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- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: SENSORS AND SWITCHES FOR DETECTING HYDROGEN

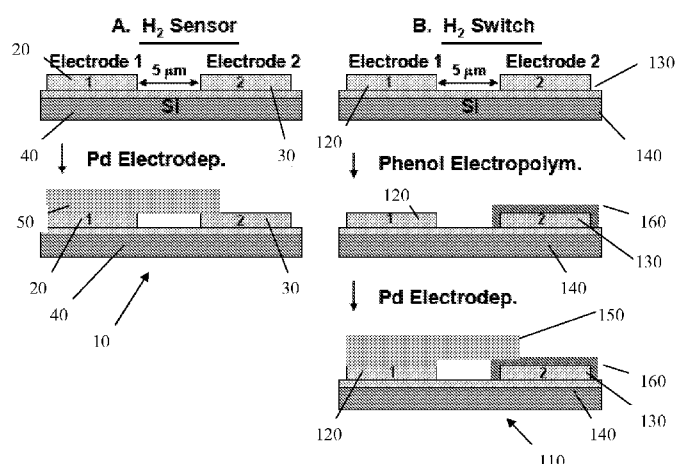


FIG. 1

(57) **Abstract:** Sensors and switches for detecting hydrogen include an electrically-insulating support; a first and second electrode; and a palladium structure alone or in combination with an organic insulating film. The palladium structures of the sensors are deposited on and contact a first electrode and a portion of the palladium structure extends to and contacts the second electrode to create a conductive path. The palladium structures of the switches are deposited on and contact a first electrode and a portion of the palladium structures extend to and contact an organic insulating film deposited on the second electrode. Upon exposure of the switch to hydrogen, portions of the palladium structure extend through the film and contact the second electrode to create a conductive path. Methods of detecting hydrogen and methods of fabricating a sensor for detecting an analyte of interest are also provided.

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SENSORS AND SWITCHES FOR DETECTING HYDROGEN

RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Serial No. 61/109,812, filed October 30, 2008, the entire disclosure of which is incorporated herein by this reference.

GOVERNMENT INTEREST

[0002] Subject matter described herein was made with U.S. Government support under Grant Number CHE-0518561 awarded by the National Science Foundation. The government has certain rights in the described subject matter.

TECHNICAL FIELD

[0003] The presently-disclosed subject matter relates to sensors and switches for detecting hydrogen, as well as methods of making and using the same. In particular, the presently-disclosed subject matter relates to sensors and switches for detecting hydrogen that make use of palladium structures alone or in combination with an organic insulating film. The presently-disclosed subject matter further describes methods of fabricating a sensor for detecting an analyte of interest whereby metal/organic/metal junctions are produced.

BACKGROUND AND GENERAL CONSIDERATIONS

[0004] Hydrogen (H₂) is a useful energy source that has the potential to reduce the need for fossil fuels in the future, and may someday replace or serve as an important alternative to the current fossil-based transportation fuels [9-11]. Indeed, a great deal of effort has been put forth to develop H₂-fueled motor vehicles in order to fulfill increasing energy demands for transportation. Also, H₂ is present as a common reagent in industry and is used as an O₂ scavenger in metallurgy, in hydrocracking for refined fuels, and in degradation of synthetic

materials. However, utilizing H_2 can be dangerous, as H_2 has one of the lowest flash points ($-253^\circ C$) of any energy source, making it highly explosive in air above 4 % H_2 by volume [12]. Accordingly, one of the aims in fuel cell research is to safely store and release H_2 in a controlled manner. For these reasons, it is important to develop simple, reliable, low-cost sensors for the detection of H_2 over a range of concentrations.

[0005] Previously, arrays of palladium (Pd) mesowires have been synthesized by electrochemical deposition of Pd on the step-edges of highly-oriented pyrolytic graphite (HOPG), and the resistance change of these arrays in the presence of H_2 has been examined after the arrays were transferred to a glass substrate and electrical contacts to the arrays were made [1,2]. In contrast to most Pd-based H_2 sensing devices, which exhibit an increase in resistance in the presence of H_2 due to the formation of the more resistive PdH_x [3,4], the Pd mesowire arrays exhibited a significant decrease in resistance due to the formation of break junctions within the mesowires upon volume expansion of the PdH_x [1,2]. These devices quantitatively detected H_2 from 2 to 10% reversibly with 75 ms response times.

[0006] H_2 sensing has also been performed with films of Pd nanoparticles prepared by physical deposition or chemical methods [5,6]. However, these Pd nanoparticle-based sensors also contain nanoscale gaps and operate on similar principles as the mesowire array [1,2]. Other nanoscale materials used for H_2 sensing include carbon [7] and Pd nanotubes [8], which operate on different principles, but display low detection limits.

[0007] In any event, known methods and devices for detecting H_2 are only capable of detecting H_2 after assembling various sensors in a complicated multi-step process involving synthesis, assembly, and contact formation, or are only capable of assembling sensors that are unable to be constructed in a highly parallel fashion or with a near 100% success rate. Furthermore, none of the known methods and devices for detecting H_2 have sufficiently provided a sensor whereby metal electrodeposition is used to make direct contact between a

deposited metal and one or more electrodes, which is of great importance in eliminating the need for multi-step processes involving synthesis, assembly, and contact formation.

SUMMARY

[0008] This summary describes several embodiments of the presently-disclosed subject matter, and, in many cases, lists variations and permutations of these embodiments. This summary is merely exemplary of the numerous and varied embodiments. Mention of one or more representative features of a given embodiment is likewise exemplary. Such an embodiment can typically exist with or without the feature(s) mentioned; likewise, those features can be applied to other embodiments of the presently-disclosed subject matter, whether listed in this summary or not. To avoid excessive repetition, this summary does not list or suggest all possible combinations of such features.

[0009] The presently-disclosed subject matter includes sensors and switches for detecting hydrogen (H_2), as well as methods of making and using the same, that make use of palladium (Pd) structures alone or in combination with an organic insulating film.

[0010] In some embodiments, a sensor for detecting H_2 is provided that includes an electrically-insulating support; a first electrode and a second electrode that are positioned at a distance from one another and affixed to the support; and a Pd structure that is deposited on and contacts the first electrode such that at least a portion of the Pd structure extends to and contacts the second electrode, thus creating a conductive path between the first electrode and the second electrode. In some embodiments, the Pd structure that is deposited on the first electrode is electrochemically deposited on the first electrode.

[0011] In some embodiments, the sensors for detecting H_2 disclosed herein are used in a method of detecting H_2 in a gas sample by: providing a sensor in accordance with the presently-disclosed subject matter; applying a voltage potential along the conductive path between the first electrode and the second electrode of the sensor; exposing the sensor to the

gas sample; and then detecting any decreases in conductivity along the conductive path between the first electrode and the second electrode to thereby detect H₂ in the gas sample.

In some embodiments of the methods for detecting H₂ disclosed herein, an exemplary sensor for detecting H₂ is used to detect a concentration of H₂ in a gas sample of as low as 0.11%.

[0012] Further provided, in some embodiments of the presently-disclosed subject matter, are switches for detecting H₂. In some embodiments, a switch for detecting H₂ is provided that includes an electrically-insulating support; a first electrode and a second electrode that are positioned at a distance from one another and affixed to the support; an organic insulating film that is deposited on the second electrode; and a Pd structure that is deposited on and contacts the first electrode such that at least a portion of the Pd structure extends to and contacts the organic insulating film. In some embodiments, upon exposure of an exemplary switch to H₂, the portion of the Pd structure, which is in contact with the organic insulating film, extends through the organic insulating film and contacts the second electrode to create a conductive path between the first electrode and the second electrode.

[0013] In some embodiments, the Pd structure that is deposited on the first electrode of an exemplary switch is electrochemically deposited on the first electrode. Further, in some embodiments, the organic insulating film that is deposited on the second electrode is deposited on the second electrode by electropolymerization. In some embodiments, the organic insulating film of an exemplary switch is comprised of phenol, aniline, pyrole, or combinations thereof. For example, in some embodiments, electropolymerizing phenol on the second electrode of an exemplary switch creates an organic insulating film on the second electrode that is a polyphenol film.

[0014] Similar to the sensors for detecting H₂ discussed above, in some embodiments, the switches for detecting H₂ disclosed herein can be used in a method of detecting H₂ in a gas sample. In some embodiments, a method of detecting H₂ in a sample includes providing a

switch for detecting H₂ in accordance with the presently-disclosed subject matter; applying a voltage potential between the first electrode and the second electrode; exposing the switch to a gas sample; and then detecting a current between the first electrode and the second electrode to thereby detect H₂ in the gas sample. In some embodiments of the methods for detecting H₂ disclosed herein, an exemplary switch for detecting hydrogen can be used to detect a concentration of H₂ in a gas sample of as low as 1.0%.

[0015] With regard to the electrodes of the exemplary sensors and switches for detecting H₂ disclosed herein, in some embodiments, the electrodes can include multiple fingers that can be aligned parallel with one another such that the first and second electrode are in an interdigitated configuration. In some embodiments of the presently-disclosed sensors and switches for detecting H₂, the distance between the first electrode and the second electrode is about 5 micrometers.

[0016] Still further provided, in some embodiments of the presently-disclosed subject matter, are methods for fabricating a sensor that is capable of detecting an analyte of interest. In some embodiments, a method of fabricating a sensor for detecting an analyte of interest is provided that comprises positioning a first electrode and a second electrode at a distance from one another on an electrically-insulating support; electropolymerizing a compound capable of producing an organic insulating film on the second electrode attached to the support; and electrodepositing a metal on the first electrode attached to the support such that at least a portion of the metal extends to and contacts the organic insulating film.

[0017] In some embodiments of the methods for fabricating a sensor disclosed herein, the metal electrodeposited on the first electrode is selected from silver (Ag), Pd, or combinations thereof. Further, in some embodiments, the compound capable of producing the organic insulating film is selected from phenol, aniline, pyrole, or combinations thereof. In some

embodiments, the compound is phenol, such that the organic insulating film that is deposited on the second electrode is a polyphenol film.

[0018] In some embodiments of the presently-disclosed methods for fabricating a sensor, a method for fabricating a sensor for detecting an analyte of interest is provided that further comprises the step of varying a thickness of the organic insulating film to change a response and a recovery time of the sensor. In some embodiments, varying the thickness of the organic insulating film is accomplished by varying a number of electropolymerization cycles.

[0019] Advantages of the presently-disclosed subject matter will become evident to those of ordinary skill in the art after a study of the description, Figures, and non-limiting Examples in this document.

DESCRIPTION OF THE DRAWINGS

[0020] FIGS. 1A and 1B are schematic diagrams showing an exemplary method for fabricating sensors for detecting hydrogen (“H₂ sensors”; FIG. 1A) and switches for detecting hydrogen (“H₂ switches”; FIG. 1B) in accordance with the presently-disclosed subject matter.

[0021] FIGS. 2A and 2B are scanning electron microscope (SEM) images of an exemplary H₂ sensor (FIG. 2A) and an exemplary H₂ switch fabricated with 10 cycles of polyphenol (FIG. 2B).

[0022] FIGS. 3A-3D are SEM images of the circled portions of the exemplary H₂ sensor shown in FIG. 2A and the exemplary H₂ switch shown in FIG. 2B (FIGS. 3A and 3B, respectively), as well as corresponding current-voltage (i-V) curves for the exemplary H₂ sensor (FIG. 3C) and H₂ switch (FIG. 3D).

[0023] FIGS. 4A and 4B are graphs showing current-time plots for an exemplary H₂ sensor (FIG. 4A) and an exemplary H₂ switch (FIG. 4B).

