Indirect photo-electrochemical detection of carbohydrates with Pt@g-C₃N₄ immobilised into a polymer of intrinsic microporosity (PIM-1) and attached to a palladium hydrogen capture membrane

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Abstract
An "indirect" photo-electrochemical sensor is presented for the measurement of a mixture of analytes including reducing sugars (e.g., glucose, fructose) and non-reducing sugars (e.g., sucrose, trehalose). Its innovation relies on the use of a palladium film creating a two-compartment cell to separate the electrochemical and the photocatalytic processes. In this original way, the electrochemical detection is separated from the potential complex matrix of the analyte (i.e., colloids, salts, additives, etc.). Hydrogen is generated in the photocatalytic compartment by a Pt@g-C₃N₄ photocatalyst embedded into a hydrogen capture material composed of a polymer of intrinsic microporosity (PIM-1). The immobilised photocatalyst is deposited onto a thin palladium membrane, which allows rapid pure hydrogen diffusion, which is then monitored by chronopotentiometry (zero current) response in the electrochemical compartment. The concept is demonstrated herein for the analysis of sugar content in commercial soft drinks. There is no requirement for the analyte to be conducting with electrolyte or buffered. In this way, samples (biological or not) can be simply monitored by their exposition to blue LED light, opening the door to additional energy conversion and waste-to-energy applications.

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1. Introduction

Photo-electroanalytical sensing [1,2] and photo-bioelectroanalytical processes [3] provide a way to detect analytes under light-activated conditions with applied current/potential and illumination (continuous or pulsed [4,5]). There have been several cases of photo-electroanalytical procedures reported previously, for example for glucose detection [6], for miRNA [7], for mercury [8], and for ascorbate [9].

In this paper, a palladium film membrane cell is employed to separate the electrochemical compartment (see Schematic 1) from the photocatalysis compartment. This separation allows any type of analytical sample, independent of chemical nature or conductivity, to be studied without direct interference during the electrochemical detection. The palladium membrane purifies the hydrogen before detection and stops the direct interaction of sample and electrode. The process relies on the well-known Pt@g-C₃N₄ photocatalyst [10,11,12] and is based on a sequence of reaction steps. First, the excitation of Pt@g-C₃N₄ (Eq. (1)) is followed by a charge separation step enhanced by the platinum deposit (Eq. (2)). Next, the photo-generated hole can be captured either by water (to give oxygen, Eq. (3)) or by a quencher such as glucose (to give oxidation products, Eq. (4)). The remaining negative charge accumulates on the nano-platinum cocatalyst (here typically 2.5 nm diameter [14]), which results in the formation of hydrogen (Eq. (5)) that then diffuses to/across the palladium membrane. After crossing the membrane, the electrochemical oxidation of...
hydrogen to protons (Eq. (6)) is responsible for the establishment of a new equilibrium potential (in competition with reactions due to ambient oxygen). This sequence of reaction steps is oversimplified due to ambient oxygen introducing further complexity on both sides of the palladium membrane (vide infra).

\[
\text{Pt@g-C}_3\text{N}_4 + h\nu \rightarrow \text{Pt@g-C}_3\text{N}_4^* \quad (1)
\]

\[
\text{Pt@g-C}_3\text{N}_4^* \rightarrow \text{Pt@g-C}_3\text{N}_4^+ \quad (2)
\]

\[
2\text{Pt@g-C}_3\text{N}_4^+ + \text{H}_2\text{O} \rightarrow 2\text{Pt@g-C}_3\text{N}_4 + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \quad (3)
\]

\[
\text{Pt@g-C}_3\text{N}_4^+ + \text{glucose} \rightarrow \text{Pt@g-C}_3\text{N}_4 + \text{products} \quad (4)
\]

\[
\text{Pt@g-C}_3\text{N}_4^+ + \text{H}^+ \rightarrow \frac{1}{2} \text{H}_2(\text{Pd}) \quad (5)
\]

\[
\text{H}_2(\text{Pd}) \rightarrow 2\text{H}^+ + 2\text{e}^- (\text{Pd}) \quad (6)
\]

