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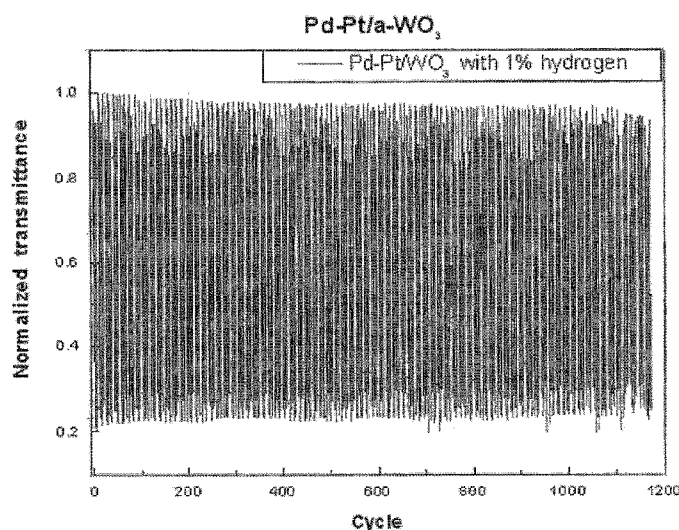
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(54) Title: GASOCHROMIC THIN FILM FOR HYDROGEN SENSOR WITH IMPROVED DURABILITY AND HYDROGEN SENSOR CONTAINING THE SAME

Fig. 8



(57) Abstract: The present invention provides a thin film for a hydrogen sensor comprising a catalytic layer which comprises (a) a gasochromic layer; and (b) palladium (Pb) and platinum (Pt) deposited on the gasochromic layer and a hydrogen sensor having the same. The hydrogen sensor of the present invention represents not only much more improved durability having its reactivity in above 1000 cycles but also much more enhanced sensitivity. The hydrogen sensor of this invention for safe utilization of hydrogen energy may be used in a photosensor for sensing a hydrogen leakage, and be also promising in its marketability in the senses that the hydrogen energy as an alternative powerful energy source is widely used.



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GASOCHROMIC THIN FILM FOR HYDROGEN SENSOR WITH IMPROVED DURABILITY AND HYDROGEN SENSOR CONTAINING THE SAME

5 BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a gasochromic thin film for a hydrogen sensor, a hydrogen sensor having the same and a method for improving a durability of a thin film for hydrogen sensor.

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BACKGROUND OF TECHNIQUE

The oil prices have recently up-risen over 100 dollars per barrel. In addition to environment problem, high-cost oil was one of most problems of fossil energy, generating increase in global demands for alternative energy. Studies and commercial services for utilization technologies of hydrogen as a prominent alternative energy source have been gradually expanded in advanced countries. The techniques to utilize hydrogen have been developed in a main axis of Department of Energy in USA, and Japan and Germany have also invested numerous manpower and capital for exploiting the techniques for utilization of hydrogen energy to substitute for fossil energy. In addition, Iceland put spurs to development and commercial service of hydrogen energy with a goal of achieving a hydrogen society in 2040. To overcome an import-dependent energy problem, Korea has also researched the storage and utilization techniques of hydrogen energy. Since a hydrogen station has been initially built in Daedeok, it was established in the heart of Seoul in 2007. It is planning to build 1700 of hydrogen stations in the whole nation until 2020.

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A hydrogen sensor for detecting hydrogen leakage is indispensable in an era emerging hydrogen energy. Because hydrogen has a danger of ignition at concentrations of above 4% in atmosphere, the hydrogen sensor for sensing hydrogen leakage has to be developed as a key technique in all areas controlling

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hydrogen energy such as hydrogen storage or hydrogen delivery for common supply of hydrogen energy. The hydrogen sensor according to its use is classified into two types: one used in production process of hydrogen and the other used in detection of hydrogen leakage. The sensor for detecting hydrogen leakage is divided into a leakage sensor to detect a micro-leakage of hydrogen and a safety sensor to be operated where hydrogen concentration reaches at a particular level in a certain place. Particularly, stability and high confidence are required in the safety sensor because it should be operated for hydrogen where hydrogen leakage is potentially generated although long period is passed. The safety sensor's structure is convenient and its fabrication cost is low due to various and universal utilization of user classes.

On the other hand, the hydrogen sensor is classified into two types according to its operation principle: electrical sensor and photographical sensor. Photographical sensor is considerable as an ideal sensor in that it enables to detect hydrogen in a long distance and has no uneasiness to the safety because electrical circuit is not involved in sensor part. It will be very helpful in the expansion of hydrogen energy to prepare a hydrogen photosensor with briefer and higher credibility and safety. Therefore, the researches to improve the durability and reactivity of sensor thin film allow a sensor to possess high credibility and safety and permit to save its production cost where optical system is easily prepared using optical pick-up set in public CD or DVD with a cost of not more than 1,000 won per a unit.

The most active field in utilization of hydrogen energy is a motorcycle technology. In particular, the study to develop hydrogen fuel cell automobile is more actively processed. The development of hydrogen sensor technique for commercial service to hydrogen fuel cell automobile also has been extensively studied.

Professor Jenshan Lin and graduate students of Department of Electrical and Computer engineering in University of Florida developed a hydrogen microsensor to express an alarm using wireless communications after detecting hydrogen leakage.

The sensor to use a micro-involved energy source as power source could be not needed to replace the battery in a plurality of sensors for detecting hydrogen leakage, and be independently operated (5). The hydrogen sensor based on Pt-gate AlGaIn/GaN heterostructure diode hydrogen sensor is operated according to the method which the electric resistance is altered whereby it is contacted with hydrogen and is not necessary to supply an additional electric power due to energy supplement using microvibration. However, as shown in most sensors using a FET method, there are several problems such as gas selectivity and a circuit necessary to wireless communication placed at the same space with sensor.

