



(51) International Patent Classification:

H01B 1/12 (2006.01) *C09D* 179/02 (2006.01)
H01G 9/042 (2006.01) *C08L* 1/12 (2006.01)
H01M 4/137 (2010.01) *C08K* 5/42 (2006.01)
H01M 4/04 (2006.01) *C08K* 5/3445 (2006.01)
H01M 4/60 (2006.01)

(21) International Application Number:

PCT/MY2012/000144

(22) International Filing Date:

25 June 2012 (25.06.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PI 2011003559 29 July 2011 (29.07.2011) MY

(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): **AHMAD, Mohd Rais** [MY/MY]; Technology Park Malaysia, 57000 Kuala Lumpur (MY). **ALVA, Sagir** [MY/MY]; Technology Park Malaysia, 57000 Kuala Lumpur (MY).

(74) Agent: **WONG, Jan Ping**; 3.02, Menara Boustead Penang, 39, Jalan Sultan Ahmad Shah, 10050 Penang (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, 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, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

[Continued on next page]

(54) Title: COMPOSITE ELECTRODE WITH IN-SITU POLYMERIZED POLYANILINE AND PREPARATION METHOD THEREOF

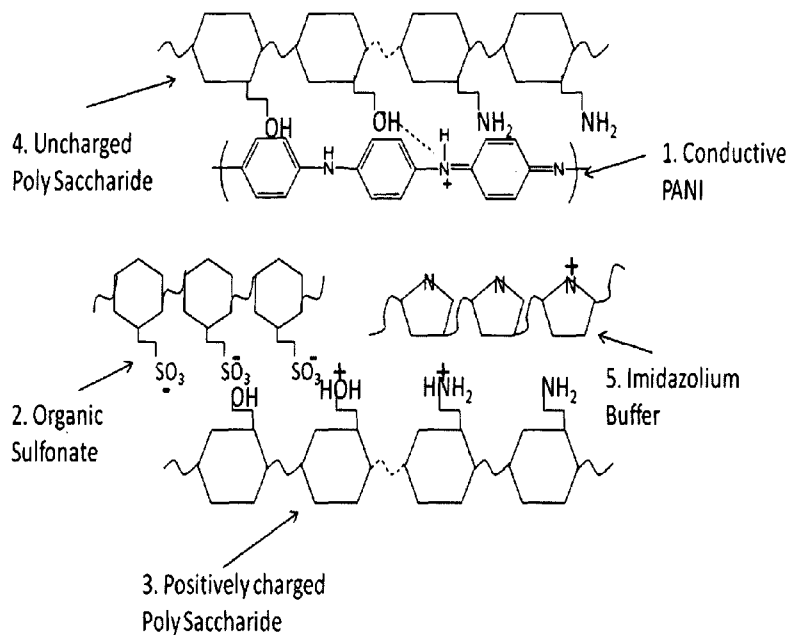


FIG. 1

(57) Abstract: The present invention relates generally to a composite electrode with *in situ* polymerized polyaniline comprising a composition of polyaniline, organic sulfonate, polysaccharide, imidazolium buffer and organic chemicals whereby said composite electrode can be used in various applications such as gas sensor, chemical sensor, electrochemical transducer, solar cell, super capacitor, corrosion protection layer etc.



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).

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

Declarations under Rule 4.17:

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

COMPOSITE ELECTRODE WITH *IN-SITU* POLYMERIZED POLYANILINE AND PREPARATION METHOD THEREOF

1. TECHNICAL FIELD OF THE INVENTION

The present invention relates generally to a composite electrode with *in situ* polymerized polyaniline comprising a composition of polyaniline, organic sulfonate, polysaccharide, imidazolium buffer and organic chemicals whereby said composite electrode can be used in various applications such as gas sensor, chemical sensor, electrochemical transducer, solar cell, super capacitor, corrosion protection layer etc.

2. BACKGROUND OF THE INVENTION

Conductive polymers such as polypyrrole, polyaniline and polythiophene have been used in a wide variety of electrochemical applications. The widespread use of these conducting polymers is due to some reasons such as ease of preparation, reproducible electrochemical characteristics, manufacturability for in volume production and low cost.

