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(54) Title: DIRECT CHEMOCHROMIC SENSING HYDRATED NICKEL HYDROXIDE COATINGS AND THEIR APPLICATION IN ALCOHOL DETECTION

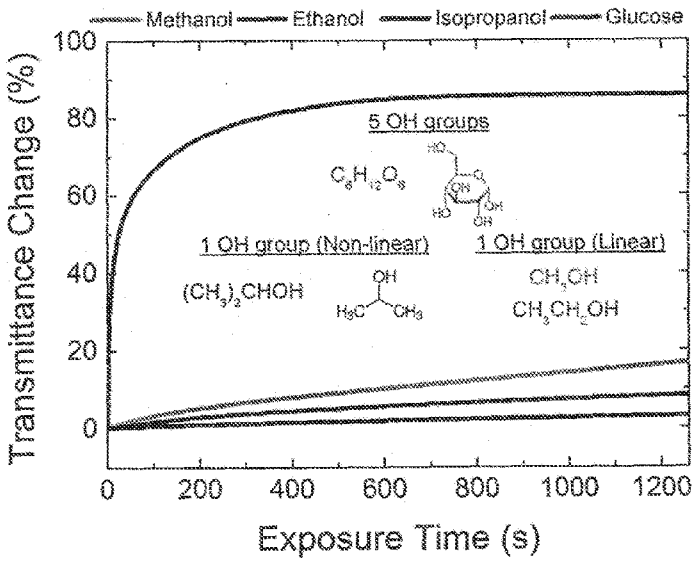

Fig. 2

(57) Abstract: The present invention demonstrates the use of hydrated nickel hydroxide, particularly in the form of thin film coatings, for the detection of reducing group containing compounds. The method of detection disclosed herein is based on chemochromic changes of the hydrated nickel hydroxide upon exposure to and contact with reducing functional groups. Furthermore, a device comprising a hydrated nickel hydroxide thin film coating deposited on an optically transparent substrate is described and exemplified by a sensor for detecting hydroxyl groups in breath alcohol. Also encompassed is a method of fabrication of such a device.

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DIRECT CHEMOCHROMIC SENSING HYDRATED NICKEL HYDROXIDE COATINGS AND THEIR APPLICATION IN ALCOHOL DETECTION

CROSS-REFERENCE TO RELATED APPLICATION

[001] The application claims the benefit of priority of Singapore Patent Application No. 10201507861T, filed September 21, 2015, the contents of which being hereby incorporated by reference in its entirety for all purposes.

FIELD OF THE TECHNOLOGY

[002] The present invention relates to the use of hydrated nickel hydroxide for the direct colorimetric sensing of reducing group containing compounds, and a method for the direct colorimetric sensing of reducing groups containing compounds, inclusive of hydroxyl groups found in alcohol. The present invention further relates to a device for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising a hydrated nickel hydroxide thin film coating and an optically transparent substrate, as well as to a method of fabrication of such a device.

BACKGROUND ART

[003] Currently, there are no easy way to detect visually the presence of reducing chemicals such as alcohols, sugars, amino acids, thiols and anti-oxidants. The impact of a visual, direct and stable detection is high since it will enable the development of personal care devices, monitoring devices or quick consumer kits that require low cost and effective indicator or sensor.

[004] The cost, in personal injury and property damage, due to accidents involving intoxicated drivers is well documented and represents an unacceptable risk to the public. Because any decrease in the frequency or severity of such accidents would be of considerable benefit, various efforts have been undertaken to develop sensors that detect the blood alcohol content (BAC) or, more typically, the breath alcohol content (BrAC).

[005] Currently, the state of the art alcohol detectors are based on 3-electrode cell measurements of electrochemical current with or without alcohol. This requires the "blow" test of bubbling one's breath into cell liquid and measuring the current from conversion of alcohol into acetic acid. This requires the need to assemble the cell and affects usability when the blower is being used. Older technologies involving a color change use color changing crystals or, more

recently, hydrogel embedded color changing crystals. Such systems are rather unstable and intended only for a single, non-cumulative use, whereby a wavelength shift can be detected. Such system also requires acid solution as a catalytic medium. Other inventions for alcohol detection involve more complex detection systems like gas chromatography or infrared spectroscopy using micro-electro-mechanical systems.

[006] U.S. Patent Application No. 20140234172 A1 discloses a breath analyzer, wherein the chemical sensor is sensitive to the concentration of an analyte in a sample of exhaled breath, and which includes a compensator for compensating the effects of variations in the amount of exhaled breath between the user and sensor location. The chemical sensor is located within a portable electronic device, and can be based on a chemomechanical principle, optical detectors, chemiresistors, or chemicapacitators.

[007] U.S. Patent No. 7,402,441 B2 discloses polyhydroxyethylmethacrylate (polyHEMA) as a holographic alcohol detector. In the method disclosed, alcohol binds to the polyHEMA film, causing it to swell, changing its absorption wavelength. The alcohol concentration is determined by measuring the reflectance wavelength of the polyHEMA film and comparing it with a calibration curve.

[008] U.S. Patent No. 8,441,357 B2 discloses the use of tin oxide as an alcohol detector. In the method disclosed, alcohol reacts with oxygen associated with tin oxide, allowing tin oxide to conduct current more readily. The alcohol concentration is determined by measuring a change of resistance of tin oxide.

[009] Kuswandi *et al.* (Sensors, 2014, 14(2), p. 2135-2149) discloses a visual ethanol biosensor based on alcohol oxidase (AOX) immobilized onto a polyaniline (PANI) film. The biosensor responds to the presence of ethanol *via* a color change from green to blue, due to the enzymatic reaction of ethanol that oxidizes the PANI film.

[0010] There is a persisting need of an easy to produce as well as easy to handle, stable, and reusable technique and apparatus for the sensing and determination of reducing group containing compounds, in particular for the sensing and determination of blood alcohol content and breath alcohol content of an individual.

SUMMARY OF THE INVENTION

[0011] In a first aspect, the present invention thus relates to the use of hydrated nickel hydroxide for the direct colorimetric sensing of one or more reducing group containing compounds in a

sample, wherein a chemochromic change of the hydrated nickel hydroxide is indicative of presence of one or more reducing group containing compounds in said sample.

[0012] In another aspect, the present invention relates to a method for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising contacting the hydrated nickel hydroxide with the sample and detecting a chemochromic change of the hydrated nickel hydroxide, wherein a chemochromic change of the hydrated nickel hydroxide is indicative of presence of one or more reducing group containing compounds in said sample.

[0013] In a further aspect, the present invention relates to a device for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising at least one optically transparent substrate sheet and a hydrated nickel hydroxide thin film coating deposited on at least one surface thereof.

[0014] In yet another aspect, the present invention also relates to a method of fabrication of a device as described herein, comprising the steps of:

(i) providing an optically transparent substrate sheet;
(ii) coating the optically transparent substrate sheet with a solution method; and
(iii) post- processing the coated substrate sheet; and
(iv) drying the substrate sheet obtained after step (iii).

[0015] Further embodiments are defined in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] **Figure 1** depicts the transmission change after 50 seconds of exposure to different concentrations of alcohol. Each set of data points across the range of concentration represents different films to test the repeatability of the growth technique.

[0017] **Figure 2** depicts the transmission change of a hydrated nickel hydroxide single layer thin film coating according to the present invention upon contact with different chemicals (at 1% concentration) after indicated exposure times. The different chemicals have different sizes and number of hydroxyl groups. The fastest reaction is the chemical with the highest reducing power, represented by the most hydroxyl groups. For chemicals with the same number of reducing groups (hydroxyl groups), the smallest chemical has the fastest speed of transmittance modulation.

[0018] **Figure 3** depicts the cumulative transmittance change of a hydrated nickel hydroxide single layer thin film coating according to the present invention with time upon exposure to different alcohol concentrations.

[0019] **Figure 4** depicts a cartoon showing possible applications of the present invention. a) As a general indicator to show presence of chemicals with reducing groups. b) As disposable, easy to use, breath analyzer to provide indication of BAC. c) As a wearable technology that indicates cumulative exposures.