10 In addition, the scientists of Argonne National Laboratory in USA have developed a flexible hydrogen sensor using a nanoparticle as a core part of hydrogen fuel-cell used in hydrogen automobile (6). The conventional hydrogen sensor used an inflexible Pd with high-purity of which cost is expensive, while a novel sensor was able to be flexible and was improved its fabrication cost and function using single-walled carbon nanotubes. The development of this sensor will be helpful in environmental and ecological manner and be expected to enhance much more safety and potential probability in hydrogen-based ecological system. The hydrogen sensor was fabricated according to two-step processes performed in high- and low-temperature. The carbon nanotube was deposited on the silicon substrate at 900°C using a chemical vapor deposition (CVD), and was then decorated on the plastic substrate at 150°C using a dry transfer printing. The delicate processes allowed carbon nanotube thin film to be formed on the plastic substrate and Pd nanoparticles to be deposited on the carbon nanotube, generating the sensor. Pd nanoparticle enhances interactions between hydrogen and carbon nanotube such that resistance of device may be changed according to exposure of hydrogen molecule on device. The sensors with excellent mechanical flexibility exhibited sensitivity (*i.e.*, the change of resistance) of ~75% for 0.05% hydrogen in air and response time of ~3 sec for 1% hydrogen at room temperature. The flexible

sensor is also operated in the same manner. In addition, it is advantageous in the senses that the plastic substrate reduces the sensor weight and prevents disruptions caused from impacts or mechanical alterations. Moreover, the sensors can enclose the flexible surface and apply to a variety of portable electric devices, automobiles or
5 airplanes. In particular, the sensor permits to prevent a major disaster by sensing very small amount of hydrogen leakage in a place such as spaceship. However, it is a problem to immediately sense hydrogen because the time to sense hydrogen is so long and is also problematic that the fabrication cost of the sensor is expensive, resulting in limitation in view of commercialization. Therefore, further studies have
10 been urgently demanded.

Throughout this application, various publications and patents are referred and citations are provided in parentheses. The disclosures of these publications and patents in their entities are hereby incorporated by references into this application in
15 order to fully describe this invention and the state of the art to which this invention pertains.

DETAILED DESCRIPTION OF THE INVENTION

The present inventors have made intensive studies to develop a hydrogen
20 sensor thin film and a hydrogen sensor having an improved durability. As results, we have discovered that the sensor with a catalytic layer comprising palladium (Pd) and platinum (Pt) has not only excellent durability but also remarkable sensitivity.

Accordingly, it is an object of this invention to provide a thin film for a hydrogen sensor.

25 It is another object of this invention to provide a hydrogen sensor.

It is still another object of this invention to provide a method for improving a durability of a thin film for a hydrogen sensor.

Other objects and advantages of the present invention will become apparent from the following detailed description together with the appended claims and drawings.

5 In one aspect of this invention, there is provided a thin film for a hydrogen sensor comprising (a) a gasochromic layer; and (b) a catalytic layer comprising palladium (Pb) and platinum (Pt) deposited on the gasochromic layer.

In another aspect of this invention, there is provided a hydrogen sensor comprising the thin film for the hydrogen sensor deposited on a substrate.

10 In still another aspect of this invention, there is provided a method for improving a durability of a thin film for a hydrogen sensor comprising the steps of:

(a) fabricating a gasochromic layer; and

(b) preparing the thin film for the hydrogen sensor by depositing a catalytic layer comprising a Pb and a Pt on the gasochromic layer.

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The present inventors have made intensive studies to develop a hydrogen sensor thin film and a hydrogen sensor having an improved durability. As results, we have discovered that the sensor with a catalytic layer comprising palladium (Pb) and platinum (Pt) has not only excellent durability but also remarkable sensitivity.

20 The present invention fundamentally senses hydrogen gas according to gasochromism. Any one of materials representing gasochromism may be used in the gasochromic layer in the thin film of the present invention.

According to a preferable embodiment, the gasochromic layer includes (i) a transition metal oxide selected from the group consisting of tungsten oxide, tungstate, nioboxide, molybden oxide, molybdate, nickel oxide, titanium oxide, banadium oxide, iridium oxide, manganese oxide, cobalt oxide and a mixture thereof; (ii) a metal hydride selected from the group consisting of $\text{La}_{1-z}\text{Mg}_z\text{H}_x$, $\text{Y}_{1-z}\text{Mg}_z\text{H}_x$, $\text{Gd}_{1-z}\text{Mg}_z\text{H}_x$, Yb_b , LaH_b , SmH_b , NiMg_2H_x , CoMg_2H_x and the mixture thereof [z

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represents 0-1; x represents 0-5; and b represents 0-3]; or (iii) a switching polymer selected from the group consisting of polyviologen, polythiophene, polyanilin and prussian blue.

5 More preferably, the gasochromic layer includes the transition metal oxide selected from the group consisting of tungsten oxide, tungstate, nioboxide, molybden oxide, molybdate, nickel oxide, titanium oxide, vanadium oxide, iridium oxide, manganese oxide, cobalt oxide and the mixture thereof.

Much more preferably, the gasochromic layer is tungsten oxide, and most preferably WO_3 .

10 It is one of most features of this invention that the catalytic layer consists of Pb and Pt. Generally, Pb and Pt may be involved in the catalytic layer using two methods:

According to the first method, the catalytic layer includes a Pb layer and a Pt layer.

15 According to the second method, the catalytic layer includes a Pb-Pt alloy layer.

Of them, the second method is preferable in view of durability and sensitivity.

Pb and Pt in the thin film for the hydrogen sensor of this invention may be deposited on the gasochromic layer according to various methods, preferably a reactive sputtering method and more preferably a RF (radio frequency) or a DC sputtering method.

The content of Pb and Pt involved in the catalytic layer preferably is 20-50 wt% and 50-80 wt%, and more preferably 30-40 wt% and 60-70 wt%, respectively.

25 The substrate on which the thin film of this invention is coated includes any one of substrates used in the sensors known to those skilled in the art. For example, the substrate is selected from the group consisting of silicone, glass, quartz, fused silica, stainless steel, mica, carbon, carbon nanotube, polymer, ceramic and porcelain enamel.

The features and advantages of the present invention will be summarized as follows:

(i) The hydrogen sensor of this invention is based on the gasochromism and includes Pb and Pt in the gasochromic layer.

(ii) The hydrogen sensor of this invention represents much more improved durability having its reactivity in above 1000 cycles.

(iii) The hydrogen sensor of this invention represents much more enhanced sensitivity.

(iv) The hydrogen sensor of this invention for safe utilization of hydrogen energy may be used in a photosensor for sensing a hydrogen leakage, and be also promising in its marketability in the senses that the hydrogen energy as an alternative powerful energy source is widely used.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 schematically represents an embodiment of the present thin film for a hydrogen sensor. The thin film for the hydrogen sensor represents a gasochromic material which is divided into a catalytic layer and a gasochromic layer. Tungsten oxide layer in the thin film for sensor is deposited on the substrate according to a sputtering method and then the catalytic layer is fabricated by an alloy sputtering Pb and Pt simultaneously. The catalytic layer is a part contacting with hydrogen in atmosphere and hydrogen gas on the thin film is disassociated into hydrogen cation and electron by catalyzer after contacting with the catalytic layer. Dissociated ions are diffused by Pb involved in the catalytic layer and are transferred to the chromic layer. The light is absorbed into the gasochromic layer through small polaron transition whereby ionic bond of tungsten is partially reduced by the transferred ions. The thin film absorbing the light is darkly changed due to properties of tungsten

oxide, a cathodic gasochromic material and hydrogen photosensor is fabricated by measuring its optical transmittance and reflection.