Polyaniline (PANI) is one of the most important intrinsically conducting polymers due to the advantages of simple preparation, good chemical stability and high conductivity. For example, PANI and its composites are widely used as

gas sensing materials for the detection of a number of chemicals. Polymerization of aniline is often catalyzed by oxidizing agent such as ammonium persulfate. The resulting polyaniline materials can appear in a number of forms depending on the charge at the nitrogen atoms. Typically different forms of polyaniline materials exhibit different degree of conductivity but invariably the polyaniline powder has no natural adhesion on electrode surface and only slightly soluble in most solvents. The low solubility of polyaniline in common organic solvents causes difficulty in preparing polyaniline for casting or printing applications.

In miniaturized sensing devices, the electrodes are close to each other and electrical contacts are often inaccessible for electro-polymerization. Electrical contacts in miniaturized cells may liable to electrical shorting when the device is immersed in monomer solution. Therefore, other methods such as drop coating, solvent casting, screen printing or inkjet printing is more appropriate for applying polyaniline materials on electrode surface when electro-polymerization of the aniline monomer is not possible due to miniature size of the electrode.

If polyaniline composite paste is to be prepared, the paste can be dispensed or printed onto the working electrode surface for a variety of applications such as in chemical sensors, amperometric cell and conductometric electrodes. Moreover, it is important that the ink or paste composition comprises binding component which is able to hold the polyaniline materials together while maintaining the conductive characteristic and electrochemical properties of polyaniline composite. In addition to this, curing

at near ambient temperature within short period of time is preferred because it will be convenient in manufacturing process as well as afford high throughput.

Therefore, adhesion of the polyaniline materials on the electrode surface is the most important requirement in the preparation of polyaniline composite electrode. Furthermore, the dispensed or printed polyaniline layer must exhibit strong adhesion to a wide range of electrode surface such as platinum, carbon, silver, silicon nitride, silicon, polysilicon, silicon oxide, polyester, FR4 or glass. Likewise if the polyaniline composite electrode is to be used as transducers in chemical sensors, the polyaniline composite layer must also able to provide good adhesion with a variety of polymeric sensing membranes such as PVC, acrylate, urethane or silicone rubber acting a sensing top layer.

It would hence be extremely advantageous to develop a method for preparing of polyaniline composite electrode through depositing homogenous phase of polyaniline conductive polymer on electrode surface by a coating technique such as solution casting method. *In situ* polymerized doped polyaniline which comprises of polyaniline, polysaccharide, organic sulfonate dopant and imidazolium buffer are drop coated to generate homogenous phase of low impedance polymeric networks. The obtained polyaniline composite not only exhibits good adhesion to electrode surface and but also affords reproducible electrochemical characteristics.

3. SUMMARY OF THE INVENTION

Accordingly, it is the primary aim of the present invention to provide a composite electrode with *in situ* polymerized polyaniline whereby the polyaniline composite exhibits good adhesion to a wide range of electrode surface.

5 It is another object of the present invention to provide a composite electrode with *in situ* polymerized polyaniline whereby the polyaniline ink can be prepared for casting or printing application.

It is another object of the present invention to provide a composite electrode with *in situ* polymerized polyaniline which can be prepared within the
10 binding matrix to produce homogenous solution of doped polyaniline.

Yet another object of the present invention is to provide a composite electrode with *in situ* polymerized polyaniline whereby the polyaniline is soluble in common organic solvent.

Yet another object of the present invention is to provide a composite
15 electrode with *in situ* polymerized polyaniline which can be drop coated to afford homogenous phase of low impedance polymeric networks.

Other and further objects of the invention will become apparent with an understanding of the following detailed description of the invention or upon employment of the invention in practice.

According to a preferred embodiment of the present invention there is provided,

A polyaniline composite electrode comprising:

an electrically-conductive substrate;

5 a composition supported on said substrate;

characterized in that said composition comprising:

polyaniline;

organic sulfonate;

polysaccharide;

10 imidazolium buffer;

organic chemicals functioning as diluents in adjusting the viscosity of polyaniline ink;

wherein *in situ* polymerized polyaniline is carried out to prepare said polyaniline composite electrode.

