



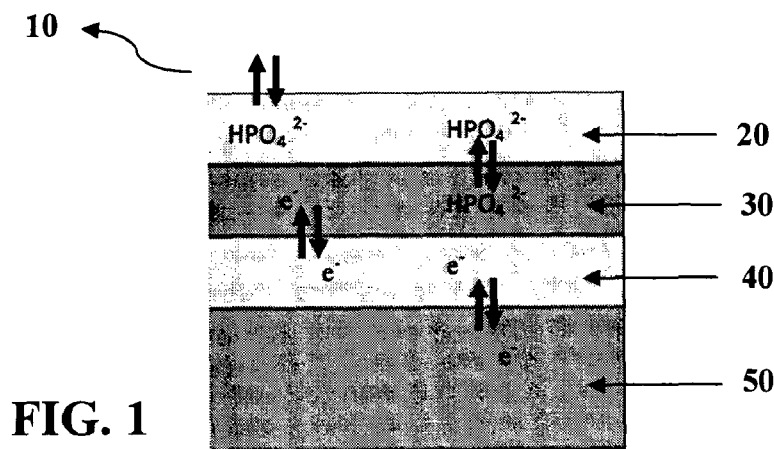
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- (71) **Applicant (for all designated States except US):** **MIMOS BERHAD** [MY/MY]; Technology Park Malaysia, 57000 Kuala Lumpur (MY).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **AIMAN SAJIDAH Binti Abd Aziz** [MY/MY]; Mimos Berhad, Technology Park Malaysia, 57000 Kuala Lumpur (MY). **MOHD RAIS Bin Ahmad** [MY/MY]; Mimos Berhad, Technology Park Malaysia, 57000 Kuala Lumpur (MY).
- (74) **Agent:** **LOK Choon Hong**; Suite 6.03.6Th Floor, Wisma Mirama, Jalan Wisma Putra, 50460 Kuala Lumpur (MY).

- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
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(54) Title: PHOSPHATE SENSOR



**FIG. 1**

(57) **Abstract:** The present invention relates to an improved phosphate sensor comprising a substrate; a thick film screen printed carbon layer; a phosphate sensing membrane; polypyrrole layer; characterized in that the polypyrrole layer is homogeneously doped on the carbon layer.

## PHOSPHATE SENSOR

### FIELD OF INVENTION

5

The present invention relates to an improved phosphate sensor for electrochemical sensing and method of preparing the same.

### BACKGROUND OF THE INVENTION

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Phosphorus (P) is a multivalent nonmetal element in the same with group nitrogen in the periodic table. It is found in nature in several allotropic forms, and is an essential element for the life of organism. Commonly, phosphorus can be found as phosphates, which consists of phosphorus atom bonded to four oxygen atoms. Phosphates are important substances in the human body. For example, calcium phosphate is a major structural component of teeth and bone. Phosphorus also is a part of DNA materials. The importance of phosphorus is not limited to human, it is also essential nutrient for early root development in plant.

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The phosphate levels in the organisms and environmental nowadays have been major concern over the years. The excessive amount of phosphate in human can cause problem to health, such as kidney damage and osteoporosis. Therefore, leaching of inorganic phosphates in the river from agricultural and industrial activity has led to eutrophication. The increasing of phosphate level could promote the growth of phosphate-dependent organisms such as algae on the water surface. These organisms use great amounts of oxygen in water and prevent the sunlight entering the water which will disrupt normal functioning of the ecosystem.

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Traditionally silver-silver chloride (Ag/AgCl) electrode has been employed as the electrochemical transducer in chemical sensors and reference electrode. While the Ag/AgCl electrode works best in the bulky glass electrode equipped with

30

comparatively large volume of liquid internal electrolyte, the miniaturized solid state version employs hydrophilic polymeric membrane as an internal layer. In a typical laboratory procedure, the internal layer is hydrated with certain concentration of the target analyte, to act as the reference concentration. Depending on storage condition and  
5 due to other factors like aging the concentration of the internal layer changes and thus causes the electrical signal to change. This requires frequent or daily calibration; else the sensor would transmit inaccurate data.