[0020] **Figure 5** depicts the transmittance change of a hydrated nickel hydroxide single layer thin film coating according to the present invention upon repeated and multiple exposures to different alcohol concentrations at 150s.

[0021] **Figure 6** depicts the transmission change of a hydrated nickel hydroxide single layer thin film coating according to the present invention with time with electrochemical cycling after alcohol exposure bleaching. The maximum obtainable transmittance is reduced after exposure to alcohol. The reason may be due to creation of inactive regions.

[0022] **Figure 7** depicts the transmittance change variation of a hydrated nickel hydroxide single layer thin film coating according to the present invention with time after multiple exposure to alcohol. The plot shows that despite the reduction in maximum obtainable transmittance, the transmittance change remains stable.

[0023] **Figure 8** depicts a reflectance Fourier transform infrared spectroscopy (FTIR) spectrum of as films at different condition. It appears that presence of hydration in the loosely bounded form is important. Single cycle also serves to replace SO_4^- with OH^- ions.

[0024] **Figure 9** depicts the transmission change variation of different hydrated nickel hydroxide thin film coatings with time, showing the speed of transmittance modulation when reacting with chemicals with hydroxyl groups. The films have been processed under different conditions. "As-prepared" film refers to a dip-coated thin film. "1 cycle" refers to a single cyclic voltammetry (CV) cathodic and anodic application of electrochemical potential in KOH solution. "Activation" refers to a known method of repeated CV cycling with the aim of increasing the hydration of the coating. It is shown that the single cycle film gives the best response speed that can be more than 10 times better than other indicated processing methods.

[0025] **Figure 10** depicts cumulative transmittance change of a hydrated nickel hydroxide single layer thin film coating according to the present invention over time at room temperature and 100 °C. The material is relatively stable at room temperature while discernible changes can be seen

at elevated temperatures. Changes at elevated temperatures are related to increase availability of OH- on the surface of the coated film.

[0026] **Figure 11** depicts the correlation between blood alcohol content (BAC) and the amount of beer consumed, which varies based on one's gender and weight. The BAC legal limit for driving in Singapore is 0.08 % (or 190 ppm).

[0027] **Figure 12** depicts the transmission change of a hydrated nickel hydroxide single layer thin film coating according to the present invention with time after exposure to different concentrations of alcohol.

[0028] **Figure 13** depicts the summarized transmittance change of a hydrated nickel hydroxide single layer thin film coating according to the present invention at different alcohol percentages. The initial change effect and saturation effect are indicated.

DETAILED DESCRIPTION OF THE INVENTION

[0029] As used in this specification, the singular forms "a," "an" and "the" include plural forms unless the context clearly dictates otherwise. Thus, for example, the term "a material" is intended to mean one or more materials, or a combination thereof.

[0030] "One or more", as used herein, relates to at least one and comprises 1, 2, 3, 4, 5, 6, 7, 8, 9 or more of the referenced species.

[0031] "About", as used in the context of the present invention, defines a range of +/- 10 %, preferably +/- 5 % of the specific value given.

[0032] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as those commonly understood to one of ordinary skill in the art to which this invention pertains. Although any known methods, devices, and materials may be used in the practice or testing of the invention, the methods, devices, and materials in this regard are described herein.

[0033] The present invention discloses for the first time the use of hydrated nickel hydroxide for the direct colorimetric sensing of one or more reducing group containing compounds.

[0034] In the context of the present invention, the term "direct colorimetric sensing" refers to a method, wherein the sensing does not require any mediator reagents and/or catalysts and wherein the sensing is based on chemochromic changes, as described herein.

[0035] The term "reducing group containing compound" refers to any compound having at least one reducing functional group. Non-limiting examples of reducing groups are OH, NH_2 and SH. Non-limiting examples of compounds containing reducing groups include methanol, ethanol, propanol, butanol, ethane-1,2-diol, propane-1,2-diol, propane-1,2,3-triol, D-(+)-glucose, D-(+)-Mannose, methyl α-D-mannopyranoside, 1-thio-β-D-glucose and D-(+)-Galactose, cysteine, serine and alanine.

[0036] According to the present invention, the one or more reducing group containing compounds, as defined herein, may be comprised in a sample.

[0037] A sample comprising reducing group containing compounds, as defined herein, may be a single reducing group containing compound as such, such as the pure form of an alcohol like ethanol, or may be a mixture of different kinds of reducing group containing compounds, such as a mixture of methanol and ethanol. Furthermore, it is anticipated that a sample comprising reducing group containing compounds refers to a sample comprising, among other components, one or more reducing group containing compounds. A sample according to the present invention may be a gaseous, liquid, solid or semi-solid sample. As non-limiting examples, blood, saliva, and human breath may be enlisted, wherein human breath relates to the air exhaled by a human individual in the process of respiration.

[0038] According to the present invention, the sensing of reducing group containing compounds is a colorimetric sensing, which is based on chemochromic changes of the hydrated nickel hydroxide, as described herein, that occur upon contact of the hydrated nickel hydroxide with at least one reducing group containing compound. The chemochromic change of the hydrated nickel hydroxide, as described herein, is detectable and manifests itself in a bleaching of the hydrated nickel hydroxide, which results in a change of transmittance of the hydrated nickel hydroxide. The sensing, as described herein, is a direct sensing and does not require any mediator reagents and/or catalysts.

[0039] "Bleaching", as used in the context of the present invention, refers to a change of color, wherein a comparably darker state is transformed into a comparably lighter state of the respective material.

[0040] Accordingly, exposure of the hydrated nickel hydroxide to one or more, that is, at least one reducing group containing compound results in a chemochromic change of the hydrated nickel hydroxide, as described herein, which is indicative of the presence of said at least one reducing group containing compound. Furthermore, if said reducing group containing compound is comprised in a sample and the hydrated nickel hydroxide is exposed to, that is, contacted with

said sample, a chemochromic change of the hydrated nickel hydroxide, as described herein, is indicative of the presence of at least one reducing group containing compound in said sample.

[0041] Thus, a first object of the present invention is the use of hydrated nickel hydroxide for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, wherein a chemochromic change of the hydrated nickel hydroxide is indicative of presence of one or more reducing group containing compounds in said sample.

[0042] According to certain embodiments, the chemochromic change of the hydrated nickel hydroxide is a change in transmittance, preferably an increase in transmittance.

[0043] According to certain embodiments, at least one of the one or more reducing group containing compound is ethanol.

[0044] According to certain embodiments, the hydrated nickel hydroxide is in the form of a thin film coating. According to preferred embodiments, the hydrated nickel hydroxide is in the form of a single layer thin film coating. A "single layer" thin film coating, as used in the context of the present invention, refers to a coating layer consisting of only the hydrated nickel hydroxide thin film coating, as described herein. Methods of fabrication of such (single layer) nickel hydroxide thin film coatings will be described herein in more detail. According to preferred embodiments, the hydrated nickel hydroxide is in the form of a single layer thin film coating, which has been treated in a 1 cycle anodic/cathodic voltammetric cycle treatment in an aqueous electrolyte solution, as will be described herein in more detail.

[0045] According to certain preferred embodiments, the hydrated nickel hydroxide thin film coating, as described herein, is located on at least one, preferably only one surface of an optically transparent substrate sheet. According to other preferred embodiments, the hydrated nickel hydroxide single layer thin film coating is located on at least one, preferably only one surface of an optically transparent substrate sheet.

[0046] "Optically transparent", as used in the context of the present invention, refers to any kind of material that is translucent, i.e. permits visible light transmittance of greater than 60 percent.

[0047] An optically transparent substrate useful in the context of the present invention may be any kind of material that satisfies the above definition and that may be coated with a hydrated nickel hydroxide thin film coating, as described herein. Non-limiting examples of materials suitable in this context include, without limitation, optically transparent glasses as well as optically transparent plastics. Also anticipated are mixtures of different kinds of optically transparent materials. An optically transparent substrate sheet according to the present invention may optionally comprise further materials or components.

[0048] According to the present invention, the optically transparent substrate material, on the surface of which a hydrated nickel hydroxide thin film coating is located on, is in the form of a sheet. In the context of the present invention, an "optically transparent substrate sheet" relates to an optically transparent substrate material, which is broad and thin in dimension. Thus, two major surfaces may be identified, wherein these two surfaces may be referred to, in the case of the sheet being in a horizontal position, as a lower and an upper surface.