15 In another aspect there is provided,

A method of preparing polyaniline composite electrode comprising steps of:

- i. mixing polysaccharide and organic sulfonic acid to produce positively charged polysaccharide and organic sulfonate salt solution;
- ii. mixing said polysaccharide-sulfonate salt solution with aniline to form doped monomer solution;
- iii. adding imidazolium buffer to said doped aniline monomer solution;
- iv. performing electropolymerization towards said doped aniline monomer solution to form doped polyaniline ink;
- v. applying said polyaniline ink on electrode surface;
- vi. curing said applied polyaniline ink under inert environment

4. BRIEF DESCRIPTION OF THE DRAWINGS

Other aspect of the present invention and their advantages will be discerned after studying the Detailed Description in conjunction with the accompanying drawings in which:

FIG. 1 is a polyaniline composite electrode of the present invention which is prepared via *in situ* polymerization of polyaniline.

FIG. 2 is a flow chart of preparation method for polyaniline composite electrode.

5 FIG. 3 is the aniline monomer solution in cellulose acetate-camphor sulfonate-methyl imidazolium dopant.

FIG. 4 is the polyaniline composite ink doped with camphor sulfonate which appears as dark colour solution.

10 FIG. 5 is the doped polyaniline composite electrode with camphor sulfonate dopant.

FIG. 6 is an exemplary of cyclic voltammetry graph of *in situ* polymerized polyaniline in cellulose acetate-camphor sulfonate.

5. DETAILED DESCRIPTION OF THE DRAWINGS

15 In the following detailed description, numerous specific details are set forth in order to provide a thorough understanding of the invention. However, it will be understood by those of ordinary skill in the art that the invention may be practised without these specific details. In other instances, well known methods, procedures and/or components have not been described in detail so as not to obscure the invention.

The invention will be more clearly understood from the following description of the embodiments thereof, given by way of example only with reference to the accompanying drawings which are not drawn to scale.

Referring to FIG. 1, there is shown the polyaniline (PANI) composite electrode of the present invention which is prepared via *in situ* polymerization of polyaniline. Said polyaniline composite electrode comprises of an electrically-conductive substrate and a composition supported on said substrate, wherein said composition comprising conductive polyaniline, organic sulfonate dopant, polysaccharide, imidazolium buffer and organic chemicals functioning as diluents in adjusting the viscosity of the doped polyaniline or polyaniline ink.

Referring to FIG. 2, there is shown a flow chart of preparation method for polyaniline composite electrode. Said preparation method for polyaniline composite electrode typically comprises of six steps, whereby said preparation method can be carried at room temperature without heat requirement. In the first step, polysaccharide-sulfonate salt solution is prepared by mixing polysaccharide and organic sulfonic acid to produce positively charged polysaccharide and organic sulfonate salt solution. Preferably, at least 1% by weight to 10 % by weight of polysaccharide and at least 1% by weight to 30 % by weight of organic sulfonic acid is used in the preparation of polysaccharide-sulfonate salt solution. For example, a solution of polysaccharide such as cellulose acetate and organic sulfonic acid such as camphor sulfonic acid is prepared by mixing the reagents in polar solvent such as tetrahydrofuran. Alternatively other polysaccharides low

impedance polymeric materials such as ethyl cellulose, cellulose, chitosan, starch, dextrin, maltodextrin, beta-glucan, chitin, mannan, galactan, fructan or combination thereof can be used in place of cellulose acetate. Other organic sulfonic acid such as dodecyl benzene sulfonic acid, polystyrene sulfonic acid, 5 toluene sulfonic acid, Nafion, apolate or combination thereof can be used in place of camphor sulfonic acid. Other solvent such as ethanol, 2-methoxyethanol, 2-propanol, acetone, 2-butanone, cyclohexanone, diethyl ether, methanol, trifluoroethanol, N-methyl pyrrolidone or combination thereof can be used in place of tetrahydrofuran. Depending on the ratio of polysaccharide to organic 10 sulfonic acid, polysaccharide-sulfonate white solid salt is precipitated out from the solution. In this case ethanol is added to re-dissolve the salt precipitate. Said organic sulfonate functions as dopant for positively charged conductive polyaniline. Said positively charged polysaccharide is used as polymeric cation counterion for organic sulfonate dopant and to provide electrical path during 15 electropolymerization. Uncharged polysaccharide is used to form low impedance polymeric networks as binder for polyaniline and other components.

