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[Continued on next page]

(54) Title: MANUFACTURING PROCESS FOR POROUS MATERIAL

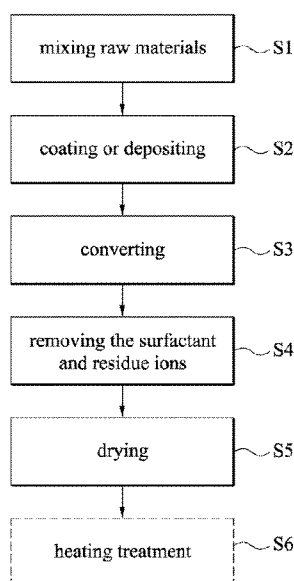


FIG. 1

(57) Abstract: A manufacturing process for a porous material is provided. The manufacturing process for a porous material includes the steps of: mixing a non-ionic surfactant with a precursor of a predetermined material to form a mixture comprising a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase; coating or depositing the mixture onto a flexible substrate; and converting the precursor of the predetermined material.



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## MANUFACTURING PROCESS FOR POROUS MATERIAL

### CROSS REFERENCE TO RELATED APPILCATIONS

[0001] This application claims the benefit of U.S. Provisional Application No.  
5 61/371,293, filed on August 6, 2010, the entirety of which is incorporated by reference  
herein.

### BACKGROUND OF THE INVENTION

#### Field of the Invention

[0002] The present invention relates to a manufacturing process for a porous material,  
10 and in particular to a manufacturing process for a porous material using surfactants as the  
pore former incorporated with continuous roll-to-roll processes.

#### Description of the Related Art

[0003] Generally, porous materials are materials with porous structures. According to  
the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be  
15 divided into three types, such as microporous, mesoporous, and macroporous materials.  
The microporous materials comprise pores of diameters substantially less than 2 nm, the  
macroporous materials comprise pores of diameters substantially greater than 50 nm, and  
the mesoporous materials comprise pores of diameters among 2-50 nm.

[0004] Surfactants typically comprise organic amphiphilic molecules having  
20 hydrophilic and hydrophobic groups and can be dissolved in organic solutions and aqueous  
solutions. When the surfactant concentration in water is low, molecules of the surfactant  
will be located at the interface between air and water. When the surfactant concentration is  
increased to a critical micelle concentration (CMC), the surfactants will aggregate to be the  
micelles. The hydrophilic group of surfactant in micelle will face outward to reduce a

contact area between the water molecules and the hydrophobic groups.

**[0005]** A hydrophilic-lipophilic balance (HLB) of a surfactant is the hydrophilic degree of the surfactants. A surfactant with higher HLB value has higher hydrophilicity. For example, surfactants with HLB values of 8 or higher have high water solubility.

5 **[0006]** Since the solution concentration is greater than the critical micelle concentration, surfactant molecules will aggregate to form the micelle. Although the micelle is typically formed in a spherical shape, the size and shape of the micelle can be gradually changed in accordance with variations in concentration and temperature. In addition, the size and shape of the micelle are also influenced by the chemical structure and  
10 molecular weight of the surfactant. Based on formation conditions and compositions, liquid crystals comprise thermotropic liquid crystals and lyotropic liquid crystals. The thermotropic liquid crystals are formed due to temperature variations, and the lyotropic liquid crystals are formed due to concentration variations.

**[0007]** Based on the organization of molecules or surfactant aggregates, liquid crystals  
15 comprise a smectic and nematic mesophase. In the nematic phase, all molecules or surfactant aggregates are aligned approximately parallel to each other with only a one-dimensional (orientational) order. In the smectic phase, all molecules or surfactant aggregates exhibit both (two-dimensional) positional and orientational order.

**[0008]** In the prior art, one of the manufacturing processes for ordered mesoporous  
20 materials uses various surfactants as structure-directing agents or so-called templates. The surfactants can be, for examples, triblock copolymers, diblock copolymers or ionic surfactants. The above method also uses alkoxides as a precursor to synthesize metal oxides or hydroxides by a sol-gel technique. Alternatively, the above method may use carbonaceous monomers or oligomers as precursors of carbons to mix with surfactants and  
25 then the surfactants are removed as the surfactants are arranged orderly and the precursors

are polymerized. The obtained polymers are then carbonized at a high temperature such that highly ordered mesoporous carbons are obtained. However, the research to date about formation of the mesoporous materials mainly focuses on changing the synthesis conditions of the precursors or the materials. For example, U.S. Patent Nos. 5,057,296, 5,108,725, 5,102,643 and 5,098,684 disclose using ionic surfactants as a template for manufacturing porous materials, wherein pore sizes thereof are greater than 5 nm. However, the formed mesoporous structures are not stable.