[0049] According to certain embodiments, the hydrated nickel hydroxide thin film coating is located on only one of the surfaces of the transparent substrate sheet. This embodiment is particularly preferred, as the sensing, that is, detecting of the chemochromic changes of the hydrated nickel hydroxide thin film coating upon contact with one or more reducing group containing compounds on the surface of the optically transparent substrate sheet may be more readily perceptible. In this case, exposure and a respective response of the entire coated surfaces may be guaranteed, whereas, in the case of a complete coating of the entire substrate surface (i.e. upper and lower surface, as defined above), certain areas of the hydrated nickel hydroxide coating may not be sufficiently exposed. Possible distortion of detecting results should be anticipated and taken into account for design.

[0050] The chemochromic change of the hydrated nickel hydroxide, which, in particularly preferred embodiments, may be in the form of a single layer thin film coating, is quite sensitive to very low concentrations of reducing group containing compounds. According to the present invention, reducing group containing compounds may be detected in concentrations of as low as double digit ppm (part per million) concentrations (**Figure 1**). However, the sensitivity of the hydrated nickel hydroxide, as disclosed herein, also depends on the amount of hydroxyl functional groups present in a respective compound as well as the molecular size of the respective compound (**Figure 2**). In general, the higher the reducing power (more hydroxyl functional groups) of a compound, the faster the response in the form of chemochromic changes of the hydrated nickel hydroxide, as disclosed herein. Furthermore, with respect to molecular sizes, the smallest molecule generally elicits the fastest response. Without wishing to be bound by theory, it is assumed that smaller molecules have a higher diffusion coefficient and lower steric hindrance, in other words, contact of the hydrated nickel hydroxide coating surface is more readily accomplished. Furthermore, the higher the concentration of a reducing compound in a sample, the faster and the more intense, in terms of transmittance change, the respective response of the hydrated nickel hydroxide, as described herein (**Figure 3**).

[0051] According to certain embodiments, a lower detection limit of reducing group containing compounds of the hydrated nickel hydroxide, as disclosed herein, is 50 ppm. This lower detection limit, in particular, holds for the detection of ethanol. In preferred embodiments, ethanol may be

detected in a gaseous sample, such as a human breath sample, using the hydrated nickel hydroxide according to the present invention, preferably in the form of a hydrated nickel hydroxide thin film coating, even more preferably in the form of a hydrated nickel hydroxide single layer thin film coating. According to certain embodiments, the lower detection limit of ethanol in an individual's breath is 50 ppm.

[0052] A further object of the present invention is a method for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising contacting the hydrated nickel hydroxide with the sample and detecting a chemochromic change of the hydrated nickel hydroxide, wherein a chemochromic change of the hydrated nickel hydroxide is indicative of presence of one or more reducing group containing compounds in said sample, as described herein. According to preferred embodiments, the hydrated nickel hydroxide is in the form of a thin film coating, as described herein. According to even more preferred embodiments, the hydrated nickel hydroxide is in the form of a single layer thin film coating. According to even more preferred embodiments, the hydrated nickel hydroxide is in the form of a single layer thin film coating, which has been treated in a 1 cycle anodic/cathodic voltammetric cycle treatment in an aqueous electrolyte solution, as will be described herein in more detail.

[0053] The method according to the present invention comprises the contacting of the hydrated nickel hydroxide, as described herein, a sample. Said contacting may be realized by any means, including, without limitation, the breathing of an individual's breath onto the hydrated nickel hydroxide, as described herein, the applying of a liquid sample comprising one or more reducing group containing compounds onto the hydrated nickel hydroxide, as described herein, the exposing of the hydrated nickel hydroxide, as described herein, to fumes and/or aerosols comprising one or more reducing group containing compounds, etc.. As detailed above, the eliciting of chemochromic changes of the hydrated nickel hydroxide is indicative of contact of the hydrated nickel hydroxide with one or more reducing group containing compounds, in other words, presence of one or more reducing group containing compounds within the sample, as defined herein. Naturally, the hydrated nickel hydroxide, as described herein, may also be contacted with a composition not containing any reducing group containing compounds, wherein the absence of any detectable chemochromic changes of the hydrated nickel hydroxide is indicative of the absence of any reducing group containing compounds within the sample.

[0054] The contacting time is not particularly limited, although a certain amount of time should be calculated for the one or more reducing group containing compounds to diffuse into the surface of the hydrated nickel hydroxide, as described herein, and for the contact responsive chemochromic change of the hydrated nickel hydroxide to occur. As indicated above, the time it takes for a chemochromic contact responsive change to occur is depending on both the quantity of hydroxyl functional groups present in the respective molecule(s) and the molecular size of the

respective molecule(s). Comparative results obtained for the chemochromic changes of a hydrated nickel hydroxide thin film coating according to the present invention are depicted in **Figure 2**. The response elicited by glucose is comparably fast and results in a maximum transmittance of 80 % after approximately 8 minutes, wherein a detectable chemochromic change is already noticeable after a few seconds of contacting time. The responses elicited by different compounds comprising only one hydroxyl functional group result in a maximum transmittance of about 5 to 20 % after approximately 20 minutes, wherein chemochromic changes may be detectable after approximately 3 to 5 minutes.

[0055] In the context of the present invention, the term "detectable" refers to both detecting of a respective response by means of one or more detecting devices, and detecting of a respective response by an observer by visual perception only. In the context of the present invention, a response to be detected is based on chemochromic changes of the nickel hydroxide, as disclosed herein. The chemochromic change of the hydrated nickel hydroxide manifests itself in a bleaching of the hydrated nickel hydroxide upon contact with reducing group containing compounds. When disposed on a transparent substrate sheet, as defined herein, a hydrated nickel hydroxide thin film coating is bleached upon contact with reducing group containing compounds, and the transmittance of the hydrated nickel hydroxide coated transparent substrate sheet is increased as compared to the formerly non-bleached state of the assembly. Depending on the quantity of hydroxyl functional groups of the respective molecule(s) to be detected, the molecular size of the respective molecule(s), the concentration of the respective molecules, as well as both contacting and response time, the chemochromic change of the hydrated nickel hydroxide may be detectable by an observer by visual perception, or may be detectable by means of a photodetector only, which measures the light transmitted through the hydrated nickel hydroxide coated transparent substrate sheet, and, in comparing transmittance before and after contacting of the hydrated nickel hydroxide with reducing group containing compounds, signals changes, which may then be processed and displayed by suitable devices for an observer to be interpreted easily and accordingly. Photodetectors are known in the art and may be chosen freely to meet varying demands. The light transmitted through the hydrated nickel hydroxide coated transparent substrate sheet as described herein may be emitted by an external source or by an internal source. In the context of the present invention, light emitted by an external light emitting source may be sunlight or any kind of artificial light emitted in the surroundings of an individual observing the detectable response of the hydrated nickel hydroxide, as described herein, to reducing group containing compounds. However, in the context of the present invention, it is also anticipated that a light emitting device intrinsically involved in the detecting of said response of the hydrated nickel hydroxide, as described herein, may serve as an internal light source, or an in-built light source. Devices suitable in this context are known in the art and include, without limitation, light emitting diodes (LEDs) and organic light emitting diodes (OLEDs).

[0056] Thus, another object of the present invention is a device for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising at least one optically transparent substrate sheet and a hydrated nickel hydroxide thin film coating deposited on at least one surface thereof.

[0057] According to certain embodiments, the hydrated nickel hydroxide thin film coating is a hydrated nickel hydroxide single layer thin film coating.

[0058] According to certain embodiments, the device according to the present invention further comprises at least one photodetector and/or at least one light emitting device.