Fig. 2 is a graph representing changes of Raman Spectra before and after hydrogen injection. (a) Pd/ α -WO₃, (b) Pd-Pt/ α -WO₃.

5 Fig. 3 is a graph representing changes of optical transmittance at an early cycling of heat-deposited Pd/ α -WO₃ and after 300 cycles of thermal-deposited Pd/ α -WO₃.

Fig. 4 is a graph representing changes of optical transmittance at an early cycling of sputtered Pd/ α -WO₃ and after 300 cycles of sputtered Pd/ α -WO₃.

10 Fig. 5 is a graph representing changes of optical transmittance at an early cycling of the present Pd/ α -WO₃ and after 300 cycles of the present Pd/ α -WO₃.

Fig. 6 is a graph representing changes of optical transmittance by the repetitive cycles of heat-deposited Pd/ α -WO₃.

15 Fig. 7 is a graph representing changes of optical transmittance by the repetitive cycles of sputtered Pd/ α -WO₃.

Fig. 8 is a graph representing changes of optical transmittance by the repetitive cycles of the present Pd/ α -WO₃.

20 The present invention will now be described in further detail by examples. It would be obvious to those skilled in the art that these examples are intended to be more concretely illustrative and the scope of the present invention as set forth in the appended claims is not limited to or by the examples.

EXAMPLES

25 Materials and Methods

Electrochromic material refers to substances that their colors are changed by injection or extraction of electric charge (cation ions or electrons) (1). Based on the fact that electrochromism is generated where ions and electrons is injected and

extracted to the thin film such as WO_3 , gasochromism by hydrogen gas has been studied (2) and the possibility to apply optical sensor for detecting hydrogen has been intensively researched (3). A representative gasochromic material is $\text{Pd}/\alpha\text{-WO}_3$ double layer thin film. Pd deposited on the WO_3 functions a catalyst material decomposing hydrogen molecule into proton and electron. Because the color of the gasochromic material is changed by contacting with hydrogen gas, hydrogen leakage could be detected by measuring the changes of its optical transmittance. Because the optical sensor for detecting hydrogen gas measures the optical transmittance of the material in an optical manner, there are diverse advantages such as (i) exclusion of electrical spark by no use of the electric current at the position of sensor material and (ii) remote detection to hydrogen by separation of sensor part and control part using optical fibers. In an optical fiber sensor for detecting hydrogen, its operation is much more stable than that of electrical sensor in that the loss in optical fiber is rare and the interference by external electromagnetic wave is not occurred (4). To apply the sensor as safety sensor detecting hydrogen for a long period, high durability in addition to hydrogen reactivity is demanded. However, in $\text{Pd}/\alpha\text{-WO}_3$ sensor, $\text{Pd}/\alpha\text{-WO}_3$ thin film is deteriorated where it is repeatedly exposed to hydrogen and the sensitivity of sensor thin film is rapidly decreased where the surface of Pd thin film is exposed in air for a long period.

Therefore, the studies to improve the durability of thin film material of sensor are compelled. In this invention, $\text{Pd-Pt}/\alpha\text{-WO}_3$ was prepared using a sputtering method to fabricate hydrogen photosensor with improved durability, and its reactivity and durability depending on exposure to hydrogen were examined using Raman spectroscopy and optical transmittance. Based on the experimental results, application possibility was tested by preparing a prototype of photosensor for detecting hydrogen.

The present inventors have intensively studied to optimize the combination of sensor thin film and catalytic thin film using a reactive sputtering method for

preparing the sensor thin film with more excellent durability and with more improved cycling compared with the conventional thin films. α -WO₃ electrochromic thin film was fabricated using RF (radio frequency) and DC sputtering method, and Pd as the catalytic thin film was deposited on its surface. As results, Pd/ α -WO₃ thin film
5 optimizerized to hydrogen response was prepared by various combinations of the thickness ratio of sensor thin film to catalytic thin film. In addition, Pt/Pd/ α -WO₃ double layer thin film and Pd-Pt/ α -WO₃ were prepared to enhance the durability of thin film. To prepare α -WO₃ layer, RF sputtering method was carried out by regulating O₂ flux in Ar gas substrate using tungsten target. Pd layer was prepared
10 according to DC sputtering method using Pd target. Pt/Pd/ α -WO₃ double layer catalytic thin film was fabricated according to the RF sputtering method utilizing Pt layer on the above-described Pd/ α -WO₃ as Pt target. Pd-Pt alloy thin film was prepared according to a co-sputtering method which two materials are simultaneously deposited using a multi-target sputtering system. The physical
15 property of the thin films was investigated by measurement of their Raman spectra depending on exposure to hydrogen and air. To test improved durability, the change of optical transmittance was measured by repeatedly exposing the sensor thin films to 1% hydrogen and air.

20 **Results**

Pd-Pt/ α -WO₃ Preparation

Pd-Pt/ α -WO₃ was prepared using DC & RF sputtering chamber (Korea Vacuum Tech., Ltd.) with multi-target system. To prepare Pd-Pt/ α -WO₃ alloy catalytic thin film, α -WO₃ was deposited on the substrate via RF sputtering with 80 of RF POWER for
25 120 min after 2×10^{-6} torr of Working pressure was given to tungsten target in the flux of 8 sccm of Ar gas and 0.4 sccm of O₂ gas according to the reactive sputtering method. Each slide glass and stainless steel was used as the substrate for testing optical transmittance and measuring *in-situ* Raman spectroscopy. The target used in

the present invention was tungsten target with 99.9% purity (Asem Tech., Co.). Since the multi-target system could utilize Pd and Pt target simultaneous, Pd-Pt alloy thin film was deposited on the above-prepared α -WO₃ using co-sputtering method after each Pd and Pt target was equipped in DC sputter gun and RF sputter gun. The co-sputtering method is a method which simultaneously deposits two materials on single substrate by concurrently sputtering two or more targets. In the present invention, it was carried out on the substrate in the flux of 5 sccm of Ar gas, in which Pd and Pt targets (Asem Tech., Co.) with 99.9% purity were used. Pd target was deposited for 3 min in a range of from 0.05 A to 0.1 A of DC POWER and Pt target was deposited for 3 min at 40 V of RF POWER. In addition, the composition of alloy measured using EPMA (Electron Probe Micro Analyzer, Japan JEOL Co., JXA-8900R) was 32% of Pd and 68% of Pt.