[0009] The conventional manufacturing processes for highly ordered mesoporous materials are typically by template-directed synthesis. The methods thereof can be divided into hard template methods and soft template methods according to features and restrictions of the template used therein. Since Kresge et al. disclosed a synthesis method for forming mesoporous silica in 1992 (C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, "Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism" *Nature*, vol 359, no. 6397, pp. 710–712, 1992), research about manufacturing mesoporous materials by template methods have been developed in the last decade. More precisely, research about manufacturing mesoporous materials by template methods that mainly focus on selections of surfactant and the conditions of material synthesizing has been carried out. For the soft template method, through selecting the surfactants and adjusting the synthesis conditions, the surfactants as a structure-directing agent will self-assemble into a highly ordered liquid crystalline phase while the concentration of the surfactant is greater than the critical micelle concentration, thereby forming various types of highly ordered mesoporous channels such as MCM-41, SBA-15 and MCM-50 having a two-dimensional high symmetry, and KIT-5, SBA-16, SBA-11, SBA-2, MCM-48, etc. having a three-dimensional high symmetry. For the hard template method, a previously prepared mesoporous silicon dioxide, such as SBA-15, is used as a template to prepare

reversed mesoporous materials. After mixing carbon precursors with SBA-15, the carbon precursors are converted to carbon. The silicon dioxide in the obtained product is removed by using hydrofluoric acid or strong bases and then the ordered mesoporous carbon named as CMK-3 is obtained. Although highly ordered mesoporous materials having microstructures can also be obtained, the cost of the hard template method is high and the structures of the obtained materials are reversed mesoporous structures.

**[0010]** The highly ordered mesoporous materials synthesized by using surfactants as structure-directing agents have characteristics such as high specific surface areas, uniform and adjustable pore sizes, and regular pore channel arrangements such that high value in applications such as separation, catalyst, electromagnetic materials, and chemical sensing can be seen, wherein the representative materials are mesoporous silicon dioxides.

**[0011]** In the prior art, the metal hydroxide or metal oxide are obtained by a precipitation, hydrolysis, condensation and redox reaction in batch process. In a batch process, the concentration gradient of reactant exists. Therefore, it is hard to control the uniformity of conversion. With a scale-up design in a conventional batch process, there are disadvantages of poor reaction uniformity and unstable quality.

## BRIEF SUMMARY OF THE INVENTION

**[0012]** In one embodiment of the present invention, a continuous process for manufacturing a porous material is provided. The manufacturing process for a porous material includes the steps of: mixing a non-ionic surfactant with a precursor of a predetermined material to form a mixture comprising a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase; coating or depositing the mixture onto a flexible substrate; and converting the precursor of the predetermined material.

**[0013]** In one embodiment of the present invention, the continuous process further

includes coating or depositing a base onto a layer comprising the precursor of the predetermined material.

**[0014]** In another embodiment of the present invention, the continuous process further includes coating or depositing a base precursor or a mixture of a base and a fugitive acid  
5 onto a layer comprising the precursor of the predetermined material.

**[0015]** In a further embodiment of the present invention, the continuous process further includes adding a base precursor or a mixture of a base and a fugitive acid into the mixture.

**[0016]** Preferably, the liquid crystalline mesophase is a smectic phase or a smectic hexagonal phase. The liquid crystalline mesophase is the form of a column having a  
10 diameter from about 2 nm to about 20 nm.

**[0017]** Preferably, the non-ionic surfactants have the HLB value from 5 to 24. More preferably, the non-ionic surfactants have the HLB value from 10 to 14.

**[0018]** The mixture comprises two continuous phases, or a continuous liquid crystalline mesophase and a continuous non-liquid crystalline phase.

15 **[0019]** In further another embodiment of the present invention, the continuous process further includes coating or depositing the mixture onto the flexible substrate in a roll-to-roll manner.

**[0020]** Preferably, the flexible substrate comprises a metal or polymer.

**[0021]** In an embodiment of the present invention, the continuous process further  
20 includes heating or drying, after converting the precursor of the predetermined material, and removing the surfactants, wherein removing the surfactants comprises washing the surfactants by a solvent or a solvent mixture.

**[0022]** The precursor is converted to obtain the predetermined material by precipitation, hydrolysis, condensation, redox reaction, polymerization, or crosslinking.

25 **[0023]** The mixture is coated or deposited onto the flexible substrate by casting,

impregnation, spraying, dipping, gravure, doctor blade, slot, slit, curtain, reverse or transfer coating, or printing.

**[0024]** The predetermined material is selected from the group consisting of silicon dioxide, titanium dioxide, nickel hydroxide, nickel oxide, and manganese oxide.

5 **[0025]** The precursor includes tetraethoxysilane, titanium salt, organotitanium, titanium alkyoxide, nickel salt, organonickel complex, manganese salt, organomanganese complex, or combinations thereof.

**[0026]** Preferably, the non-ionic surfactants comprise a block, graft, or branch copolymer.

10 **[0027]** More preferably, the non-ionic surfactants comprise ethylene oxide (EO) copolymer, propylene oxide (PO) copolymer, butylene oxide copolymer, vinyl pyridine copolymer, vinyl pyrrolidone, epichlorohydrin copolymer, styrene copolymer, acrylic copolymer, or combinations thereof.

