

Pd Doped SnO₂ Resistive Film As A Non-Enzymatic Glucose Sensor

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Abstract

A new sugar sensor based on metal oxide is presented here. The variation on the sensor resistance is studied against different glucose and fructose concentrations (1 - 360 mg/dl). The study is done for three different resistive films (i) pristine palladium oxide (PdO_x); (ii) tin oxide (SnO₂) and (iii) palladium doped tin oxide (Pd-SnO₂). The chemical reactions of glucose and fructose with surface species were studied. Pd-SnO₂ films show excellent and reliable response to glucose and fructose solution in comparison with the bare films (PdO_x and SnO₂). Sensor performance was checked for blood of normal (120 mg/d) and diabetic (240 mg/d) patient. The sensor showed remarkable response of ~2 and 12 for normal and diabetic patient respectively. The non-enzymatic sensor showed a good stability, repeatability and reproducibility. The structure and morphology of these films were characterized by X-ray diffractometer, Transmission Electron Microscopy (TEM).

Key Words: Palladium, Tin oxide, Glucose, non-enzyme, Fructose, Sensor, Resistive film.

Introduction:

The rising demand of glucose sensor has driven tremendous research efforts for decades [22, 30]. Researchers are looking for a reliable, reproducible, sensitive and fast response glucose sensor along with low cost, low power consumption and small size. Glucose oxidase is widely used in sensor fabrication, [6,8,12,17,25,28,29,33,35] It catalyses the oxidation of glucose to gluconolactone. The enzymatic sensor of glucose is highly sensitive and selective. However, the poor stability and interference of oxidizable species that the sensor is subjected, are counted as common problems. The activity of glucose oxidase enzyme is highly affected by temperature, pH value, humidity and toxic chemicals [30].

Great attention has been paid to develop enzyme-free sensor to detect the glucose and fructose. In developing the enzyme-free polaro sensor, the sensor is tested with the direct electro-oxidation of glucose using different substrates such as platinum [26], gold [16], alloys [23], copper [5, 10, 18, 31] and mercury [20]. However, these electrodes are intoxicated due to surface adsorption of intermediates and chlorides. These contaminated electrodes lead to low sensitivity and selectivity along with poor reusability. Reliable fructose sensors could be more useful in measuring the quantity of sugar in food

products such as fruit juice and high-fructose corn syrup. The sensor is also useful in clinical samples including blood serum and seminal plasma. An enzymatic spectrophotometric assay is available for fructose determination; however it is time intensive, tedious and costly [21]. Several groups have recently used the immobilization of *Gluconobactersp* and fructose dehydrogenase to construct various amperometric biosensors for fructose. However, it may be useful to explore new materials which can be developed as better non-enzymatic glucose and fructose sensor.

Tin oxide has wide application in solar cells, sensors, opacifiers and bio-chemical applications [1,2,13,15,24,27]. The compound attracts many researchers due to its useful electric properties, low cost and the chemical stability. Doped and undoped tin oxide have widely used in biosensor. These materials are used as an electrode with a specific immobilized enzyme deposited on surface of the material [1,15,27]. The specific enzyme is used as an electrocatalyst. Similarly, in non-enzymatic sensors, the modified materials on the surface of the electrodes are also act as the electrocatalysts [32].

In this work, the fast, simple and low cost SSTD method is customized to demonstrate new non-enzymatic glucose sensor using spin coating technique to fabricate three different metal oxides. The sensor was designed to work similar to a resistive gas sensor, but with sample liquid drop in order to have cheap and simple way to check sugar quantity in blood. The variation of sensor resistance was studied when liquid (glucose) interfaces solid (film).

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Experimental:

All the reagents, Acetone, glucose, fructose, Na₂HPO₄, NaCl, SnCl₂ and PdCl₂ were of analytical grade and the solutions were freshly prepared with double distilled water.