In the second step aniline monomer solution is prepared by adding approximately 5 % by weight to 30 % weight of aniline to the polysaccharide-sulfonate salt solution, for example cellulose acetate-camphor sulfonate doped 20 electrolyte. Positively charged polysaccharide is formed along with camphor sulfonate dopant.

In the third step approximately 1 % by weight to 5 % by weight of imidazolium buffer such as methyl imidazole-methyl imidazolium solution, dodecyl imidazole, decyl imidazole or other polymeric imidazolium ion such as poly(4-vinyl imidazole) or combination thereof is added to said aniline monomer
5 solution to increase the conductivity of the mixture as well as to provide stable electrical current path during electropolymerization in a potentiostat setup and assists oxidation of aniline.

In the fourth step reference electrode such as silver-silver chloride reference electrode, counter electrode such as platinum counter electrode and
10 inert working electrode such as glassy carbon working electrodes are immersed into the buffered aniline monomer solution. *In situ* electropolymerization occurs towards said aniline monomer solution to form doped polyaniline. In a potentiostat setup the aniline monomer is polymerized by controlling the current density across the solution. The solution turns into dark in colour as doped
15 polyaniline is formed.

In the fifth step, the doped polyaniline or the polyaniline ink can be applied on said electrically-conductive substrate or electrode surface using the preferred coating technique such as screen printing, stencil printing, inkjet printing, solution casting and spin coating. The conductive polyaniline function as active sensing
20 agent or as electrochemical transducer. Approximately 25 % by weight to 85 % by weight of organic chemical or solvent is added as diluents in each mixing to adjust the viscosity of the polyaniline ink. Said organic chemicals comprises of

the chemicals such as 2-methoxyethanol, n-methyl pyrrolidone, carbitol, butyl glycol, acrylic acid, pyruvic acid, ethyl acetate, tetrahydrofuran, toluene, xylene, propanol or combination thereof. Therefore, the concentration of said doped polyaniline can be controlled by the volume of organic chemicals to be added.

5 In the sixth step, the applied polyaniline ink is cured under inert environment to evaporate off the solvents under continuous flow of nitrogen gas. The deposited doped conductive polyaniline is characterized by performing cyclic voltammetry between -1V to 1V in potassium chloride solution. The example of the CV plot is described in FIG. 6.

10 Exemplary embodiment of the method of the invention is described hereinafter and should not be construed to limit the scope of the present invention.

Example 1

Preparation of polyaniline-cellulose acetate-camphor sulfonate composite 15 solution:

Polysaccharide-sulfonate salt solution was prepared by mixing 500 mg cellulose acetate and 74.8 mg camphor sulfonic acid (0.322 mmol). 10 ml of tetrahydrofuran (THF) was added into the mixture to achieve homogenous colourless solutions. After that, said homogenous solutions were mixed with 0.3 g
20 (3.22 mmol) aniline and 500 μ L methyl imidazole-methyl imidazolium buffer

solution. The mixture was stirred continuously until colourless viscous aniline monomer solution is obtained as illustrated in FIG. 3. The material was then electrochemically polymerized by using potentiostat such as Autolab PGSTAT Model 128N for 600 seconds. The polymerization cycles were repeated for 10
5 times at 2 mA cm^{-2} current density in a three-electrode cell, whereby platinum stick as counter electrode, silver-silver chloride (Ag/AgCl) wire as reference electrode and glassy carbon stick as working electrode. The polyaniline composite ink doped with camphor sulfonate is obtained which appears as dark solution as shown in FIG. 4. FIG. 5 shows the polyaniline composite electrode
10 prepared by *in situ* polymerization of aniline monomer in cellulose-camphor sulfonate solution.

Example 2

Preparation of PANI-CSA Nano Composite Electrode

Screen printed carbon electrodes (SPE) with 4 mm diameter were cleaned
15 ultrasonically with deionized water for 1 minute. 30 μL of PANI-CSA ink composition was dropped onto the cleaned carbon surface and dried over an hour under continuous flow of nitrogen gas. The Electrode was characterized with cyclic voltammetric using potentiostat such as Autolab PGSTAT Model 128N with scan at -1V to +1V and scan rate at 0.1V/s in 0.1 M KCl solution. The cyclic
20 voltammetry graph is shown in FIG. 6.