**[0028]** Alternatively, the non-ionic surfactants comprise polyoxyethylene alkylether  
15 having a chemical formula of  $C_xH_{2x+1}(EO)_yH$ , where EO represents an ethylene oxide, x is not less than 12, and y is not less than 6.

**[0029]** Preferably, the molecular weight of the non-ionic surfactants is between 500 and 20000. More preferably, the molecular weight of the non-ionic surfactants is between 600 and 10000.

20 **[0030]** In an embodiment of the present invention, the continuous process further includes adding a swelling agent into the mixture.

**[0031]** In another embodiment of the present invention, a process for manufacturing a porous material includes the steps of: mixing a non-ionic surfactant with a precursor of a predetermined material and either a base precursor or a first mixture of a base and a fugitive  
25 acid to form a second mixture comprising a continuous phase and a liquid crystalline

mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase; coating or depositing the second mixture onto a flexible substrate; heating or illuminating the base precursor or the first mixture of the base and the fugitive acid; and converting the precursor of the predetermined material.

5   **[0032]**     Preferably, the base precursor or the mixture of the base and the fugitive acid is a nitrogen-containing compound, guanidine, urea, amine, imine, or derivatives thereof. The base precursor or the mixture of the base and the fugitive acid is heated under a temperature ranging from 30 °C to 150 °C.

10   **[0033]**     In further another embodiment of the present invention, a process for manufacturing a porous material includes the steps of: mixing a non-ionic surfactant with a precursor of a predetermined material to form a mixture comprising a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase; coating or depositing the mixture onto a flexible substrate; coating or depositing a base precursor or a mixture of a base and a  
15   fugitive acid onto a layer comprising the precursor of the predetermined material; heating or illuminating the base precursor or the mixture of the base and the fugitive acid; and converting the precursor of the predetermined material.

20   **[0034]**     In one embodiment of the present invention, a continuous process for manufacturing an electrode includes the steps of mixing a non-ionic surfactant with a precursor of a predetermined material to form a mixture comprising a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase; coating or depositing the mixture onto a metal substrate; and converting the precursor of the predetermined material.

25   **[0035]**     In another embodiment of the present invention, a continuous process for manufacturing porous material includes the steps of: mixing a surfactant with a nickel salt

or organonickel complex to form a mixture; adding a silver halide and a developing agent or reducing agent into the mixture; coating or depositing the mixture onto a flexible substrate; reacting the silver halide with the developing agent or reducing agent under illumination; and converting the nickel salt or organonickel complex to obtain nickel hydroxide.

**[0036]** In a further embodiment of the present invention, a continuous process for manufacturing an electrode includes the steps of: mixing a surfactant with a nickel salt or organonickel complex to form a mixture; adding a silver halide and a developing agent or reducing agent into the mixture; coating or depositing the mixture onto a metal substrate; reacting the silver halide with developing agent or reducing agent under illumination; and converting nickel salt or organonickel complex to obtain nickel hydroxide.

**[0037]** Preferably the developing agent or reducing agent comprises an organic compound, hydroquinone, aminophenol, phenylene diamine, derivatives thereof, or combinations thereof. More preferably, the developing agent or reducing agent comprises methyl p-aminophenol, N-methyl-p-aminophenol salt, 1-phenyl-3-pyrazolidinone, derivatives thereof, or combinations thereof.

## BRIEF DESCRIPTION OF THE DRAWINGS

The present invention can be more fully understood by reading the subsequent detailed description and examples with references made to the accompanying drawings, where:

**[0038]** FIG. 1 is a flow chart of a manufacturing process for porous materials of the invention;

**[0039]** FIGs. 2a, 2b and 2c are schematic diagrams showing a continuous roll-to-roll coating process of the invention, respectively;

[0040] FIGs. 3a and 3b are schematic diagrams showing a continuous roll-to-roll removing, drying, and scraping steps of the invention, respectively;

[0041] FIG. 4 is a schematic diagram showing a continuous roll-to-roll electrode cutting step of the invention;

5 [0042] FIGs. 5a, 5b, 5c, 5d, and 5e are schematic diagrams showing a roll-to-roll manufacturing process for silver-containing porous materials of the invention;

[0043] FIG. 6a is a plot for the isotherm of the porous nickel hydroxide of Example 1;

[0044] FIG. 6b is a plot for the pore size distribution of the porous nickel hydroxide of Example 1;

10 [0045] FIG. 7a is a plot for the isotherm of the porous nickel hydroxide of Example 2; and

[0046] FIG. 7b is a plot for the pore size distribution of the porous nickel hydroxide of Example 2.

## DETAILED DESCRIPTION OF THE INVENTION

15 [0047] The following description is made for the purpose of illustrating the general principles of the invention and should not be taken in a limiting sense.