The immobilisation of the photocatalyst onto the palladium membrane surface can be achieved with a polymer of intrinsic microporosity. The use of a polymer of intrinsic microporosity (or PIM) is not only a simple scaffold to hold the catalyst without binding to the photocatalyst surface, but it is also beneficial, based on recent progress, in controlling the transport of gas molecules (under triphasic conditions) at electrode surfaces [15]. PIMs have been developed a decade ago [16] as a novel class of glassy (molecularly rigid) porous materials with excellent processability. Recently, these materials have emerged as useful components in electrochemical processes [17] due to the ability to stabilise surfaces, immobilise catalysts [18], and to capture gases such as hydrogen under “triphasic” conditions in the presence of aqueous electrolytes [19]. PIM-1 offers a surface area (BET) of typically 750 m² g⁻¹ [20] and pores of around 1–2 nm [21].

In this report, exploratory data are presented to demonstrate the concept of an “indirect” carbohydrate sensor, based on an indirect electrochemical process (via palladium membrane) and driven by blue light (λ = 385 nm) in a photo-catalytic reaction. The Pt@g-C₃N₄ photocatalyst is employed in conjunction with the hydrogen capturing PIM-1 polymer of intrinsic microporosity. Different types of carbohydrates (reducing and non-reducing) are shown to produce detectable photoresponses. Potential for application of “indirect sensing” is demonstrated with commercial softdrinks.

2. Experimental

2.1. Reagents

All chemicals were purchased from Sigma-Aldrich and used without any further purification. Palladium membrane (0.025 mm thickness, 99.95% purity, light tested) was purchased from Goodfellow Ltd. PIM-1 was prepared following a literature procedure [22]. Commercial softdrinks (a glucose-containing soft-drink “Innocent Coconut Water” (Innocent UK) and a sweetener-containing softdrink “Oasis Aquashock Chilled Cherry” (Coca Cola UK)) were bought from a local supermarket. Deionized water (18.2 MΩ cm at 20 °C obtained from a CE Instruments Ltd. water purification system) was used to prepare electrolyte solutions. All experiments are conducted in an ambient environment (T = 22 ± 2 °C).

2.2. Instrumentation

Electrochemical measurements were conducted with a potentiostat system (μAUTOLAB III, Metrohm, Herisau, Switzerland). GPES software was used to record the data. A KCl-saturated calomel electrode (SCE) was used as the reference electrode together with a platinum wire as the counter electrode. Transmission electron microscopy (TEM) images for Pt@g-C₃N₄ materials were captured with a JEOL JSM-2010Plus (JEOL U.K. Ltd, Welwyn Garden City, UK). An LED light source wavelength 385 nm was employed (Thorlabs, Inc., M385LP1). 1H NMR spectra was recorded on a Bruker 500 MHz spectrometer. Mass spectrometry analyses were performed on an Automated Agilent QTOF (Waltuk) used with HPLC (4 chromatography columns) and variable wavelength detector (VWD). LC-MS analyses were performed using an Agilent QTOF 6545 with Jetstream ESI spray source coupled to an Agilent 1260 Infinity II Quat pump HPLC with 1260 autosampler, column oven compartment and variable wavelength detector (VWD).
2.3. Procedures

**Synthesis of Pt@g-C$_3$N$_4$.** First, melamine (Sigma-Aldrich, 99% purity) was added into a ceramic boat with lid, which was then placed into the centre of an Elite horizontal tube furnace (TSH12/65/550) and heated to 500 °C for three hours. After cooling overnight, the final g-C$_3$N$_4$ was obtained as pale-yellow powder. Next, potassium hexachloroplatinate(IV) ($K_2PtCl_6$) (purchased from Sigma-Aldrich, >99.9% purity) (40 mg) and 0.4 g of the synthesised g-C$_3$N$_4$ were added into 25 mL of saturated sodium oxalate solution in a glass vial. In order to deposit platinum nanoparticles (Pt$_0$) onto the g-C$_3$N$_4$, the reaction mixture was irradiated with blue light ($\lambda = 385$ nm) for 60 h with continuous stirring. Pt@g-C$_3$N$_4$ catalyst was finally separated and collected by centrifuging, washing, and drying in an oven.

