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(54) **Title**: A PHOSPHATE SENSOR AND METHOD OF FORMATION THEREOF

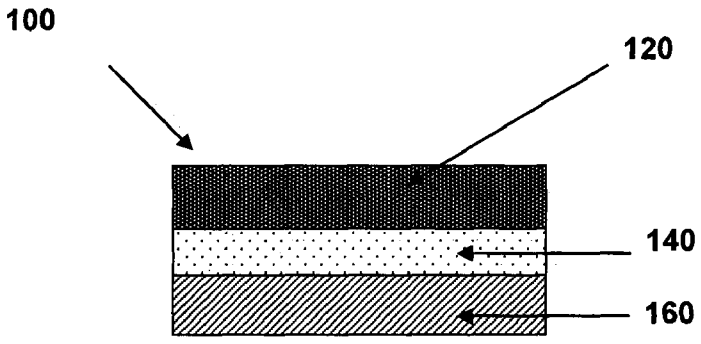

FIGURE 1

(57) **Abstract**: The present invention relates to a phosphate sensor (100) for detecting and measuring inorganic phosphate anions. The phosphate sensor (100) is characterised by a substrate (160), a conductor layer (140) disposed on the substrate, and a cobalt nanoparticles composite layer (120) disposed on the conductor layer (140). A method of forming the phosphate sensor (120) is also provided.

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A PHOSPHATE SENSOR AND METHOD OF FORMATION THEREOF

FIELD OF INVENTION

The present invention relates to a phosphate sensor and a method of formation thereof.

BACKGROUND OF THE INVENTION

Phosphate is a frequently analysed substance in the water treatment industry. Phosphate analysis is also common in environmental monitoring, in clinic diagnosis, and in other industrial places such as mining and metallurgical processes.

Phosphate fertilizers are widely used to increase nutrient level for most crops and lawn plants. When properly applied the inorganic phosphate binds well with soil components, and will not contribute to water pollution. However, inorganic phosphate is commonly applied on soil surface and it is easily washed away to rivers, lakes, drainage and ground water.

Inorganic and organic phosphate pollutant from fertilizer runoff causes eutrophication in rivers and lakes, where the nutrients cause excessive growth of algae and weeds. This results in oxygen deficiency in the aquatic eco system and makes it unsuitable for fish and other species. Therefore, monitoring of phosphate level in sources of fresh water is important to ensure water quality for drinking, household use, as well as to keep proper balance in the aquatic eco-system.

A conventional phosphate sensor device comprises a sensing membrane that embeds chemical components in the polymeric matrix. An example of the phosphate sensor device is disclosed in US 6,540,894 which relates to a phosphate ion selective electrode, with the detection limit is made small to enable measurement of phosphate ion concentrations of down to low concentration, and a method of manufacturing the abovementioned phosphate ion selective electrode, wherein a sensing membrane of an ion selective electrode A is comprised of a solid membrane having a slightly soluble metal salt as the main component thereof.

However, the chemical component of the phosphate sensor of this device tends to leach out, and results in functional failure of the sensor device. Moreover, prolonged exposure in harsh environment causes delamination of the sensing membrane whereby the polymeric matrix is peeled off from the transducer electrode surface of the sensor device.

Hence, there is a need to provide a phosphate sensor that obviates from the functional failure of the sensor device due to the delamination of the sensing membrane under prolonged exposure to harsh aqueous environment.

SUMMARY OF INVENTION

The present invention relates to a phosphate sensor **(100)** for measuring inorganic phosphate anions and a method for producing the phosphate sensor **(100)**. The phosphate sensor **(100)** is characterised by a substrate **(160)**; a conductor layer **(140)** disposed on the substrate; and a cobalt nanoparticles composite layer **(120)** disposed on the conductor layer **(140)**. The phosphate sensor **(100)** is suitably used for detecting inorganic phosphate in dibasic inorganic phosphate form.

Preferably, the conductor layer **(140)** is selected from the following materials: screen printed silver, electrode deposited silver, electroplated silver, screen printed carbon, electroplated platinum or a combination thereof.

Preferably, the cobalt nanoparticles composite layer **(120)** is prepared by embedding cobalt nanoparticles in low impedance nano-porous material.

Preferably, the cobalt nanoparticles composite layer **(120)** comprises of 10% to 50% cobalt nanoparticles by weight and 50% to 90% cellulose acetate by weight.