### Manufacturing of porous materials

[0048] Synthesis methods capable of mass production are provided to synthesize the porous materials using the surfactants as the pore former. According to the present invention, the continuous process for manufacturing a porous material includes the steps of mixing a non-ionic surfactant with a precursor of the predetermined material to obtain a mixture and coating or depositing the mixture onto the flexible substrate in a roll to roll manner. Next, conversion is performed to obtain a composite sol. After removing the non-ionic surfactants and residue ions, the porous material is obtained. In addition,

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depending on the porous materials, a heating treatment may optionally be performed to conduct a dehydration or phase transformation after the drying step.

**[0049]** In a batch process, the concentration gradient of reactant is existed such that it is hard to control the uniformity of the conversion. According to embodiments of the invention, diffusion distances of reactant can be controlled with an adjustable film thickness in the converting step to achieve uniform conversions in the continuous mass production.

**[0050]** FIG. 1 is a flow chart showing an exemplary continuous process for manufacturing a porous material. As shown in FIG. 1, in a mixing step S1, raw materials such as at least one non-ionic surfactant and a precursor of a predetermined material are mixed to obtain a mixture. The mixture comprises a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants. The precursor is essentially located in the continuous phase, wherein the mixture comprises two continuous phases, or a continuous liquid crystalline mesophase and a continuous non-liquid crystalline phase.

**[0051]** Preferably, the liquid crystalline mesophase is a smectic phase. More preferably, the liquid crystalline mesophase is a smectic hexagonal phase. A column of a smectic hexagonal phase has a diameter from about 2 nm to about 20 nm.

**[0052]** In a coating or depositing step S2, as shown in FIG. 2, the mixture is coated or deposited onto a flexible substrate (e.g., a substrate 200 as shown in FIGs. 2a~2c) during a continuous process (e.g., performed by a coater 202 as shown in FIGs. 2a~2c). The flexible substrate can be metal or polymer. After the coating or depositing step, the precursor of the predetermined material is located in the continuous phase comprising the non-ionic surfactants and can be converted to the predetermined material. Methods for the conversion way can be precipitation, hydrolysis, condensation, redox reaction, polymerization, crosslinking or combinations thereof. In the coating or depositing step S2, the mixture is coated or deposited onto the flexible substrate to obtain the film (e.g., a film

204) by casting, impregnation, spraying, dipping, gravure, doctor blade, slot, slit, curtain, reverse or transfer coating, or printing .

**[0053]** Conversion uniformity can be controlled by adjusting the film thickness and diffusion distance of reactant in a continuous process. Furthermore, when a base precursor or the mixture of a base and a fugitive acid is added into the mixture, the hydroxyl ion concentration can be controlled by heating or illuminating. Because a base precursor or the mixture of a base and a fugitive acid and precursor can be well mixed before the converting step, the conversion uniformity can be controlled both for a batch or a continuous process.

**[0054]** The predetermined material can be oxide or hydroxide, such as silicon dioxide, titanium dioxide, nickel hydroxide, nickel oxide, manganese oxide and combinations thereof. For example, if the predetermined material is silicon dioxide, tetraethoxysilane (TEOS) can be used as precursors. If the predetermined material is titanium dioxide, titanium salt, organotitanium complexes or titanium alkoxide can be used as precursors. If the predetermined material is nickel hydroxide or nickel oxide, nickel salts or organonickel complexes can be used as precursors. If the predetermined material is manganese oxide ( $\text{MnO}_x$ ), organomanganese complexes, manganese salts such as potassium permanganate and manganese sulfate, or potassium permanganate and manganese acetate can be used as precursors.

**[0055]** The non-ionic surfactants can be block, graft or branch copolymers. In addition, the non-ionic surfactants can be selected from the group consisting of ethylene oxide (EO) copolymer, propylene oxide (PO) copolymer, butylene oxide copolymer, vinyl pyridine copolymer, vinyl pyrrolidone, epichlorohydrin copolymer, styrene copolymer, acrylic copolymer, and combinations thereof. Further, the non-ionic surfactants may include the polyoxyethylene alkylether, such as  $\text{C}_x\text{H}_{2x+1}\text{EO}_y\text{H}$ , where x is not less than 12

and y is not less than 6.

**[0056]** Preferably, the molecular weight of the non-ionic surfactant is between 500 and 20000. More preferably, the molecular weight of the non-ionic surfactant is between 600 and 10000.

5 **[0057]** Preferably, the non-ionic surfactants may have an HLB value from 5 to 24. More preferably, the non-ionic surfactants may have an HLB value from 10 to 14.