Daily calibration is difficult for field deployed integrated sensors.  
10 Another problem caused by the hydrophilic internal layer is its incompatibility with the sensing membranes. The sensing membrane is usually highly lipophilic and its adhesion to hydrated hydrophilic internal layer is marginal and this results in peeling of the sensing membrane.

15 Conductive polymers have been introduced as electrochemical transducer and it has been shown that chemical sensors employing conductive polymer can produce fast response and stable signal without the use of additional internal layer. Polypyrrole, polythiophene and polyaniline have been used as conductive polymers for chemical sensors.

20

Polypyrrole has been the most widely used due to numerous advantages. Doping the polypyrrole increases the conductivity of the conducting polymer and this is usually achieved by electropolymerization from solution of pyrrole monomer containing electrolyte of chloride or nitrate salts of potassium. This causes a problem because the  
25 doping electrolyte is aqueous solution, whereas the pyrrole monomer is only moderately soluble in this electrolyte. Therefore, vigorous shaking and continuous stirring are required to achieve homogenous mixture and to maintain homogeneity of the doped polypyrrole on a phosphate sensor.

30 Hence, there is still a need in the art for an improved phosphate sensor for electrochemical sensing.

**SUMMARY OF THE INVENTION**

According to a first aspect of the invention, there is provided a phosphate sensor comprising:

- 5           a substrate,
- a thick film screen printed carbon layer,
- a phosphate sensing membrane;
- polypyrrole layer;
- characterized in that the polypyrrole layer is homogeneously doped on the
- 10          carbon layer.

According to a second aspect of the invention, there is provided the phosphate sensor is used in the manufacture of an ion selective electrode (ISE) and an ion sensitive field effect transistor (ISFET) phosphate sensing device.

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According to a third aspect of the invention, there is provided a method of depositing doped polypyrrole electrochemical transducer layer comprising;

- a) preparing a pyrrole monomer doped electrolyte solution and a hydrophilic dopant in a polar solvent;
- 20          b) immersing a carbon electrode, a counter electrode and a reference electrode into the doped pyrrole electrolyte solution; and
- c) depositing the doped polypyrrole electrochemically .

The provision of the method is advantageous as it results in producing a stable electrical signal and maintains homogeneity of the doped polypyrrole on a phosphate sensor.

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**BRIEF DESCRIPTION OF THE DRAWINGS**

For a fuller understanding of the nature of the present invention, reference should be made to the following detailed description taken in connection with the accompanying drawings in which:

**FIG. 1:** illustrates an electron transfer mechanism of phosphate ion inside the phosphate sensor with doped polypyrrole.

**FIG.2:** illustrates hydrophilic organic salts for polypyrrole doping.

**FIG.3:** illustrates a doped polypyrrole conducting polymer.

**FIG.4:** illustrates molecular structures of methyl methacrylate (2) and tetrahydrofurfuryl acrylate (3) monomers.

**FIG.5:** illustrates a cyclic voltammograms of Ppy(Cl) from 50% v/v methanol solvent on Pt in 0.1M KCl with 90, 150, 300 and 500 sec electropolymerisation time.

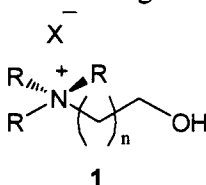
**FIG.6:** illustrates a potentiometric response of phosphate sensor with various electropolymerisation times.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to a miniaturized solid state phosphate sensor 10 as illustrated in FIG.1 based on doped polypyrrole wherein the doping electrolytes are hydrophilic organic salts, as illustrated in FIG.2 dissolved in polar organic solvent, mixture of polar solvents or mixture of polar solvent and deionized water. In one embodiment, the miniaturized solid state phosphate sensor 10 based on doped polypyrrole electrochemical transducer that gives stable electrical signal. The phosphate sensor 10 does not require the use of hydrophilic internal layer and is easy to fabricate.