Based on the results to compare *in-situ* Raman spectrum of Pd-Pt/ α -WO₃ with that of Pd/ α -WO₃ for, W⁵⁺=O bond was shifted to W⁶⁺=O before and after hydrogen injection, demonstrating that gasochromic phenomenon of Pd-Pt/ α -WO₃ is similar to that of Pd/ α -WO₃ (Fig. 2).

Measurement of Optical Transmittance Change of Pd-Pt/ α -WO₃

Optical transmittance was measured in the condition of hydrogen injection for practical application of Pd-Pt/ α -WO₃ as a sensor material. Artificial air containing 1% of hydrogen, 80% of nitrogen and 20% oxygen was repetitively injected for predetermined period at a rate of 2,000 sccm and then the optical transmittance of Pd-Pt/ α -WO₃ was measured. In comparison with heat-deposited Pd-Pt/ α -WO₃, sputtered Pd-Pt/ α -WO₃ and Pd-Pt/ α -WO₃, the present inventors demonstrated that in others except heat deposition, each response time was within 1 sec and optical transmittance lowed by hydrogen injection was more rapidly restored where hydrogen injection was finished and then oxygen was injected. In injection of each hydrogen and oxygen for 60 sec per a cycle, it could be appreciated that the

decrease and restoration of optical transmittance was improved in alloy even after 500 cycles. These results demonstrated that irrespective of contacting with hydrogen for a long period, the operation of the decrease and restoration of optical transmittance to hydrogen response is more excellent in the present invention than
5 in a conventional method (Figs. 3-5).

Durability Measurement of Pd-Pt/ α -WO₃

The present inventors investigated changes of optical transmittance according to repetitive cycling. The durability of heat-deposited Pd-Pt/ α -WO₃ is lower than that
10 of sputtered Pd-Pt/ α -WO₃. Continuous changes of optical transmittance were observed in sputtered Pd-Pt/ α -WO₃ even and in Pd-Pt/ α -WO₃ even after 500 cycling and above 1,200 cycling, respectively (Figs. 6-8), suggesting that the durability of sensor thin film comprising the alloy is improved as compared with that of a conventional Pd/ α -WO₃. In addition, the catalytic activity of alloy layer permits the
15 present thin film to enhance the resistance potential to contaminant materials. As shown in changes of optical transmittance, its change in Pd/ α -WO₃ was about 35% while that in Pd-Pt/ α -WO₃ was not less than about 80%, representing that the catalytic layer including Pd and Pt is more effective than that including only Pd. Accordingly, the durability and sensitivity of Pd-Pt/ α -WO₃ was improved much higher
20 than that of Pd/ α -WO₃ prepared by the conventional sputtering method because the change of α -WO₃, the gasochromic layer, was remarkably facilitated via efficient decomposition of hydrogen by Pt.

Having described a preferred embodiment of the present invention, it is to be
25 understood that variants and modifications thereof falling within the spirit of the invention may become apparent to those skilled in this art, and the scope of this invention is to be determined by appended claims and their equivalents.

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What is claimed is:

1. A thin film for a hydrogen sensor comprising (a) a gasochromic layer; and (b) a catalytic layer comprising palladium (Pd) and platinum (Pt) deposited on the gasochromic layer.
2. The thin film for the hydrogen sensor according to claim 1, wherein the gasochromic layer comprises (i) a transition metal oxide selected from the group consisting of tungsten oxide, tungstate, nioboxide, molybden oxide, molybdate, nickel oxide, titanium oxide, vanadium oxide, iridium oxide, manganese oxide, cobalt oxide and a mixture thereof; (ii) a metal hydride selected from the group consisting of $\text{La}_{1-z}\text{Mg}_z\text{H}_x$, $\text{Y}_{1-z}\text{Mg}_z\text{H}_x$, $\text{Gd}_{1-z}\text{Mg}_z\text{H}_x$, Yb_b , LaH_b , SmH_b , NiMg_2H_x , CoMg_2H_x and the mixture thereof [z represents 0-1; x represents 0-5; and b represents 0-3]; or (iii) a switching polymer selected from the group consisting of polyaniline, polythiophene, polyaniline and prussian blue.
3. The thin film for the hydrogen sensor according to claim 2, wherein the gasochromic layer comprises the transition metal oxide selected from the group consisting of tungsten oxide, tungstate, nioboxide, molybden oxide, molybdate, nickel oxide, titanium oxide, vanadium oxide, iridium oxide, manganese oxide, cobalt oxide and the mixture thereof.
4. The thin film for the hydrogen sensor according to claim 1, wherein the catalytic layer comprises a Pd layer and a Pt layer.
5. The thin film for the hydrogen sensor according to claim 1, wherein the catalytic layer comprises a Pd-Pt alloy layer.
6. The thin film for the hydrogen sensor according to claim 1, wherein the

catalytic layer is deposited on the gasochromic layer using a reactive sputtering method.

7. The thin film for the hydrogen sensor according to claim 6, wherein the
5 reactive sputtering method is a RF (radio frequency) method or a DC sputtering method.

8. The thin film for the hydrogen sensor according to claim 1, wherein the
10 catalytic layer comprises 20-50 wt% of Pb and 50-80 wt% of Pt.

9. A hydrogen sensor comprising the thin film for the hydrogen sensor according
to any one of claims 1-8 deposited on a substrate.

10. The hydrogen sensor according to claim 9, wherein the substrate is selected
15 from the group consisting of silicone, glass, quartz, fused silica, stainless steel, mica, carbon, carbon nanotube, polymer, ceramic and porcelain enamel.

11. A method for improving a durability of a thin film for a hydrogen sensor
comprising the steps of:

20 (a) fabricating a gasochromic layer; and
(b) preparing the thin film for the hydrogen sensor by depositing a catalytic layer comprising a Pb and a Pt on the gasochromic layer.