A method for producing the phosphate sensor **(100)** includes the steps of preparing and disposing a conductor layer **(140)** onto a substrate **(160)**; preparing a cobalt nanoparticles-cellulose acetate paste; coating the cobalt nanoparticles-cellulose acetate paste onto the conductor layer **(140)** to produce the phosphate sensor **(100)**; and characterising the phosphate sensor **(100)**.

Preferably, disposing the conductor layer **(140)** on the substrate **(160)** comprises the steps of screen printing a silver paste on a substrate **(160)**; and curing the silver paste at approximately 120°C for 30 minutes.

Preferably, the cobalt nanoparticles-cellulose acetate paste is prepared by the steps of dissolving and mixing cellulose acetate solution in tetrahydrofuran; stirring the mixture of cellulose acetate solution and tetrahydrofuran under nitrogen atmosphere; and adding cobalt nanoparticles into the mixture with a continuous stirring and under continuous flow of nitrogen gas.

A method for regenerating an oxidised phosphate sensor **(100)** is also provided. The method comprises the steps of providing the oxidised phosphate sensor **(100)** as working electrode; providing a reference electrode; providing a platinum rod as a counter electrode; connecting the working electrode, reference electrode and counter electrode into an electrochemical condition; immersing the working electrode, reference electrode and counter electrode into an acidic solution; applying a cyclic voltammetry method; and repeating the cyclic voltammetry method until the oxidised cobalt nanoparticles of the phosphate sensor **(100)** return to an original uncharged state.

Preferably, the acidic solution used for immersing the working electrode, reference electrode and counter electrode is 0.1M hydrochloric solution.

Moreover, the cyclic voltammetry method is suitably swept between 1.2V to 0V for at least once.

Advantageously, the phosphate sensor of the present invention does not tend to delaminate under prolonged exposure to harsh environment.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

FIGURE 1 illustrates a cross sectional view of a phosphate sensor **(100)** in accordance to an embodiment of the present invention.

FIGURE 2 illustrates a flow chart for a method of producing a phosphate sensor **(100)** in accordance to an embodiment of the present invention.

FIGURE 3 illustrates a graph plot of an electromotive force (emf) signals versus log activity of dibasic phosphate of a phosphate sensor buffered at pH 8 with reference electrode in calibration solution.

FIGURE 4 illustrates a cyclic voltammetry graph plot of cobalt nanoparticles-cellulose acetate composite of a phosphate sensor of the present invention in 0.1M hydrochloric (HCl) solution during regeneration.

DESCRIPTION OF THE PREFFERED EMBODIMENT

A preferred embodiment of the present invention will be described herein below with reference to the accompanying drawings. In the following description, well known functions or constructions are not described in detail since they would obscure the description with unnecessary detail. In the following specification and the claims which follow, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise.

Referring now to **Figure 1**, there is shown a phosphate sensor **(100)** according to an embodiment of the present invention.The phosphate sensor **(100)** comprises of a substrate **(160)**, a conductor layer **(140)** disposed on the substrate and a cobalt nanoparticles composite layer **(120)** disposed on the conductor layer **(140)**. Preferably, the conductor layer **(140)** is of the following materials: screen printed silver, electrode deposited silver, electroplated silver, screen printed carbon, electroplated platinum or a combination thereof. The cobalt nanoparticles composite layer **(120)** is fabricated by embedding cobalt nanoparticles in low impedance nano-porous material. The term "nanoparticles" generally describes particles with diameters of about 1 to 100 nm. Metal nanoparticles can have electromagnetic properties different from the bulk metal. This can be caused by surface effects due to the high surface area to volume ratio. Inorganic phosphate anions in water are detected in three forms of ionic and mainly dependent on pH level. Among others,

monobasic inorganic phosphate ($H_2PO_4^-$), dibasic inorganic phosphate (HPO_4^{2-}), and tribasic inorganic phosphate (PO_4^{3-}).Preferably, the phosphate sensor of the present invention is used to detect inorganic phosphate in dibasic inorganic phosphate form i.e. the predominant species detected at pH 6-8.

Figure 2 illustrates a flow chart for a method of producing a phosphate sensor **(100)** in accordance to an embodiment of the present invention.