**[0058]** Precipitation refers to at least one kind of metal ions being converted to obtain the undissolvable material. For example,  $\text{Co}(\text{OH})_2$  can be obtained by reacting the cobalt salt with hydroxyl ions. The hydroxyl ions can be produced from a base, base precursor  
10 or the mixture of the base and the fugitive acid. For a base, hydroxyl ion concentrations can be increased by dissolving a base into an aqueous solution. For example, sodium hydroxide and potassium hydroxide are the commonly used base. For a base precursor or the mixture of a base and a fugitive acid, the hydroxyl ion concentration is gradually increased by heating or illuminating, and the reaction rate can be controlled when the base  
15 precursor or the mixture of the base and the fugitive acid is decomposed. The base precursor or the mixture of the base and the fugitive acid can be the nitrogen-containing compound, such as guanidine, urea, amine, imine or derivatives thereof.

**[0059]** As shown in FIG. 1, after the coating or depositing step S2, the flexible substrate is conveyed to the next station by a continuous roll-to-roll process (e.g., a process  
20 performed by a roll-to-roll type conveyer 222 shown in FIGs. 2a, 2b and 2c).

**[0060]** After the mixture containing precursor and non-ionic surfactants are coated or deposited onto flexible substrate as shown in as FIG. 2a, a converting step S3, as shown in FIG. 1, is applied to convert the precursor to the predetermined material. In another embodiment, after the mixture is coated or deposited onto a flexible substrate (e.g. the  
25 substrate 200) to form a film (e.g. the film 204), a base, base precursor or the mixture of the

base and the fugitive acid can be coated or deposited onto a flexible substrate. The method of coating or depositing can be a dipping, spraying (refer to the sprayer 206 in FIG. 2b), coating (refer to the coater 208 in FIG. 2c), attaching, casting, impregnation, gravure, doctor blade, slot, slit, curtain, reverse, or printing, thereby obtaining the predetermined materials. When a base precursor or the mixture of the base and the fugitive acid is used as a reactant, a heating or illuminating treatment step (not shown) is required in the converting step S3 to obtain the predetermined material.

**[0061]** As shown in FIG. 2a, the base precursor or the mixture of the base and the fugitive acid as a reactant, can be mixed in the mixture obtained at the step S1.

**[0062]** As shown in FIG. 1, after the converting step S3, a removing step S4 is performed to remove the non-ionic surfactants and residue ions in the composite sol over the flexible substrate, wherein the composite sol contains the predetermined material, non-ionic surfactants and residue ions. After removing the non-ionic surfactants and residue ions, porous materials are obtained. In preferred embodiments, water or suitable solvents can be used for removing the non-ionic surfactants and residue ions. In the removing step S4, a spray washing (e.g. by a sprayer 310) can be directly performed on the substrate to obtain the porous material as shown in FIG. 3a. After the removing step S4, the porous materials are dried (e.g. by a dryer 312), scraped (e.g. by a scraper 314) and collected. In another embodiment, after the converting step S3, the composite sol is scraped (e.g. by a scraper 314) into a washing tank (e.g. by a tank 316) to remove non-ionic surfactants and residue ions, as shown in FIG. 3b.

**[0063]** As shown in FIG. 1, after removing non-ionic surfactants and residue ions in step S4, a drying step S5 is then performed by a spray drying, freeze drying, or continuous tunnel drying or by using a batch oven to remove the solvent or the water, as shown in FIGS.

3a and 3b.

[0064] As shown in FIG. 1, a heating treatment S6 may optionally be performed after the drying step S5 to conduct a dehydration or phase transformation. For example, the TiO<sub>2</sub> crystalline phase can be changed from anatase to rutile after a heating treatment.

[0065] The process of the invention can be synthesized by using the surfactants as the pore former and is not limited to only synthesizing the specific materials, porous metal oxide, hydroxides, or the like.

[0066] In the preferred embodiment of the invention, tetraethoxysilane (TEOS) is used as the precursor to be incorporated with a non-ionic surfactant, such as P123 (a triblock copolymer produced by BASF<sup>®</sup> Corp.) or C<sub>16</sub>H<sub>33</sub>EO<sub>10</sub>H for obtaining SiO<sub>2</sub> by using a sol-gel method. After removal of P123 or C<sub>16</sub>H<sub>33</sub>EO<sub>10</sub>H, porous SiO<sub>2</sub>. A titanium salt or organotitanium complex, such as titanium alkyoxide, can be used as precursors for obtaining TiO<sub>2</sub>. For example, titanium isopropoxide or titanium butoxide is mixed with non-ionic surfactants and then coated or deposited onto a flexible substrate. After a converting step, a removing step is performed to remove the non-ionic surfactants to obtain the porous TiO<sub>2</sub>.

[0067] In order to enhance conductivity of the predetermined material, an additive can be added into the mixture. The additive can be metal salt or a conductive agent. For example, cobalt salt or organocobalt complexes can be added into the mixture of the nickel salt or organonickel complexes, C<sub>16</sub>H<sub>33</sub>EO<sub>10</sub>H or P123 surfactants. After the converting and removing steps, the porous material of the cobalt-doped nickel hydroxide can be obtained. In another embodiment, the conductive agent, such as graphite, graphene, carbon black, carbon nanotube (CNT) or metal particles which comprises Ti, Pt, Ag, Au, Al, Ru, Fe, V, Ce, Zn, Sn, Si, W, Ni, Co, Mn, In, Os, Cu, or Nb can be added into the mixture. The precursor is converted to the predetermined material, and then a removing step is performed to obtain the composite with porous structure.