[0059] According to certain embodiments, the device is a breath alcohol sensor device. The design of the device according to the present invention is not particularly limited, as long as contact of reducing group containing compounds may be enabled and a respective response in the form of chemochromic changes of the hydrated nickel hydroxide may be detectable and observable. Therefore, anticipated are loose sheets composed of only the optically transparent substrate sheet and the (single layer) hydrated nickel hydroxide thin film coating, as described herein, optionally further comprising components that facilitate handling of the device, such as protective sheeting or casing partially affixed to the sheet according to the present invention. Furthermore, it is anticipated that the device according to the present invention be incorporated into an electronic device, such as a cell phone or general operating modular units as employed in the automotive field. Incorporation of a device as disclosed herein may be temporary or permanent. By way of example, **Figure 4** depicts possible embodiments of the device according to the present invention. **Figure 4a** illustrates a general indicator in the form of a loose sheet to signal presence of chemicals with reducing groups. **Figure 4b** illustrates a disposable, easy to use, breath analyzer to provide indication of BAC, also in the form of a loose sheet. **Figure 4c** illustrates a wearable technology as anticipated by the present invention, wherein the device according to the present invention is incorporated into a wearable detecting device.

[0060] The device according to the present invention may be a disposable device for one time use only, or it may be a device suitable for repeated use and the cumulative detecting of the presence of reducing group containing compounds in a sample. As evidenced in **Figure 5**, wherein depicted is the change of transmittance after multiple use of a hydrated nickel hydroxide thin film, a device according to the present invention is suitable for repeated usage. In **Figure 6**, transmittance changes of a hydrated nickel hydroxide thin film coating according to the present invention before and after several rounds of exposure to reducing group containing compounds are depicted. In **Figure 7**, the effect of repeated exposure of a hydrated nickel hydroxide thin film coating to reducing group containing compounds with respect to transmittance changes is

illustrated. The results depicted in both **Figure 6** and **Figure 7** prove reusability of the device according to the present invention, as only slight degradation of the film after repeated exposure is observable.

[0061] A further object of the present invention is a method of fabrication of a device as disclosed herein, wherein the device comprises an optically transparent substrate sheet, as defined herein, and a hydrated nickel hydroxide thin film coating located on at least one surface thereof. The method according to the present invention comprises the steps of (i) providing an optically transparent substrate sheet, as defined herein, (ii) coating the optically transparent substrate sheet with a solution method, (iii) post-processing the coated substrate sheet, and (iv) drying the coated substrate sheet obtained after step (iii).

[0062] The coating of the optically transparent substrate according to the present invention is realized by a solution method. A solution method according to the present invention encompasses the contacting the substrate with a coating solution, wherein a coating solution according to the present invention may be prepared to be comprising nickel sulfate, potassium persulfate, and aqueous ammonia (solution method 1), or to be comprising nickel nitrate (solution method 2). According to preferred embodiments, the solution of solution method 1 contains only nickel sulfate, potassium persulfate, and aqueous ammonia, in particular 4 parts of 1 M nickel sulfate, 3 parts of 0.25 M potassium persulfate and 1 part of 25 % aqueous ammonia. According to other preferred embodiments, the solution of solution method 2 contains only nickel nitrate, preferably 0.5 M nickel nitrate. The contacting of the substrate with a solution according to the present invention may encompass, for instance and without limitation, the dipping of the substrate into the solution, the immersing of the substrate into the solution, the spraying of the solution onto the substrate, application of the solution onto the substrate in roll-to-roll coating processes etc.. According to solution method 1, the coating is achieved by vertical dip coating of the substrate into freshly prepared solution according to solution method 1 for 1 to 60 minutes at room temperature. According to solution method 2, the coating is achieved by immersing the substrate into the solution according to solution method 2, followed by application of a -0.8 – 1.1 V voltage, relative to Ag/AgCl reference electrode, for a duration of 30 seconds to 10 minutes, at room temperature.

[0063] The post-processing of the coated optically transparent substrate sheet according to the present invention is realized by immersing the coated substrate into an aqueous electrolyte solution, followed by conducting one or more cyclic anodic/cathodic voltammetric cycles. According certain embodiments of the present invention, the aqueous electrolyte solution is a KOH solution, preferably a 0.1-1M KOH solution. The one or more, that is, at least one, cyclic anodic/cathodic voltammetric cycles may be performed by applying at least one cyclic sweep

voltage, preferably between -0.2 to 0.8 V, relative to an Ag/AgCl reference electrode. At least one cyclic sweep refers to a minimum of one complete cycle at room temperature.

[0064] The drying of the coated substrate sheet obtained after step (iii) of the process according to the present invention may be realized by any drying means known in the art and may encompass, for instance, the drying of the coated substrate sheet by natural air drying, or blow drying, or hot plate drying.

[0065] It has been found that conducting cyclic anodic/cathodic voltammetric cycles on the coated substrate sheet, as described above, further improves the overall sensing sensitivity of the hydrated nickel hydroxide thin film coating.

[0066] By conducting anodic/cathodic voltammetric cycles on the coated substrate sheet, ionic species intercalated in the molecular lattice of the hydrated nickel hydroxide coated onto the surface of the substrate sheet, such as SO_4^- ions, are removed, thereby promoting subsequent hydration of the coating (**Figure 8**).

[0067] It has been found by the inventors that hydrated nickel hydroxide thin film coatings prepared in a solution method 1 according to the present invention and treated in only one complete anodic/cathodic voltammetric cycle are most efficient in the sensing of reducing group containing compounds, as defined herein. **Figure 9** illustrates time-dependent transmittance change percentages of hydrated nickel hydroxide thin film coatings prepared by different methods. "As prepared" refers to a hydrated nickel hydroxide thin film coating, wherein the optically transparent substrate sheet is dip coated with a solution containing $NiSO_4$, $K_2S_2O_8$ and aqueous ammonia. "1 cycle" refers to a hydrated nickel hydroxide thin film coating prepared by a method according to the present invention, wherein the optically transparent substrate sheet is dip coated with a solution consisting of $NiSO_4$, $K_2S_2O_8$ and aqueous ammonia and subsequently treated in a 1 cycle anodic/cathodic voltammetric cycle treatment in KOH solution. "Activation" refers to a hydrated nickel hydroxide thin film coating prepared by dip coating the optically transparent substrate sheet with a solution consisting of $NiSO_4$, $K_2S_2O_8$ and aqueous ammonia, and subsequent repeated cyclic voltammetry (CV) treatment of the coated substrate sheet in order to increase hydration of the coating. "Sputtered" refers to a nickel oxide thin film coated using physical vapor deposition.

[0068] The results obtained with respect to transmittance change of the respective coatings upon contact with reducing group containing compounds as indicated in **Figure 9** show that best results are achieved using a hydrated nickel hydroxide thin film coating prepared by a method according to the present invention, wherein the optically transparent substrate sheet is dip coated with a solution consisting of $NiSO_4$, $K_2S_2O_8$ and aqueous ammonia and subsequently treated in a 1 cycle

anodic/cathodic voltammetric cycle treatment in KOH solution. Treatment of the coating according to the present invention in more than one CV cycle will cause densification of the film and, eventually, detachment of layers. The optimum with respect to reducing group containing compound detection is achieved with just one CV cycle, which serves the purpose of removing intercalated ion species and allows for subsequent hydration of the coating. This variation of processing results in an enhancement of speed of transmittance change from 3-10 % per minute to more than 35 % per minute, approximately 39 % per minute.

[0069] According to certain embodiments, only one cyclic voltammetric cycle is conducted on the substrate obtained after step (iii). This embodiments is especially useful when the coating of the optically transparent substrate sheet is realized according to solution method 1, as described herein.

[0070] According to other embodiments, more than one cyclic voltammetric cycles are conducted on the substrate obtained after step (iii). This embodiments is especially useful when the coating of the optically transparent substrate sheet is realized according to solution method 2, as described herein.

[0071] As indicated in **Figure 10**, the transmittance profile of the hydrated nickel hydroxide coating is open circuit stable at room temperature. At higher temperatures, however, changes in the transmittance profile cab be observed. Thus, another object anticipated by the present invention is the detection of changes in temperature using hydrated nickel hydroxide as described herein, in particular hydrated nickel hydroxide in the form of a thin film coating, in the presence of one or more reducing group containing compounds. **Figure 10** shows a cumulative transmittance change of a hydrated nickel hydroxide thin film coating on a transparent substrate according to the present invention at different temperatures can be observed. Without wishing to be bound by theory it is assumed that, with elevated temperatures, the availability of hydroxyl functional groups on the surface of the coating is increased, resulting in detectable transmittance changes, as described herein.