Initially, as in step **220**, a conductor layer **(140)** is disposed on the substrate **(160)**. Preferably, the conductor layer **(140)** is disposed on the substrate by screen printing silver paste on a FR4 or PCB substrate and curing the silver paste at approximately 120°C for 30 minutes to give a final dry thickness of 100 µm. The silver paste printed on the substrate is shaped in a circular form with 2 to 3 mm diameter and it is printed on copper-gold wire trace of the substrate that is connected to at least one electrical contact for connecting the phosphate sensor **(100)** with an external circuit. The advantage of the screen printed silver paste covering the wire trace is that it minimizes copper corrosion of the wire trace. Preferably, an insulator layer is disposed on the substrate surface while exposing the screen printed silver paste and the electrical contact. The insulator layer is suitably made of solder mask paste or red epoxy glue printed on the substrate and cured in the oven at approximately 120°C for 30 minutes. A silver electrode is now ready to be used.

Thereon, as in step **222**, cobalt nanoparticles composite paste is prepared by mixing cobalt nanoparticles with cellulose acetate (CA) solution in tetrahydrofuran to afford a cobalt nanoparticles-cellulose acetate paste. The mixture of cobalt nanoparticles having cellulose acetate comprising of 10 to 50% by weight of cobalt nanoparticles and 50 to 90% by weight of cellulose acetate. Preferably, the cobalt nanoparticles composite paste is prepared by initially weighing, dissolving and adding the cellulose acetate solution into 10 ml tetrahydrofuran in a glass vial to provide a mixture with 5% by weight of cellulose acetate. Thereon, the glass vial is tightly capped and the mixture is magnetically stirred under nitrogen atmosphere for approximately 1 hour until homogenous clear solution is achieved. The cobalt nanoparticles are then gradually added into the mixture under continuous stirring to afford 40% weight of cobalt nanoparticles. The mixture is magnetically stirred for approximately 3 hours under continuous flow of nitrogen gas to produce the cobalt

nanoparticles-cellulose acetate paste. In a preferred embodiment cobalt nanoparticles are mixed with cellulose acetate (CA) solution in tetrahydrofuran to afford a thick black paste wherein it comprises 50% by weight of cobalt nanoparticles.

In step of **224**, the cobalt nanoparticles-cellulose acetate paste as prepared in step **222** is applied and coated on top of the screen printed silver to completely cover the silver surface of the silver electrode as prepared in step **220**. It has to be ensured that no part of the silver material is exposed to the analyte solution when used in measuring the phosphate concentration. The electrode coated with cobalt nanoparticles-cellulose acetate paste is dried at ambient temperature under continuous flow of nitrogen gas for approximately 20 minutes to 1 hour to completely dry the paste to produce the phosphate sensor **(100)**. The metal nanoparticles coated substrate may be made in a variety of ways, including but not limited to contacting the substrate with a metal nanoparticles composition to give the metal nanoparticles coated substrate.

In the step **226**, a potentiometric measurement and characterization of the phosphate sensor **(100)** to detect dibasic phosphate ion are tested during this step. The phosphate sensor **(100)** as formed in step **224** and a reference electrode are connected to an ion meter. Both electrodes are immersed in calibration solution of potassium dibasic phosphate buffered by acetic acid at pH 7-8. The electromotive force (emf) responses at each calibration solution are recorded and the data are plotted as illustrated in **Figure 3**. Sensor response of the phosphate sensor **(100)** reaches to near ideal Nernstian behaviour of -22.8 mV/decade for dibasic inorganic phosphate, and with a good correlation coefficient of 0.99 is observed when the phosphate sensor **(100)** is successfully prepared and calibrated. The emf readings of the phosphate sensor are shown in **Table 1**. The phosphate sensor **(100)** is now ready to be used.

$[HPO_4^{2-}]$	mV 1	mV 2	mV 3	AVG
-1	-11.1	-14.6	-12.3	-12.7
-2	9.3	6.3	5.6	7.1
-3	37.8	26.9	34.4	33.0
M				-22.9
C				36.6
r^2				0.99

Table 1: EMF readings of the phosphate sensor prepared from cobalt nanoparticles composite with dibasic phosphate solutions

For measuring and detecting dibasic phosphate ion, the cobalt nanoparticles of the composite layer **(120)** of the phosphate sensor **(100)** are in tendency to be oxidised as shown in the equation below.