[0024] FIGS. 5A-5F are SEM images of exemplary H₂ switches fabricated with 10 cycles of phenol, including: a perspective view of an entire H₂ switch (FIG. 5A); an expanded view

of a Pd structure (FIG. 5B); a top view of a single Pd structure (FIG. 5C) as compared to a side view of a Pd structure showing its proximity with a polyphenol layer on a second electrode (FIG. 5D); and, a side view of another exemplary H₂ switch (FIG. 5E) and an expanded image of the region depicted by the dashed box in FIG. 5E (FIG. 5F).

[0025] FIGS. 6A and 6B are graphs showing current-time plots of an exemplary H₂ sensor (FIG. 6A) and an exemplary H₂ switch (FIG. 6B) measured at -0.3 V in the presence of N₂ initially and in the presence of various concentrations of H₂ (H₂ “on”, •) and 100 % N₂ (H₂ “off”, °), as indicated.

[0026] FIGS. 7A and 7B are graphs showing the percent response versus H₂ concentration for various H₂ sensors over the entire range of 0.11 to 9.6 % H₂ (FIG. 7A) and over the linear range of 0.11 to 0.78 % H₂. The percent response was defined as $(i_t - i_b)/i_b \times 100$, where i_t is the current in the presence of H₂ and i_b is the baseline current in the presence of N₂ before exposure to H₂.

[0027] FIGS. 8A and 8B are graphs showing current-time plots for H₂ switches fabricated with 10 cycles of phenol (FIG. 8A) at 1 % H₂, and a different H₂ switch showing shorter response and recovery times at various concentrations of H₂ measured at -0.3 V in the presence of N₂ initially and in the presence of various concentrations of H₂ (H₂ “on”, •) and 100 % N₂ (H₂ “off”, °), as indicated.

[0028] FIGS. 9A and 9B are an atomic force microscopy (AFM) image showing a portion of an electrode with electrodeposited polyphenol after scratching away an area of the polyphenol film (FIG. 9A) and a graph showing the cross-sectional analysis of the scratched area of the polyphenol film showing that the thickness is approximately 5.9 nm in that area.

[0029] FIGS. 10A and 10B are schematic diagrams showing the mechanisms involved in an exemplary H₂ sensor (FIG. 10A) and an exemplary H₂ switch (FIG. 10B).

[0030] FIGS. 11A and 11B are graphs showing current-time plots for H₂ switches with a polyphenol film electrodeposited on a second electrode with 4 cycles of phenol (FIG. 11A) and with 5 cycles of phenol (FIG. 11B), measured at -0.3 V in the presence of N₂ initially and in the presence of various concentrations of H₂ (H₂ “on”, •) and 100 % N₂ (H₂ “off”, °), as indicated.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0031] The details of one or more embodiments of the presently-disclosed subject matter are set forth in this document. Modifications to embodiments described in this document, and other embodiments, will be evident to those of ordinary skill in the art after a study of the information provided in this document. The information provided in this document, and particularly the specific details of the described exemplary embodiments, is provided primarily for clearness of understanding and no unnecessary limitations are to be understood therefrom.

[0032] While the following terms are believed to be well understood by one of ordinary skill in the art, definitions are set forth to facilitate explanation of the presently-disclosed subject matter.

[0033] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the presently-disclosed subject matter belongs. Although any methods, devices, and materials similar or equivalent to those described herein can be used in the practice or testing of the presently-disclosed subject matter, representative methods, devices, and materials are now described.

[0034] Following long-standing patent law convention, the terms “a,” “an,” and “the” refer to “one or more” when used in this application, including the claims. Thus, for example, reference to “a sensor” includes a plurality of such sensors, and so forth.

[0035] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification and claims are approximations that can vary depending upon the desired properties sought to be obtained by the presently-disclosed subject matter.

[0036] As used herein, the term “about,” when referring to a value or to an amount of mass, weight, time, volume, concentration or percentage is meant to encompass variations of in some embodiments $\pm 20\%$, in some embodiments $\pm 10\%$, in some embodiments $\pm 5\%$, in some embodiments $\pm 1\%$, in some embodiments $\pm 0.5\%$, and in some embodiments $\pm 0.1\%$ from the specified amount, as such variations are appropriate to perform the disclosed methods.

[0037] The presently-disclosed subject matter provides sensors and switches for detecting hydrogen (H_2), as well as methods of making and using the same, whereby palladium (Pd) structures are utilized either alone or in combination with an organic insulating film.

[0038] It has been observed that by electrodepositing a metal (e.g., Pd) or by combining electrodeposition of a metal and electropolymerization of an organic compound capable of producing an organic insulating film (e.g., phenol) at micro-gap electrodes, metal-electrode or metal-organic-electrode junctions can be created that advantageously can be used to provide controlled responses to H_2 , such that sensors and switches for detecting H_2 can effectively be created that avoid the problems present in prior sensors and switches for detecting H_2 . In particular, the sensors and switches for detecting H_2 described herein include the benefits of: 1) forming a direct contact between metal structures and electrodes during synthesis, which eliminates the need for multi-step processes involving transfer, assembly, and contact formation that is common in electronic-based micro-/nano-sensing

devices, and which lead to long fabrication times and device failures; 2) providing a simple, fast, highly parallel process with a near 100 % success rate; and, 3) providing an approach for fabricating sensors and switches that may be used in fabricating a wide range of metal/organic/metal junctions. As such, the presently-disclosed subject matter also provides a method for fabricating a sensor, which may be used to fabricate a variety sensing devices for various applications.

[0039] FIG. 1A is a schematic diagram showing an exemplary method of making a sensor for detecting H₂ in accordance with the presently-disclosed subject matter. In this exemplary implementation, an exemplary sensor 10 for detecting H₂ is fabricated by initially positioning a first electrode 20 and a second electrode 30 at a distance from one another and affixing the electrodes 20, 30 to an electrically-insulating support 40. Various materials that resist the flow of electrical current can be used to provide an electrically-insulating support in accordance with the presently-disclosed subject matter, and thus can be used to support or separate electrical conductors (e.g., electrodes) while still providing low background conductivity or without allowing current to travel via the support itself. For example, in some embodiments, the exemplary electrically-insulating support 40 can be comprised of materials such as silicon/silicon oxide, other silicate materials such as micas and silicon nitrides, glass, porcelain, composite materials, polymers such as plastics, and ceramics. As will be recognized by those of ordinary skill in the art, each of the foregoing materials can be used to provide an electrically-insulating support onto which a first electrode and a second electrode can be affixed.

[0040] The first electrode 20 and the second electrode 30 of an exemplary sensor 10 for detecting H₂ can be comprised of any electrically-conductive material through which an electric current may enter and leave. Such electrodes are known to those of ordinary skill in the art and include, but are not limited to, silver, gold, platinum, chromium, titanium,

palladium, copper, indium-tin-oxide, or conductive carbon electrodes. Further, as will also be recognized by those of ordinary skill in the art, various methods can be used to affix electrodes to a support such as evaporating, sputtering, or electrochemically depositing electrodes on an electrically-insulating support, as well as the utilization of conductive paints or photolithography procedures. For example, in some embodiments of the presently-disclosed subject matter, gold electrodes can be fabricated by photolithography and affixed to a silicon support by sputtering and depositing gold over a suitable adhesion layer such as a titanium adhesion layer.

[0041] As noted, an exemplary sensor 10 for detecting H₂ of the presently-disclosed subject matter is comprised of at least a first electrode 20 and a second electrode 30 that are positioned at a distance from one another. Typically, and as discussed further below with respect to the Pd structures 50 utilized in conjunction with the presently-disclosed subject matter, a criterion regarding the distance between the two electrodes 20, 30 is that the Pd structures 50 deposited on the first electrode 20 are able to extend across the gap between the electrodes 20, 30 and thus contact the second electrode 30 to create a conductive path between the first electrode 20 and the second electrode 30. The ability of a Pd structure to form a connection between two electrodes can occur at distances as long as tens to hundreds of micrometers depending on the length and amount of Pd materials used to make the connection. In some embodiments, however, to allow the Pd structures 50 to make a connection in a reasonable amount of time (e.g., a few minutes) and provide sufficient conductive path between the two electrodes 20, 30, a distance of less than 10 micrometers between the two electrodes 20, 30 is used. In the schematic diagram shown in FIG. 1A, the distance between the electrodes 20, 30 is about 5 micrometers.

[0042] In some embodiments of the presently-disclosed sensors for detecting H₂, the electrodes 20, 30 can include one or more fingers such that the first electrode 20 and the

second electrode 30 can be arranged in an interdigitated configuration. For example, as shown in FIGS. 2A and 2B, in some embodiments, the first electrode 20 and the second electrode 30 are each comprised of about 5 to about 7 fingers that are aligned parallel to each other such that the fingers interlock without touching one another and form an array. By arranging the first electrode 20 and the second electrode 30 in such a configuration, an exemplary sensor 10 for detecting H₂ can be provided such that there is a greater likelihood of a conductive path being established between the first electrode 20 and the second electrode 30 subsequent to a deposition of Pd structures 50.

[0043] Regardless of the particular configuration of the electrodes on an exemplary sensor for detecting hydrogen, however, and referring again to FIG. 1A, once the first electrode 20 and second electrode 30 have been positioned at a distance from one another and affixed to the electrically-insulating support 40, a Pd structure 50 is then deposited on and contacts the first electrode 20 with at least a portion of the Pd structure 50 extending to and contacting the second electrode 30, thus creating a conductive path between the first electrode 20 and the second electrode 30. In some embodiments, the Pd structures 50 utilized in accordance with the presently-disclosed subject matter can be Pd molecules that are deposited on a first electrode 20 by electrochemically depositing the Pd on the first electrode 20. For example, in some embodiments, Pd may be deposited on the first electrode 20 by electrochemical deposition, wherein an electric current is run through a Pd solution until a sufficient amount of charge passes through the solution. In this regard, Pd deposition can be performed by attaching a wire lead to the first electrode 20 and to a potentiostat, and then holding the potential at a specified voltage versus a reference electrode.

[0044] In such embodiments, the Pd molecules forming the Pd structures 50 can further form dendritic or flower-like structures (see, e.g., FIGS. 3A and 3B) that, once deposited on a first electrode 20, may cross over to a second adjacent electrode 30 and form a conductive

path between the two electrodes 20, 30. In these embodiments, the dendritic or flower-like Pd structures 50 are typically about 1-10 micrometers in length and about 0.5 to about 1.0 micrometer in width, such that, in some embodiments, the Pd structures 50 are essentially Pd nanostructures that extend from the first electrode 20 and contact a small area on the second electrode 30. Based on the conductivity of the exemplary sensors 10 for detecting H₂ disclosed herein, as well as the conductivity of pure Pd ($94,800 \Omega^{-1}\text{cm}^{-1}$), the estimated contact area of the Pd structures 50 on the second electrode 30 is about 83 nanometers by about 83 nanometers. As such, it is believed that the connection between the Pd structures 50 and the second electrode 30 is not through the larger micron dimensions of the Pd structures 50, but is instead through one of the smaller dendritic branches that are on the order of about 10 to about 100 nanometers or more. As shown in FIGS. 5A-5F, scanning electron microscope (SEM) images show that Pd electrodeposits upward and outward on the first electrode 20, and preferentially at the edges of the first electrode 20, such that only a small percentage of these Pd structures 50 grow long enough to make a connection to the second electrode 30 in the pre-determined time period that is used for an exemplary deposition of Pd on a first electrode 20. As such, in some embodiments, the number of connections between the electrodes 20, 30 can be between about 1 to about 25 connections per sensor 10 out of the approximately 100 to 1000 Pd structures 50 that grow into dendritic or flower-like Pd structures 50 on the first electrode 20. Furthermore, by providing a contact area on the second electrode 30 that is on the order of nanometers, it is thought that the sharper connection points provide more control over an exemplary sensor for detecting H₂ and also provide a more sensitive sensor that is capable of detecting lower concentrations of H₂ in a gas sample.