**Immobilisation of photocatalyst into PIM-1.** Pt@g-C$_3$N$_4$ catalyst was dispersed together with the polymer of intrinsic microporosity (PIM-1) in a chloroform solution. The mixture was ultrasonicated in a water bath for 15 mins before use. Deposits were formed by drop-casting.

**Preparation of Pd membrane.** A piece of commercial document lamination foil was firstly punctured with a hole with a 2 mm diameter. A Pd foil (0.025 mm thickness, 0.5 cm x 0.5 cm, Goodfellow Ltd.) was then placed between the two pieces of the laminate (see Fig. 1A). A strip of copper film was placed in contact with the Pd foil for electrical connection. The laminate was then sealed with a hot iron to achieve sealing. Fig. 1B and C show schematic drawings of the photocatalyst deposited with a PIM-1 coating and a mixed coating with both photocatalyst and PIM-1. The latter proved to be a more robust methodology and was applied throughout the study. In Fig. 1D TEM images are shown revealing platinum nanoparticles of typically 2.5 nm diameter.

3. Results and discussion

3.1. Pt@g-C$_3$N$_4$ photopotential responses due to hydrogen from glucose

The production of hydrogen from glucose by the Pt@g-C$_3$N$_4$ photocatalyst can be revealed due to rapid hydrogen diffusion through the adjacent palladium film [23]. The diffusion coefficient for hydrogen in palladium has been reported as approximately $3 \times 10^{-11}$ m$^2$ s$^{-1}$ at room temperature [24,25] and therefore the response time delay due to hydrogen diffusing through the $L = 25$ µm membrane will be typically $\tau \approx \frac{L^2}{D} = 20$ s. The advantage of the palladium film separating the electrochemical compartment and the photocatalysis compartment (see Schematic 1) is based on the purification of the hydrogen transiting the palladium. In this way it is possible to suppress any interfering redox response from the sample.

Chronoamperometry at zero current was chosen to follow the photoresponse in terms of an equilibrium potential signal. Fig. 2A shows some typical chronoamperometry data traces. Only distilled water (i) does not lead to a significant potential response due to oxygen on both sides of the palladium membrane dominating the redox equilibrium. Trace (ii) shows a slight negative shift, but with a stable equilibrium potential when 0.1 M NaOH is added into

![Fig. 1.](image1.png)

![Fig. 2.](image2.png)
the catalysis compartment. The presence of glucose in the aqueous solution makes a significant difference. In both, water with glucose (iii) and 0.1 M NaOH with glucose (iv), a delayed and pronounced shift to negative potentials (0.00 and −0.12 V vs. SCE, respectively) is observed. This shift can be attributed to the photocatalytic hydrogen evolution due to glucose acting as a hole quencher. Perhaps interestingly, the delay is more pronounced in 0.1 M NaOH, but the final potential is also substantially more negative (more hydrogen is produced). The delay is (at least in part) due to the need to locally consume oxygen present on both sides of the palladium membrane (vide infra). Due to the complexity of the chemistry of glucose in alkaline media and the additional benefit of not requiring any electrolyte in the photocatalysis compartment, the following experiments were conducted in pure water.

Data in Fig. 2B were obtained with different concentrations of glucose dissolved in water. An amount of 60 μg Pt@g-C3N4 photocatalyst was immobilized together with 12 μg PIM-1. A signal can be measured for a concentration as low as 10 mM glucose. However, the delay is substantial (300 s) and the final potential does not significantly shift. When increasing the glucose concentration, the hydrogen response is observed to be faster (within 60 s) and the shift in equilibrium potential is more pronounced. A dependence of the final equilibrium potential on the glucose concentration is observed.

Next, the effect of the PIM-1 polymer is investigated. Fig. 3 shows chronooamperometry (zero current) data obtained for (A) 60 μg Pt@g-C3N4 with 24 μg PIM-1 and (B) 60 μg Pt@g-C3N4 with no PIM-1. The presence of the polymer of intrinsic microporosity does affect the behaviour of the photocatalyst. An increase in PIM-1 appears to slow down the photoresponse as well as shifting the final equilibrium potential slightly more positive. This increase and shift is consistent with the additional PIM-1 either slowing diffusion access to the photocatalyst or somewhat lowering the light intensity at the location of the photocatalyst.