[0072] Using a device as described herein, the presence of reducing group containing compounds in a sample, as defined herein, may be detected in real time, and the concentration of a known reducing group containing substance, such as ethanol in a human breath sample, may be determined using a calibrated reference table.

[0073] The methods of usage and the device according to the present invention require no supplementary reagents, such as catalysts or triggering chemicals, as opposed to the state of the art methods and devices. The material as disclosed herein is open circuit stable at ambient temperature. For lower concentrations of reducing group containing compounds in a sample, detection at concentrations in the range of ppm levels is possible and may be facilitated by the

employment of cameras or photodetectors with or without in-built light sources. At higher concentrations of reducing group containing compounds, the response elicited, as described herein, is visible within seconds. Thus, at higher concentrations of reducing group containing compounds, the detection device requires no electronics, no external bias, and no external energy supply. The final effect of the sensing is cumulative. For this reason, the device according to the present invention may be used as an indicator to show cumulative or instant exposure to chemical fumes or chemical spills in the relevant industry. The device may be deigned in the form of a wearable coated patch or pre-installed indicator device, whereby the cumulative sensing capability of hydroxyl functional groups, over long periods of time, can be achieved and visually observed.

[0074] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject-matter from the genus, regardless of whether or not the excised material is specifically recited herein. Other embodiments are within the following claims. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0075] One skilled in the art would readily appreciate that the present invention is well adapted to carry out the objects and obtain the ends and advantages mentioned, as well as those inherent therein. Further, it will be readily apparent to one skilled in the art that varying substitutions and modifications may be made to the invention disclosed herein without departing from the scope and spirit of the invention. The compositions, methods, procedures, treatments, molecules and specific compounds described herein are presently representative of preferred embodiments are exemplary and are not intended as limitations on the scope of the invention. Changes therein and other uses will occur to those skilled in the art which are encompassed within the spirit of the invention are defined by the scope of the claims. The listing or discussion of a previously published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

[0076] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising”, “including,” containing”, etc. shall be read expansively and without limitation. The word "comprise" or variations such as "comprises" or "comprising" will accordingly be understood to imply the inclusion of a stated integer or groups of integers but not the exclusion of any other integer or group of integers. Additionally, the terms and expressions

employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by exemplary embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0077] The content of all documents and patent documents cited herein is incorporated by reference in their entirety.

EXAMPLES

[0078] **Example 1:** A hydrated nickel hydroxide coated substrate sheet according to the present invention may be prepared as described in the following:

[0079] A coating solution 1 according to solution method 1, as described herein, containing 4 parts of 1M nickel sulfate, 3 parts of 0.25 M potassium persulfate and 1 part of 25% aqueous ammonia is prepared. The coating is achieved by vertical dip coating of the substrate into freshly prepared solution 1 for 1 to 60 minutes at room temperature.

[0080] Alternatively, a coating solution according to solution method 2, as described herein, containing 0.5 M nickel nitrate is prepared. The coating is achieved by immersing the substrate into solution 2, followed by application of a -0.8 to 1.1 V voltage, relative to Ag/AgCl reference electrode, for a duration of 30 seconds to 10 minutes, at room temperature.

[0081] The substrate obtained after either method is then rinsed with water followed by natural drying or drying with air gun.

[0082] The post processing step is achieved by immersing the coated substrate obtained according to solution method 1 or solution method 2 into a 0.1 to 1 M KOH solution, followed by application of at least one cyclic sweep voltage between -0.2 to 0.8 V, relative to an Ag/AgCl reference electrode. At least one cyclic sweep refers to a minimum of one complete cycle, at room temperature.

CLAIMS

1. Use of hydrated nickel hydroxide for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, wherein a chemochromic change of the hydrated nickel hydroxide is indicative of presence of one or more reducing group containing compounds in said sample.

2. The use according to claim 1, wherein the hydrated nickel hydroxide is in the form of a thin film coating, preferably a single layer thin film coating.

3. The use according to claim 2, wherein the hydrated nickel hydroxide thin film coating is located on at least one, preferably only one surface of an optically transparent substrate sheet.

4. The use according to any one of the preceding claims, wherein chemochromic change of the hydrated nickel hydroxide is a change in transmittance, preferably an increase in transmittance.

5. Method for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising contacting the hydrated nickel hydroxide with the sample and detecting a chemochromic change of the hydrated nickel hydroxide, wherein a chemochromic change of the hydrated nickel hydroxide is indicative of presence of one or more reducing group containing compounds in said sample.

6. Device for the direct colorimetric sensing of one or more reducing group containing compounds in a sample, comprising at least one optically transparent substrate sheet and a hydrated nickel hydroxide thin film coating deposited on at least one surface thereof.

7. The device according to claim 6, further comprising at least one photodetector and/or at least one light emitting device.

8. The device according to claim 6 or 7, wherein the device is a breath alcohol sensor device.

9. Method of fabrication of a device according to claim 6, comprising the steps of:
   (i) providing an optically transparent substrate sheet;

(ii) coating the optically transparent substrate sheet with a solution method; and

(iii) post-processing the coated substrate sheet; and

(iv) drying the substrate sheet obtained after step (iii).

10. The method according to claim 9, wherein the post-processing of step (iii) s realized by immersing the coated substrate sheet obtained after step (ii) into an aqueous electrolyte solution and conducting one or more cyclic anodic/cathodic voltammetric cycles.

11. The method according to claim 10, wherein only one cyclic voltammetric cycle is conducted on the substrate obtained after step (iii).

12. The method according to claim 10, wherein more than one cyclic voltammetric cycles are conducted on the substrate obtained after step (iii).

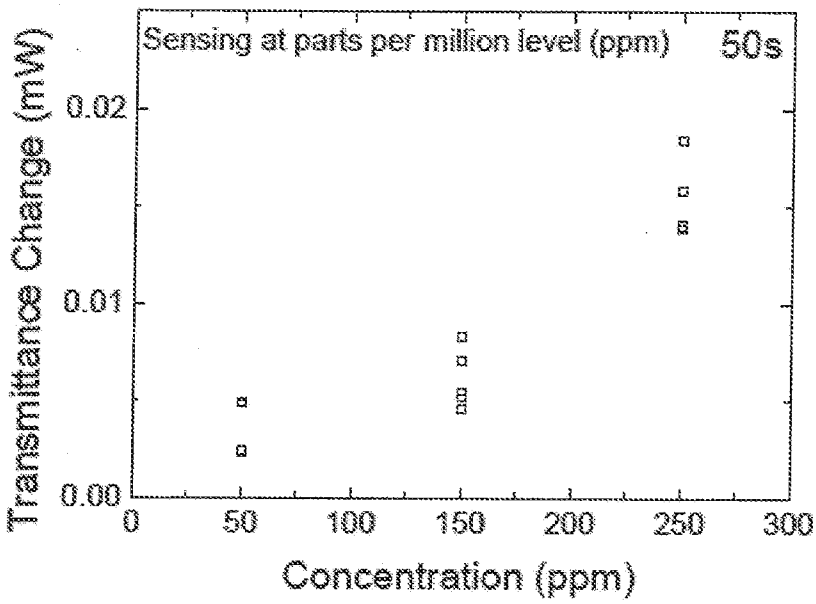
Sensing at parts per million level (ppm)
50s
Transmittance Change (mW)
0.02
0.01
0.00
0
50
100
150
200
250
300
Concentration (ppm)