[0068] Preferably, the manufacturing process further includes the steps of adding a swelling agent into the mixture, wherein the swelling agent is selected from the group consisting of 1, 3, 5-trimethylbenzene (TMB), cholesterol, polystyrene, polyethers, polyetheramines, polyacrylate, polyacrylic and derivatives thereof.

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#### Manufacturing electrodes with porous materials

[0069] For the manufacturing of an electrode, a metal substrate made of nickel, copper, or aluminum can be applied. Without scraping the composite sol from the metal substrate, the porous materials can be obtained on the metal substrate after the removing step of the non-ionic surfactants and residue ions and the drying step. Electrodes comprising porous materials can be manufactured by using an adequate cutting step (e.g. by the cutter 318 shown in FIG. 4) in a continuous process. The electrodes can be applied to batteries, super capacitors or fuel cells.

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[0070] In order to enhance conductivity of predetermined material, an additive can be added into a mixture. The additive can be metal salt or a conductive agent. For example, the nickel salt or organonickel complexes,  $C_{16}H_{33}EO_{10}H$  or P123 surfactants and cobalt salt or organocobalt complexes are mixed to obtain a mixture and coated or deposited onto a metal substrate. After the converting and removing steps, the porous material of the cobalt doped nickel hydroxide on the metal substrate can be obtained. In another embodiment, the conductive agent, such as graphite, graphene, carbon black, carbon nanotube (CNT) or metal particles which comprises Ti, Pt, Ag, Au, Al, Ru, Fe, V, Ce, Zn, Sn, Si, W, Ni, Co, Mn, In, Os, Cu, or Nb can be added into the mixture. The mixture is converted to the composite sol. After a step of removing the non-ionic surfactants and residue ions and a step of drying, electrodes with porous material can be obtained by an adequate cutting step.

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Manufacturing electrodes with porous materials containing silver particles

**[0071]** In order to increase the conductivity of predetermined materials, silver halide, such as silver chloride, silver bromide, and silver iodide, and a developing agent or reducing agent can be added into the mixture. During manufacturing of the electrodes, silver halide is reduced to silver particles in the porous materials. Under illumination (e.g. by the illumination device 520 shown in Fig. 5a), few silver ions will be reduced to silver atoms as the nuclei. In the existence of silver atoms, a developing agent or reducing agent can be used to reduce the residue silver ions to silver particles. Typically, the developing agent or reducing agent is an organic compound including hydroquinone, aminophenol, phenylene-diamine, derivatives thereof, and combinations thereof. Preferably, the developing agent or reducing agent can be methyl p-aminophenol, N-methyl-p-aminophenol salt, 1-phenyl-3-pyrazolidinone, derivatives thereof, and combinations thereof.

**[0072]** In another embodiment, as shown in FIGs. 5a-5b, silver halide, such as silver chloride, silver bromide, and silver iodide, and a developing agent or reducing agent can be added into the mixture. A coating or depositing step is performed after the mixing step. Before the converting step, silver halide is reduced to silver particles by reacting with the developing agent or reducing agent under illumination (e.g. by illumination device 520 shown in FIGs. 5a and 5b). A base is coated or deposited (e.g. by the sprayer 206 or the coater 208 shown in FIGs. 5a and 5b, respectively) onto a flexible substrate to convert the precursor to  $\text{Ni}(\text{OH})_2$ . The residue silver ions can be further reduced to silver particles under the basic condition. After the removing step (e.g. by a sprayer 310 as shown in FIG. 5c) and drying step (e.g. by a dryer 312 as shown in FIG. 5c), a porous  $\text{Ni}(\text{OH})_2$  containing silver particles is obtained as shown in FIGs. 5c. In another embodiment shown in FIG.

5d, the composite sol is scraped (e.g. by a scraper 314) into a washing tank (e.g. by a tank 316) to remove non-ionic surfactants and residue ions. Then the porous  $\text{Ni}(\text{OH})_2$  containing silver particles is obtained after a drying step.

**[0073]** In another embodiment of the invention, silver halide, such as silver chloride, silver bromide, and silver iodide, and a developing agent or reducing agent can be added into the mixture. The mixture is coated or deposited onto a metal substrate. The metal substrate can be nickel, copper, or aluminum. After the converting step, the composite sol is not scraped from the metal substrate. Electrodes with porous  $\text{Ni}(\text{OH})_2$  containing silver particles can be obtained by a removing step and a cutting step (e.g. by a cutting 318 as shown in FIG. 5e). The electrodes can be applied to batteries, super capacitors or fuel cells.

