



(43) International Publication Date
20 September 2012 (20.09.2012)

- (51) **International Patent Classification:**
G01N 27/26 (2006.01) *G01N 33/53* (2006.01)
G01N 27/30 (2006.01)
- (21) **International Application Number:**
PCT/MY2012/000037
- (22) **International Filing Date:**
29 February 2012 (29.02.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
PI2011000954 2 March 2011 (02.03.2011) MY
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- (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, QA, RO, RS, RU, RW, 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.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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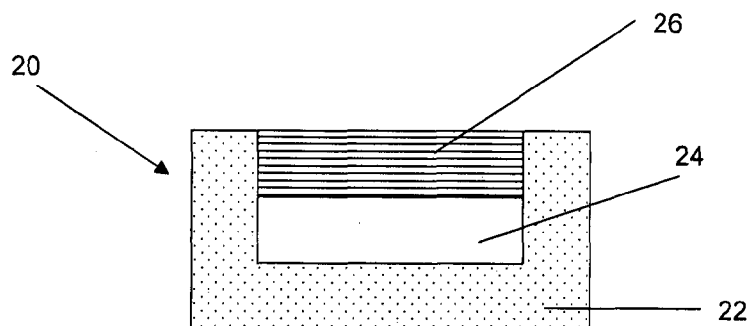
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

- with international search report (Art. 21(3))

(54) **Title:** ALLOY ELECTRODE SENSOR FOR DETECTING HEAVY METAL

Fig. 1



(57) **Abstract:** The present invention provides a nanoparticles alloy electrode [20] sensor comprising a casing [22], such as Teflon layer, followed by a conductor [24] layer, preferably one or in combination of screen printed silver, electroless deposited silver, electroplated silver, screen printed carbon and electroplated platinum, and a nanoparticles alloy [26] preferably silver nanoparticles-mercury alloy layer, deposited on top of each layer respectively. The membraneless nanoparticles alloy electrode [20] based on stripping voltammetry is capable to detect trace level of heavy metals simultaneously in water. The parameters are particularly: lead, cadmium, zinc, nickel, arsenic and copper ions which are automatically analyzed via stripping voltammetric analytical method.



Description

Title of Invention: ALLOY ELECTRODE SENSOR FOR DETECTING HEAVY METAL

- [1] The present invention relates to an alloy electrode sensor for heavy-metal detection and a method to fabricate thereof.

Background Art

- [2] Heavy metals such as mercury, lead, cadmium, zinc, copper and arsenic are extremely toxic to human even in trace amount. Through polluted waters, these heavy metals can get into the human body via fishes and drinking water. To ensure that heavy metal pollutants do not harm humans through contaminated fish and polluted water, sensor systems to monitor the heavy metal levels are proposed.
- [3] At present, a prior art listed an electrochemical metal analysis sensor for heavy metal detection. This sensor has a printed electrode with a layer of mercury compound or salt and a permeable polymer layer which is added with inert particulate matter. It uses the stripping voltammetric analytical method and the sample has to be treated with de-naturant prior to analysis.
- [4] Another prior art listed the use of stripping voltammetry for arsenic measurement where conventional gold, graphite, glassy carbon and thin diamond electrodes are used to detect arsenic.
- [5] Current chemical sensor systems are deployed in remote places and have difficult access for regular maintenance. The systems are sometimes bulky as it has to accommodate different sensors to detect different parameters. Sensors for trace amount detection faces surface fouling problem as surface fouling causes trace amount of contamination on the sensor surface which is sufficient to lead to create false signal and therefore give inaccurate result. This is evident in sensors with membrane layer.
- [6] Due to these reasons, innovation needs to be made on the alloy electrodes. The present invention is made in view of the need to address the disadvantages of ion selective or membraned sensors while retaining the stripping voltammetric analytical method to detect trace amount of heavy metals.