[0045] In some embodiments of the presently-disclosed subject matter, the sensors for detecting H₂ can thus be used in a method of detecting H₂ in a gas sample by: providing a sensor in accordance with the presently-disclosed subject matter; applying a voltage potential

along the conductive path between the first electrode and the second electrode of the sensor; exposing the sensor to a gas sample; and detecting a decrease in conductivity along the conductive path between the first electrode and the second electrode to thereby detect H₂ in the gas sample. In some embodiments of the methods for detecting H₂ in a gas sample, which make use of a sensor of the presently-disclosed subject matter, the H₂ is present in the gas sample at a concentration of as low as 0.11%.

[0046] It is appreciated that hydrogen spontaneously adsorbs to Pd as atomic hydrogen and diffuses into a Pd lattice to form the more resistive PdH_x. In this regard, the initial α -phase Pd becomes β -phase PdH_x through an α - β phase transition and the Pd lattice spacing changes throughout these phase changes, depending on the hydrogen concentration in the surrounding atmosphere. These phase transitions and changes in lattice spacing lead to measurable changes in the optical properties, resistance, and mass of the Pd, and can thus be utilized as an effective means to detect hydrogen.

[0047] For example, in one exemplary implementation of a method for detecting H₂ in a gas sample using a sensor of the presently-disclosed subject matter, a voltage potential (e.g., -0.3 V) can be applied to an exemplary sensor such that current flows along the conductive path between the first electrode and the second electrode that is formed by the Pd structure. When this sensor is subsequently exposed to a certain concentration of H₂ (e.g., a concentration above about 0.11%), the Pd structure of the sensor then transitions into the more resistive PdH_x and the conductivity along the conductive path between the first and second electrode decreases reversibly such that the decrease in conductivity can then be measured by methods known to those of ordinary skill in the art to thereby detect H₂ in the gas sample.

[0048] With further regard to the detection of H₂ in a gas sample, an exemplary sensor of the presently-disclosed subject matter can be utilized to determine the presence or absence of

H₂ in a sample, but may also be used to measure the amount of H₂ in a particular gas sample. As such, “detecting” H₂, as used herein, can refer to a determination of whether H₂ is present or absent in a sample of interest as well as quantifying the amount of H₂ that is present in a sample of interest. For example, to quantify the amount of hydrogen present in a sample, a calibration curve can be obtained by measuring the response of a sensor, or the analytical signal, to known H₂ concentrations, i.e. standards. In these quantification methods, the analytical signal used for the detection of H₂ can be calculated as the percent response as described by the following equation:

$$\% \text{ Response} = (i_r - i_b) / i_b \times 100\%$$

where i_b is the initial sensor baseline current in the presence of 100% N₂ and i_r is the sensor current in the presence of a H₂/N₂ mixture of a certain standard percent H₂. A negative value is equal to a decrease in the current upon exposure to H₂ and vice-versa. The calibration curve is then obtained by plotting H₂ concentration (x-axis) versus the percent response (y-axis). From this curve, the concentration of H₂ in unknown samples can thus be determined.

[0049] FIG. 1B is a schematic diagram showing an exemplary method for making a switch 110 for detecting H₂ in accordance with the presently-disclosed subject matter. Similar to the exemplary sensor 10 shown in FIG. 1A, the exemplary switch 110 for detecting H₂ is fabricated by initially providing an electrically-insulating support 140 onto which a first electrode 120 and a second electrode 130 are positioned at a distance from one another and affixed. The exemplary electrically-insulating support 140 and the electrodes 120, 130 of the exemplary switch 110 can be comprised of the same materials and fabricated by the same methods that are utilized to fabricate the exemplary sensor 10 described above with reference to FIG. 1A. In the exemplary implementation shown in FIG. 1B, however, prior to depositing a Pd structure, onto the first electrode 120 of the switch 110, an organic insulating film 160 is deposited on the second electrode 130 to provide an electrically-

insulating (i.e., resistive) barrier. In some embodiments, this organic insulating film 160 is comprised of an organic compound that, in the absence of hydrogen, prevents the Pd structure 150 from extending to and contacting the second electrode 130. In the presence of H₂, however, the Pd structure 150, which is deposited on and contacts the first electrode 120 of the exemplary switch 110 with at least a portion of the Pd structure 150 extending to and contacting the organic insulating film 160, extends through the organic insulating film 160 and contacts the second electrode 130.

[0050] In the exemplary implementation shown in FIG. 1B, the organic insulating film 160 is a polyphenol film (i.e., a polymer comprised of monomer phenol molecules that are connected to one another through carbon-oxygen-carbon bonds). Of course, other compounds capable of producing an organic insulating film can also be used without departing from the spirit and scope of the subject matter disclosed herein. For example, in some embodiments, the organic insulating film can be comprised of phenol, aniline, pyrrol, or combinations thereof.

[0051] As also shown in FIG. 1B, in some embodiments, the organic insulating film 160 is deposited on the second electrode 130 of the exemplary switch 110 by an electropolymerization process in which a current is applied through a solution containing one or more monomers of an organic compound that is capable of forming an organic insulating film, such as those described above. For example, in some embodiments, the organic insulating film 160 can be deposited on the second electrode 130 of the exemplary switch 110 by electropolymerizing phenol on the second electrode 130 by cycling from 0.0 to 1.2V at 100 mV/s in a 5 mM phenol solution in 0.1 M sulfuric acid (H₂SO₄). Of course, to the extent it may be desired, other methods can also be utilized to deposit the organic insulating film 160 on the second electrode 130 including methods whereby the films are chemically-assembled and/or physically deposited onto the second electrode 130.

[0052] In some embodiments of the presently-disclosed subject matter, the switches for detecting H_2 can be used in a method of detecting H_2 in a gas sample. In some embodiments, a method for detecting H_2 in a gas sample is provided that includes providing a switch in accordance with the presently-disclosed subject matter, applying a voltage potential between the first and second electrode; exposing the switch to a gas sample, and then detecting a current between the first electrode and the second electrode to thereby detect H_2 in the gas sample.

[0053] As noted, in the exemplary switch of the presently-disclosed subject matter, the organic insulating film can act as a resistive barrier that reduces or prevents electrical contact between the Pd structures and the second electrode. When the exemplary switch is exposed to a gas sample containing H_2 , PdH_x forms and the Pd structures expand in volume allowing the Pd structures to expand through the polyphenol layer and make direct contact with the second electrode. The contact between the two electrodes thus causes an increase in current and forms a "switch," wherein current flows between the electrodes in the presence of a particular H_2 concentration, but rapidly decreases such that when the H_2 concentration drops below a threshold concentration negligible current flows between the two electrodes.

[0054] For example, in one exemplary implementation of a method of detecting H_2 that makes use of an exemplary switch, a voltage potential (e.g., -0.3 V) can be applied to an exemplary switch such that current initially flows along through the first electrode and along the Pd structure, but ceases to flow, or only flows negligibly, once the current reaches the organic insulating film. When this switch is subsequently exposed to H_2 , such as what may be present in a gas sample of interest, the Pd structure then transitions into PdH_x and expands in volume to extend through the organic insulating layer and contact the second electrode. Once contact is made with the second electrode, the current between the first electrode and the second electrode is then able to increase by 7-8 orders of magnitude such that the current

between the electrodes can then be measured by methods known to those of ordinary skill in the art to thereby detect H₂ in the gas sample. In some embodiments, the methods of detecting H₂ in a gas sample utilizing a switch of the presently-disclosed subject matter can detect H₂ that is present in gas sample at a concentration of as low as 1.0%.

[0055] Thus, the sensors, switches, and methods of detecting H₂ described herein allow for electrodeposition of metals, such as Pd, to produce a sensor for controlled sensing behavior, or a combination of electrodeposition of metals and electropolymerization of one or more compounds capable of producing an organic insulating film, such as phenol, on electrodes in order to produce switches for controlled switching behavior. The sensors, switches, and methods of the presently-disclosed subject matter further allow the direct contact of a metal to the electrodes to be made by metal electrodeposition, thus eliminating the need for multistep processes involving synthesis, assembly, and contact formation which are common in electronic-based sensing devices, but also providing beneficial methods for controlling metal/organic/metal junctions in a fast parallel manner that can be used in other sensing or molecular electronics applications.

[0056] In this regard, the presently-disclosed subject matter further provides, in some embodiments, methods of fabricating a sensor for detecting an analyte of interest that can be used to fabricate useful sensors that, in some embodiments, can include metal electrode/metal structure/organic/metal electrode junctions. In some embodiments, a method for fabricating a sensor for detecting an analyte of interest is provided that includes positioning a first electrode and a second electrode at a distance from one another on an electrically insulating support; electropolymerizing a compound capable of producing an organic insulating film on the second electrode attached to the support; and electrodepositing a metal on the first electrode attached to the support such that at least a portion of the metal extends to and contacts the organic insulating film.

[0057] As one exemplary implementation of a method for fabricating a sensor for detecting an analyte of interest, a sensor for detecting an analyte of interest can be provided where, similar to the exemplary switches for detecting H₂ described herein above, the metal deposited on the first electrode can be Pd, and, in some embodiments, the organic insulating layer can be produced by a compound capable of producing an organic insulating film, such as phenol, aniline, pyrrole, or combinations thereof. In some embodiments, the organic insulating film is a polyphenol film.

[0058] In some embodiments of the presently-disclosed methods for fabricating a sensor for detecting an analyte of interest, the thickness of the organic insulating film deposited on the second electrode is varied to change a response and recovery time of an exemplary sensor. In some embodiments, varying the thickness of the organic insulating film comprises varying the number of electropolymerization cycles, which, in some embodiments, can comprise about 4 to about 10 cycles.

[0059] For example, in one exemplary implementation of a method for fabricating a sensor for detecting an analyte of interest, where a Pd structure is deposited on the first electrode subsequent to the electropolymerization of phenol on the second electrode such that a portion of the Pd structure on the first electrode contacts the polyphenol film, it has been observed that as the number of phenol electropolymerization cycles increases, an increasingly thicker film of polyphenol is deposited on the second electrode and the response and recovery time, as well as the magnitude of response, decreases. Accordingly, for some applications where faster switching behavior is preferred, it may be desirable to use a thinner polyphenol layer, and vice versa.

[0060] Although the exemplary methods for fabricating a sensor for detecting an analyte of interest are described herein with reference to a method where the deposited metal is palladium and the organic insulating layer is comprised of organic compounds such as

phenol, aniline, and/or pyrrole, as a further refinement, it is contemplated that the metal deposited on the second electrode can be selected from silver or combinations of silver and palladium and that the organic insulating layer can further be comprised of various other organic molecules. For example, in some embodiments, the deposited metal can comprise a silver nanowire where the silver nanowire itself can change its conductivity in the presence of various molecules (e.g., ammonia) or can be functionalized with further materials to make the silver nanowire respond to analytes that would not typically change the conductivity of silver. As another example, in some embodiments, the organic insulating film itself can change in conductivity by reacting to a particular analyte of interest, such that, upon exposure to the analyte of interest, conductivity is increased between the metal structure contacting the organic insulating film and a change in current can be detected to thereby detect an analyte of interest. In this regard, it is contemplated that polyethylene dioxythiophene: polystyrene sulphonate (PEDOT:PSS) materials can be used to create an organic insulating layer and then used in a sensor to detect nitric oxide, methanol, ethanol, acetone, ammonia, glucose, and/or calcium ions; polyaniline (PANI) can be used to detect NO₂, pH, chloroform, methanol, and glucose; sulfonate-functionalized water-soluble conjugated polymers, which contain bipyridine units, can be used to detect transition metal ions; and material-based heterojunctions consisting of hexadecafluorinated nickel phthalocyanine and Nickel phthalocyanine (Au/Ni(F₁₆Pc)/NiPc/Al) can be used to detect O₃ and NH₃.