FIG.1 shows a phosphate sensor 10 comprising; a substrate 50, a thick film screen printed carbon layer 40, a phosphate sensing membrane 20; polypyrrole layer 30; wherein the polypyrrole layer 30 is homogeneously doped on the carbon layer 40. FIG.1 also shows that the polypyrrole conducting polymer 30 is deposited on top of screen printed thick film carbon 40 electrode. The carbon 40 surface must first be cleaned by sonication, and the pyrrole monomer is electropolymerized from the doping electrolyte.

In one embodiment of the phosphate sensor 10, the doped polypyrrole layer 30 having doping electrolyte of the following structure;



X = Cl, Br, I, BF<sub>4</sub>, PF<sub>6</sub>, OAc, CF<sub>3</sub>CO<sub>2</sub>, NO<sub>3</sub>, Fe(CN)<sub>6</sub>, oxalate, tosylate

n = 1, 2, 3

R = H, methyl, ethyl, butyl, allyl

In one embodiment of the phosphate sensor 10, the phosphate sensing membrane 20 is photo-cured co-polymer of methyl methacrylate and tetrahydrofurfuryl acrylate

containing photoinitiator, diacrylate crosslinker, lipophilic ammonium salt and phosphate ionophore.

5 In another embodiment of the phosphate sensor **10**, the phosphate sensing membrane **20** is bulk co-polymer of methyl methacrylate and tetrahydrofurfuryl acrylate containing photoinitiator, diacrylate crosslinker, lipophilic ammonium salt and phosphate ionophore.

10 The phosphate sensor **10** of the present invention is usable in the manufacture of an ion selective electrode (ISE) phosphate sensing device. Also, the phosphate sensor **10** is usable in the manufacture of an ion sensitive field effect transistor (ISFET) phosphate sensing device.

15 The polymerization process of the pyrrole monomer releases two moles of electrons for each mole of the monomer. In the oxidized state polypyrrole exists as a polyradical cation, and at this state, anions such as chloride, are attracted electrostatically into the polymerized film as counter ions or dopants as illustrated in **FIG.3**.

20 The electrolytes of hydrophilic organic salts are prepared by dissolution in polar organic such as ethanol, methanol, 2-methoxy ethanol, dimethyl sulfoxide, acetonitrile or tetrahydrofuran. Mixture of polar organic solvents or mixture of the organic solvent and deionized water can also be used to dissolve the salts and the pyrrole monomer. Pyrrole exhibits very high solubility in these solvents and vigorous shaking or stirring is not required for mixing or in keeping homogeneity during electropolymerization.

25

A method of depositing doped polypyrrole electrochemical transducer layer comprising;

- a) preparing a pyrrole monomer doped electrolyte solution and a hydrophilic dopant in a polar solvent;
  - b) immersing a carbon electrode, a counter electrode and a reference electrode into the doped pyrrole electrolyte solution; and
- 30

c) depositing the doped polypyrrole electrochemically .

5 In one example, in step (a) the pyrrole monomer doped electrolyte solution having concentration ranges from 0.1M to 3M of pyrrole monomer and the hydrophilic dopant in a polar solvent having a concentration ranges from 0.1M to 3M. Preferably, the hydrophilic dopant is choline chloride.

10 In one example, the depositing step (c) is by electrochemical polymerization of constant current method with current density of 0.1 to 10 mA per square centimetre.

In another example, the depositing step (c) is by electrochemical polymerization utilising cyclic voltammetry method with scans between -1V and +1V.

15 In one example, pyrrole electropolymerization process takes place at the screen printed carbon **40** working electrode while conventional double-junction reference electrode and platinum or glassy carbon electrode counter electrode complete the chronopotentiometry setup.