Fig. 1

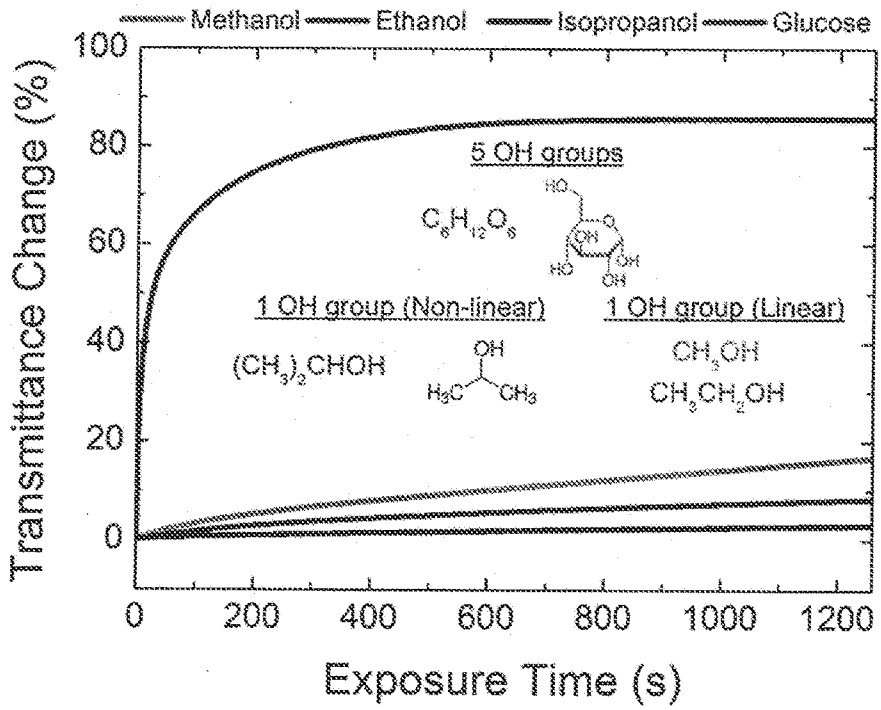
Methanol
Ethanol
Isopropanol
Glucose
Transmittance Change (%)
100
80
60
40
20
0
0
200
400
600
800
1000
1200
Exposure Time (s)
5 OH groups
C6H12O6
1 OH group (Non-linear)
(CH3)2CHOH
1 OH group (Linear)
CH3OH
CH3CH2OH

Fig. 2

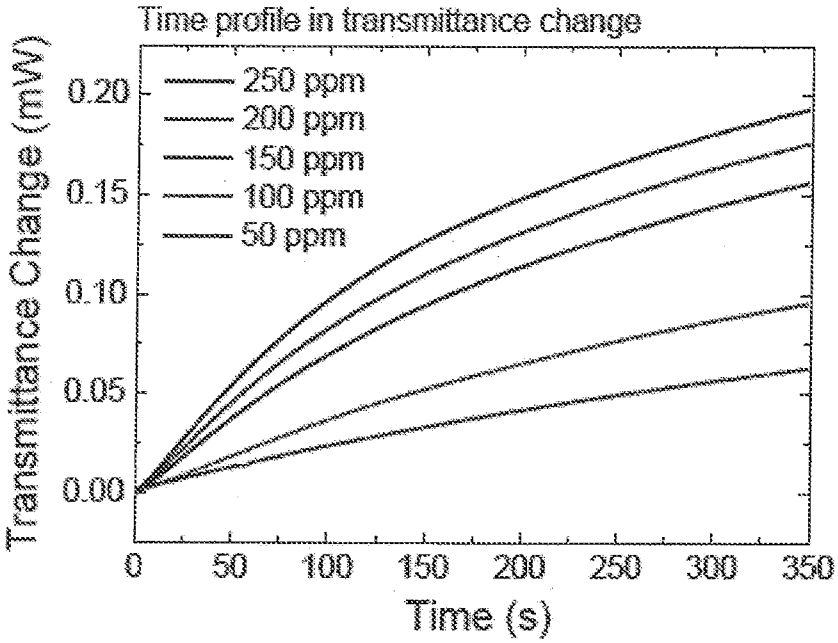
Time profile in transmittance change
Transmittance Change (mW)
0.20
0.15
0.10
0.05
0.00
250 ppm
200 ppm
150 ppm
100 ppm
50 ppm
0
50
100
150
200
250
300
350
Time (s)

Fig. 3

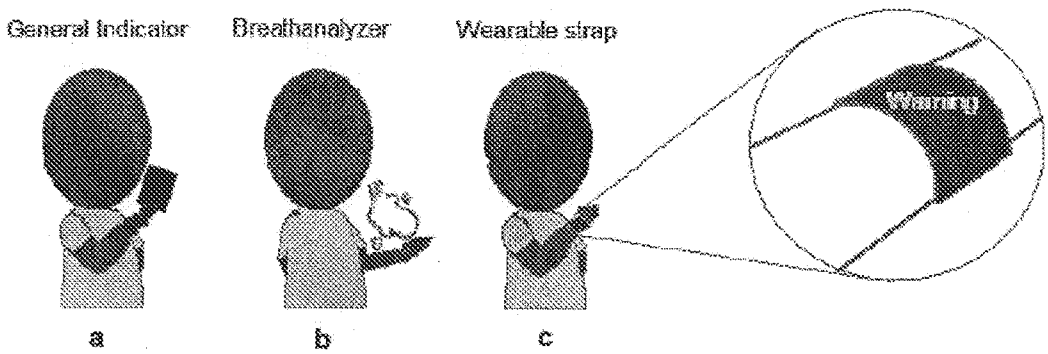
General Indicator
Breathanalyzer
Wearable strap
Warning
a
b
c

Fig. 4

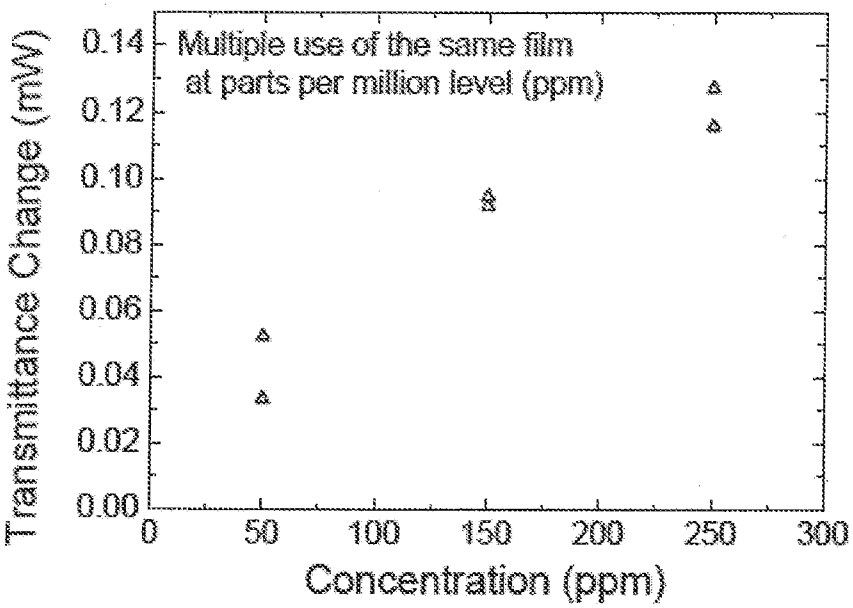
Multiple use of the same film
at parts per million level (ppm)
Transmittance Change (mW)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
300
Concentration (ppm)

Fig. 5

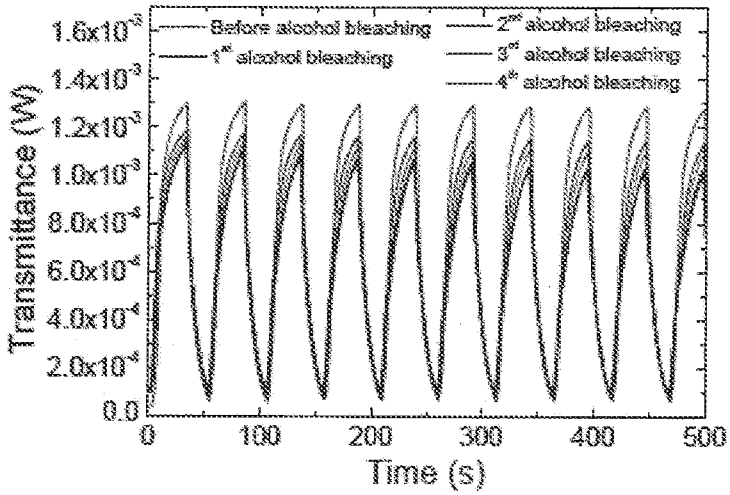
Before alcohol bleaching
1st alcohol bleaching
2nd alcohol bleaching
3rd alcohol bleaching
4th alcohol bleaching
Transmittance (W)
1.6x10-3
1.4x10-3
1.2x10-3
1.0x10-3
8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
0
100
200
300
400
500
Time (s)