In the absence of PIM-1 (see Fig. 3B), the equilibrium potential response is significantly delayed and observed only for very high concentrations of glucose (for less than 0.5 M glucose the process occurs not within 1000 s). This can be explained with the competing fluxes of hydrogen and oxygen to the photocatalyst. Fig. 3D shows a schematic diagram indicating production of hydrogen at the photocatalyst and diffusion of oxygen from outside into the PIM-1 layer. As a microporous polymer, PIM-1 is open to small molecule diffusion, e.g. glucose, protons, water, and to gas diffusion, e.g. hydrogen and oxygen. However, under triphasic conditions transport of oxygen may be slowed down during hydrogen production. Therefore, the PIM-1 material not only provides mechanical stabilisation of the Pt@g-C3N4 photocatalyst, but also a protection against oxygen improving the flux of hydrogen into the palladium membrane. The optimum effects are observed with 60 μg Pt@g-C3N4 and 12 μg PIM-1.

Data plotted in Fig. 3C shows the effect of PIM-1 when equilibrium potential data is plotted versus glucose concentration. Without PIM-1 present a delayed and dramatic change is observed. With the PIM-1 present, a more gradual change occurs, and this could be useful when analytically detecting glucose or other types of carbohydrates.

Fig. 3. (A) Chronopotentiometry (zero current) with 60 μg Pt@g-C3N4 and 24 μg PIM-1 on palladium in (i) 0.01, (ii) 0.05, (iii) 0.1, (iv) 0.2, (v) 0.5, and (vi) 1 M glucose in water. (B) As before but for only 60 μg Pt@g-C3N4 and no PIM-1. (C) Summary plot of end potential (at 1000 s) as a function of glucose concentration in water for (i) no PIM-1, (ii) 24 μg PIM-1, and (iii) 12 μg PIM-1. (D) Schematic drawing of the photocatalytic hydrogen production under a PIM-1 film competing with oxygen ingress.
3.2. Pt@g-C3N4 photopotential responses due to hydrogen produced from different carbohydrates

The effects of the carbohydrate molecular structure on the phototresponse was investigated, in particular in view of the behaviour of reducing versus non-reducing sugars. Fig. 4 shows chronopotentiometry (zero current) data for glucose, fructose (reducing) as well as sucrose and trehalose (non-reducing). It is clear that both reducing and non-reducing sugars give significant phototresponses. It has previously been suggested that the reaction of the sugar is likely to be associated with its adsorption onto the g-C3N4 photocatalyst [14] and therefore holes of high energy (2.7 eV band gap [26]) may be sufficiently energetic to trigger oxidation even for non-reducing carbohydrates. For trehalose (Fig. 4A), the phototresponse is delayed and observed only for concentrations higher than 0.1 M. However, for sucrose (Fig. 4B) only a weak delayed signal is observed. Both glucose (Fig. 2B) and fructose (Fig. 4C) show phototresponses over the complete concentration range. The plot in Fig. 4D summarises and compares the final equilibrium potential data (at 1000 s) for the four types of carbohydrate.

3.3. Pt@g-C3N4 photopotential responses due to hydrogen generation from soft drink samples

A potential area of application of the photopotential generation for carbohydrates could be in monitoring of commercial products containing sugars. The palladium membrane is dense separating the electrochemical compartment from the photocatalysis compartment. Complex samples of any type (even in oils etc.) could be in contact and used to generate phototresponses.

Here, commercial softdrink samples were purchased and tested. Fig. 5A shows the phototresponse for a sugar containing softdrink (see experimental). Filtration was necessary as turbidity affected the measurement. However, in future this could be avoided by shortening the optical path length (here 15 mm). By diluting the sample systematically, a set of data points was recorded. NMR analysis of the product (see supporting information) revealed the presence of an aqueous glucose: fructose: sucrose solution with molar ratio 1: 4.95: 2.42 and with total content of 0.355 g glucose + 1.75 g fructose + 1.3 g sucrose in 100 mL water. An artificial solution of identical composition was used for comparison purposes. Data in Fig. 5B show very similar phototresponses upon dilution. A softdrink with sweetener (no carbohydrates) did not give any significant phototresponse (Fig. 5C). The plot in Fig. 5D shows data for two repeat data sets of the sugar-containing softdrink together with the data for the artificial mixture of sugars showing a good agreement.