20 Referring to **FIG.4**, co-polymer of acrylates, methyl methacrylate (**2**) and tetrahydrofurfuryl acrylate (**3**) has been employed as the phosphate sensing membranes **20** based on doped polypyrrole. The monomers can be photo-polymerized from a cocktail containing the monomers, photoinitiator, crosslinker, lipophilic ammonium salt and phosphate ionophore.

25 Likewise, bulk co-polymer of the above monomers can also be used as the sensing membrane **20**. In another example of preparation, the bulk co-polymer is first synthesized by refluxing the desired ratios of the monomers and benzoyl peroxide in benzene. After purification and drying, samples from the bulk polymer are dissolved with methylene chloride or tetrahydrofuran, along with the above components for  
30 phosphate sensing membrane **20**. A few microliters of the bulk cocktail is dispensed



coated on the sonicated polypyrrole electrode and the solvent air dried before testing for phosphate response can be conducted.

Polypyrrole is a conducting polymer due to its conjugated network of double  
5 bonds. In this manner it acts as a molecular wire and thus employed to conduct electrical current. Polypyrrole has another property that is of interest in chemical sensing – it undergoes reversible oxidation-reduction cycle at well-defined potentials. This property allows the use of polypyrrole as electrochemical transducer in chemical and biosensors.

10 Advantageously, the method of depositing doped polypyrrole electrochemical transducer layer increases the potential of obtaining homogeneously doped polypyrrole layer on the phosphate sensor.

Advantageously, the preparation of the phosphate sensor takes shorter time by  
15 utilizing the method of depositing doped polypyrrole electrochemical transducer layer.

The invention now being generally described, the same will be better understood by reference to the following detailed examples which are provided for purposes of illustration only and are not to be limiting of the invention unless so specified.

20

### EXAMPLE 1

#### **Phosphate sensor based on polypyrrole film doped with choline-Cl in 50% Methanol/deionised water (varied electropolymerisation time)**

##### 25 i) Formation of Polypyrrole film

The screen printed electrodes (SPE) with 4 mm diameter were cleaned ultrasonically with deionized water for 1 min. The electrochemical polymerization was performed in a conventional three-electrode cell with a platinum as auxiliary electrode and the Ag/AgCl double junction as reference electrode using Autolab PGSTAT  
30 MODEL 128N for 90, 150, 300 and 500 seconds. The polypyrrole (Ppy) films were generated with current density of  $2 \text{ mA cm}^{-2}$  in aqueous solution of 0.5M pyrrole

monomer containing 1M choline chloride dopant and 50% v/v methanol solvent. After forming electropolymerisation, cyclic voltammetry experiments were conducted between -1.0 V and +1.0 V with a potential sweep rate of 100 mV sec<sup>-1</sup> in 0.1M potassium chloride (KCl) solution. The plot is shown as in **FIG.5**.

5

### (ii) Phosphate sensor fabrication

Phosphate cocktail were prepared by mixing poly(vinyl) chloride (PVC), 2-nitrophenyl octyl ether (NPOE), bis-thiourea derivative ionophore, tetradodecylammonium chloride (TDACl) and tetrahydrofuran (THF) solvent. Then, the homogenous cocktail was deposited on top of Ppy film with 50% v/v methanol as solvent formed on top of SPE and dried overnight at room temperature. This phosphate sensor was tested using commercial Ag/AgCl double junction reference electrode. The results were shown in Table 1 and in **FIG.6**. All the results have shown satisfactory phosphate sensitivity value with good regression value more than 0.9.