Preparation and characterization of sensor films:

Tin chloride as well as palladium chloride solution were separately prepared in acetic acid. The third solution was prepared by dissolving mixer of PdCl₂ and SnCl₂ (ratio 3:97 by weight) in acetic acid. The solid to liquid ratio for all the three solutions was 3:6 by wt. The films were deposited on soda-lime glass substrate. The substrates were cleaned using chromic acid several times and then followed by rinsing with distilled water. Films were deposited by spinning 0.5 ml of the prepared solution. Both speed and time of spinning were controlled to get approximately equal thickness. The dried films were annealed at 550°C for 40 min. The firing temperature and firing time were optimized for tin oxide films [3]. Minimum 3 samples were made for each solution types and all the oxide films showed a good adhesion to soda-lime substrate. The used ratio of PdCl₂ to SnCl₂ and the firing temperature are optimized for the present sensor.

Fabrication of the present resistive sensor can be briefly described as follow: the annealed film was cut into 1X2 cm² pieces. Silver paste was printed on the two sides of the film using screen printing technique. The printed electrodes were allowed to dry for 1 hour under an infra red lamp (IR) to which copper wires were soldered. Active area of the prepared sensor is made to be 1X1 cm² so that the test drop was made to be located on the center of the active area without touching the electrodes of the sensor.

The small angle X-ray diffraction (SAXRD) of these annealed films was carried out using X-ray diffractometer (Bruker AXS D8 Advance model) using Cu K α radiation ($\lambda = 1.5418\text{\AA}$) at grazing angle of 1°. UV-Vis spectra of these films were recorded on spectrophotometer (Jasco V-670). Microstructure analysis of the film was carried out using transmittance electron microscope (JEOL, Model JSM-6360A). The powder of all the three samples, that was used to perform the transmission electron microscopy (TEM) test, were obtained from film by scraping the powder off the film using a blade.

Preparation of glucose and fructose solutions:

Glucose and fructose solutions were prepared in

(i) phosphate buffer saline (PBS) having pH of 7.4 as well as in (ii) distilled water. Various concentrations of 1, 5, 10, 60, 100, 200, 300 and 360 mg/dl were prepared and tested. All the experiments of testing glucose and fructose were done at room temperature (25°C). When samples were tested by the solid resistive film, care was taken to locate the drop at the middle and no sample part was reaching sensor electrodes.

Sensing Characterization:

The sensing characterization was done by noting the variation in the resistance of sensor for each glucose/fructose concentrations. Half bridge method was used to determine the resistance of sensor [3]. In half bridge method a 100 k Ω resistance is connected in series with the sensor and 20 volts was applied between the standard resistance (series resistance) and the sensor. The variation in sensor resistance, in presence and absence of glucose/fructose, was determined by noting the change in voltage drop of the standard resistance. For voltage measurements, three-and-half-digits digital multimeter was used.

Sensor response (R_s) is defined as the ratio of resistance of a sample without glucose (R_o) to its resistance in presence of test glucose (R_G):

$$R_s = \frac{R_o}{R_G}$$

2 microlitre (μ l) of glucose solution (size of the drop \sim 3 mm) was put on the centre of the film using a Micropipette. The change in voltage drop across series resistance was noted before and after putting glucose. Three sets of measurements were carried out for each oxide film in order to check the repeatability. After each measurement, the sensor was cleaned by acetone and kept to dry. We define the Response time as the time taken by the sensor when its resistance undergoes a 90% change with respect to the maximum resistance that sensor showing.

Results and Discussion:**Characterization of PdO_x, SnO₂ and pd-SnO₂ films:**

Thickness of the film was measured by FTM-7 and it was found to be (300 \pm 50 nm). Figure 1(a) illustrates the SAXRD pattern of the films deposited on soda-lime glass substrate annealed at 550°C for 40 min. The XRD data was recorded for films prepared using SnCl₂ and PdCl-SnCl₂ solutions. For both sample, the XRD data showed that all the diffraction peaks are well indexed to the tetragonal SnO₂ structure. There was no observable shift in the diffraction peaks position when Pd was introduced.

Additionally, there was no observable impurity phases related to the Pd, PdO or PdO₂ in the patterns of the film prepared using PdCl-SnCl₂. The data was confirmed by comparing with the Joint Committee on Powder Diffraction Standards (JCPDS) data (Card No. 72-1147) and the highest intensity was recorded for the diffraction peak corresponding to (110) which is located at $2\theta = 33.9^\circ$. Two peaks were observed

(not seen here) for the film prepared from PdCl₂ solution. The peaks are related to tetragonal phase of PdO. Therefore, we feel that the undetected signal of PdO_x in Pd-SnO₂ films was probably due to the low amounts of Pd loaded in the crystallite SnO₂. The peaks may probably overlapped with high intensity peak of pure SnO₂ at $2\theta = 33.6^\circ$.