While the polyaniline conducting polymers is applied for chemical sensor in the aforementioned embodiment, the present invention is not restricted to this but may alternatively be applied to other applications such as a gas sensor, electrochemical transducer, solar cell, super capacitor, electrode in lithium
5 battery, corrosion protection layer etc.

While the preferred embodiment of the present invention and its advantages has been disclosed in the above Detailed Description, the invention is not limited thereto but only by the scope of the appended claim.

WHAT IS CLAIMED IS:

1. A polyaniline composite electrode comprising:

an electrically-conductive substrate;

a composition supported on said substrate;

- 5 characterized in that said composition comprising:

polyaniline;

organic sulfonate;

polysaccharide;

imidazolium buffer;

- 10 organic chemicals functioning as diluents in adjusting the viscosity of said polyaniline solution;

wherein *in situ* polymerized polyaniline is carried out to prepare said polyaniline composite electrode.

2. A polyaniline composite electrode as claimed in Claim 1 wherein
15 said organic sulfonate is camphor sulfonate, dodecyl benzene sulfonate, polystyrene sulfonate, toluene sulfonate, Nafion, apolate

or combination thereof with a range of 1 % by weight to 30 % by weight of organic sulfonic acid is used.

3. A polyaniline composite electrode as claimed in Claim 1 wherein said polysaccharide is cellulose acetate, ethyl cellulose, cellulose, chitosan, starch, dextrin, maltodextrin, beta-glucan, chitin, mannan, galactan, fructan or combination thereof with a range of 1 % by weight to 10 % by weight of polysaccharide is used.

4. A polyaniline composite electrode as claimed in Claim 1 wherein approximately 5 % by weight to 30 % weight of aniline is added to prepare aniline monomer solution.

5. A polyaniline composite electrode as claimed in Claim 1 wherein said imidazolium buffer is methyl imidazole-methyl imidazolium solution, dodecyl imidazole, decyl imidazole, poly(4-vinyl imidazole) or combination thereof with a range of 1 % by weight to 5 % by weight of imidazolium buffer is used.

6. A polyaniline composite electrode as claimed in Claim 1 wherein said organic chemicals is 2-methoxyethanol, n-methyl pyrrolidone, carbitol, butyl glycol, acrylic acid, pyruvic acid, ethyl acetate, tetrahydrofuran, toluene, xylene, propanol or combination thereof with a range of 25 % by weight to 85 % by weight of organic chemicals is used.

7. A polyaniline composite electrode as claimed in Claim 1 wherein said polyaniline composite electrode can be used as a chemical sensor, gas sensor, electrochemical transducer, solar cell, super capacitor, electrode in lithium battery and corrosion protection layer.
- 5 8. A method of preparing polyaniline composite electrode comprising steps of:
 - i. mixing polysaccharide and organic sulfonic acid to produce positively charged polysaccharide and organic sulfonate salt solution;
 - 10 ii. mixing said polysaccharide-sulfonate salt solution with aniline to form doped aniline monomer solution;
 - iii. adding imidazolium buffer to said doped aniline monomer solution;
 - iv. performing electropolymerization towards said doped aniline monomer solution to form doped polyaniline;
 - 15 v. applying said polyaniline on electrically-conductive substrate;
 - vi. curing said applied polyaniline under inert environment.

9. A method of preparing polyaniline composite electrode as claimed in Claim 8 wherein solvent comprising of ethanol, tetrahydrofuran, 2-methoxyethanol, 2-propanol, acetone, 2-butanone, cyclohexanone, diethyl ether, methanol, trifluoroethanol, N-methyl pyrrolidone or combination thereof is added after said step of mixing polysaccharide and organic sulfonic acid to obtain homogeneous solution of said polysaccharide-sulfonate salt solution.
10. A method of preparing polyaniline composite electrode as claimed in Claim 8 wherein said method of preparing polyaniline composite electrode is carried out at room temperature without heat requirement.