12. The method according to claim 11, wherein the gasochromic layer comprises
25 (i) a transition metal oxide selected from the group consisting of tungsten oxide, tungstate, nioboxide, molybden oxide, molybdate, nickel oxide, titanium oxide, banadium oxide, iridium oxide, manganese oxide, cobalt oxide and the mixture thereof; (ii) a metal hydride selected from the group consisting of $\text{La}_{1-z}\text{Mg}_z\text{H}_x$, Y_{1-z}

$z\text{Mg}_z\text{H}_x$, $\text{Gd}_{1-z}\text{Mg}_z\text{H}_x$, Yb_b , LaH_b , SmH_b , NiMg_2H_x , CoMg_2H_x and the mixture thereof [z represents 0-1; x represents 0-5; and b represents 0-3]; or (iii) a switching polymer selected from the group consisting of polyviologen, polythiophene, polyanilin and prussian blue.

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13. The method according to claim 12, wherein the gasochromic layer comprises the transition metal oxide selected from the group consisting of tungsten oxide, tungstate, nioboxide, molybden oxide, molybdate, nickel oxide, titanium oxide, banadium oxide, iridium oxide, manganese oxide, cobalt oxide and mixtures thereof.

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14. The method according to claim 11, wherein the catalytic layer comprises the Pb layer and the Pt layer.

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15. The method according to claim 11, wherein the catalytic layer comprises the Pb-Pt alloy layer.

16. The method according to claim 11, wherein the catalytic layer is deposited on the gasochromic layer using the reactive sputtering method.

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17. The method according to claim 16, wherein the reactive sputtering method comprises the RF (radio frequency) or the DC sputtering method.