[0061] The above-described sensors, switches, and methods for detecting for H₂, as well as the methods for fabricating a sensor for detecting an analyte of interest, are important for both producing useful H₂ sensors and switches that exhibit controlled responses to H₂, but are also important for developing other sensing, nanoelectronic, and molecular electronics applications in which a metal/organic/metal junction may be desirable. Furthermore, by uniquely combining metal electrodeposition and organic compound electropolymerization at

microgap electrodes, the methods and devices of the presently-disclosed subject matter provide a unique way of producing metal/organic/metal junctions. Thus, the devices and methods of the presently-disclosed subject matter provide convenient alternatives to current fabrication processes, with the added benefit that the presently-disclosed methods eliminate the need for multi-step processes involving transfer, assembly, and contact formation.

[0062] The presently-disclosed subject matter is further illustrated by the following specific but non-limiting examples.

EXAMPLES

[0063] Example 1 - Fabrication and Characterization of Exemplary Hydrogen Sensors and Switches

[0064] Interdigitated gold array electrodes with 10 or 14 fingers separated by a 5 μm gap were fabricated in a clean room by photolithography on a Si/SiO_x substrate. Briefly, the photolithography procedure followed a positive resist procedure in which good adhesion of the photoresist was ensured by depositing hexamethyldisilazane (HDMS) onto the Si/SiO_x substrate ("wafer"). A spin coater was then turned on and run at the following settings: a) 500 revolutions per minute (rpm) for 0.2 seconds (s); b) 4000 rpm for 10 s; and, (c) 0 rpm for 0.2 s. A positive resist "1813" solution was then deposited on the wafer and spun at the same settings. After coating the wafer with HDMS and 1813, the wafer was baked at 90°C for 1 min ("soft bake"). A mask and the wafer were placed in an AB-M aligner and exposed to ultraviolet (UV) light for 6.0s using a contact vacuum. The wafer was then soaked in toluene for 1 min and dried with a nitrogen gun. The solvent was then baked out at 90°C for 15 s. The areas of photoresist were developed by immersing the wafer in MF-319 developer (95 % water, less than 1 % surfactant, and 2.2 % tetramethylammonium hydroxide) for approximately 1 to 2 min.

[0065] Deposition procedures were performed using an Argon (Ar^+) ion source that bombards a solid target and consequently produces gas-phase atomic ions that then deposit on top of the wafer. Titanium targets were used as adhesion layers and Au was then deposited. The Au-coated wafers were immersed in acetone, and ultrasonics and a cotton swab were used for the lift-off procedure. Finally, the wafers are coated with 1813 and dicing was performed to separate the individual devices for further use.

[0066] Wire leads were attached to Au contact pads on the devices with Ag epoxy (cured 8-12 h, 80°C), followed by further insulation with an overlayer of Torr seal epoxy (cured 8-12 h, 80°C). The electrodes were cleaned by rinsing them in ethanol, acetone, nanopure water, and isopropyl alcohol before drying under N_2 . The electrodes were then placed in an UVO ozone cleaner (Jelight Company Inc., Irvine, CA) for 10 min and were also cleaned electrochemically by cycling the electrodes in 0.1 M H_2SO_4 from 0.0 to 1.2 V.

[0067] FIG. 1 illustrates two methods used to electrochemically fabricate exemplary devices on interdigitated array (IDA) electrodes (10 or 14 fingers) separated by a 5 μm gap. Consistent with the exemplary methods shown in FIG. 1, the first procedure (FIG. 1A) was used to fabricate an exemplary sensor for detecting hydrogen (“ H_2 sensor”) and involved Pd electrodeposition on a first electrode (Electrode 1) from a 5 mM PdCl_4^{2-} solution in 0.1 M H_2SO_4 . Deposition was performed by hooking up one wire lead to a potentiostat and was performed in chronocoulometric mode. The potential was held at -0.1 V versus an Ag/AgCl reference electrode until 1.2×10^{-3} coulombs of charge passed. Platinum wire was used as a counter electrode. The amount of charge passed depended on the distance between the electrodes. It was experimentally determined that 1.2×10^{-3} coulombs was preferred for a 5 micrometer electrode separation and that a larger separation or smaller separation required a larger amount or smaller amount of charge, respectively.

[0068] The second procedure (FIG. 1B) was used to fabricate an exemplary switch for detecting hydrogen (“H₂ switch”) and involved electropolymerization of phenol on a second electrode (Electrode 2) by cycling from 0.0 to 1.2 V at 100 mV/s in a 5 mM phenol solution in 0.1 M H₂SO₄ for 4 to 10 cycles. Pd was then deposited on a first electrode (Electrode 1) by following the same Pd electrodeposition procedure that was used in the first procedure.

[0069] FIG. 2 shows scanning electron microscopy (SEM) images of an entire 10-finger IDA for an exemplary H₂ sensor and for an exemplary H₂ switch (10 cycles of phenol). FIG. 3 shows SEM images of Pd/electrode junctions on a portion of the 10-finger IDAs depicted in FIG. 2 (circled portions), including images of portions of both an H₂ sensor (FIG. 3A) and an H₂ switch (FIG. 3B). The Pd metal deposited on Electrode 1 crossed over to Electrode 2 and has a dendritic or flowerlike structure [13]. Electrode 2 appears darker in FIG. 3B due to the presence of the insulating polyphenol film.

[0070] FIG. 3C and FIG. 3D show current-voltage (i-V) curves for an exemplary H₂ sensor and an exemplary H₂ switch, respectively. A difference between the two devices is the observed resistance. The H₂ sensor is ohmic, exhibiting a current of 13 mA at -1.0 V ($R = 77 \Omega$), while the H₂ switch exhibits a current of 2.09 nA at -1.0 V ($R = 478 \text{ M } \Omega$). Current time plots of the H₂ sensor and H₂ switch (FIGS. 4A and 4B, respectively) show that the current is constant in the mA range with time for the H₂ sensor, but exponentially decays by 1 to 2 orders of magnitude down to the 10 to 100 pA range with time for the H₂ sensor. Based on the known conductivity of Pd ($94,800 \Omega^{-1}\text{cm}^{-1}$), the current observed for the H₂ sensor corresponds to a contact area of 83 nm x 83 nm. This value is much smaller than the apparent contact area observed from the top view SEM images (FIGS. 2 and 3). Side-view SEM images of an exemplary H₂ switch (see, FIGS. 5A-5F) reveal that the Pd deposits vertically and horizontally from the first electrode and preferentially at the edges of the first

electrode, indicating that some of the apparent connections viewed from the top in FIGS. 2 and 3 may not actually be in connection with the second electrode.

[0071] Table 1 provides information about the current, resistance, number of apparent connections from top views, and contact areas based on the resistance for various exemplary H₂ sensors and H₂ switches. The number of apparent connections varied while the current was within one order of magnitude for at least three samples of each type of device. The differences did not qualitatively affect the highly reproducible responses to H₂.

H ₂ Sensor					
sample	# of fingers in IDA	# of apparent connections (top view)	Current at -1V from I-V curve (A)	Resistance at -1V(Ω)	Contact Area
1*†	10	6	1.30×10^{-2}	76.9	83×83 nm
2	10	1	1.37×10^{-2}	73.0	85×85 nm
3	10	5	8.29×10^{-3}	122	66×66 nm
H ₂ Switch-10 cycles Phenol					
sample	# of fingers in IDA	# of apparent connections (top view)	Current at -1V from I-V curve (A)	Baseline current from current-time plots (pA)	
1	14	19	8.25×10^{-3}	10-100	
2†	10	3	1.30×10^{-3}	10-100	
3	14	24	8.60×10^{-3}	10-100	
4‡	---	---	1.30×10^{-3}	10-100	
5*‡	10	4	2.09×10^{-3}	10-100	

Table 1. Number of connections, current, resistance, and contact area for exemplary H₂ sensors and H₂ switches ((*) SEM images of these samples are shown in FIGS. 2A and 2B and in FIGS. 3A and 3B); (#) current-voltage plots of these samples are shown in FIG. 3C and 3D); (†) current-time sensing plots of these samples are shown in FIGS. 6A and 6B); (‡) current-time sensing plots of these samples are shown in FIGS. 8A and 8B).

[0072] Example 2 - Detection of Hydrogen Using Exemplary Hydrogen Switches and Sensors

[0073] FIGS. 6A and 6B show the current at -0.3 V as a function of time for a 10-finger IDA H₂ sensor and H₂ switch (10 cycles polyphenol), respectively, in the presence of 100 % N₂ (H₂ “off”, ○) and various H₂ concentrations as indicated in N₂ carrier gas (H₂ “on”, •). The current was initially stable in 100 % N₂ and then decreased reversibly in the presence of H₂

for the H₂ sensor, as shown in FIG. 6A. The decrease can be due to the formation of PdH_x, which is more resistive compared to Pd. There was a non-linear increase in the response between 1.0 % and 3.1 % H₂ that can be due to the well-known α - to β - phase-transition that occurs during the formation of PdH_x. Above 3.1 %, the response was similar indicating hydrogen saturation of the Pd. Calibration curves from 0.0 to 0.78 % H₂ (FIGS. 7A and 7B) for three H₂ sensors reveal an average slope and theoretical limit of detection of 0.58 ± 0.11 and 0.04 ± 0.03 % H₂, respectively, as is also shown in Table 2. The average response and recovery time ranged from 20 to 60 s (Table 3), and the 3 % change in the Pd resistance for the H₂ sensor at 9.6 % H₂ was smaller than what has been previously reported in other sensing devices [3]. Without wishing to be bound by any particular theory, it is thought that the resistance increase observed with the formation of PdH_x in the H₂ sensors is counteracted by a resistance decrease that is caused by an increase in contact area upon expansion of PdH_x, thus leading to a smaller increase in resistance than what would typically be expected (see, e.g., FIG. 10A).

Sample	1	2	3		
% H ₂	% response	% response	% response	AVG	STD
9.6	2.61±0.01	2.74±0.02	2.77±0.06	2.71	0.09
6.0	2.12±0.12	2.69±0.01	2.64±0.04	2.48	0.32
3.1	1.93±0.23	2.48±0.01	2.22±0.01	2.21	0.27
1.0	0.76±0.02	0.80±0.02	0.98±0.01	0.84	0.11
0.78	0.37±0.02	0.44±0.14	0.52±0.02	0.44	0.08
0.48	0.24±0.01	0.25±0.01	0.37±0.01	0.28	0.07
0.21	0.10±0.01	0.13±0.01	0.17±0.02	0.13	0.04
0.11	0.04±0.02	0.04±0.01	0.08±0.01	0.05	0.01
Sample	1	2	3		
Linear slope (% res./%H ₂)	0.48	0.56	0.69	0.58	0.11
Limit of detection {%H ₂ }	0.06	0.05	0.01	0.04	0.03

Table 2. Percent responses for three different H₂ sensors as a function of H₂ concentration along with the linear slope and limit of detection for each device.