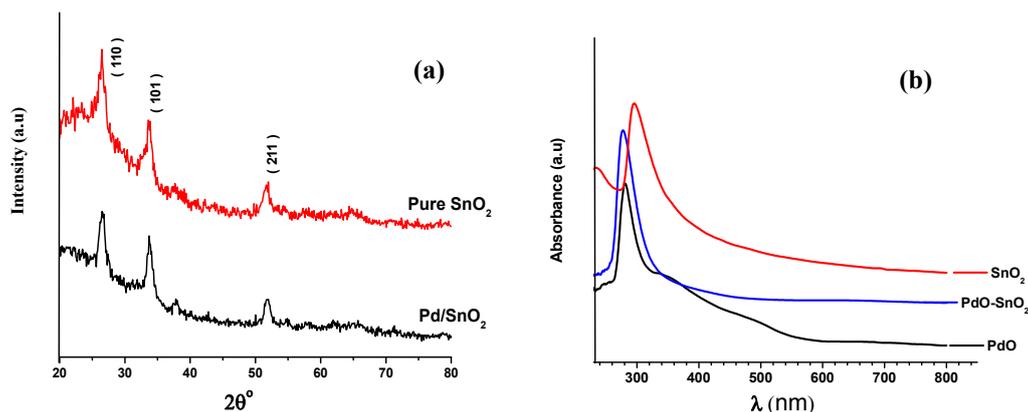


Figure 1: (a) X-ray diffractogram and (b) UV-Vis of single step thermal decomposition nano-particle SnO₂ and Pd/SnO₂ film deposited on glass substrate.

UV-Vis spectra of these oxide films (Fig. 1b), shows a single narrow optical absorption "peaks". The absorption peak is located at 295 nm for SnO₂ which corresponds to band gap energy of ~4.2 eV. PdO_x and Pd-SnO₂ exhibit an absorption peak located at 280 and 276 nm respectively. The corresponding optical energy band gap of Pd-SnO₂ film (4.48 eV) is blue-shift with respect to that of the pristine SnO₂ (Fig. 1b).

Shifting of the absorption edge/peak to a higher energy with respect to that of the bulk might be due to small-sized particles and / or morphology. The effect of quantum confinement is expected in semiconductor when the particle size is comparably smaller than Bohr radius. The material is expected to exhibit discrete electron energy levels with high oscillator strength [7,14].

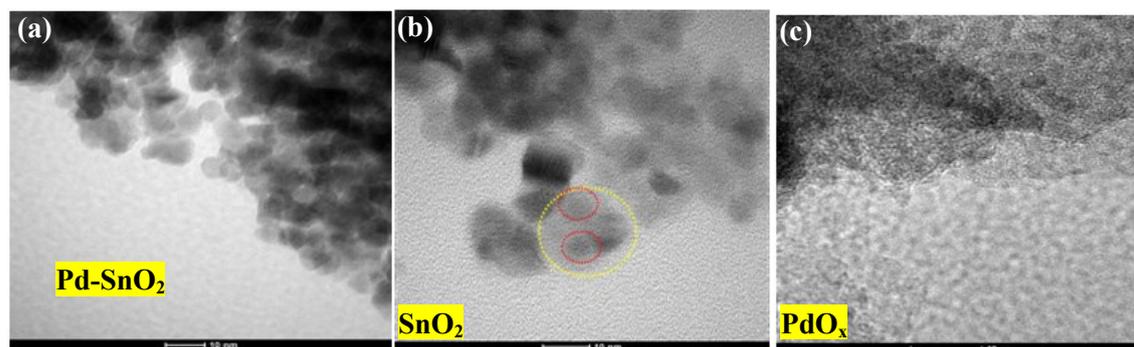


Figure 2: TEM of (a) Pd-SnO₂ (b) pristine SnO₂ and (c) pristine PdO_x deposited on glass substrate