15

Log (HPO <sub>4</sub> <sup>2-</sup> )	50% Methanol in 0.5M Pyrrole, 1M Choline chloride							
	90 sec well 1	90 sec well 3	150 sec well 1	150 sec well 3	300 sec well 1	300 sec well 3	500 sec well 1	500 sec well 3
-3	39.0	61.9	82.5	120.3	132.9	167.4	270.3	227.4
-2	8.5	34.2	54.2	92.9	104.2	139.8	241.1	200.4
-1	-30.0	-3.2	16.6	56.4	67.4	104.5	204.3	165.3
Sensitivity (mV/dec)	-34.5	-32.6	-33.0	-32.0	-32.8	-31.5	-33.0	-31.0
Intercept	-63.2	-34.1	-14.9	25.3	36.0	74.3	172.5	135.7
R <sup>2</sup>	0.9956	0.9928	0.9934	0.9934	0.9950	0.9950	0.9956	0.9944

Table 1: Phosphate sensor response (50% v/v methanol platform) with varied polymerisation time

20

Although the invention has been described with reference to particular embodiment, it is to be understood that the embodiment is merely illustrative of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made to the illustrative embodiment that other arrangements may be devised without departing from the scope of the present invention as defined by the appended claims.

25

## CLAIMS

- 5        2. A phosphate sensor comprising:

a substrate;

a thick film screen printed carbon layer;

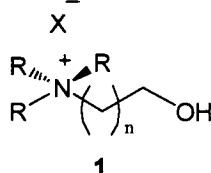
a phosphate sensing membrane;

polypyrrole layer;

- 10       characterized in that the polypyrrole layer is homogeneously doped on the carbon layer.

3. The phosphate sensor as claimed in Claim 1, characterized in that the doped polypyrrole layer having doping electrolyte of the following structure;

15



X = Cl, Br, I, BF<sub>4</sub>, PF<sub>6</sub>, OAc, CF<sub>3</sub>CO<sub>2</sub>, NO<sub>3</sub>, Fe(CN)<sub>6</sub>, oxalate, tosylate

n = 1, 2, 3

R = H, methyl, ethyl, butyl, allyl

20

4. The phosphate sensor as claimed in Claim 1, characterized in that the phosphate sensing membrane is photo-cured co-polymer of methyl methacrylate and tetrahydrofurfuryl acrylate containing photoinitiator, diacrylate crosslinker,
- 25       lipophilic ammonium salt and phosphate ionophore.

5. The phosphate sensor as claimed in Claim 1, characterized in that the phosphate sensing membrane **12** is bulk co-polymer of methyl methacrylate and tetrahydrofurfuryl acrylate containing photoinitiator, diacrylate crosslinker,
- 30       lipophilic ammonium salt and phosphate ionophore..

6. Use of the phosphate sensor according to any preceding claim in the manufacture of an ion selective electrode (ISE) phosphate sensing device.
7. Use of the phosphate sensor according to claim 1 to 4 in the manufacture of an ion sensitive field effect transistor (ISFET) phosphate sensing device.
- 5 8. A method of depositing doped polypyrrole electrochemical transducer layer comprising;
  - a) preparing a pyrrole monomer doped electrolyte solution and a hydrophilic dopant in a polar solvent;
  - 10 b) immersing a carbon electrode, a counter electrode and a reference electrode into the doped pyrrole electrolyte solution; and
  - c) depositing the doped polypyrrole electrochemically.
- 15 9. A method of depositing doped polypyrrole electrochemical transducer layer according to Claim 7, characterized in that in step (a) the pyrrole monomer doped electrolyte solution having concentration ranges from 0.1M to 3M of pyrrole monomer and the hydrophilic dopant in a polar solvent having a concentration ranges from 0.1M to 3M.
- 20 10. A method of depositing doped polypyrrole electrochemical transducer layer according to Claim 8, characterized in that the hydrophilic dopant is choline chloride.
- 25 11. A method of depositing doped polypyrrole electrochemical transducer layer according to Claim 7, characterized in that the depositing step (c) is by electrochemical polymerization of constant current method with current density of 0.1 to 10 mA per square centimetre.
- 30 12. A method of depositing doped polypyrrole electrochemical transducer layer according to Claim 4, characterized in that the depositing step (c) is by

electrochemical polymerization utilising cyclic voltammetry method with scans between -1 V and +1 V.