Summary of Invention

- [7] The present invention proposes a nanoparticles alloy electrode sensor based on stripping voltammetry which is capable of detecting trace level of heavy metals simultaneously in water. The alloy electrode sensor [20] for detecting heavy metal, comprising: a sensing layer [26], sensitive towards heavy metal; a conductor layer [24], to provide electrical contact between sensing layer and external readout circuit; a casing [22] layer to encapsulate conducting layer while exposing part of sensing layer;

characterised in that, the sensing layer [26] is silver nanoparticle-mercury alloy. The parameters are particularly: lead, cadmium, zinc, nickel, arsenic and copper ions which are automatically analyzed via stripping voltammetric analytical method. The proposed membraneless sensor system is a miniaturized, self-powered and calibration free system. It is equipped with microcontroller, application software and wireless transmitter to perform self-cleaning cycle to avoid surface fouling and to transmit data, status of power supply and condition of the sensor to a central database.

Brief Description of Drawings

- [8] Fig. 1 is a sectional drawing of the trace level heavy metal sensor.

Description of Embodiments

- [9] Hereinafter, the present invention is described in detail.
- [10] The invention involves a nanoparticles alloy electrode [20] for detection of heavy metals in trace amounts in water. The heavy metals detected simultaneously and analyzed automatically are particularly; lead, cadmium, zinc, nickel, arsenic and copper ions. The sectional drawing of the nanoparticles alloy electrode [20] is shown in Fig. 1.
- [11] The nanoparticles alloy electrode [20] comprises a casing [22] layer which partially encapsulates a conductor [24] layer on top of the casing [22] layer. The top of the conductor [24] layer is then layered with a sensing layer [26], a nanoparticles alloy layer, preferably silver nanoparticles-mercury alloy.
- [12] The casing [22] layer, made of material such as Teflon, provides mechanical strength to the electrode structure and allows it to withstand harsh field environment and polluted media. The conductor [24] layer provides electrical contact between the nanoparticles alloy and external readout circuitry. The material is at least one or combination of preferably, screen printed silver, electroless deposited silver, electroplated silver, screen printed carbon and electroplated platinum. The nanoparticles alloy [26] layer, preferably silver nanoparticles-mercury alloy, functions as the sensing element, which is sensitive towards heavy metal, in detecting trace quantities of the various heavy metals ions in polluted water.
- [13] In a preferred embodiment, silver wire is used as the electrical conductor [24]. The said silver wire with 0.3 mm to 0.8 mm diameter is coiled at one end to make 2 to 3 turns, and with the desired diameter so that it can be tightly secured at the bottom of Teflon casing [22]. The silver wire passes through the hole at the bottom of the casing [22] for electrical contact. The silver wire is further secured at this position using epoxy glue, such as Araldite adhesive.
- [14] In order to achieve better electrical contact and to further support the mechanical structure, a conductor [24] layer is deposited onto the coiled silver wire. Silver layer is

deposited using electroless deposition technique by reduction of silver nitrate or silver acetate solution with triethanolamine. In a preferred embodiment, silver nitrate solution (0.2 mL, 0.1 M) is pipetted into the cylindrical casing [22] to cover the silver wire. Three drops of triethanolamine were added in the casing [22] and mixed well with the silver nitrate solution. The electrode is then heated in the oven at 60 °C to 120 °C for 20 to 60 minutes to create silver layer on the coiled silver wire.