H ₂ Sensor	Response time				
% H ₂	sample 1	sample 2	sample 3	AVG	STD
9.6	17	29	24	23	8
6.0	29	25	24	26	3
3.1	31	37	25	31	4
1.0	57	61	58	59	2
0.78	46	61	58	55	6
0.48	55	50	59	55	5
0.21	47	53	51	50	3
0.11	30	38	34	34	4
H ₂ Sensor	Recovery time				
% H ₂	sample 1	sample 2	sample 3	AVG	STD
9.6	46	43	46	46	3
6.0	49	47	47	47	1
3.1	38	31	28	32	4
1.0	51	50	52	51	1
0.78	59	55	56	57	2
0.48	43	45	51	46	4
0.21	44	46	50	47	3
0.11	32	38	40	37	4

Table 3. Response and recovery times for three different H₂ sensors as a function of H₂ concentration.

[0074] The current-time plot for the H₂ switch in FIG. 6B is different compared to that of the H₂ sensor. Instead of exhibiting a decrease in current, the current dramatically increased by 7-8 orders of magnitude above 1.0 % H₂ (see FIGS. 8A and 8B for responses of exemplary H₂ switches to 1.0 % H₂). For example, at 3.1 % the current increased from 1.0×10^{-11} A to 1.1×10^{-3} A. The dramatic increase in current can be due to a connection being made between the electrodeposited Pd and the second electrode (see, e.g., FIG. 3B) as PdH_x forms and expands in volume and through the approximately 4 to 10 nm thick polyphenol layer, such as the 5.9 nm thick polyphenol layer shown in FIGS. 9A and 9B, leading to direct contact with the second electrode (see, e.g., FIG. 10B).

[0075] The mechanism depicted in FIG. 10B is supported by three observances. First, a threshold detection is observed at about 1.0 % H₂, which is where the Pd transition from α -phase to β -phase occurs. Below this threshold, the volume expansion of PdH_x is not

sufficient to form a direct connection to second electrode. Second, the current of an exemplary H₂ switch above 1.0 % H₂ is on the same order of magnitude as the current (10^{-3} to 10^{-4} A) of the directed connected Pd in an exemplary H₂ sensor (see, FIG. 6A, and Tables 4 and 5), which indicates that direct contact is made in the H₂ switches. Third, current-voltage curves of the H₂ switch in the presence of H₂ exhibit symmetric, linear curves as does the directly connected Pd depicted in FIG. 3C, making it unlikely that Schottky barriers lead to the switching behavior.

10 cycles of Phenol					
sample 1	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	1.29×10^{-3}	1.28×10^{-3}	1.25×10^{-3}	1.27×10^{-3}	0.02×10^{-3}
6.0	1.28×10^{-3}	1.28×10^{-3}	1.20×10^{-3}	1.25×10^{-3}	0.04×10^{-3}
3.1	1.11×10^{-3}	1.15×10^{-3}	1.10×10^{-3}	1.12×10^{-3}	0.03×10^{-3}
sample2	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	2.47×10^{-3}	2.48×10^{-3}	/	2.48×10^{-3}	0.01×10^{-3}
6.0	1.89×10^{-3}	2.19×10^{-3}	/	2.04×10^{-3}	0.21×10^{-3}
3.1	1.73×10^{-3}	2.20×10^{-3}	/	1.97×10^{-3}	0.33×10^{-3}
sample 3	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9	4.19×10^{-3}	3.88×10^{-3}	/	3.93×10^{-3}	0.37×10^{-3}
6	3.86×10^{-3}	2.11×10^{-3}	/	2.99×10^{-3}	1.24×10^{-3}
3	3.56×10^{-3}	1.96×10^{-3}	/	2.76×10^{-3}	1.13×10^{-3}
sample 4	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	1.19×10^{-3}	/	/	/	/
6.0	1.18×10^{-3}	/	/	/	/
3.1	1.11×10^{-3}	/	/	/	/
1.0	0.96×10^{-3}	/	/	/	/
sample 5	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	2.25×10^{-3}	/	/	/	/
6.0	1.98×10^{-3}	/	/	/	/
3.1	0.35×10^{-3}	/	/	/	/
1.0	0.28×10^{-3}	/	/	/	/
5 cycles Phenol					
sample 1	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	0.42×10^{-3}	0.38×10^{-3}	/	0.40×10^{-3}	0.02×10^{-3}
6.4	0.26×10^{-3}	0.30×10^{-3}	/	0.28×10^{-3}	0.03×10^{-3}
3.1	0.17×10^{-3}	0.22×10^{-3}	/	0.19×10^{-3}	0.04×10^{-3}
sample2	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	3.12×10^{-3}	2.97×10^{-3}	/	3.05×10^{-3}	0.11×10^{-3}
6.0	3.06×10^{-3}	2.88×10^{-3}	/	2.97×10^{-3}	0.13×10^{-3}
3.1	2.87×10^{-3}	2.56×10^{-3}	/	2.72×10^{-3}	0.22×10^{-3}
4 cycles Phenol					
sample 1	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	0.74×10^{-3}	0.72×10^{-3}	/	0.73×10^{-3}	0.01×10^{-3}
6.0	0.45×10^{-3}	0.45×10^{-3}	/	0.45×10^{-3}	0.004×10^{-3}
3.1	0.30×10^{-3}	0.29×10^{-3}	/	0.29×10^{-3}	0.006×10^{-3}
sample2	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	1.56×10^{-3}	1.49×10^{-3}	/	1.53×10^{-3}	0.05×10^{-3}
6.0	1.54×10^{-3}	1.36×10^{-3}	/	1.45×10^{-3}	0.13×10^{-3}
3.1	0.60×10^{-3}	0.62×10^{-3}	/	0.61×10^{-3}	0.02×10^{-3}

Table 4. Final currents at different H₂ concentrations for each trial of various H₂ switches.

Sample	10 Cycles Phenol		5 Cycles Phenol		4 Cycles Phenol	
% H ₂	AVG	STD	AVG	STD	AVG	STD
9.6	2.56×10^{-3}	1.32×10^{-3}	1.72×10^{-3}	1.32×10^{-3}	1.13×10^{-3}	0.39×10^{-3}
6.0	2.09×10^{-3}	0.88×10^{-3}	1.62×10^{-3}	1.34×10^{-3}	0.95×10^{-3}	0.50×10^{-3}
3.1	1.95×10^{-3}	0.82×10^{-3}	1.45×10^{-3}	1.26×10^{-3}	0.45×10^{-3}	0.16×10^{-3}
1.0	$0.62 \times 10^{-3*}$	$0.48 \times 10^{-3*}$	/	/	$0.22 \times 10^{-3\#}$	/

Table 5. Average final currents at various H₂ concentrations for H₂ switches as a function of the number of electrochemical cycles in phenol (for 10 cycles phenol, the average is from three exemplary H₂ switches (sample 1, 2, and 3); (*) the value at 1.0% H₂ represents the average for two devices (samples 4 and 5); for 4 and 5 cycles phenol, the average is from two different devices (samples 1 and 2); (#) the value at 1.0 % H₂ is for one device (sample 2).

[0076] H₂ switches fabricated with polyphenol using 4 or 5 electrochemical cycles also operated as effective H₂ switches (FIG. 11), but with less than 100 % success, which is observed in H₂ switches fabricated with 10 cycles of phenol. However, in those devices fabricated with 4 or 5 cycles of phenol, the response and recovery times were generally shorter than H₂ switches fabricated using 10 electrochemical cycles to deposit the polyphenol layer (see, Tables 6 and 7), which was attributed to faster penetration of PdHx through a thinner, more porous polyphenol film. Indeed, as the polyphenol thickness decreases, the % response increases and the response and recovery times decrease. As such, for certain applications, a thinner polyphenol layer may thus be preferable for faster and larger switching behavior.

10 Cycles Phenol										
Sample 1	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	29	44	36	36	8	172	182	157	170	13
6.0	34	48	39	41	7	131	153	72	119	42
3.1	46	28	41	38	25	67	36	52	52	16
Sample 2	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	22	24	/	23	1	68	76	/	72	6
6.0	40	55	/	48	11	67	73	/	70	4
3.1	56	35	/	46	15	72	41	/	57	22
Sample 3	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	29	12	/	21	12	144	222	/	183	55
6.0	21	20	/	21	1	48	117	/	83	49
3.1	72	41	/	57	22	108	51	/	86	40
Sample 4	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	27	/	/	/	/	76	/	/	/	/
6.0	32	/	/	/	/	63	/	/	/	/
3.1	48	/	/	/	/	48	/	/	/	/
1.0	830	/	/	/	/	27	/	/	/	/
Sample 5	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	13	/	/	/	/	12	/	/	/	/
6.0	16	/	/	/	/	10	/	/	/	/
3.1	19	/	/	/	/	9	/	/	/	/
1.0	24	/	/	/	/	8	/	/	/	/

5 Cycles Phenol									
Sample 1	Response time				Recovery time				
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD	
9.6	20	18	18	3	32	29	31	2	
6.0	26	25	26	1	15	15	15	0	
3.1	24	27	26	2	32	25	29	5	
Sample 2	Response time				Recovery time				
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD	
9.6	8	15	13	5	26	25	26	4	
6.0	9	14	13	2	17	34	26	11	
3.1	33	32	33	1	26	17	22	4	

4 Cycles Phenol									
Sample 1	Response time				Recovery time				
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD	
9.6	11	12	12	1	31	22	27	6	
6.0	13	11	12	10	27	25	26	1	
3.1	20	15	18	4	5	7	6	1	
Sample 2	Response time				Recovery time				
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD	
9.6	7	9	8	1	22	23	23	1	
6.0	14	6	10	6	22	23	23	1	
3.1	23	22	23	1	15	11	13	3	
1.0	110	/	/	/	9	/	/	/	

Table 6. Response and recovery time at different H₂ concentrations for each trial of various H₂ switches.

H ₂ Switch	Response time					
Sample	10 Cycles Phenol		5 Cycles Phenol		4 Cycles Phenol	
% H ₂	AVG	STD	AVG	STD	AVG	STD
9.6	27	9	16	5	10	2
6.0	37	14	20	10	11	1
3.1	47	9	30	5	21	4
1.0	428 [*]	570 [*]	/	/	110 [#]	/
H ₂ Switch	Recovery time					
Sample	10 Cycles Phenol		5 Cycles Phenol		4 Cycles Phenol	
% H ₂	AVG	STD	AVG	STD	AVG	STD
9.6	142	61	29	4	25	3
6.0	91	25	21	7	25	2
3.1	63	15	26	5	10	5
1.0	17 [*]	13 [*]	/	/	9 [#]	/

Table 7. Average response and recovery times for H₂ switches to various concentrations of H₂ as a function of the number of electrochemical cycles in phenol. (for 10 cycles phenol, the average is from three exemplary H₂ switches (sample 1, 2, and 3); (*) the value at 1.0 % H₂ represents the average for two devices (samples 4 and 5); for 4 and 5 cycles phenol, the average is from two different devices (samples 1 and 2); (#) the value at 1.0 % H₂ is for one device (sample 2).

[0077] Throughout this document, various references are mentioned. All such references are incorporated herein by reference, including the references set forth in the following list:

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13. Cheng, C., Gonela, R.K., Gu, Q., Haynie, D.T. *Nano lett.* 2005, 5, 175-178.

[0078] It will be understood that various details of the presently disclosed subject matter can be changed without departing from the scope of the subject matter disclosed herein. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation.