Fig. 6

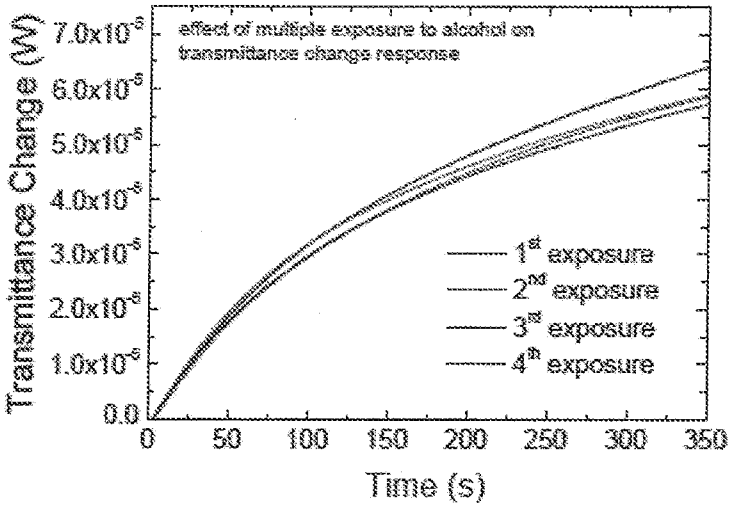
effect of multiple exposure to alcohol on transmittance change response
Transmittance Change (W)
7.0x10⁻⁵
6.0x10⁻⁵
5.0x10⁻⁵
4.0x10⁻⁵
3.0x10⁻⁵
2.0x10⁻⁵
1.0x10⁻⁵
0.0
0
50
100
150
200
250
300
350
Time (s)
1st exposure
2nd exposure
3rd exposure
4th exposure

Fig. 7

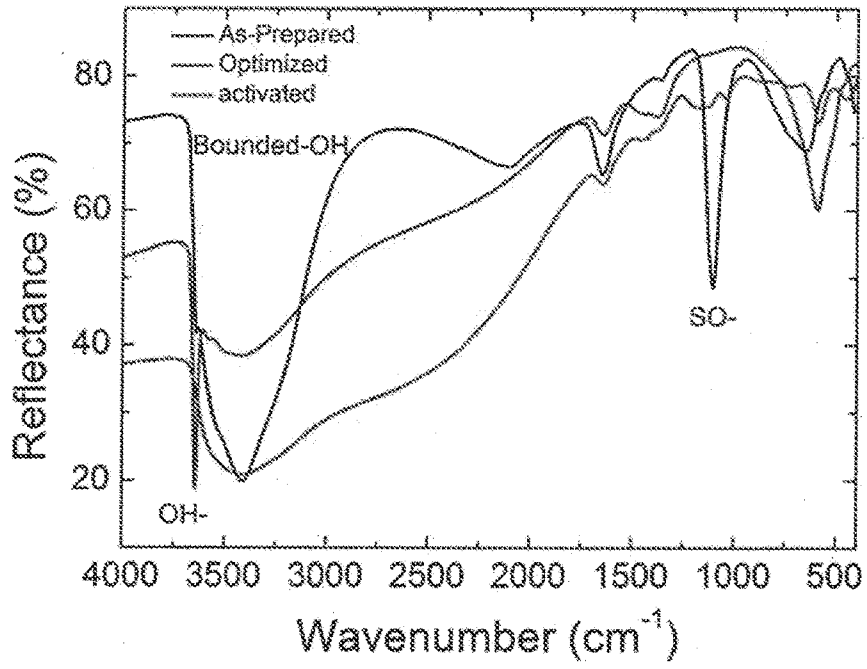
As-Prepared
Optimized
activated
Bounded-OH
SO-
OH-
Reflectance (%)
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

Fig. 8

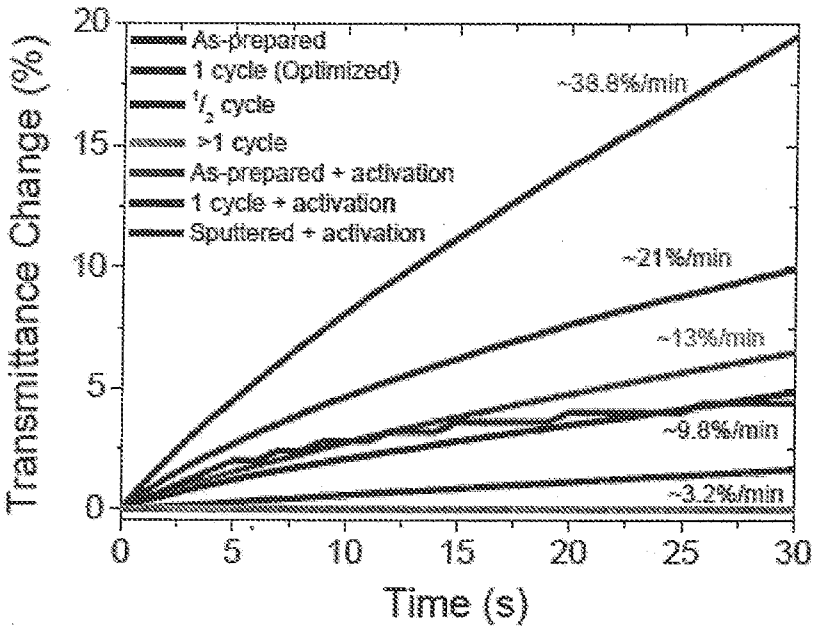
Transmittance Change (%)
Time (s)
As-prepared
1 cycle (Optimized)
½ cycle
>1 cycle
As-prepared + activation
1 cycle + activation
Sputtered + activation
~38.8%/min
~21%/min
~13%/min
~9.8%/min
~3.2%/min
0
5
10
15
20
25
30

Fig. 9

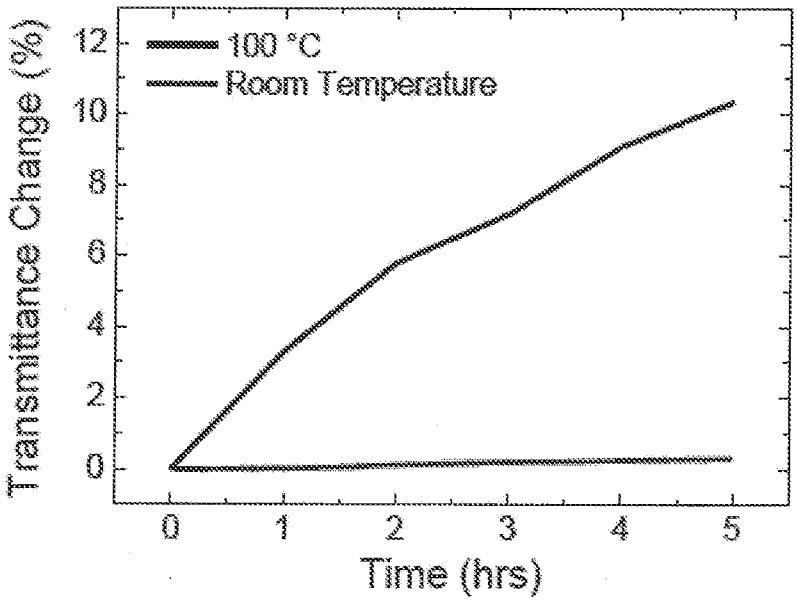
Transmittance Change (%)
Time (hrs)
100 °C
Room Temperature
0
2
4
6
8
10
12
0
1
2
3
4
5