18. The method according to claim 11, wherein the catalytic layer comprises 20-50 wt% of Pb and 50-80 wt% of Pt.

25

Fig. 1

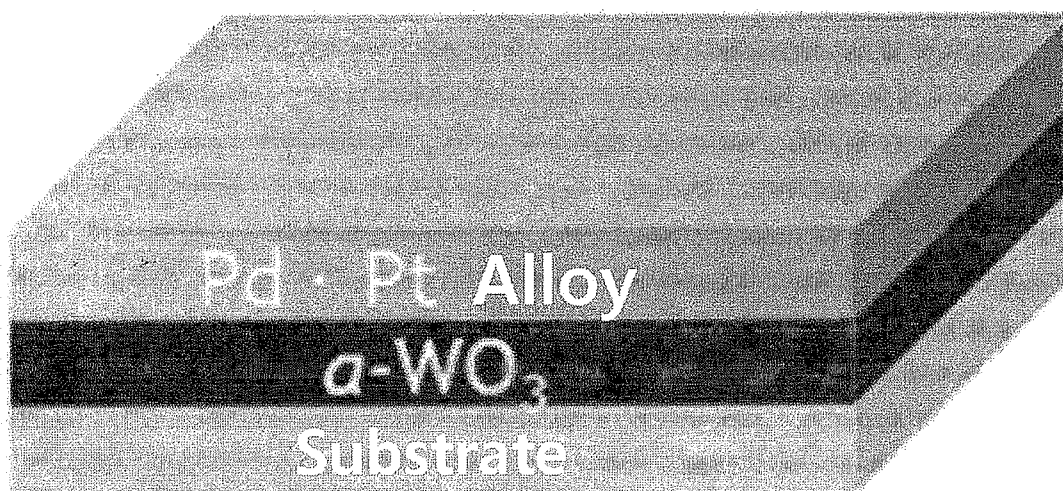


Fig. 2

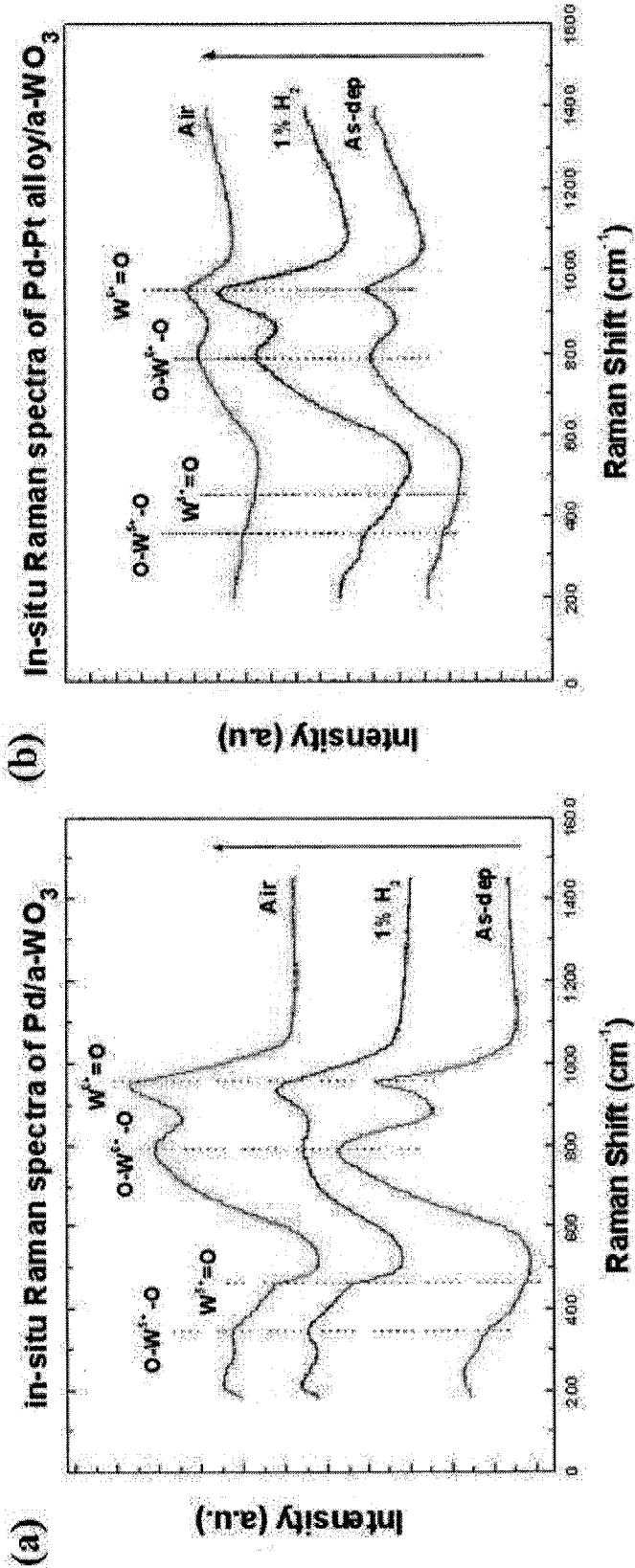


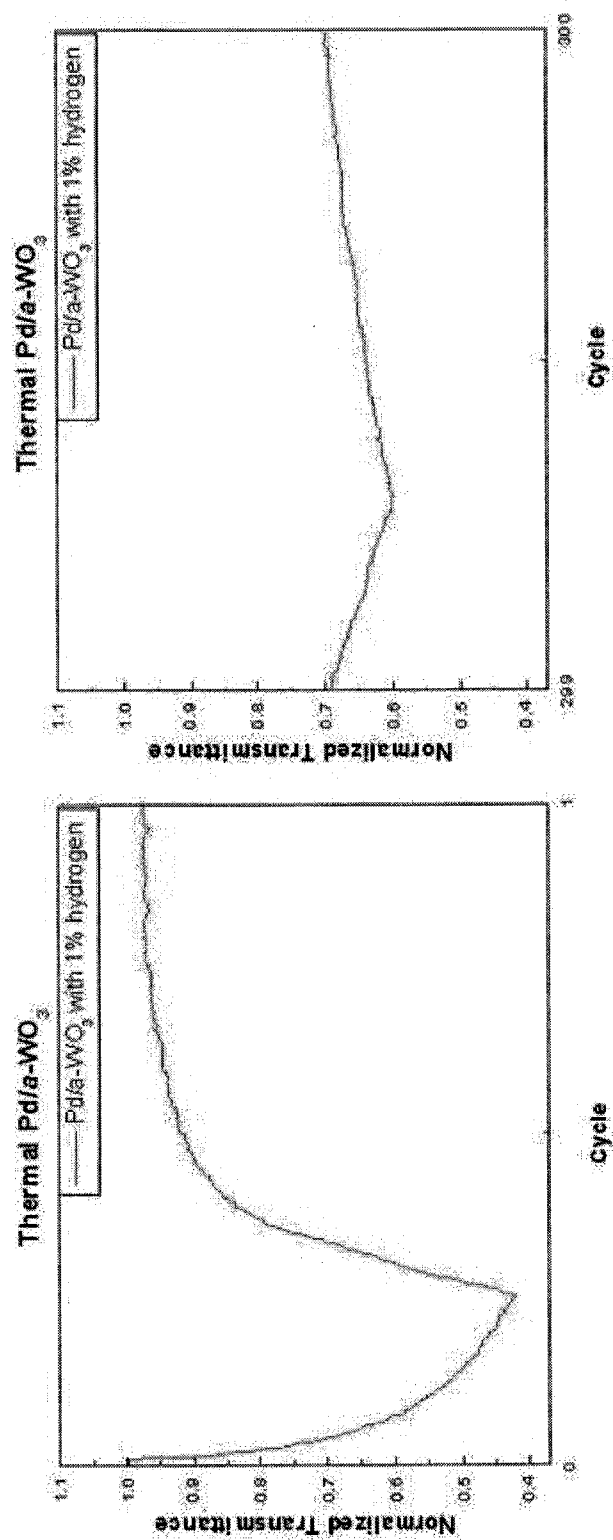
Fig. 3

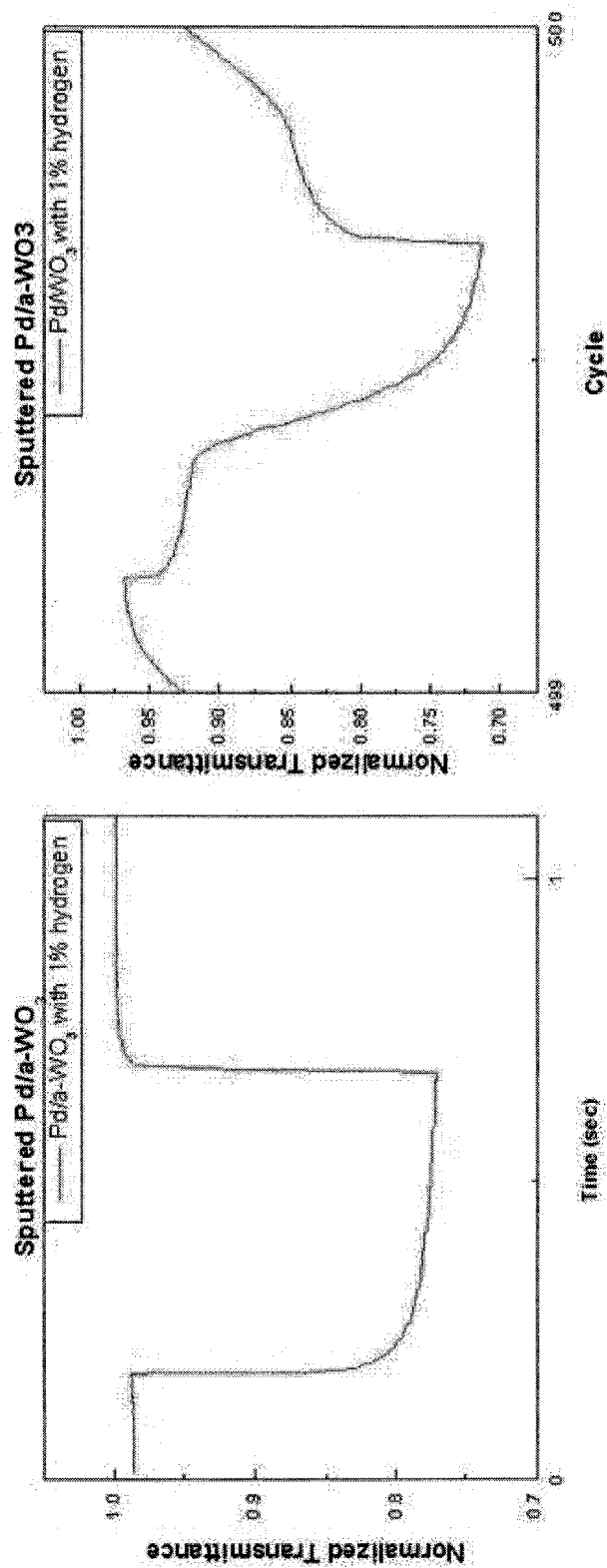
Fig. 4

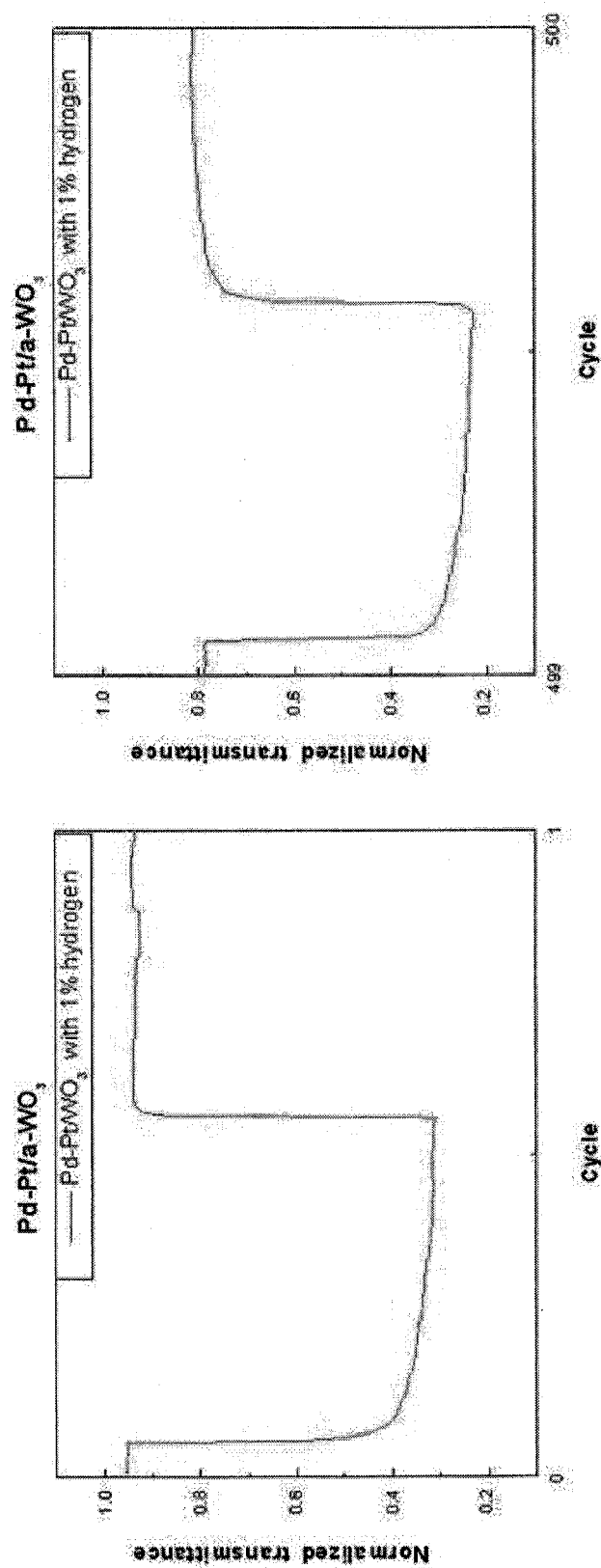
Fig. 5

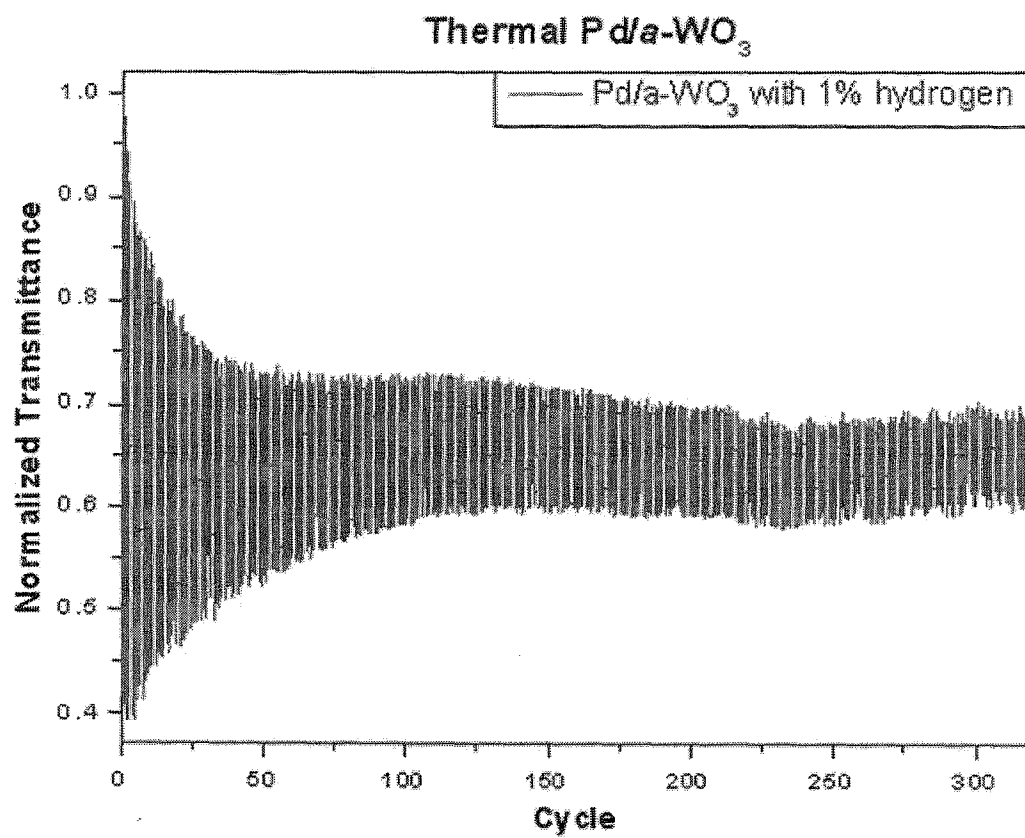
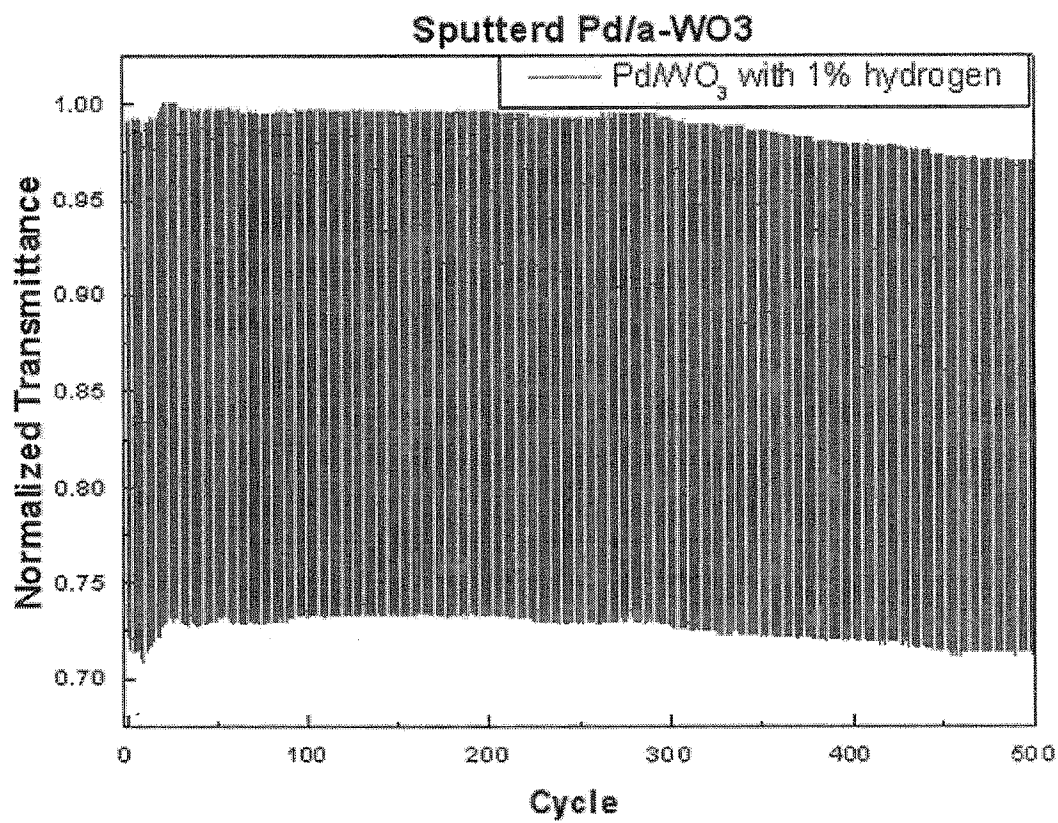
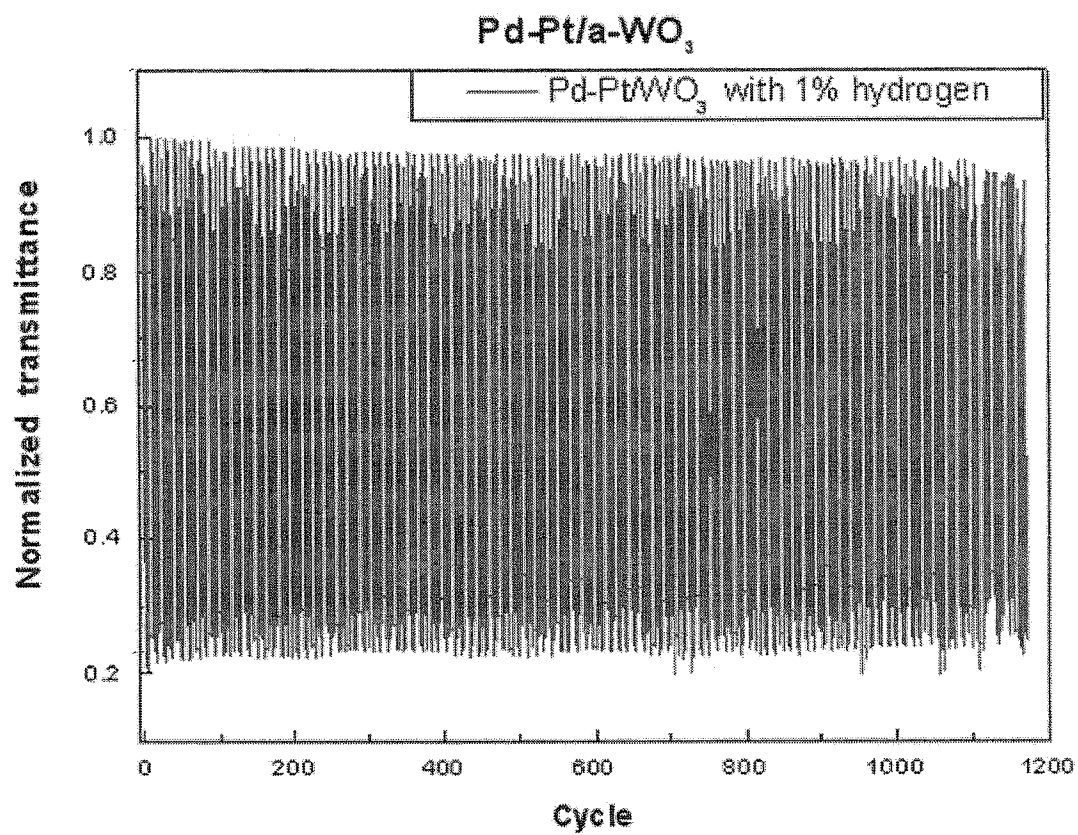
Fig. 6

Fig. 7

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Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2008/006324**A. CLASSIFICATION OF SUBJECT MATTER****G01N 