CLAIMS

What is claimed is:

1. A sensor for detecting hydrogen, comprising:
 - an electrically-insulating support;
 - a first electrode and a second electrode positioned at a distance from one another and affixed to the support; and
 - a palladium structure deposited on and contacting the first electrode with at least a portion of the palladium structure extending to and contacting the second electrode, thus creating a conductive path between the first electrode and the second electrode.
2. The sensor of claim 1, wherein the first electrode and the second electrode are in an interdigitated configuration.
3. The sensor of claim 1, wherein the distance between the first electrode and the second electrode is about 5 micrometers.
4. The sensor of claim 1, wherein the palladium structure is electrochemically deposited on the first electrode.
5. A method of detecting hydrogen in a gas sample, comprising:
 - providing a sensor, including
 - an electrically-insulating support,
 - a first electrode and a second electrode positioned at a distance from one another and affixed to the support, and
 - a palladium structure deposited on and contacting the first electrode

with at least a portion of the palladium structure extending to and contacting the second electrode, thus creating a conductive path between the first electrode and the second electrode;

applying a voltage potential along the conductive path between the first electrode and the second electrode;

exposing the sensor to the gas sample; and

detecting a decrease in conductivity along the conductive path between the first electrode and the second electrode to thereby detect hydrogen in the gas sample.

6. The method of claim 5, wherein the hydrogen is present in the gas sample at a concentration of as low as about 0.11 %.

7. A switch for detecting hydrogen, comprising:

an electrically-insulating support;

a first electrode and a second electrode positioned at a distance from one another and affixed to the support;

an organic insulating film deposited on the second electrode; and

a palladium structure deposited on and contacting the first electrode with at least a portion of the palladium structure extending to and contacting the organic insulating film on the second electrode;

wherein, upon exposure to hydrogen, the portion of the palladium structure contacting the organic insulating film extends through the organic insulating film and contacts the second electrode, thus creating a conductive path between the first electrode and the second electrode.

8. The switch of claim 7, wherein the first electrode and the second electrode are in an interdigitated configuration.
9. The switch of claim 7, wherein the distance between the first electrode and the second electrode is about 5 micrometers.
10. The switch of claim 7, wherein the palladium structure is electrochemically deposited on the first electrode.
11. The switch of claim 7, wherein the organic insulating film is deposited on the second electrode by electropolymerization.
12. The switch of claim 7, wherein the organic insulating film is comprised of phenol, aniline, pyrole, or combinations thereof.
13. The switch of claim 12, wherein the organic insulating film is a polyphenol film.
14. A method of detecting hydrogen in a gas sample, comprising:
providing a switch, including
 - an electrically-insulating support,
 - a first electrode and a second electrode positioned at a distance from one another and affixed to the support,
 - an organic insulating film deposited on the second electrode, and
 - a palladium structure deposited on and contacting the first electrode with at least a portion of the palladium structure extending to and contacting the organic insulating

film on the second electrode, such that, upon exposure to hydrogen, the portion of the palladium structure contacting the organic insulating film extends through the organic insulating film and contacts the second electrode;

applying a voltage potential between the first electrode and the second electrode;

exposing the switch to a gas sample; and

detecting a current between the first electrode and the second electrode to thereby detect hydrogen in the gas sample.

15. The method of claim 14, wherein the hydrogen is present in the gas sample at a concentration of as low as about 1.0 %.

16. The method of claim 14, wherein the organic insulating film is comprised of phenol, aniline, pyrole, or combinations thereof.

17. The method of claim 16, wherein the organic insulating film is a polyphenol film.

18. A method of fabricating a sensor for detecting an analyte of interest, comprising:
positioning a first electrode and a second electrode at a distance from one another on an electrically insulating support;

electropolymerizing a compound capable of producing an organic insulating film on the second electrode attached to the support; and

electrodepositing a metal on the first electrode attached to the support such that at least a portion of the metal extends to and contacts the organic insulating film.

19. The method of claim 18, wherein the compound capable of producing the organic insulating film is selected from the group consisting of phenol, aniline, pyrrole, and combinations thereof.
20. The method of claim 19, wherein the organic insulating film is a polyphenol film.
21. The method of claim 18, wherein the metal electrodeposited on the first electrode is selected from the group consisting of silver, palladium, or combinations thereof.
22. The method of claim 18, further comprising varying a thickness of the organic insulating film to change a response and a recovery time of the sensor.
23. The method of claim 22, wherein the varying the thickness of the organic insulating film comprises varying a number of electropolymerization cycles.
24. The method of claim 23, wherein the number of electropolymerization cycles is about 4 to about 10 cycles.