**[0074]** The present invention provides two exemplary embodiments of the manufacturing of porous nickel hydroxide as follows.

#### Example 1

**[0075]** A surfactant  $\text{C}_{16}\text{H}_{33}\text{EO}_{10}\text{H}$ , methanol, and nickel chloride are mixed in water to form a mixture. The content of  $\text{C}_{16}\text{H}_{33}\text{EO}_{10}\text{H}$  in the mixture is 60 wt.%. The mixture is deposited onto substrate to form a film with thickness of 4 mm. The converting step is conducted by spraying a NaOH solution under  $25^\circ\text{C}$  to obtain a  $\text{Ni}(\text{OH})_2$  composite sol. After washing by water and ethanol, a drying step is performed at  $60^\circ\text{C}$  to obtain a porous nickel hydroxide. As shown in FIG. 6a, the isotherm plot of the nickel hydroxide exhibits a capillary condensation step at relative pressure from 0.4 to 0.8 and exhibits the pores structure in the nickel hydroxide. As shown in FIG. 6b, the pore size distribution of the porous nickel hydroxide is narrow and the specific surface area and pore diameter of the porous nickel hydroxide are  $525.0\text{ m}^2/\text{g}$  and approximately 6.1 nm, respectively.

Example 2

[0076] A surfactant  $C_{16}H_{33}EO_{10}H$ , urea, and nickel chloride are mixed in water to form a mixture. The content of  $C_{16}H_{33}EO_{10}H$  in the mixture is 60 wt.%. The converting step is conducted by heating at  $65^{\circ}C$  to obtain a  $Ni(OH)_2$  composite sol. After washing by water and ethanol, a drying step is performed at  $60^{\circ}C$  to obtain a porous nickel hydroxide. FIG. 7a shows the isotherm of the porous nickel hydroxide of Example 2. As shown in FIG. 7a, the isotherm plot of the nickel hydroxide exhibits a capillary condensation step at relative pressure from 0.4 to 0.8 and exhibits the pores structure in the nickel hydroxide. As shown in FIG. 7b, the pore size distribution of the porous nickel hydroxide is narrow and the specific surface area and pore diameter of the porous nickel hydroxide are  $285.5\text{ m}^2/\text{g}$  and approximately 3.8 nm, respectively.

[0077] While the invention has been described by way of example and in terms of the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, it is intended to cover various modifications and similar arrangements (as would be apparent to those skilled in the art). Therefore, the scope of the appended claims should be accorded the broadest interpretation so as to encompass all such modifications and similar arrangements.

## CLAIMS

1. A continuous process for manufacturing a porous material, comprising:  
mixing a non-ionic surfactant with a precursor of a predetermined material to form a  
mixture comprising a continuous phase and a liquid crystalline mesophase  
5 comprising the non-ionic surfactants, wherein the precursor is essentially  
located in the continuous phase;  
coating or depositing the mixture onto a flexible substrate; and  
converting the precursor of the predetermined material.

2. The continuous process of claim 1, further comprising coating or depositing a  
10 base onto a layer comprising the precursor of the predetermined material.

3. The continuous process of claim 1, further comprising adding a base precursor or  
a mixture of a base and a fugitive acid into the mixture.

4. The continuous process of claim 1, wherein the liquid crystalline mesophase is a  
smectic phase or a smectic hexagonal phase.

15 5. The continuous process of claim 1, wherein the liquid crystalline mesophase is  
the form of a column having a diameter from about 2 nm to about 20 nm.

6. The continuous process of claim 1, wherein the non-ionic surfactants have an  
HLB value from 5 to 24.

7. The continuous process of claim 6, wherein the non-ionic surfactants have the  
20 HLB value from 10 to 14.

8. The continuous process of claim 1, wherein the mixture comprises two  
continuous phases, or a continuous liquid crystalline mesophase and a continuous  
non-liquid crystalline phase.

9. The continuous process of claim 1, further comprising coating or depositing the  
25 mixture onto the flexible substrate in a roll-to-roll manner.

10. The continuous process of claim 1, wherein the flexible substrate comprises a metal or polymer.

11. The continuous process of claim 1, further comprising heating or drying after converting the precursor of the predetermined material.

5 12. The continuous process of claim 1, further comprising removing the surfactants.

13. The continuous process of claim 12, wherein removing the surfactants comprises washing the surfactants by a solvent or a solvent mixture.

14. The continuous process of claim 1, wherein the precursor is converted to obtain the predetermined material by precipitation, hydrolysis, condensation, redox reaction,  
10 polymerization, or crosslinking.

15. The continuous process of claim 1, wherein the mixture is coated or deposited onto the flexible substrate by casting, impregnation, spraying, dipping, attaching, gravure, doctor blade, slot, slit, curtain, reverse or transfer coating, or printing.

16. The continuous process of claim 1, wherein the predetermined material is  
15 selected from the group consisting of silicon dioxide, titanium dioxide, nickel hydroxide, nickel oxide, and manganese oxide.

