properties of Tungsten Trioxide by Optimized Pd Doping
Type of the Article	Research Paper

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PART 1: Review Comments

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
Compulsory REVISION comments	<p>This paper reported the gasochromic properties of a PdCl₂-doped WO₃ towards H₂. The topic is not new, and the authors did not provide enough new findings that may be useful or instructive to readers working in related areas. Moreover, much more work is needed to complement the research paper. In all, the authors just provided an experimental report with little discussion and quite limited experimental results. Detailed comments are provided as follows:</p> <p>(1) English writing needs to be further improved. Sometimes the grammatical errors greatly hindered the understanding;</p> <p>(2) In the Introduction section, the authors need to reorganize the paragraphs. It should be developed in a logical way, and it is quite improper to emphasize the advantage of the gasochromic sensor over resistive sensor at the end of this section. Moreover, the authors should make a comprehensive literature review to reflect the up-to-date progress in the research area, and clearly show the features or the advantages of their research work over</p>	<p>By comparing the present work with similar ones, significant improvement could be observed. For example The Pd/WO₃ response time (T₉₀) for the 2.4% H₂ was 3s and the recovery time was 25 s, which is a significant reduction from the results (60 s) of Lin et al. [9].</p> <p>In addition, the transmission modulation change ($\Delta T_1\%$) increased 12% and the concentration of H₂ decreased about 2%.</p> <p>1) We did our best</p> <p>2) In the Introduction section, the catalytic role of Pd and the mechanism of gasochromic coloration by H₂ were added. Furthermore, a description about operation of resistive sensors was added to explain these metal-oxide resistive sensors are made in the same way that the gasochromic sensors are made, but only act at working</p>



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	<p>previous achievements;</p>	<p>temperatures above 150°C, while the present gasochromic sensor works at room temperature and so reducing energy consumption and increasing the stability of this type of sensor. These are major advantages compared to other types.</p> <p>To show the advantages of our research over previous achievements, we added an explanation at the end of the Results and Discussion section and compare our research work with similar one.</p> <p>To express our general contribution in improving the gasochromic properties of sensor, we can say the sol-gel method makes the WO₃ film more porous than those obtained in other methods. Its porous structure increased the surface area and the dissociation sites. Also the size of the grains decreased by sol-gel and Kudo method and the surface-to-volume ratio increased, which improved the efficiency of the gasochromic sensor.</p> <p>By direct adding of the PdCl₂ solution on the surface of the WO₃-coated glass and its chemical reduction by annealing, we increased the possibility of collisions between H₂ atoms and Pd particles and</p>
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	<p>(3) In the Material and Methods section, the authors should provide the details of their measurement setup, and the parameters such as the gasflow speed, the composition of tested hydrogen and oxygen, the measurement temperature. They said that “the colored films are flushed with 10 lit/min O₂ gas for 1min to meet 10% of their initial transmissions. Finally, the samples are exposed to the air to achieve their initial transmissions”. What does this mean? Why did they do so? Do they mean that all the gasochromic sensors could “meet 10% of their initial transmissions by flushing with oxygen for the same time of 1 min?</p>	<p>thus, the gasochromic efficiency improved. We tested 3 concentrations of catalyst and 4 different annealing temperatures and regard to the obtained experimental results; we chose optimum condition to improve the transmission variation and response and recovery times. These comparisons are mentioned at the end of the results and discussion by details.</p> <p>3) About the measurement setup, the technical specifications and models of the devices and equipments for each measurement techniques listed into the paper. For example for spectrophotometer we added: 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 gas flow of Oxygen and Hydrogen gases are mentioned 10liter/min and 2.7%, respectively. About the temperature, primary annealing was done for each sample at 70°C for 10min after each deposition step using both WO₃ and Pd solutions so that the PdCl₂ chemical reduction occurred on the surface of the</p>
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		<p>layer. Then, in order to investigate the effect of different baking temperatures and consequently the effect of surface morphology (crystalline or amorphous phases) on sensing performances of the gasochromic layers, they annealed at 200, 300, 400 and 500°C.</p> <p>In the statement of “the colored films are flushed with 10 liter/min O₂ gas for 1min to meet 10% of their initial transmissions. Finally, the samples are exposed to the air to achieve their initial transmissions”, the value of "10%" removed, since as you mentioned, all samples don't meet 10% of their initial transmission value after applying 1 min O₂ gas flow and this amount varies for different samples.</p> <p>As it is explained in the text, after colouring process of samples, they exposed to oxygen gas flow of 10liter/min for 1 min. Of course flushing with Oxygen for 1min, not provide the recovery of layers to 90% of initial transmission, and this time (1min) is not considered as recovery time. But it is a suitable criterion for comparison the bleaching amount of the samples. We made samples again like previous ones and exposed to air in a controllable air chamber to reach 90% initial transparency. Of course the recovery time according to its</p>
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	<p>(4) They claimed that it is a thin film device, and thus the thickness of the film must be provided. They provided transmission spectrum in Fig. 7. The wavelength range from 350 to 850 nm. Why did they use glass instead of quartz as the substrate for film preparation?</p> <p>(5) How did the response time and recovery time defined? In the paper, the authors did not provide any figure showing the real-time response of the sensor to hydrogen and oxygen or air. It is therefore impossible to evaluate the dynamics of the sensor and compare the sensing properties of the PdCl₂-doped sensor with the literature results;</p> <p>(6) The discussion on the effect of annealing temperature on the sensing performance is just hypothesis without the support of any proof. The so-called effect of PdCl₂ concentration on the sensing behaviors of WO₃ is not at all acceptable. Anyway, it is impossible to make a</p>	<p>definition (as it is defined in the text and also is given in answer to question 5) was only measured in a controllable air chamber.</p> <p>(4) The glass of course is cheaper than quartz and furthermore since the glass has also a wide transmission spectrum in visible and near IR region, we used glass instead of quartz.</p> <p>(5) 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.</p> <p>(6) The annealing temperature generally affect on grain size and crystallization. As the SEM images show, as temperature increased, the grains joined and the grain size increased and the structure being more regular. If the size of the grains is smaller,</p>
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	<p>conclusion for the “trend” with only three data. Moreover, the WO_3 was doped with PdCl_2 instead of Pd since no reduction of PdCl_2 occurs before the exposure to hydrogen, and it is therefore improper to use the phrase “Pd-doped”;</p> <p>the surface-to-volume ratio increases, which improves the efficiency of the gasochromic sensor. Contrariwise, 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 decreased and the sensing performance decreased. Meanwhile, the films developed by the sol-gel method have a porous structure and with increasing the temperature, the number of holes decreases due to the heat treatment. So ions penetration into the network becomes harder.</p> <p>On the other hand, 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.</p> <p>About the effect of PdCl_2 concentration on sensing behavior of WO_3, we can refer to the similar works that used PdCl_2 as a catalyst (like [9] of the references), and also provided limited number of PdCl_2 concentrations (for example 2 concentrations of Pd:W molar ratio) to</p>
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		<p>investigate the effect of catalyst concentration on samples transparency. So we chose 3 concentrations of this catalyst solution (0.01, 0.05 and 0.1M) and by comparing transmission modulation we selected the optimum concentration. It is evident that precise optimization needs to wider range experiment.</p> <p>Primary annealing after each steps of deposition for both WO_3 and Pd solutions, at 70°C for 10min, reduces PdCl_2. So we assume that the reduction of PdCl_2 occurs before the exposure to hydrogen. However according to similar works (like references of [9] and [14] and so on) we changed "Pd-doped WO_3" to "pd/ WO_3".</p>
	<p>(7) The authors provided the SEM figures of the PdCl_2-doped WO_3, but no comments were seen in the paper. What did the figure imply? Do they just want to provide the experimental data and ask the readers to make analysis and comments?</p>	<p>(7) As SEM images show, nano particles have spherical shape and uniform distribution. As the SEM images show, as temperature increased, the grains joined and the grain size increased and the structure being more regular. This expression was added to the text.</p>
	<p>(8) The XRD figures should be combined into one diagram so as to more directly reflect the evolution of crystallization with the annealing temperature. No need to use four figures;</p>	<p>(8) The XRD figures were combined into one diagram. XRD spectra of the samples annealed at 200°C, 300°C and 400°C belong to pure WO_3 thin film and the</p>