Figure (2a-2c) shows the TEM images of the Pd-SnO₂, SnO₂ and PdO_x powder that scraped from the films after firing at 550°C. The images (not shown) of selected area electron diffraction

pattern (SAED) reveal that all the samples were of poly-crystalline structures. TEM image of Pd-SnO₂ shows nearly similar spherical particles with size of 2-5 nm. The TEM of pristine SnO₂

(Fig. 2b) shows spherical particles of size 5 nm along with some particles with bigger size of 10-15 nm. A bimodal distribution of SnO₂ (2-5 nm particles distributed on the surface of the 10-15 nm particle) was also noted by the atomic force microscopy (AFM) for the SnO₂ [4]. This bimodal distribution is not seen clearly by TEM and that would probably be due to the film morphology that was disturbed to obtain powder. TEM results of Pd-SnO₂ shows that palladium could have influence on keeping particles shape identical and smaller. Tan et al [24] observed an influence in particle size of SnO₂ when a Pd was used as dopant. These results could probably due to the presence of the Pd additive that modifies the growth kinetic of SnO₂ nanoparticles. Similarly to what Luo et al [19] reported for Cerium (Ce) added to tungsten (W) and Fardindoost et al [9] for the Pd added to W. They have suggested that because of the lower ionic radius of W⁺⁶ (56 pm) comparing to the ionic radius of the additive (Ce and Pd), the catalyst particles may get accumulated in the grain boundaries of tungsten. This accumulation prevented grain growth of the tungsten during the heat treatment. In our case, the identical and smaller size that the Pd-SnO₂ films having, is probably because of the Pd. The ionic radius of Pd (78 pm) will accumulate in grain boundaries of Sn⁴⁺ (71 pm) preventing grain growth of the SnO₂. It could be said that palladium works as a capping agent in the present reaction.

Sensitivity of Pd- SnO₂ to glucose without enzyme:

The chemical adsorption activity is presented here for all the three different oxide towards glucose in buffer and in water. The sensitivity of the sensors was also noted against fructose in buffer and in water. 2 µl of testing sample was determined to be the maximum volume that could stand exactly in between the sensor electrodes. Figure (3a) shows the behavior of all the three sensors against glucose solution in the buffer. The change in sensor resistance was noted when the glucose solution was dropped on the active area of the film. A decrease in sensors resistance was observed for all the sensors (PdO_x, SnO₂ and Pd-SnO₂) when glucose was exposed. PdO_x and SnO₂ showed a response (R_o/R_G) of 1.5 and 4 for PdO_x and SnO₂ film respectively when 1 mg/dl of glucose was tested. As the glucose concentration increased to 360 mg/dl, the response of PdO_x sensor reached the value of 28 while the response of SnO₂ sample reached to 140. However, The Pd-SnO₂ sample noted a response of 100 and 800 for concentrations of 1 mg/dl and 360 mg/dl respectively. The noted higher response of Pd-SnO₂ sample, which is higher than what the bare samples noted, indicates that the recorded fall in resistance of Pd-SnO₂ sensor, could be attributed to the existence the catalyst (Pd) that was introduced to SnO₂ sample [10,12].