Cobalt (s) ⟶ **Cobalt (II) + 2e**

The oxidisation of the cobalt nanoparticles produces potential difference based on the potential of a reference electrode such as silver-silver chloride or chloride reference cell which is shown in the equation below.

AgCl (s) ⟶ **Ag(s) + 1e**

In order for the phosphate sensor to be re-used, the oxidised phosphate sensor **(100)** is required to be regenerated. Step **228** illustrates a regeneration step of the oxidised phosphate sensor **(100)** after it has been used for detecting dibasic phosphate ion. A cyclic voltammetry method is used for regeneration of the oxidised phosphate sensor **(100)** by reducing the oxidised cobalt material of the phosphate sensor **(100)** to return to an original uncharged state of cobalt as shown in the equation below.

Cobalt (II) + 2e ⟶ **Cobalt (s)**

This method is used to reduce cobalt (II) to cobalt (0). The oxidised phosphate sensor **(100)** is used as the working electrode, whereas silver-silver chloride and

platinum rod are used as reference electrode and counter electrode, respectively. All three electrodes are connected in electrochemical condition and immersed in 0.1M solution of hydrochloric acid and repeated sweeps between -1.2V to 0.0V are performed three to six times as illustrated in **Figure 4**. After the regeneration treatment, the phosphate sensor **(100)** is recycled and reused for detection of dibasic phosphate ion.

The following examples are included to provide additional guidance to those skills in the art. These examples are not intended to limit the scope of the invention in any manner.

EXAMPLES

Examples of the experiments conducted for steps **220** to **228** of **Figure 2** are described herein below.

1) Preparation of Screen Printed Silver Electrode

Silver paste was screen printed on FR4 or PCB substrate and oven cured at 120°C for 30 minutes to give a final dry thickness of 100µm. A round shaped silver electrode with 2 to 3mm diameter was printed on copper-gold wire trace that functions as electrical contact for the phosphate sensor. Small portion of the wire trace overlapped with the silver layer to provide electrical contact but to minimize copper corrosion. Solder mask paste or red epoxy glue was then printed over the whole sensor surface with the sensor window and pin contacts were open to expose the silver circular structure and pin traces. The insulator layer was cured in the oven at 120°C for 30 minutes.

2) Preparation of Cobalt Nanoparticles Composite Paste

Cellulose acetate was weighed and dissolved and added into 10 mL tetrahydrofuran in a glass vial to afford 5% solution by weight. The glass vial was tightly capped and the mixture magnetically stirred under nitrogen atmosphere for 1 hour until homogenous clear solution was achieved. Cobalt nanoparticles were gradually added into the mixture under continuous stirring to afford a thick black paste with 40% cobalt nanoparticles by weight. The mixture was magnetically stirred for additional 3 hours under continuous flow of nitrogen gas.

3) Preparation and Characterization of Cobalt Nanoparticles Phosphate Sensor

The cobalt nanoparticles-cellulose acetate paste was applied on top of screen printed silver electrode to completely cover the silver surface. Special care needed to be taken to ensure that no part of the silver material was exposed to the analyte solution. The electrode covered with cobalt nanoparticles-cellulose paste was dried at ambient temperature under continuous flow of nitrogen gas for 1 hour to give a completely dry composite electrode. The cobalt nanoparticles-cellulose composite electrode and a double-junction Ag-AgCl reference electrode were attached to an ion meter and both electrodes were immersed in freshly prepared calibration solutions of potassium dibasic phosphate buffered by acetic acid at pH 7-8. The emf response at each calibration solution was recorded and the data plotted as shown in **Figure 3**. Sensor response near to ideal Nernstian behavior of -22.8 mV/decade for dibasic inorganic phosphate, and with a correlation coefficient of 0.99 is observed.

4) Regeneration of Cobalt Nanoparticles Composite Sensor Surface by Cyclic Voltammetry

The cobalt nanoparticles-cellulose acetate composite phosphate sensor used for detecting dibasic inorganic phosphate as described earlier was electrochemically treated to regenerate the oxidized surface. The used sensor, double-junction silver-silver chloride reference electrode and platinum counter electrode were immersed in 0.1M hydrochloric solution and the cyclic voltammetry voltage was repeatedly swept between -1.2V and 0V for 3 to 6 times at slow sweep rates to reduce the oxidized cobalt nanoparticles to its original uncharged state. The regenerated phosphate sensor is now ready for next use.