27/12(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC G01N 27/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

D/B : eKIPASS

KEY WORD : Gasochromic layer, Hydrogen sensor, Thin film

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 7233034 B2 (Ping Liu et al.) 19 JUN. 2007 see column 3 line 66 - column 5 line 15; figures 1	1, 4-5, 9-11, 14-15
A	US 2004-23595 A1 (Ping Liu et al.) 5 FEB. 2004 see the whole document	1-18
A	US 6723566 B2 (Lee Se Hee et al) 20 APR. 2004 see the whole document	1-18
A	Transactions of the Korean Hydrogen and New Energy Society vol.16(1): 9-16 (Cheong Hyeon-Sik et al.) DEC. 2005 "Optical Hydrogen Sensor Based on Gasochromic RuO ₂ .xH ₂ O Thin Film" see the whole document -----END OF DOCUMENT-----	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

27 MAY 2009 (27.05.2009)

Date of mailing of the international search report

27 MAY 2009 (27.05.2009)

Name and mailing address of the ISA/KR

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Authorized officer

CHOI, SOK JIN

Telephone No. 82-42-481-8472



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2008/006324

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7233034 B2	19.06.2007	US 2007-039372 A1	22.02.2007
US 6723566 B2	20.04.2004	EP 1279030 A2 US 2004-0037745 A1	29.01.2003 26.02.2004
US 2004-23595 A1	05.02.2004	NONE	