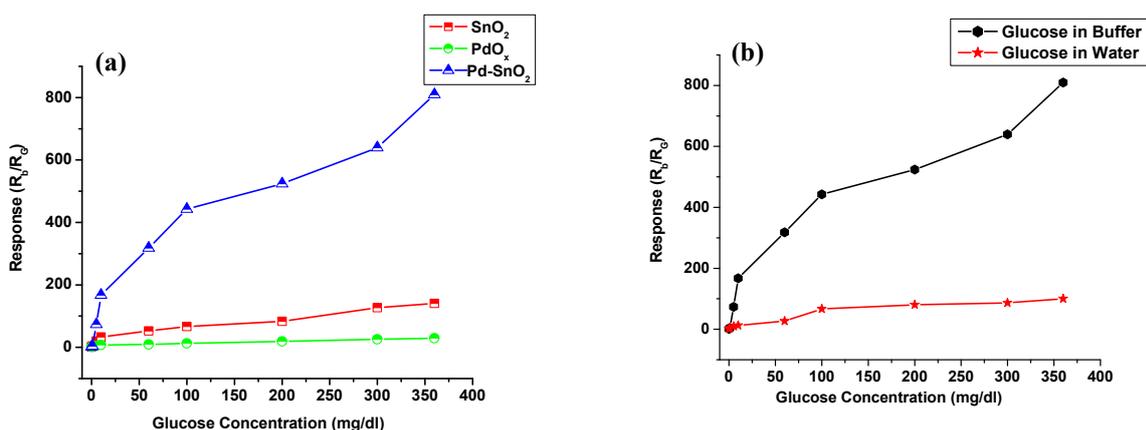


Fig 3:(a) Sensor response versus variation of glucose concentration in buffer for Pd-SnO₂, SnO₂ and PdO_x films. (b) Response versus concentration graph of glucose in buffer and water for Pd-SnO₂ film

Figure (3b) shows the response variation of Pd-SnO₂ sensor for glucose in water and glucose in buffer for a different concentrations. The Pd-SnO₂ sensor gives lower response to the glucose

in water than the glucose in buffer. The response for glucose in water was found to be 25 and 100 for concentration of 1 and 360 mg/dl respectively.

When fructose was replacing glucose in buffer, the sensor shows higher response of 90 for 1 mg/dl and the response reached to 1015 for 360 mg/dl (Figure 4a). So, there is a significant increase in the response when glucose and fructose are dissolved in buffer as compared to, glucose and fructose in distilled water. These obtained results (higher response for glucose in PBS than glucose in water) could be due to the

difference in the pH value of the solvent, something similar to what Kang et al reported [11]. They observed a reduction in their response. The sensor was made of nanorods arrays of ZnO on which the glucose oxidase (GO_x) was immobilized on the surface of ZnO. The reduction of 80% on the activity of GO_x was noted when pH value 6-5 and this activity will drop down when the pH is greater than 8.

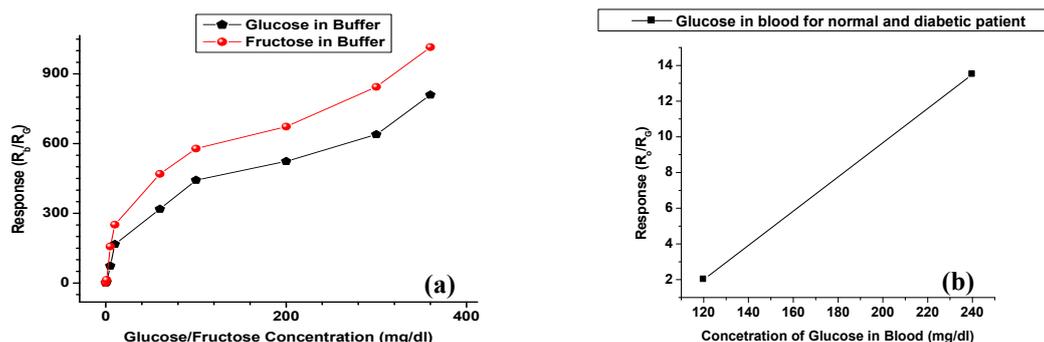


Figure 4: (a) Comparison graph of response versus concentration of glucose and fructose in buffer. (b) PdSnO₂ response of sugar present in blood of normal and diabetic patients.

The response time is defined as the time required for a sensor to attain the 90% of change in resistance when sensor is exposed to a test glucose/fructose. The recovery time is the time taken to get back 90% of the original resistance when glucose/fructose removed. It was seen that the time required to reach the saturation in the resistance was 20 seconds (sec) for glucose as well as for fructose. As compared to the Pd-SnO₂ sensor, PdO and SnO₂ films show a response of ~40 sec. To get back to the original resistance of the sensor, the sensor surface was cleaned by acetone and left to dry. During drying process,

the sensor resistance had increased back to reached a 90% of the original resistance. The sensor was used several times with good repeatability. The recovery time was measured to be 2-3 minutes and it depends on the drying time. PdO and SnO₂ films taking longer time to recover. All the data from this non-enzymatic glucose sensor showed that the sensor has faster response time. This may be attributed to the fact that the glucose/ fructose react with the adsorbed oxygen on the surface of the Pd-SnO₂ film increasing electron number in the conduction band of the Pd-SnO₂.