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	<p>(9) I have doubt on the reversibility of the gasochromic sensors based on PdCl₂ doped WO₃, and the authors did not comment on whether the sensor could restore its original data by flushing with air. What is the meaning of the change in transparency of sensors by flushing with oxygen for 1 min? This should not be regarded as a measure of response time and response magnitude.</p> <p>(10) What is the function of PdCl₂ doping? The authors did not explain clearly the sensing mechanism of PdCl₂ doped WO₃.</p>	<p>spectra of sample annealed at 500°C, belongs to pd/ WO₃ thin film to show the difference between graphs and the peaks of Pd were added too.</p> <p>(9) The long time stability characteristic has been obtained and shown in Figure 8. The optimum sample was switched 1000 times over 3 months without a significant change in performance. The figure shows that the difference between transmissions graphs of the sample is negligible after 3 months.</p> <p>As it is said in previous sections, flushing with Oxygen for 1min, don't provide the recovery of layers to 90% of initial transmission, but it is a suitable criterion to compare samples and of course the corresponding time (1min) is not regarded as a measure of response time.</p> <p>(10) the function of PdCl₂ doping is explained in the text as the following steps:</p> <ol style="list-style-type: none"> 1. Adsorption and dissociation of H₂ on to the Pd catalyst. 2. Transfer of H from the Pd on to the WO₃ film surface. 3. Diffusion of H into the interior of WO₃ film pore surface. 4. Formation of an intermediate state
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		<p>having WO_3 and two H.</p> <p>5. Formation of $\text{WO}_2 + \text{H}_2\text{O}$.</p> <p>6. Diffusion of the oxygen vacancy.</p> <p>7. Escape of the H_2O.</p> <p>Steps 1 to 3 are quick; steps 4, 5 or 6 are slow; step 7 is slower than 4, 5 and 6.</p> <p>According to Faughman, the coloration of WO_3 thin films occurs because of the valence change in tungsten ($\text{W}^{+6}-\text{W}^{+5}$) that causes ray absorbance and the diffusion of electrons and positive ions into the WO_3 lattice that completes the coloration process.</p> <p>More explanation exists in the introduction section of the text.</p>
<u>Minor</u> REVISION comments		
<u>Optional/General</u> comments		