The phosphate sensor **(100)** can be deployed in the field for measuring plant nutrient levels as well as chemical pollution due to fertilizers run-off to rivers and ground water. The phosphate sensor **(100)** is incorporated into a sensing system that sends data using a transmitter device to a central database. The data at the database can be analysed to understand trends and relationship with other parameters such as crop yield, in order to optimize the use of fertilizers and monitor contamination caused by fertilizer run-off.

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrated and describe all possible forms of

the invention. Rather, the words used in the specifications are words of description rather than limitation and various changes may be made without departing from the scope of the invention.

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CLAIMS

1. A phosphate sensor **(100)** for measuring inorganic phosphate anions is characterised by:
   a) a substrate **(160)**;
   b) a conductor layer **(140)** disposed on the substrate; and
   c) a cobalt nanoparticles composite layer **(120)** disposed on the conductor layer **(140)**.

2. The phosphate sensor **(100)** as claimed in Claim **1**, wherein the conductor layer **(140)** is selected from the following materials: screen printed silver, electrode deposited silver, electroplated silver, screen printed carbon, electroplated platinum or a combination thereof.

3. The phosphate sensor **(100)** as claimed in Claim **1**, wherein the cobalt nanoparticles composite layer **(120)** is prepared by embedding cobalt nanoparticles in low impedance nano-porous material.

4. The phosphate sensor **(100)** as claimed in Claim **1**, wherein the cobalt nanoparticles composite layer **(120)** comprises of 10% to 50% cobalt nanoparticles by weight and 50% to 90% cellulose acetate by weight.

5. The phosphate sensor **(100)** as claimed in any of the preceding claims, wherein the phosphate sensor **(100)** is used to detect inorganic phosphate in dibasic inorganic phosphate form.

6. A method for producing a phosphate sensor **(100)**, comprising the steps of:
   a) preparing and disposing a conductor layer **(140)** onto a substrate **(160)**;
   b) preparing a cobalt nanoparticles-cellulose acetate paste;
   c) coating the cobalt nanoparticles-cellulose acetate paste onto the conductor layer **(140)** to produce the phosphate sensor **(100)**; and
   d) characterising the phosphate sensor **(100)**.

7. The method as claimed in step **(a)** of Claim **6**, wherein the conductor layer **(140)** is disposed on the substrate **(160)** comprising the steps of:
   a) screen printing a silver paste on a substrate **(160)**; and

b) curing the silver paste at approximately 120°C for 30 minutes.

8. The method as claimed in step **(b)** of Claim **6**, wherein the cobalt nanoparticles-cellulose acetate paste is prepared by the steps of:
   a) dissolving and mixing cellulose acetate solution in tetrahydrofuran;
   b) stirring the mixture of cellulose acetate solution and tetrahydrofuran under nitrogen atmosphere; and
   c) adding cobalt nanoparticles into the mixture with a continuous stirring and under continuous flow of nitrogen gas.

9. A method for regenerating an oxidised phosphate sensor **(100)** as claimed in Claim **1**, comprising the steps of:
   a) providing the oxidised phosphate sensor **(100)** as working electrode;
   b) providing a reference electrode;
   c) providing a platinum rod as a counter electrode;
   d) connecting the working electrode, reference electrode and counter electrode into an electrochemical condition;
   e) immersing the working electrode, reference electrode and counter electrode into an acidic solution;
   f) applying a cyclic voltammetry method; and
   g) repeating the cyclic voltammetry method until the oxidised cobalt nanoparticles of the phosphate sensor **(100)** return to an original uncharged state.

10. The method as claimed in step **(e)** of Claim **9**, wherein the acidic solution is 0.1M hydrochloric solution.

11. The method as claimed in step **(g)** Claim **9** wherein the cyclic voltammetry method is swept between 1.2V to 0V for at least once.