Fig. 10

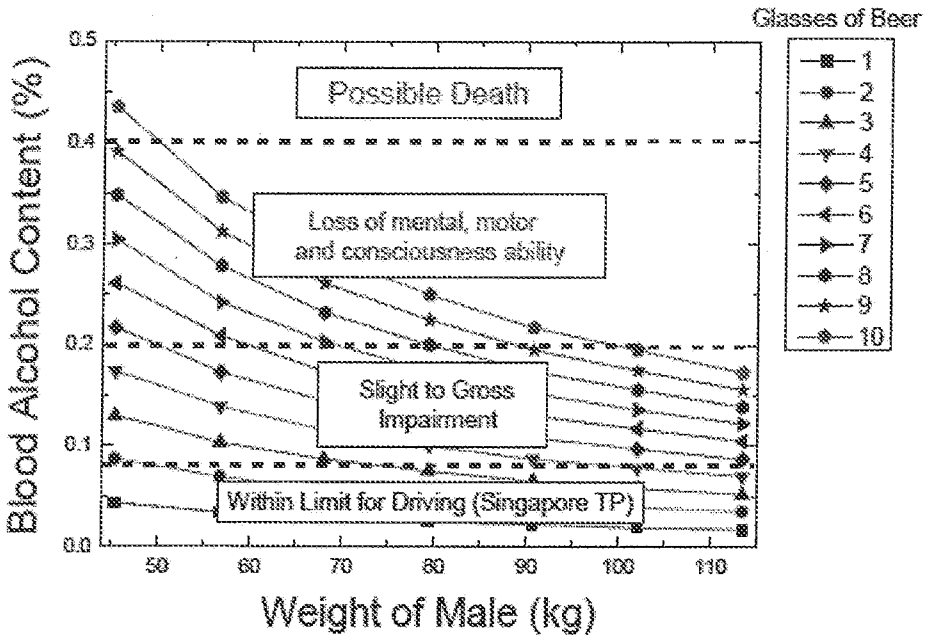
Glasses of Beer
1
2
3
4
5
6
7
8
9
10
Possible Death
Loss of mental, motor and consciousness ability
Slight to Gross Impairment
Within Limit for Driving (Singapore TP)
Blood Alcohol Content (%)
0.0
0.1
0.2
0.3
0.4
0.5
50
60
70
80
90
100
110
Weight of Male (kg)

Fig. 11

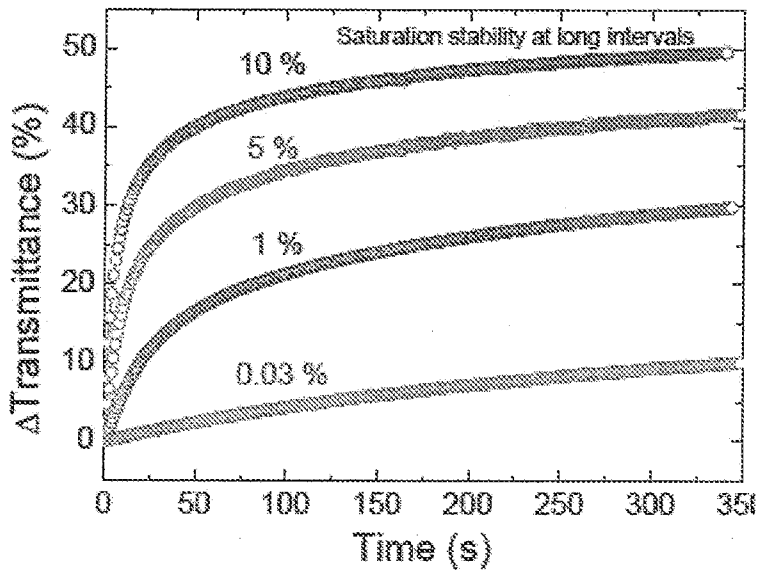
Saturation stability at long intervals
10 %
5 %
1 %
0.03 %
ΔTransmittance (%)
0
10
20
30
40
50
0
50
100
150
200
250
300
350
Time (s)

Fig. 12

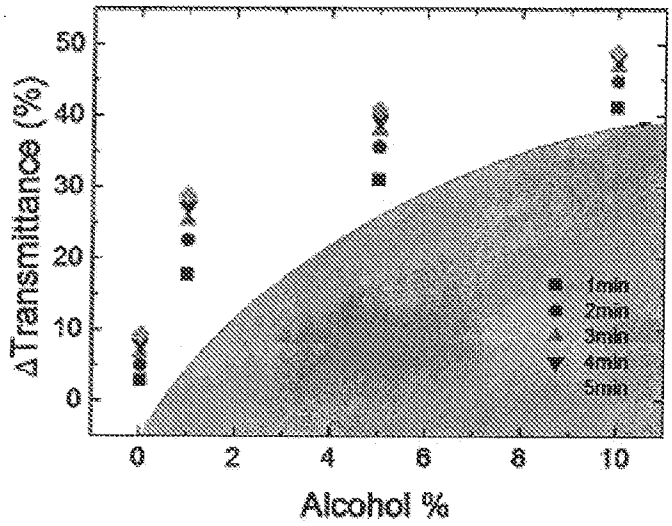
ΔTransmittance (%)
0
10
20
30
40
50
0
2
4
6
8
10
Alcohol %
1min
2min
3min
4min
5min

Fig. 13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050458

A. CLASSIFICATION OF SUBJECT MATTER

G01N 21/78 (2006.01) G01N 33/98 (2006.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G01N

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)

EPODOC/WPIAP/CAplus/EMBASE/BIOSIS/MEDLINE: hydrated nickel hydroxide/nickel oxyhydroxide (NiOH/NiOOH), reducing groups, hydroxyl groups, colorimetric, colourimetric, chemichromic, chemochromic, thin flim, breadth alcohol, sensor, device, analyzer and equivalent terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MORTIMER, R.J. ET AL., An *in situ* colorimetric measurement study of electrochromism in the thin-film nickel hydroxide/oxyhydroxide system. *J. Solid State Electrochem.* , 21 September 2014, Vol. 18, pages 3359-3367 [Retrieved on 2016-11-28] <DOI: 10.1007/S10008-014-2618-5> Whole document, particularly page 3362, left column (first paragraph), right column (first paragraph), Equation 18; Figure 1.	1-7 & 9-12
X	REN, Y. ET AL., The coloration and degradation mechanisms of electrochromic nickel oxide. *Sol. Energ. Mat. Sol. Cells*, 11 May 2013, Vol. 116, pages 83-88 [Retrieved on 2016-11-28] <DOI: 10.1016/J.SOLMAT.2013.03.042> Whole document, particularly page 84, left column (first paragraph), right column (first paragraph); page 85, Equation 4; Figure 4.	1-7 & 9-12
X	US 4,605,285 A (FUJIWARA, R. AND SHIMIZU, I.) 12 August 1986 Whole document, particularly column 1, lines 7-9; column 3, lines 24-49; Example 1; Figures 4 & 6.	1-7 & 9-12

☒ 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 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

Date of the actual completion of the international search	Date of mailing of the international search report
28/11/2016 *(day/month/year)*	05/12/2016 *(day/month/year)*

Name and mailing address of the ISA/SG	Authorized officer
Intellectual Property Office of Singapore 51 Bras Basah Road #01-01 Manulife Centre Singapore 189554 Email: pct@ipos.gov.sg	Teclise Ng (Dr) IPOS Customer Service Tel. No.: (+65) 6339 8616

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050458

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HALL, D.S. ET AL., Nickel hydroxides and related materials: a review of their structures, synthesis and properties. *Proc. R. Soc. A*, 25 October 2014, Vol. 471, pages 20140792: 1-65 [Retrieved on 2016-11-28] <DOI: 10.1098/RSPA.2014.0792> Whole document, particularly page 26, last paragraph to page 27, first paragraph.	-
P,X	HU, C-W. ET AL., Fabrication of nickel oxyhydroxide/palladium (NiOOH/Pd) thin films for gasochromic application. *J. Mater. Chem. C*, 3 May 2016, Vol. 4, pages 5390-5397 [Retrieved on 2016-11-28] <DOI: 10.1039/C6TC01541G> Whole document.	1-7 & 9-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2016/050458

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4,605,285 A	12/08/1986	JPS59182428 A	17/10/1984
		JPS59182427 A	17/10/1984
		JPS59214017 A	03/12/1984