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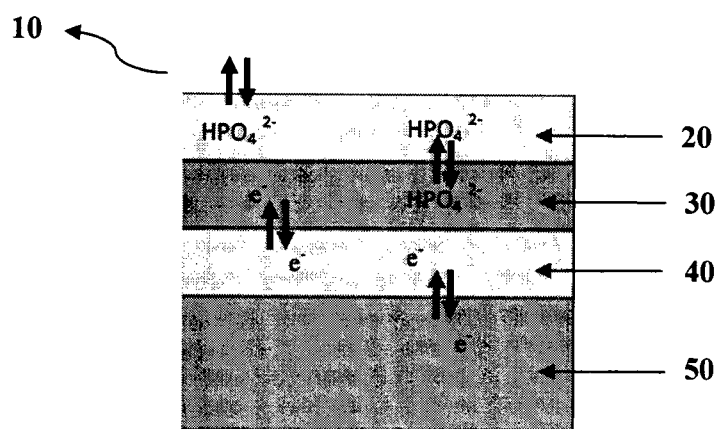


FIG. 1

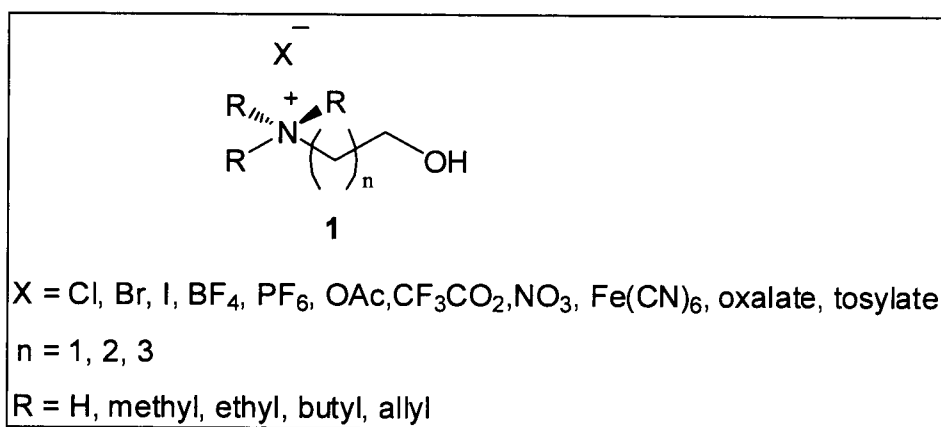


FIG. 2

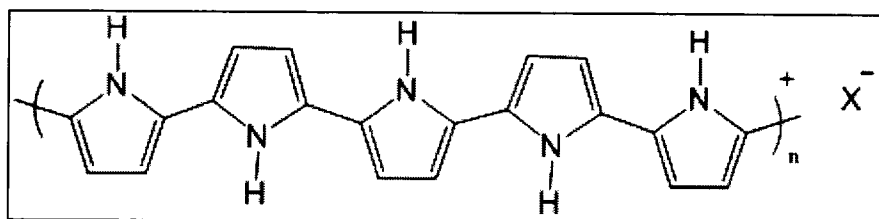


FIG. 3

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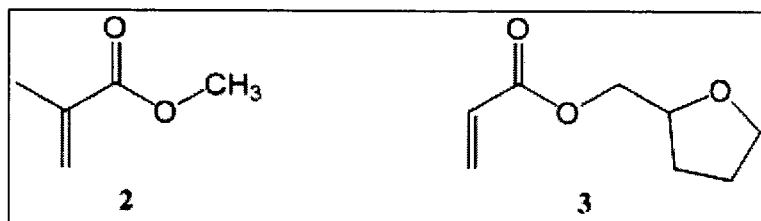