- [15] In another preferred embodiment, the silver wire tracing and conductor [24] along with insulating layer is screen printed on printed-circuit board substrate and Teflon retaining dam is glued forming a circle surrounding the printed silver electrode. The printed silver paste and insulator pastes are cured in the oven at 120 °C.
- [16] In a preferred embodiment, silver nanoparticles are synthesized by reducing pentaerythritol stabilized silver ions. The aqueous solution of silver nitrate or silver acetate with pentaerythritol is gently heated to reduce silver ions to silver nanoparticles. 1 part of 0.05 M to 0.5 M silver salt solution is added into 5 to 30 parts of pentaerythritol in deionized water, both by weight, and heating the mixture at 60 °C to 100 °C for 1 to 3 hours. In another approach, catalytic amount of hydroquinone is added to the reaction mixture before heating.
- [17] The silver nanoparticles prepared in this matter can be precipitated by adding dilute sodium chloride solution or without addition of salt solution but with centrifuge. The precipitated and dried silver nanoparticles were characterized for particle size and regularity with scanning electron microscope. The synthesized silver nanoparticles are cautiously added to 0.5 mL of high purity mercury liquid in 2 mL glass vial, just the right amount to convert the shiny mercury liquid to shiny metallic silver nanoparticles-mercury (Ag NP - Hg) alloy by continuous mixing with plastic or Teflon spatula. The parts of silver nanoparticles added to the mercury are 1 to 10 parts to 99 to 90 parts respectively. The mixture is stirred for 5 to 15 minutes for each addition. The shiny Ag NP - Hg alloy lump is then transferred from the glass vial onto clean Kim Wipers and rolled onto the wipers to remove loose silver particles.
- [18] The nanoparticles alloy [26] lump is then carefully packed into the cylindrical or planar silver electrode described earlier, with small stainless steel spatula to give good contact with the silver surface and to give flat and shiny sensor surface. The completed silver nanoparticles-mercury alloy comprises, by weight, 10 % to 30 % of silver nanoparticles and 70 % to 90 % mercury.
- [19] The surface of the silver nanoparticles-mercury alloy electrode is electrochemically cleaned prior to the sensing step by performing repeated cyclic voltammetry steps from -1.2 V to 0 V for five times in TRIS sulphate buffered solution. After this electrochemical cleaning cycle differential pulse voltammetry of the sensing electrode in the same buffered solution from -1.2 V to 0 V shows very clean background spectrum.

- [20] Accordingly, the invention disclosed a nanoparticles alloy electrode [20] sensor based on stripping voltammetry, comprising a casing layer [22], such as Teflon, followed by a conductor [24] layer, preferably one or in combination of screen printed silver, electroless deposited silver, electroplated silver, screen printed carbon and electroplated platinum, and a nanoparticles alloy [26] preferably silver nanoparticles-mercury alloy layer, deposited on top of each layer respectively. The membraneless nanoparticles alloy electrode [20] is capable to detect trace level of lead, cadmium, zinc, nickel, arsenic and copper ions simultaneously in polluted water.

Claims

- [Claim 1] An alloy electrode sensor [20] for detecting heavy metal based on stripping voltammetry, comprising:
a sensing layer [26], sensitive towards heavy metal;
a conductor layer [24], to provide electrical contact between sensing layer and external readout circuit;
a casing [22] layer to encapsulate conducting layer while exposing part of sensing layer;
characterised in that,
the sensing layer [26] is silver nanoparticle-mercury alloy.
- [Claim 2] An electrode according to claim 1, wherein the nanoparticles alloy electrode [20] sensor is a calibration free system connected to external microcontroller, and application software to perform self-cleaning cycle to avoid surface fouling.
- [Claim 3] An electrode according to claim 1, wherein the casing layer [22] is made of mechanically strong material such as Teflon.
- [Claim 4] An electrode according to claim 1, wherein the conductor [24] material is at least one or combination of preferably, screen printed silver, electroless deposited silver, electroplated silver, screen printed carbon and electroplated platinum.
- [Claim 5] An electrode according to claim 1, wherein the silver nanoparticles-mercury alloy comprises, by weight, 10 % to 30 % silver nanoparticles and 70 % to 90 % mercury.
- [Claim 6] A method of fabricating nanoparticles alloy electrode, comprising:
securing an electrical conductor at the bottom of casing layer [22];
depositing a conductor [24] layer on top of the casing [22]; and
packing carefully silver nanoparticles-mercury alloy [26] layer onto the conductor [24] layer.
- [Claim 7] A method according to claim 6, wherein the step of securing an electrical conductor at the bottom of sensing layer and depositing a conductor layer on top of casing is conducted with:
screen-printing an electrical conductor tracing and conductor [24] along with insulating layer on printed-circuit board substrate; and
forming casing [22] circle surrounding printed electrode.
- [Claim 8] A method according to claim 6 or 7, wherein the preferred embodiment of electrical conductor is coiled silver wire.
- [Claim 9] A method according to claim 6 or 7, wherein the preferred embodiment

of the conductor [24] layer is silver.