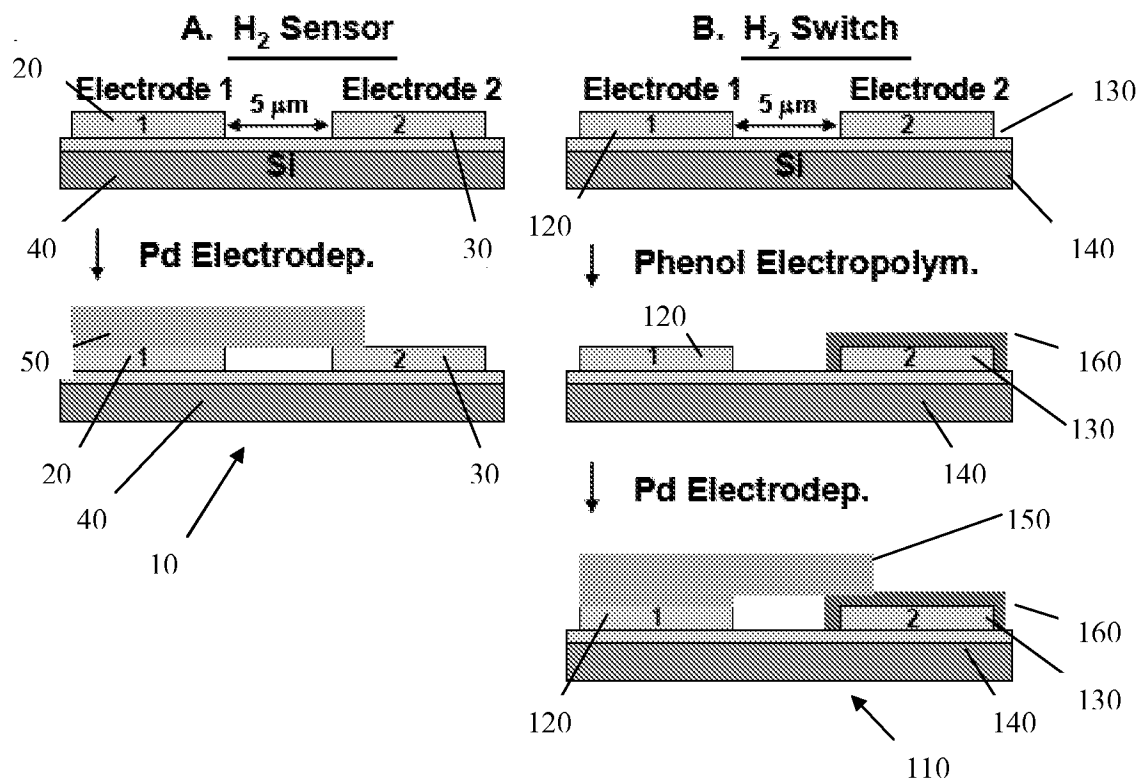


FIG. 1

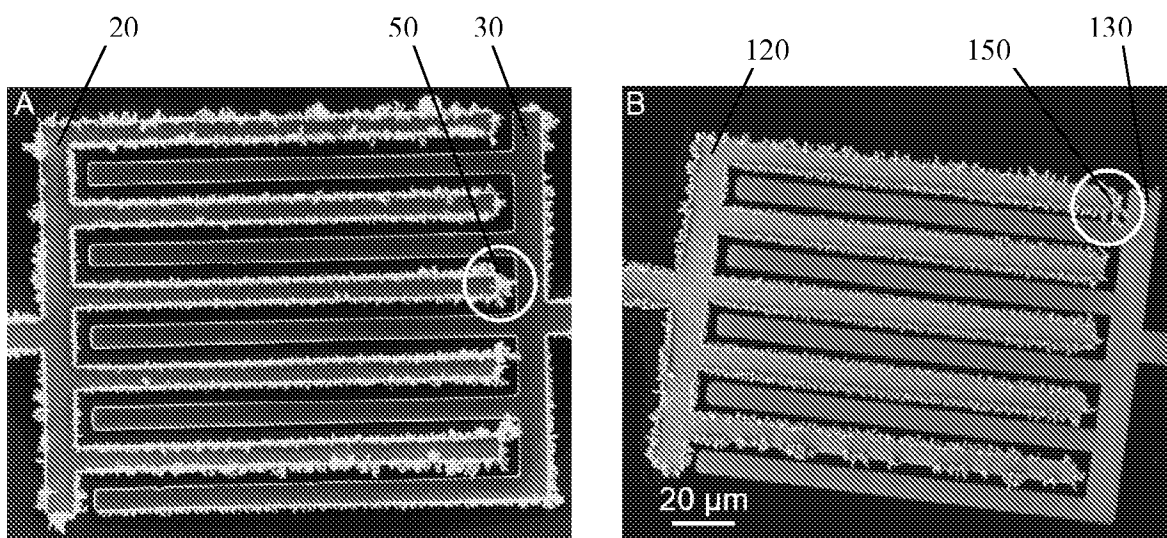


FIG. 2

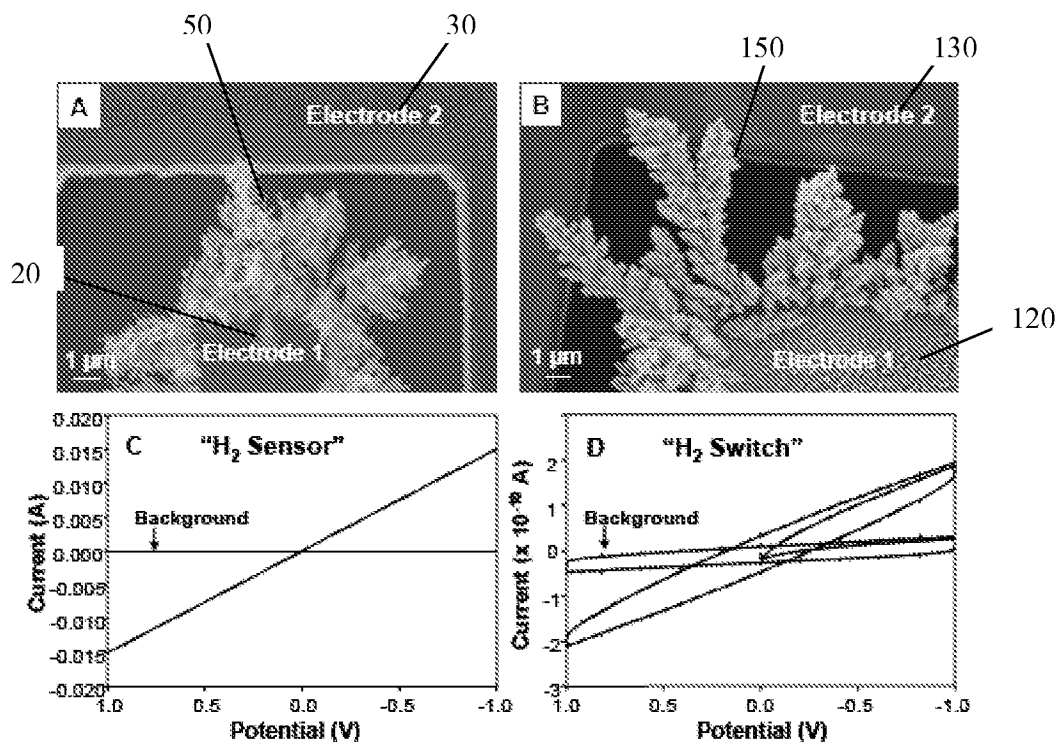


FIG. 3

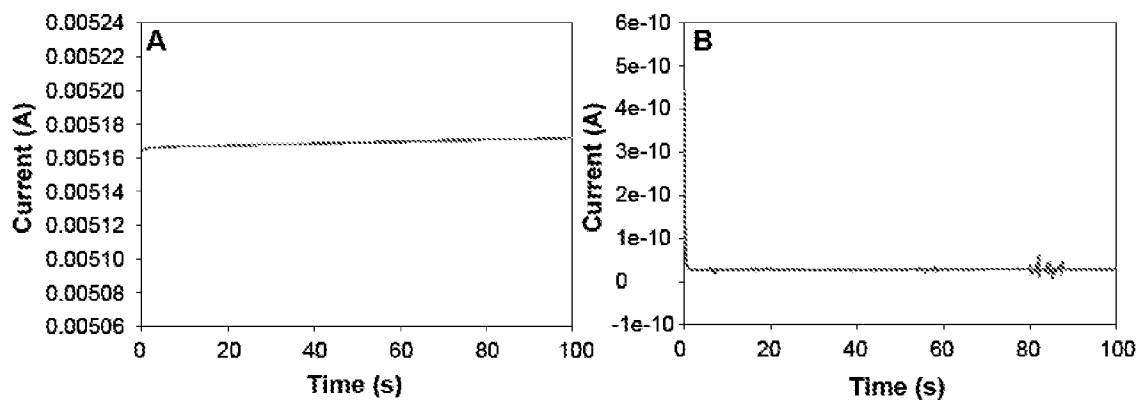


FIG. 4

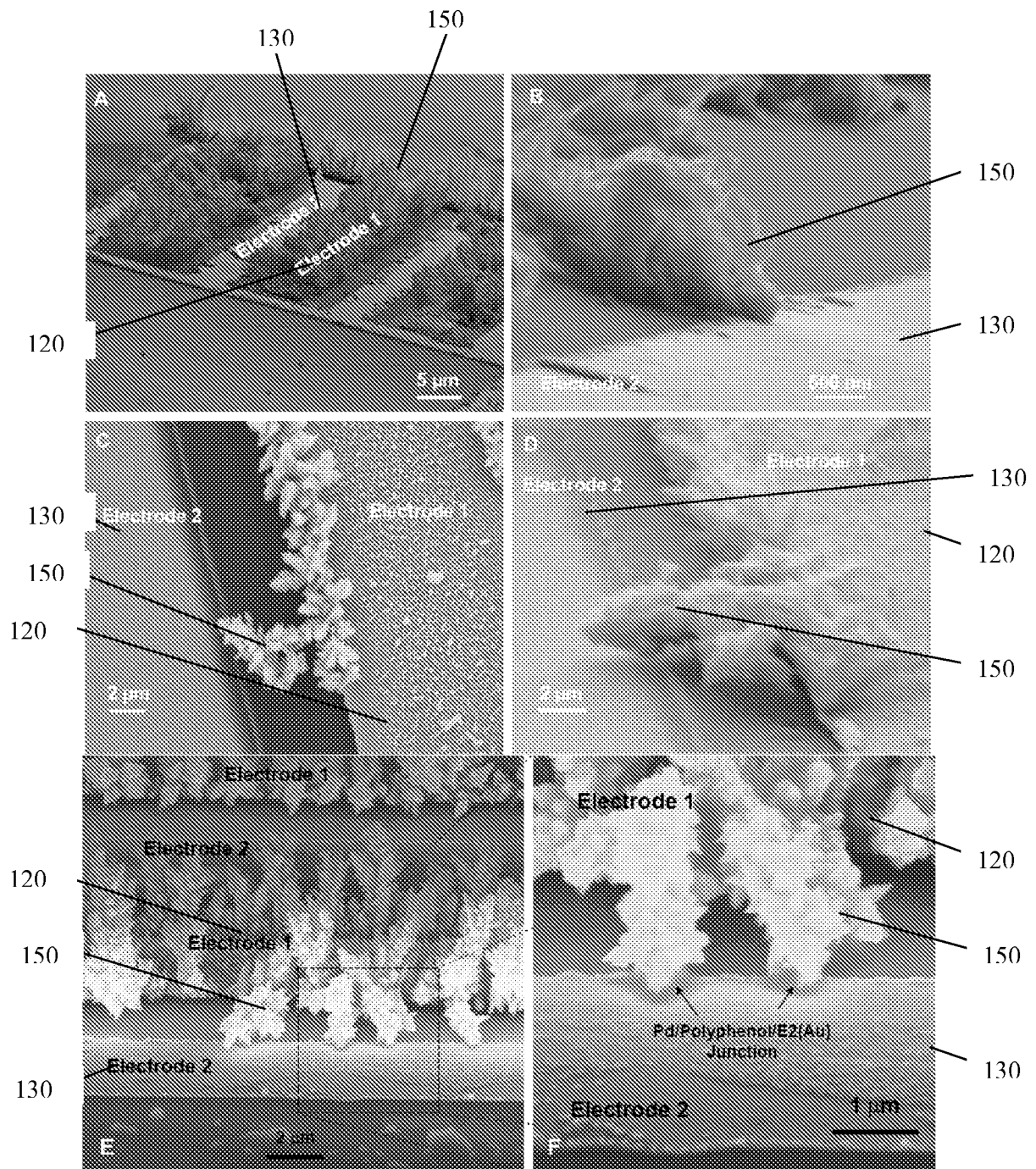


FIG. 5

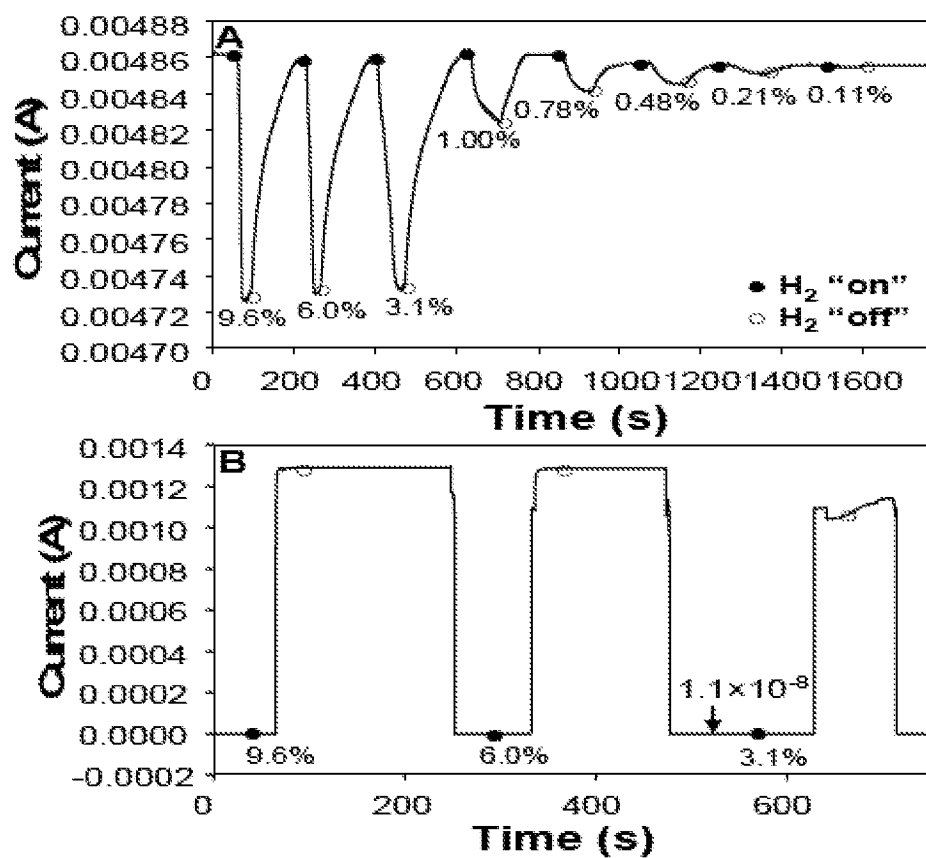


FIG. 6

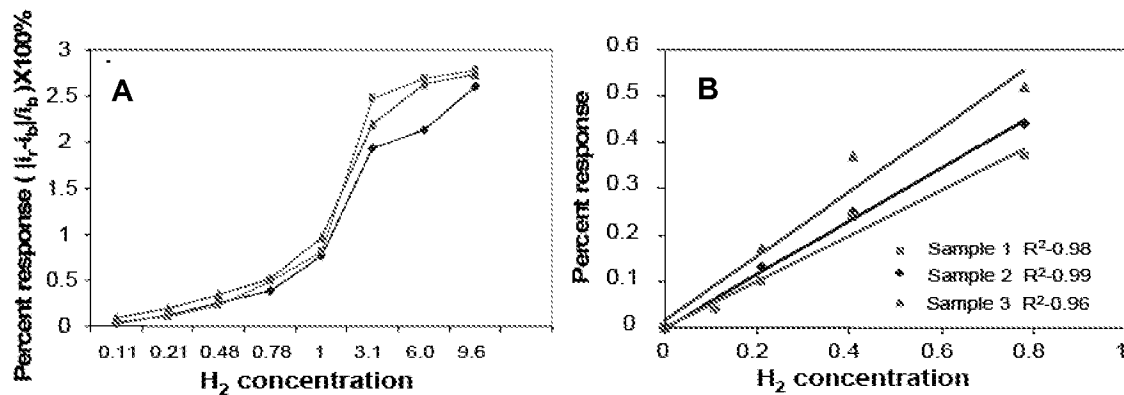


FIG. 7

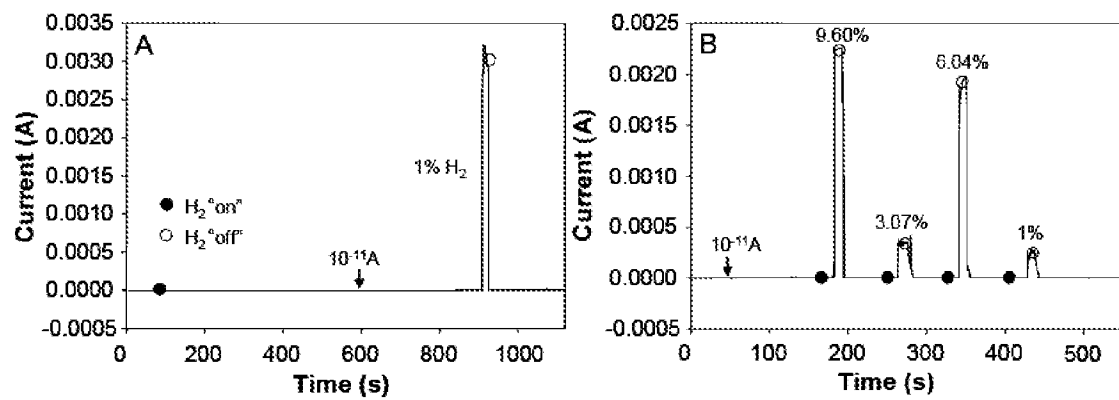


FIG. 8

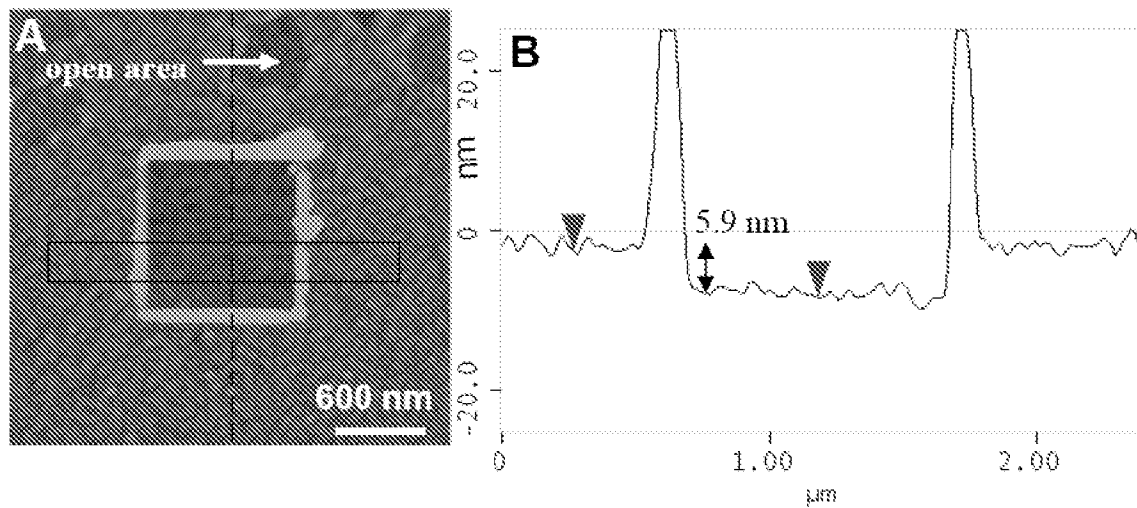


FIG. 9

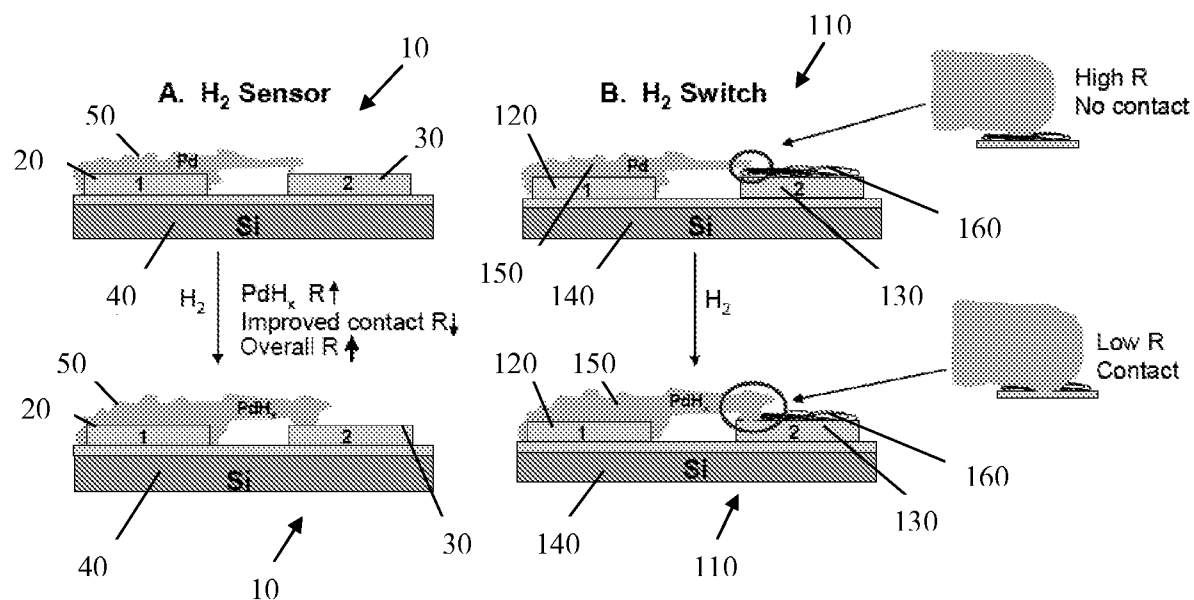


FIG. 10

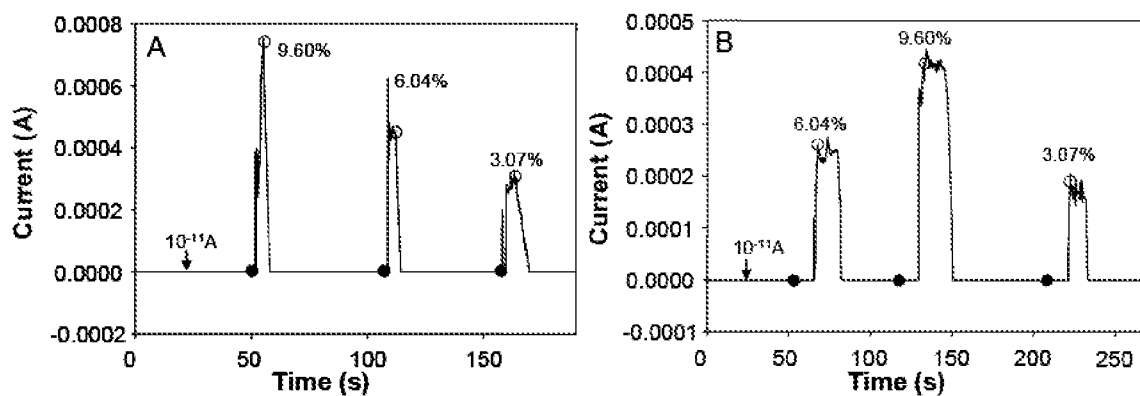


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/62787

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - G01N 27/407 (2009.01) USPC - 73/23.2 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) USPC - 73/23.2 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 73/31.06. IPC(8) - G01N 7/00, 27/00, 27/407 (2009.01). Term search-- see search terms below. Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST(USPT,PGPB,EPAB,JPAB); Dialogweb (344, 347, 348, 349, 371, 652, 654, 345, 351, 315, 35, 440, 155); USPTO online search; Google Scholar; Google Patents. Search terms: sensor, hydrogen, electrode, palladium, deposited, deposition, electrodeposition, film, polymer, polymerization, phenol, aniline, pyrrole, insulating, electropolymerization																																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 7,171,841 B2 (XU et al.) 06 February 2007 (06.02.2007), title; abstract; col 4, ln 21-37; col 5, ln 2-5; col 5, ln 13-14; col 5, ln 57-59; col 6, ln 62-64; FIGS. 2A, 4, 5A, 7</td> <td>5, 6</td> </tr> <tr> <td>X</td> <td>YUN et al., "Electrochemically Grown Wires for Individually Addressable Sensor Arrays." Nano Letters, 4(3): 419-422, March 2004 (03.2004), p. 421, col. 1, last full paragraph; p. 421, col. 2, first full paragraph; p. 422, col. 1, first paragraph; FIGS. 1, 4</td> <td>1, 3, 4</td> </tr> <tr> <td>Y</td> <td></td> <td>2, 9, 10, 18-24</td> </tr> <tr> <td>X</td> <td>BANEZ et al., "Reactivity of Hydrogen with Solid-State Films of Alkylamine- and Tetraoctylammonium Bromide-Stabilized Pd, PdAg, and PdAu Nanoparticles for Sensing and Catalysis Applications." Journal of the American Chemical Society, 130(2): 622-633, 16 January 2008 (16.01.2008), p. 624, col. 2, first full paragraph; p. 626, col. 1, last paragraph, running onto col. 2; p. 627, col. 1, first full paragraph; FIGS. 1, 3B, 4</td> <td>7, 14, 15</td> </tr> <tr> <td>Y</td> <td></td> <td>8-13, 16, 17</td> </tr> <tr> <td>Y</td> <td>US 2007/0140908 A1 (MIZUGUCHI, et al.) 21 July 2007 (21.07.2007), para [0057]; FIG. 1</td> <td>2, 8</td> </tr> <tr> <td>Y</td> <td>US 6,814,845 B2 (WILSON et al.) 09 November 2004 (09.11.2004), col 1, ln 47-60; col 3, ln 54-col 4, ln 8; col 4, ln 10-12</td> <td>11-13, 