FIG. 4

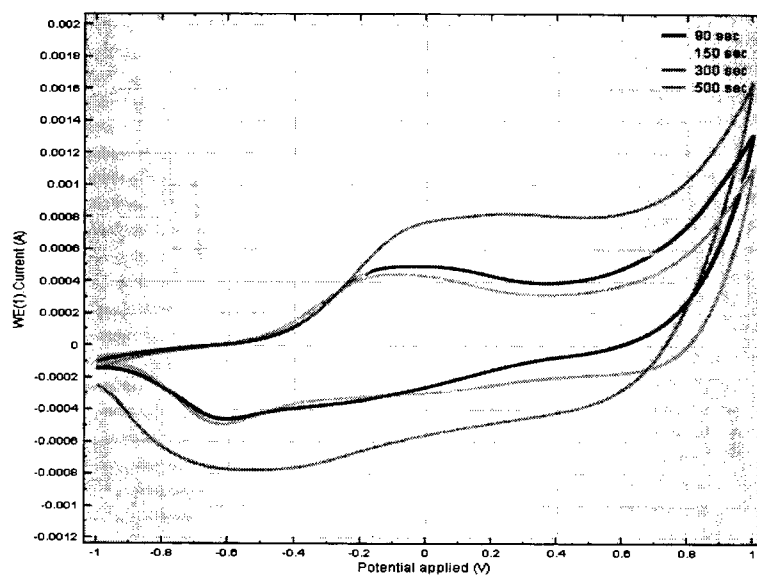


FIG. 5

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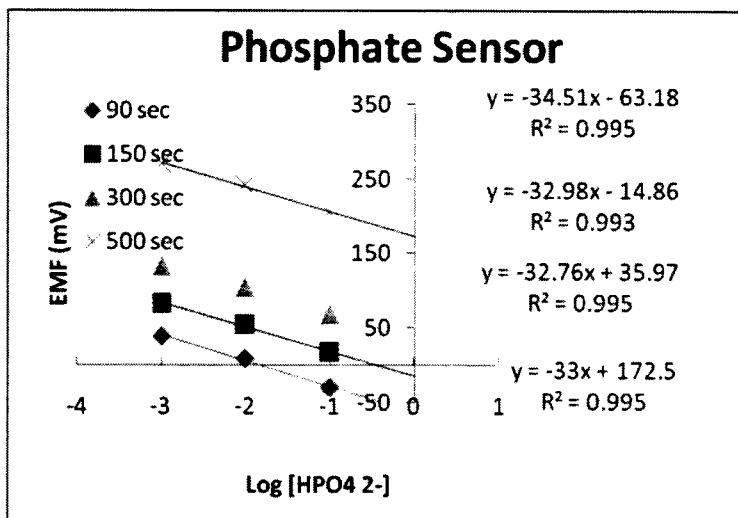


FIG. 6



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/MY2011/000155

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

G01N 27/333 (2006.01)

C25B 11/04 (2006.01)

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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, WPI, INSPEC, GOOGLE: (Or Poly\_pyrrole?, PPy, pyrrole?, PPyCl, poly\_pyrrole?, pyrrole?); (Or +electrode?, +sensor?, transducer?, C25B11/low/ic/ec/ecno, ISE, ISFET, transistor?, SPE, g01n27/30/low/ic/ec/ecno); Phosphate?; (dop+, nitrate, choline, chloride); (carbon, graphite); screen w print+ and similar terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XU, H. <i>et. al.</i> : "A glucose oxidase sensor based on screen-printed carbon electrodes modified by polypyrrole", Proceedings of the 2005 IEEE, Engineering in Medicine and Biology 27th Annual Conference, Shanghai, China, September 1-4, 2005, pg. 1917-1920	
Y	Refer to the whole document and in particular to section titled "B. Fabrication of Enzyme Electrode" & "E. Optimization of Experimental Conditions"; Fig. 1	8
		10