[Claim 10]

A method according to claim 9, wherein the silver conductor [24] is prepared, comprising:

dispensing a mixture of silver salt solution and triethanolamine onto the coiled silver conducting wire; and

heating the mixture at 60 °C to 120 °C for 20 to 60 minutes in the oven.

[Claim 11]

A method according to claim 6, wherein the silver nanoparticles-mercury alloy is prepared, comprising adding 1 to 10 parts of silver nanoparticles to 90 to 99 parts of mercury, both by weight.

[Claim 12]

A method according to claim 6, wherein the silver nanoparticles-mercury alloy is prepared, comprising:

adding 1 part of 0.05 M to 0.5 M silver nitrate or silver acetate into 3 to 30 parts of pentaerythritol in deionized water, both by weight;

heating gently the mixture at 60 °C to 100 °C for 1 to 3 hours to reduce silver ions to silver nanoparticles;

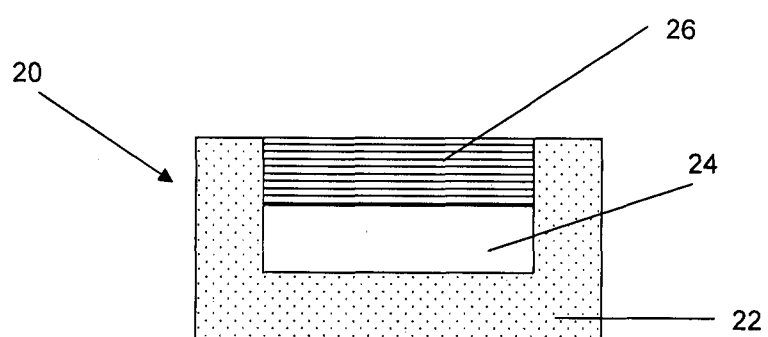
precipitating the silver nanoparticles solution with sodium chloride or centrifuging without addition of salt solution;

checking dried silver nanoparticles for particle size and regularity with scanning electron microscope;

adding cautiously 1 to 10 parts of silver nanoparticles to 90 to 99 parts of high purity mercury liquid; both by weight, in a glass vial while stirring for 5 to 15 minutes with each addition to convert to silver nanoparticles-mercury alloy lump;

transferring silver nanoparticles-mercury alloy lump from glass vial onto wipers and rolling onto wipers to remove loose silver particles.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/MY2012/000037

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

G01N 27/26 (2006.01)

G01N 27/30 (2006.01)

G01N 33/53 (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)

WPI & EPO - IPC & keywords- strip, heavy metal, silver, mercury, nano, electrode, layer and other like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101620202 A (EAST CHINA NORMAL UNIVERSITY) 1 June 2010 English abstract retrieved from WPI database. Abstract	
A	WO 2009/151306 A1 (EL BAKOURI) 17 December 2009 English translation retrieved from Espace. Abstract	
A	US 2010184062 A1 (STEINMULLER-NETHL et al.) 22 July 2010 Abstract and claim 16	



Further documents are listed in the continuation of Box C



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Date of the actual completion of the international search
10 May 2012Date of mailing of the international search report
25 May 2012Name and mailing address of the ISA/AU
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2012/000037

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			
CN	101620202	NONE			
WO	2009151306	NONE			
US	2010184062	AT	505495	EP	2173894
		WO	2009003208	JP	2010531978
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.					
END OF ANNEX					