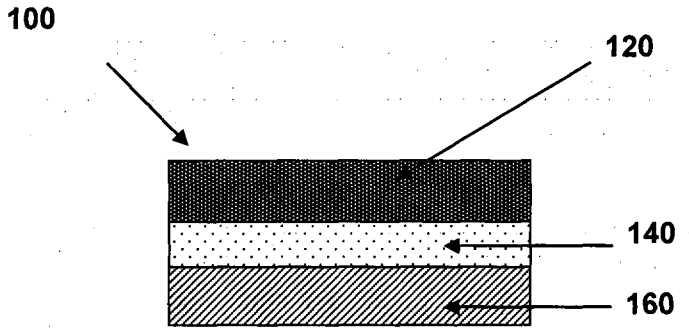

FIGURE 1

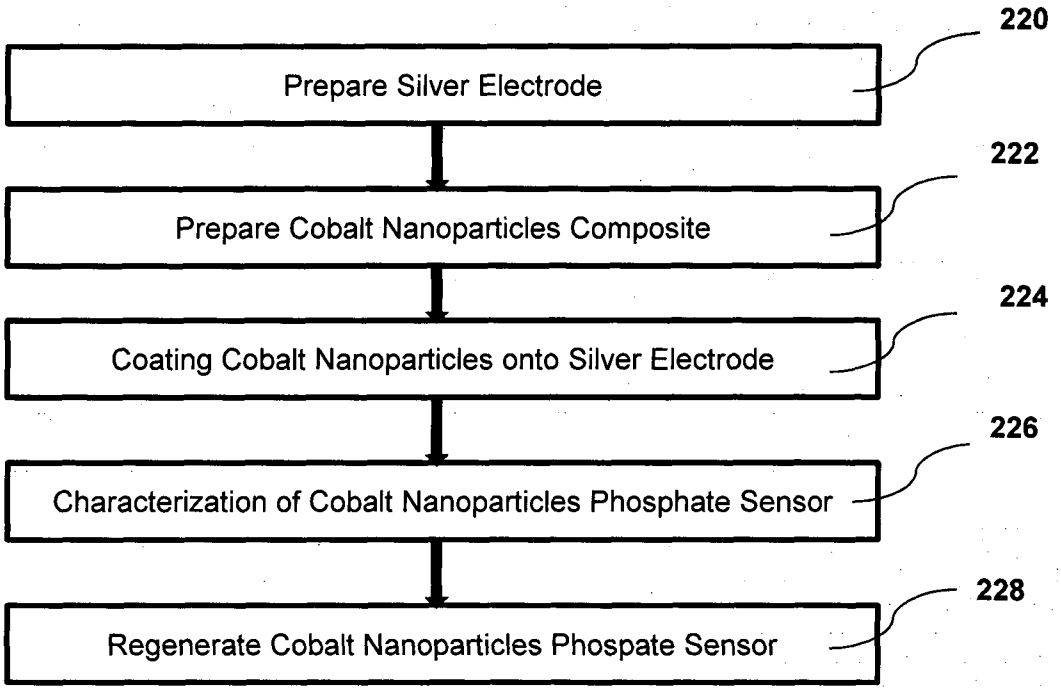

FIGURE 2

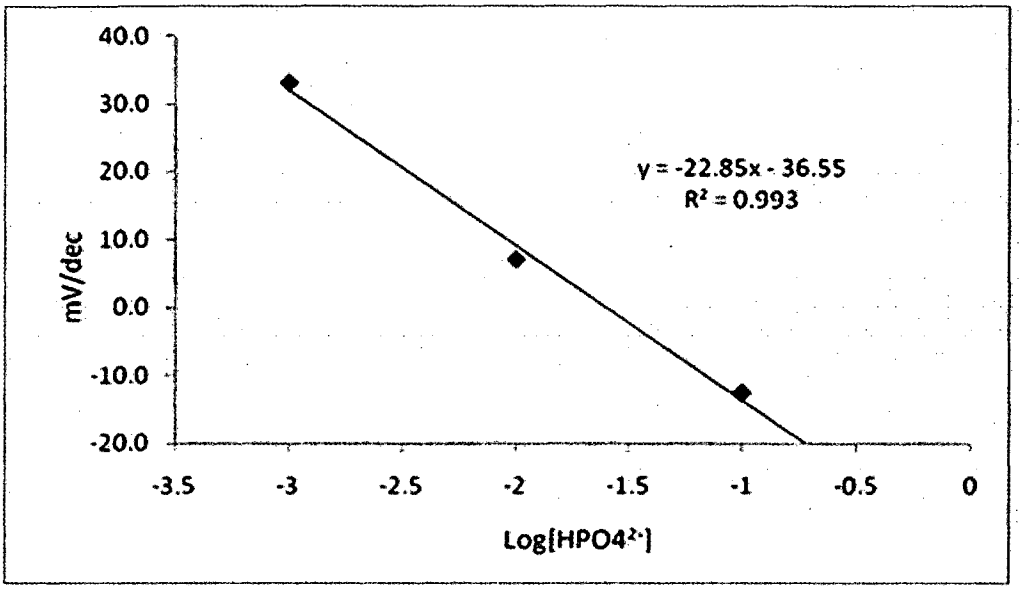

FIGURE 3

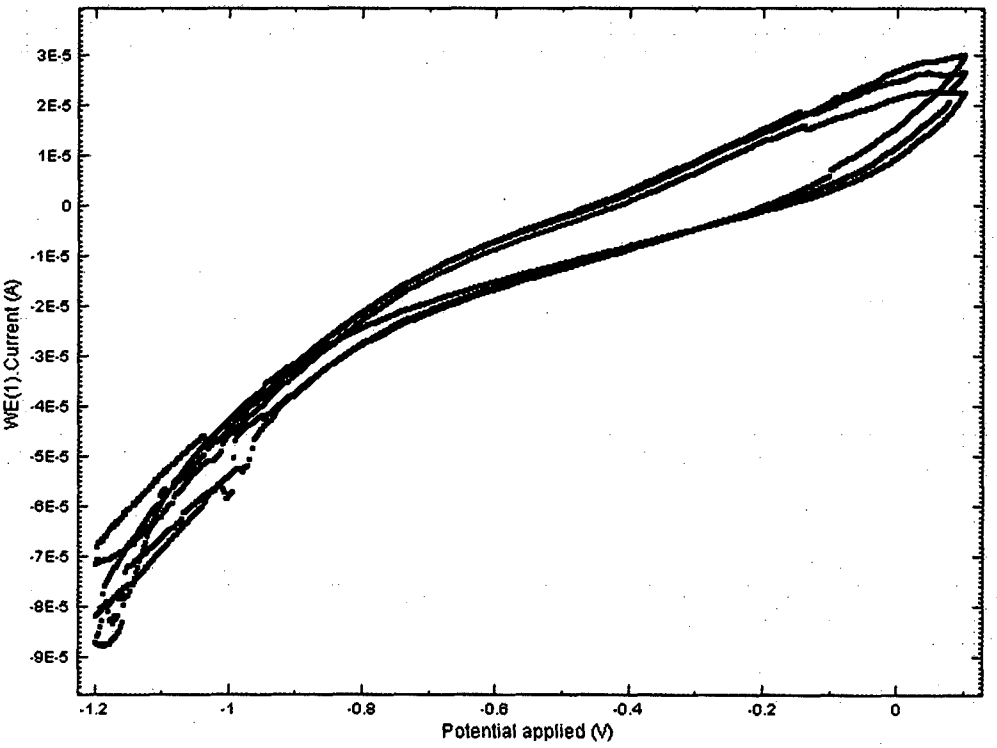

FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2012/000092

A. CLASSIFICATION OF SUBJECT MATTER

G01N 27/333 (OCT 2005)

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)

Databases : WPI, EPODOC, INSPEC, GOOGLE

Keywords:

Phosphate, phosphorous, Sensor, detector, selection, cobalt, nano, diaphragm, membrane, ion, composite, cellulose-accetate, polymer, contact, electrode, substrate, wafer 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.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

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"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
20 July 2012	20 July 2012

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INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/MY2012/000092**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 1098502 A (UNIV HUNAN) 08 February 1995 Abstract, and description of Fig. 1, Fig. 1	1-11
Y	CN 101915793 A (INST SEMICONDUCTORS CAS) 15 December 2010 Abstract, and description of Figs. 1-3, Figs. 1-3	1-11
Y	US 2010/0035047 A1 (AJAYAN ET AL.) 11 February 2010 Paragraphs 0010-0022, 0053, 0116-0118, 0138	1-11

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/MY2012/000092**

This Annex lists known 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/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
CN 1098502 A	08 Feb 1995	CN 1098502 A	08 Feb 1995
CN 101915793 A	15 Dec 2010	CN 101915793 A	15 Dec 2010
US 2010/0035047 A1	11 Feb 2010	US 2010035047 A1	11 Feb 2010
		US 2010120942 A1	13 May 2010

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.