It should be noted that these measurements were all performed in the presence of ambient oxygen and this affects the equilibrium potential data (as oxygen will react with hydrogen at the palladium surface). Additional experiments (not shown) with argon de-aeration cause a shift of the final equilibrium to more negative potentials. Argon de-aeration only on the sample side does not speed up the phototresponse but results in a shift in final potential.

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**Fig. 4.** (A) Chronopotentiometry (zero current) data obtained with 60 µg Pt@g-C3N4 and 12 µg PIM-1 at a palladium membrane for (i) 0.05, (ii) 0.1, (iii) 0.2, (iv) 0.5, and (v) 1 M trehalose in water. (B) As above but for sucrose. (C) As above but for fructose. (D) Plot of the final equilibrium potential (at 1000 s) versus carbohydrate concentration in water for (i) trehalose, (ii) glucose, (iii) sucrose, and (iv) fructose.
by approximately −50 mV. However, when argon de-aerating both sides of the palladium membrane, the final equilibrium potential with the softdrink approaches −0.2 V vs. SCE. Therefore, the conditions (oxygen content) on both sides of the palladium membrane during the analytical detection are important. Applications of this methodology seem most plausible for approximation/monitoring of total carbohydrate content in the presence of ambient oxygen. In future, improvements in the analytical performance are likely for example with thinner palladium composite membranes, with photo-chronoamperometric techniques, or based on voltammetric read-out of photocurrents.

4. Conclusions and outlook

It has been shown that a palladium film can be employed to separate an anolyte compartment with glucose and an electrochemical compartment filled with aqueous 10 mM HCl. Production of hydrogen in the anolyte compartment driven by a blue LED (385 nm) and catalysed by a Pt@g-C$_3$N$_4$ photocatalyst deposit causes the equilibrium potential of the palladium working electrode to respond. In future work, a wider range of photocatalysts and hydrogen evolution catalysts could be employed and tested, for example including materials based on oxygen deficient oxides [27].

A PIM-1 matrix for the Pt@g-C$_3$N$_4$ photocatalyst was employed to help capturing the hydrogen, protect against oxygen, and to provide a mechanically stable catalyst film. In the future, additional work will be required to explore other types of PIM materials and more generally the robustness of this type of sensor. There are three potential failure modes based on (i) the photocatalyst failing, (ii) the palladium membrane becoming brittle, or (iii) the PIM-1 material itself undergoing degradation. Currently, there is no experimental data to predict the longevity of this type of indirect sensor in continuous operation.

When glucose was introduced as a hole quencher, significant photo-responses are recorded as change in equilibrium potential. The process is effective in distilled water, in commercial softdrink, or fruit juice samples. The measurable glucose concentrations range appeared to be from about 10 mM to approximately 300 mM in the presence of ambient oxygen. However, other types of carbohydrates such as fructose (reducing), or sucrose, trehalose (non-reducing) give photoresponses with similar characteristics. For commercial samples only the total content for a given mixtures of carbohydrates is measured. Distinguishing between the different types of quenchers is not possible under these conditions. Traditional techniques such as flow-through NMR or optical viscosity probes [28] could be employed as alternatively approaches. A biosensor array [29] for disaccharides and a flow injection biosensor based on enzymes to selectively/simultaneously detect glucose, fructose, and sucrose have been reported previously to monitor complex saccharide mixtures [30].

The “indirect electrochemical sensor” methodology is novel in that the separation of electrochemical and analysis compartments...
allows the electrochemical detection to be separated from complex matrix elements (colloids, salts, additives, etc.). There is no requirement for the analyte to be conducting with electrolyte or buffered. Samples (biological or non-biological) can be monitored simply in contact to the membrane and exposed to blue light from an LED light source. In the future, a wider range of applications may be possible. However, the sensitivity as well as the response time of the sensor need to be improved for example by introducing much thinner types of membranes, or introducing alternative membranes based on graphene composites. Further applications beyond sensor development are possible in energy conversion and in waste-to-energy applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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