16-24</td> </tr> <tr> <td>Y</td> <td>US 2006/0021881 A1 (SOUNDARRAJAN et al.) 02 February 2006 (02.02.2006), para [0105], [0110]</td> <td>22-24</td> </tr> <tr> <td>A</td> <td>US 7,367,215 B2 (MONTY et al.) 06 May 2008 (06.05.2008), Summary Section; FIGS. 3, 4</td> <td>1, 4, 5</td> </tr> <tr> <td>A</td> <td>US 2008/0221806 A1 (BRYANT et al.) 11 September 2008 (11.09.2008), abstract; FIG. 1</td> <td>1, 5</td> </tr> <tr> <td>A</td> <td>US 7,416,702 B2 (YAMAGUCHI et al.) 26 August 2008 (26.08.2008), abstract; FIG. 1</td> <td>1, 5, 7, 14</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 7,171,841 B2 (XU et al.) 06 February 2007 (06.02.2007), title; abstract; col 4, ln 21-37; col 5, ln 2-5; col 5, ln 13-14; col 5, ln 57-59; col 6, ln 62-64; FIGS. 2A, 4, 5A, 7	5, 6	X	YUN et al., "Electrochemically Grown Wires for Individually Addressable Sensor Arrays." Nano Letters, 4(3): 419-422, March 2004 (03.2004), p. 421, col. 1, last full paragraph; p. 421, col. 2, first full paragraph; p. 422, col. 1, first paragraph; FIGS. 1, 4	1, 3, 4	Y		2, 9, 10, 18-24	X	BANEZ et al., "Reactivity of Hydrogen with Solid-State Films of Alkylamine- and Tetraoctylammonium Bromide-Stabilized Pd, PdAg, and PdAu Nanoparticles for Sensing and Catalysis Applications." Journal of the American Chemical Society, 130(2): 622-633, 16 January 2008 (16.01.2008), p. 624, col. 2, first full paragraph; p. 626, col. 1, last paragraph, running onto col. 2; p. 627, col. 1, first full paragraph; FIGS. 1, 3B, 4	7, 14, 15	Y		8-13, 16, 17	Y	US 2007/0140908 A1 (MIZUGUCHI, et al.) 21 July 2007 (21.07.2007), para [0057]; FIG. 1	2, 8	Y	US 6,814,845 B2 (WILSON et al.) 09 November 2004 (09.11.2004), col 1, ln 47-60; col 3, ln 54-col 4, ln 8; col 4, ln 10-12	11-13, 16-24	Y	US 2006/0021881 A1 (SOUNDARRAJAN et al.) 02 February 2006 (02.02.2006), para [0105], [0110]	22-24	A	US 7,367,215 B2 (MONTY et al.) 06 May 2008 (06.05.2008), Summary Section; FIGS. 3, 4	1, 4, 5	A	US 2008/0221806 A1 (BRYANT et al.) 11 September 2008 (11.09.2008), abstract; FIG. 1	1, 5	A	US 7,416,702 B2 (YAMAGUCHI et al.) 26 August 2008 (26.08.2008), abstract; FIG. 1	1, 5, 7, 14
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☐ Further documents are listed in the continuation of Box C. ☐																																						
<table border="0"> <tr> <td colspan="2"> * 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 another 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 </td> <td> "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 </td> </tr> </table>			* 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 another 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																																	
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Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774																																				