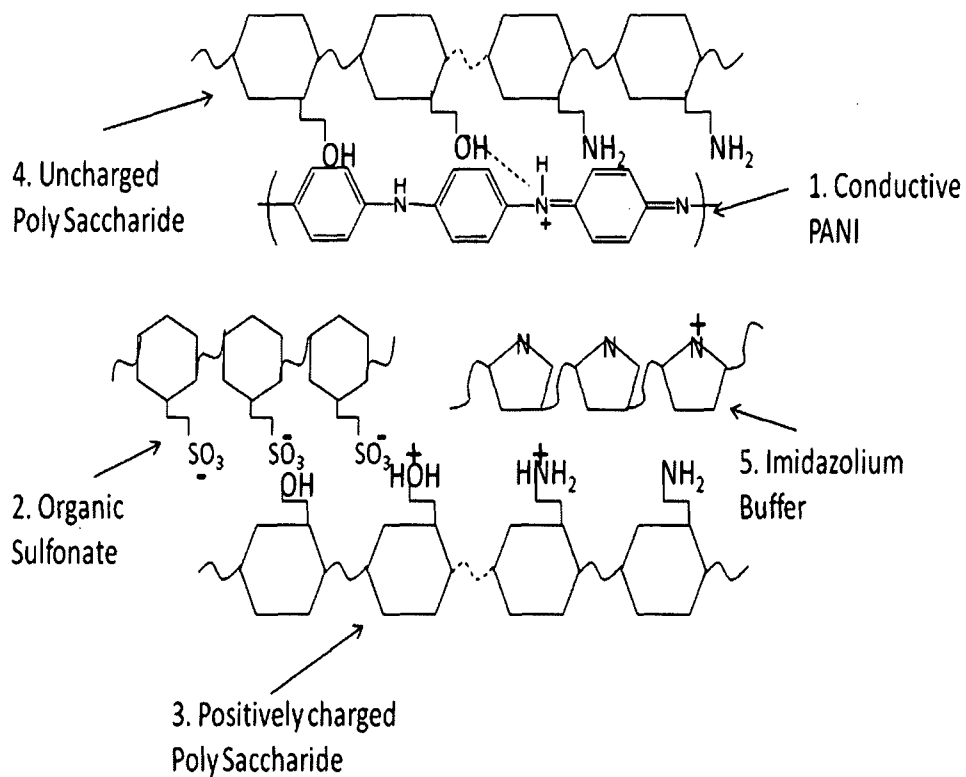


FIG. 1

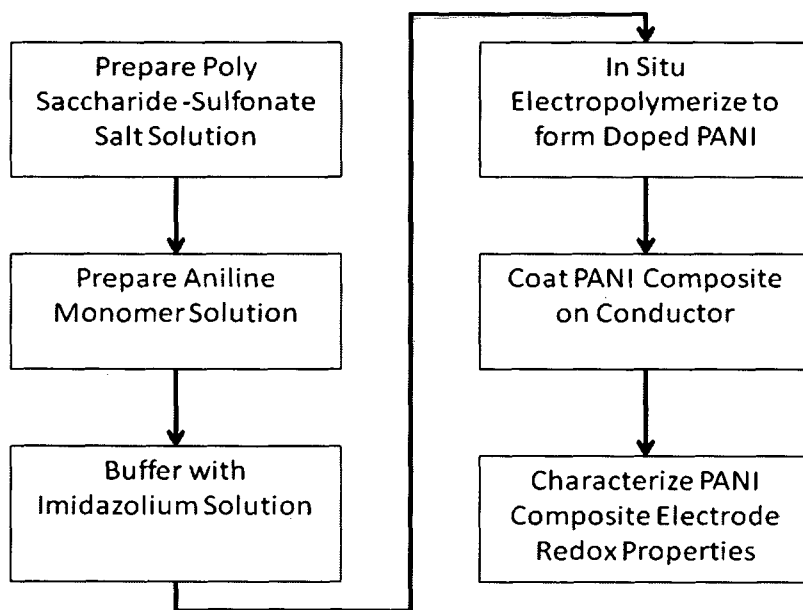


FIG. 2

2/3

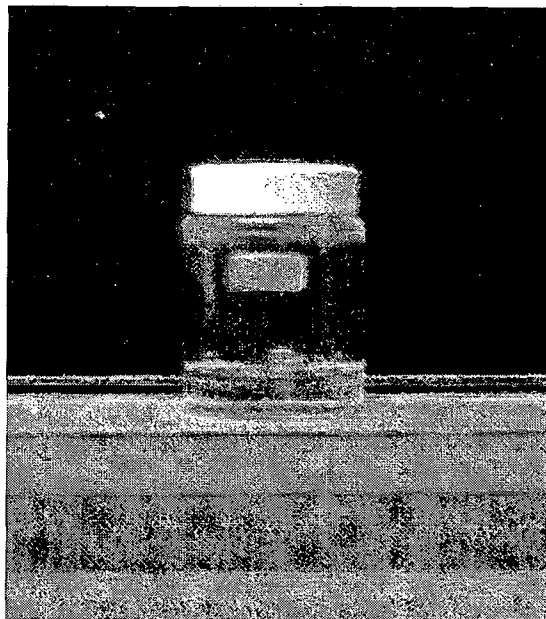


FIG. 3

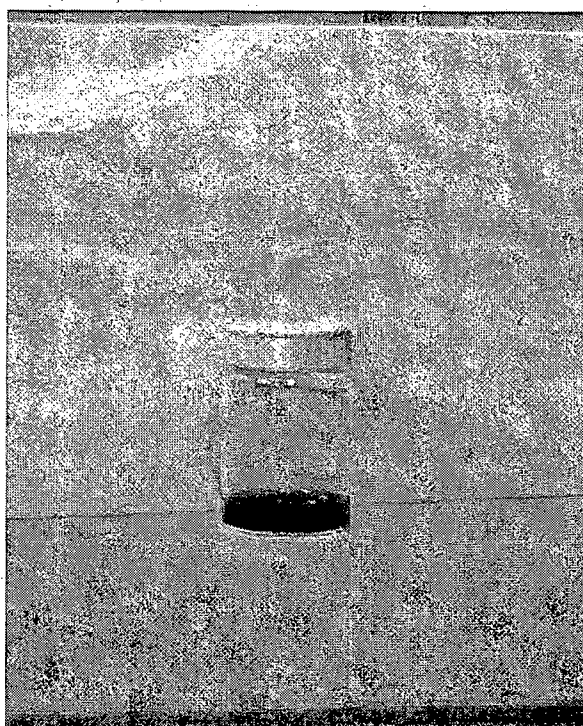


FIG. 4

3/3

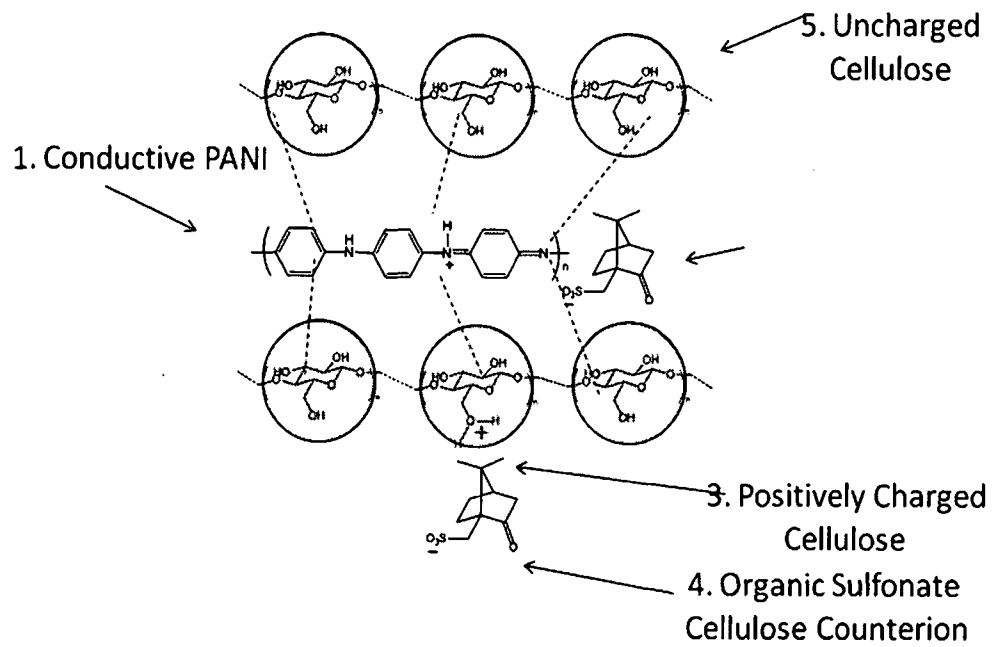


FIG. 5

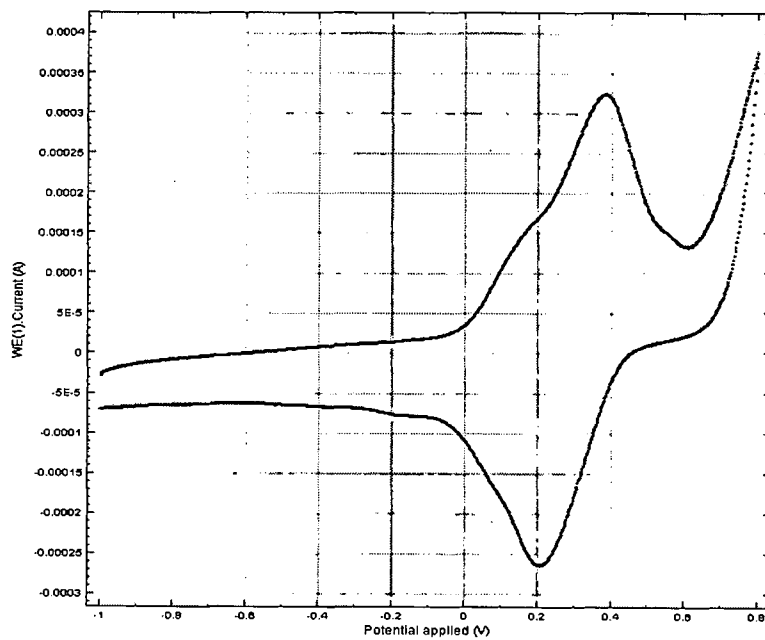


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/MY2012/000144

A. CLASSIFICATION OF SUBJECT MATTER INV. H01B1/12 H01G9/042 H01M4/137 H01M4/04 H01M4/60 C09D179/02 ADD. C08L1/12 C08K5/42 C08K5/3445 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) C08G C08L C09D C09J H01M H01B 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) EPO-Internal, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 194 129 B1 (KASONO OSAMU [JP] ET AL) 27 February 2001 (2001-02-27) column 4, line 51 - column 5, line 17 -----	1-10