☒ 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
04 October 2011

Date of mailing of the international search report  
11/10/2011

Name and mailing address of the ISA/AU  
AUSTRALIAN PATENT OFFICE  
PO BOX 200, WODEN ACT 2606, AUSTRALIA  
E-mail address: pct@ipaustalia.gov.au  
Facsimile No. +61 2 6283 7999

Authorized officer  
**FIROOZEH RABBANI**  
AUSTRALIAN PATENT OFFICE  
(ISO 9001 Quality Certified Service)  
Telephone No : +61 2 6283 2287

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/MY2011/000155

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	BENDIKOV, T. A. <i>et. al.</i> : "Development and environmental application of a nitrate selective microsensor based on doped polypyrrole films", Sensors and Actuators B, Vol. 106, 2005, pg 512-517, available online 21 September 2004	
X	Refer to the whole document and in particular to section titled "2.2 Preparation of nitrate-doped polypyrrole (PPy(NO <sub>3</sub> -)) microelectrodes".	8-9, 11
Y	US 5605617 A (BIDAN <i>et. al.</i> ) 25 February 1997	10
X	Refer to the whole document and in particular to Fig. 3, col. 7, ln 32-47, Example 1; col. 8, ln 9-20; col. 9, ln 10-15	8, 12
Y	BIDAN G., <i>et. al.</i> : "Electrode Modified by sulfonated calixarenes immobilised into a polypyrrole film: a step towards new ion-sensitive layers" Synthetic Metals, Vol. 84, 1997, pg 255-256	10
X	Refer to the whole document and in particular to section titled 2. Experimental	8
Y	WO 2010/022353 A1 (INNOVA MATERIALS, LLC) 25 February 2010	10
Y	Refer to the whole document and in particular to paragraphs [0010]-[0011]; [0036]	10
	WO 2009/073927 A1 (MONASH UNIVERSITY) 18 June 2009	
X	Refer to the whole document and in particular to pg 2 lines 5-9; pg 78, ln 1-8	2, 3, 6, 7

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/MY2011/000155**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:  
Continued in Supplemental Box

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

**Supplemental Box III(1)**

(To be used when the space in any of Boxes I to IV is not sufficient)

**Continuation of Box No: III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 2-7 are directed to a phosphate sensor comprising a phosphate sensing membrane, a polypyrrole layer homogeneously doped on a carbon layer. The feature of "a phosphate sensing membrane" is specific to this group of claims.
- Claims 8-12 are directed to a method of depositing doped polypyrrole electrochemical transducer layer. The feature of electrochemically depositing a doped polypyrrole layer is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is a doped polypyrrole layer. However this feature does not make a contribution over the prior art because it is disclosed in:

XU, H. *et. al.*: "A glucose oxidase sensor based on screen-printed carbon electrodes modified by polypyrrole", Proceedings of the 2005 IEEE, Engineering in Medicine and Biology 27th Annual Conference, Shanghai, China, September 1-4, 2005, pg. 1917-1920

BENDIKOV, T.A. *et. al.*: "Development and environmental application of a nitrate selective microsensor based on doped polypyrrole films", Sensors and Actuators B Vo. 106, (2005), pg 512-517, available online 21 September 2004

US 5605617 A (BIDAN *et. al.*) 25 February 1997

BIDAN G., *et. al.*: "Electrode Modified by sulfonated calixarenes immobilised into polypyrrole film: a step towards new ion-sensitive layers" Synthetic Metals 84, (1997), pg 255-256

WO 2009/073927 A1 (MONASH UNIVERSITY) 18 June 2009

Therefore in the light of these documents (list being non-exhaustive) this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2011/000155

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5605617	EP	0642661	FR	2703463	JP	H07507636
		WO	9423291				
WO	2010022353	AU	2009282691	CA	2734864	CN	102186643
		EP	2328731	US	2011217544		
WO	2009073927	AU	2008336264	EP	2232249	US	2011042225
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							