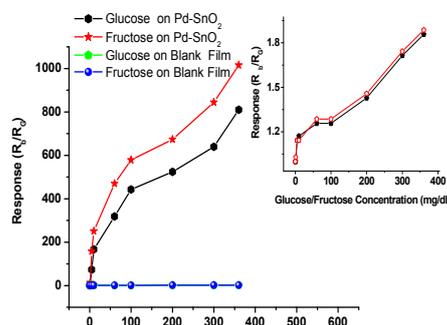
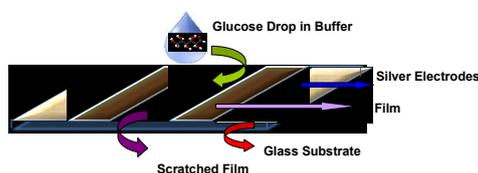


Figure 5: (a) Schematic diagram of films with no film deposited on the middle of the film. (b) Comparison graph of glucose and fructose response for Pd-SnO₂ with and without active material. Inset: Response versus glucose concentration of Pd-SnO₂- film with no active material.

The performance of Pd-SnO₂ sensor was checked for sugar in blood by examining two blood samples of normal and diabetic patient. The glucose in the blood samples was measured clinically and it was found to be 120 mg/dl and 240 mg/dl for normal and diabetic patient respectively. The blood samples were put directly, without any treatment, on the active area of the sensor. No change was observed in sensor resistance of PdO and SnO₂ while Pd-SnO₂ sensor showed response of ~2 and ~ 12 for the samples of the normal and diabetic patient respectively (Figure 4b). Although there are many substances in blood and it cannot be insured that the reduction of Pd-SnO₂ resistance is because of glucose only. But the results indicate that the Pd doped SnO₂ sensor can be used to test blood sugar with no specific enzymes (Glucose Oxidase) and many experiments needed to be performed to clarify what substances else in the blood could react with Pd-SnO₂ surface. Also experiments need to be done to identify the detection process of sugar on metal oxide surface.

Gas detection is generally evaluated by measuring the change in metal oxide conductivity. The conductivity increases when electrons are transferred to the conduction band of the oxide due to the reaction of the test gas with the surface absorbed oxygen species. Generally, the reaction on metal oxide surface requires an activation energy which is provided commonly either by thermal heat or/and adding catalyst. So SnO₂ and PdO sensors showed no response to glucose/fructose, probably because the insufficient activation energy that room temperature provided. In amperometric, the electrodes are playing a good role in detecting glucose by checking the electrolyte conduction change. We feel that the detection of our glucose/fructose metal oxide resistive sensor is similar to gas detection. Glucose/fructose reacts with oxygen species at the surface of metal oxide. This reaction releases electrons to the conduction band and as a sequence the resistance of metal oxide decreases. The suggested interpretation of our glucose sensor is proved by special experiment. Films of Pd-SnO₂ were prepared with no material deposited on the center of the glass substrate (see Figure 5). As the center part of the film is left to be blank, drop of glucose and fructose was put on the center part. A precaution was taking to make the drop touch of the two sides (electrodes) of the film. With a different concentration of glucose and fructose,

the film showed absolutely no effect on resistance value of the sensor. Because there is no adsorbed layer below the test drop, the resistance of the film probably does not fall. Figure 5b shows the response of glucose and fructose for Pd-SnO₂ film and the blank centered film. Apparently, no response was observed for the modified films (film with blank center), when tested for glucose and fructose (Inset figure 5b). The film shows very small response which is probably due to the absorption of glucose and fructose by the edge.

To interpret the higher response that Pd-SnO₂ sensor showed for glucose in buffer, the response of the Pd-SnO₂ sensor was checked for the buffer with no glucose. The response was 1.1 and was very low for both SnO₂ and PdO_x sensor. The higher conductivity of Pd-SnO₂ sensor is probably due to the reaction of Pd with the organic compound that leads to release electrons to the conduction band of SnO₂ substrate. This reaction is highly effected by pH value of the solution.