A	US 6 235 220 B1 (PRON ADAM [FR] ET AL) 22 May 2001 (2001-05-22) claims 1-6; table 1 -----	1-10
A	CRUZ-SILVA ET AL: "Enzymatic synthesis of pH-responsive polyaniline colloids by using chitosan as steric stabilizer", EUROPEAN POLYMER JOURNAL, PERGAMON PRESS LTD. OXFORD, GB, vol. 43, no. 8, 4 August 2007 (2007-08-04), pages 3471-3479, XP022183197, ISSN: 0014-3057, DOI: 10.1016/J.EURPOLYMJ.2007.05.027 abstract; table 1 ----- -/-	1-10
☒ 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 "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 12 November 2012		Date of mailing of the international search report 20/11/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Meiners, Christian

INTERNATIONAL SEARCH REPORT

International application No

PCT/MY2012/000144

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 277 450 B1 (KATOOT MOHAMMAD W [US]) 21 August 2001 (2001-08-21) claims 6,8; example 2 -----	1-10
A	US 2003/091899 A1 (MATSUBARA KEIKO [JP] ET AL) 15 May 2003 (2003-05-15) paragraphs [0010] - [0012], [0029] - [0031], [0067]; table 1 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/MY2012/000144

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6194129	B1	27-02-2001	JP 3611955 B2 19-01-2005
			JP 11120625 A 30-04-1999
			US 6194129 B1 27-02-2001

US 6235220	B1	22-05-2001	DE 69731536 D1 16-12-2004
			DE 69731536 T2 24-11-2005
			EP 0916141 A1 19-05-1999
			FR 2751660 A1 30-01-1998
			JP 4142106 B2 27-08-2008
			JP 2001501017 A 23-01-2001
			US 6235220 B1 22-05-2001
			WO 9805040 A1 05-02-1998

US 6277450	B1	21-08-2001	NONE

US 2003091899	A1	15-05-2003	CN 1409418 A 09-04-2003
			US 2003091899 A1 15-05-2003