Glucose and fructose are monosaccharides they are compounds containing aldehyde or ketone group and 2 or more hydroxyl groups. Glucose is a crystalline solid and the backbone of glucose is comprised of unbranched carbon chains in which all the carbon atoms are linked by single bonds. In open-chain form, one of the carbon atoms is double bonded to an oxygen atom to form a carbonyl group; each of the other carbon atoms has a hydroxyl group. If the carbonyl group is at the end of the carbon chain, it is an aldehyde group. And if the carbonyl group is at any other position it is a ketone group as in case of fructose.

In gas sensor, it is gas phase adsorption reaction while in the present case, it is liquid phase adsorption process. As in gas sensing, it is observed that film resistance of the present sensor is the highest in air and with water and buffer, it falls but with glucose, it falls drastically and with fructose, it still falls further. This means that glucose and fructose gives more and more electrons to SnO₂ conduction band. When the adsorbed oxygen is reacting with glucose/fructose, electrons are released due to the removal of oxygen species from film surface. The reaction is catalyzed by palladium.

It is well reported that in polarimetry (H, ⁻CH₃ Alkyl group) are more electron releasing (I type) groups and ⁻OH is further electron withdrawing (I type) by electrostatic induction effect for mesomeric chain. Now combining

these two: i) gas sensor and ii) polarimetry, one may say that in present case, with alkyl group of glucose ($^+\delta$) induces electrostatically more negative charge on substrate, than the water (H^+ , OH^-) thus releasing electrons to conduction band of SnO₂ and decreases its resistance. With two alkyl groups in fructose, resistance of film is still lower. We have not considered effects of other groups which may be present in glucose and fructose nor the groups present in buffer used.

Conclusion:

A novel non-enzymatic glucose sensor based on Pd doped SnO₂ films is obtained. The palladium doped tin oxide films were prepared by the single step thermal decomposition at the optimized firing temperature of 550°C. Comparing with SnO₂ and PdO_x the palladium doped tin oxide sensor showed a good response towards glucose and fructose. The chemical adsorption reaction of Pd doped SnO₂ with sugar showed that the

response increases with increasing in concentration of both glucose and fructose. The newly developed non-enzymatic glucose and fructose sensor presents a number of attractive features such as good stability, reproducibility as well as fast response time of 20 sec. Palladium in tin oxide films plays an important catalytic role in glucose and fructose sensing. It is confirmed by proper sensor film geometry that the reaction is adsorption dependent and not liquid state polarimetric. The surface of the film is mechanically and chemically stable and its surface can be easily regenerated by cleaning it with acetone.

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غشاء أكسيد القصدير المقاوم و المطعم بالبلاديوم كمتحسس غير إنزيمي للجلوكوز

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ملخص

هذا البحث يعرض جهاز استشعار السكر القائم على أساس أغشية أكسيد المعادن الرقيقة وذات المقاومة الكهربائية العالية. تم في هذا البحث دراسة الاختلاف في مقاومة المستشعر ضد تراكيز مختلفة من الجلوكوز والفركتوز (1-360 mg/dl). أجريت الدراسة لثلاثة أغشية رقيقة مختلفة (1) أكسيد البالاديوم (PdO_x)؛ (2) أكسيد القصدير (SnO_2) و (3) أكسيد القصدير المطعم بالبلاديوم ($Pd-SnO_2$). أغشية الرقيقة تظهر استجابة عالية وموثوقاً بها للجلوكوز و الفركتوز بالمقابلة مع الأغشية العارية (PdO_x و SnO_2). تم فحص أداء المستشعر لعينات من دم المريض العادي (120 mg/d) ومرضى السكري (240 mg/d). وأظهرت أجهزة الاستشعار استجابة ملحوظة من 2~ و 12 للمريض العادي ومريض السكري على التوالي. وأظهرت أجهزة الاستشعار غير الأنزيمية الاستقرار جيدة، والتكرار واستتساخه. وقد تم فحص هيكل ومورفولوجية هذه الأغشية باستخدام الأشعة السينية (X-ray diffractometer)، والمجهر الإلكتروني (Transmission Electron Microscopy).

الكلمات المفتاحية: أكسيد القصدير، بلاديوم، جلوكوز، فركتوز، متحسس، غشاء رقيق