17. The continuous process of claim 1, wherein the precursor comprises tetraethoxysilane, titanium salt, organotitanium, titanium alkyoxide, nickel salt, organonickel complex, manganese salt, organomanganese complex, or combinations  
20 thereof.

18. The continuous process of claim 1, further comprising adding an additive, metal salt, conductive agent, carbon nano-tube, carbon black, graphite, graphene or metal particles into the mixture.

19. The continuous process of claim 1, wherein the non-ionic surfactants comprises  
25 a block, graft, or branch copolymer.

20. The continuous process of claim 1, wherein the non-ionic surfactants comprises ethylene oxide (EO) copolymer, propylene oxide (PO) copolymer, butylene oxide copolymer, vinyl pyridine copolymer, vinyl pyrrolidone, epichlorohydrin copolymer, styrene copolymer, acrylic copolymer, or combinations thereof.

5           21. The continuous process of claim 1, wherein the non-ionic surfactants comprises polyoxyethylene alkylether having a chemical formula of  $C_xH_{2x+1}(EO)_yH$ , where EO represents an ethylene oxide, x is not less than 12, and y is not less than 6.

22. The continuous process of claim 1, wherein the molecular weight of the non-ionic surfactants is between 500 and 20000.

10           23. The continuous process of claim 22, wherein the molecular weight of the non-ionic surfactants is between 600 and 10000.

24. The continuous process of claim 1, further comprising adding a swelling agent into the mixture.

15           25. The continuous process of claim 1, further comprising coating or depositing a base precursor or a mixture of a base and a fugitive acid onto a layer comprising the precursor of the predetermined material.

26. The continuous process of claim 25, wherein the base precursor or the mixture of the base and the fugitive acid is a nitrogen-containing compound.

20           27. The process of claim 25, wherein the base precursor or the mixture of the base and the fugitive acid comprises guanidine, urea, amine, imine, or derivatives thereof.

28. The continuous process of claim 25, wherein the base precursor or the mixture of the base and the fugitive acid is heated under a temperature ranging from 30 °C to 150 °C.

29. The continuous process of claim 28, wherein the base precursor or the mixture of the base and the fugitive acid is heated under a temperature ranging from 30 °C to 70 °C.

30. A process for manufacturing a porous material, comprising:

- 5 mixing a non-ionic surfactant with a precursor of a predetermined material and either a base precursor or a first mixture of a base and a fugitive acid to form a second mixture comprising a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase;
- 10 coating or depositing the second mixture onto a flexible substrate;
- heating or illuminating the base precursor or the first mixture of the base and the fugitive acid; and
- converting the precursor of the predetermined material.

31. A continuous process for manufacturing a porous material, comprising:

- 15 mixing a non-ionic surfactant with a precursor of a predetermined material to form a mixture comprising a continuous phase and a liquid crystalline mesophase comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase;
- coating or depositing the mixture onto a flexible substrate;
- 20 depositing a base precursor or a mixture of a base and a fugitive acid onto a layer comprising the precursor of the predetermined material;
- heating or illuminating the base precursor or the mixture of the base and the fugitive acid; and
- converting the precursor of the predetermined material.

25 32. A continuous process for manufacturing an electrode, comprising:

- mixing a non-ionic surfactant with a precursor of a predetermined material to form a mixture comprising a continuous phase and a liquid crystalline mesophase

comprising the non-ionic surfactants, wherein the precursor is essentially located in the continuous phase;  
coating or depositing the mixture onto a metal substrate; and  
converting the precursor of the predetermined material.

5 33. A continuous process for manufacturing a porous material, comprising:  
mixing a surfactant with a nickel salt or organonickel complex to form a mixture;  
adding a silver halide and a developing agent or reducing agent into the mixture;  
coating or depositing the mixture onto a flexible substrate;  
reacting the silver halide with the developing agent or reducing agent under  
10 illumination; and  
converting the nickel salt or organonickel complex to obtain nickel hydroxide.

34. The continuous process of claim 33, wherein the developing agent or reducing agent comprises an organic compound.

15 35. The continuous process of claim 33, wherein the developing agent or reducing agent comprises hydroquinone, aminophenol, phenylenediamine, derivatives thereof, or combinations thereof.

36. The continuous process of claim 33, wherein the developing agent or reducing agent comprises methyl p-aminophenol, N-methyl-p-aminophenol salt, 1-phenyl-3-pyrazolidinone, derivatives thereof, or combinations thereof.

20 37. A continuous process for manufacturing an electrode, comprising:  
mixing a surfactant with a nickel salt or organonickel complex to form a mixture;  
adding a silver halide and a developing agent or reducing agent into the mixture;  
coating or depositing the mixture onto a metal substrate;  
reacting the silver halide with developing agent or reducing agent under  
25 illumination; and  
converting nickel salt or organonickel complex to obtain nickel hydroxide.

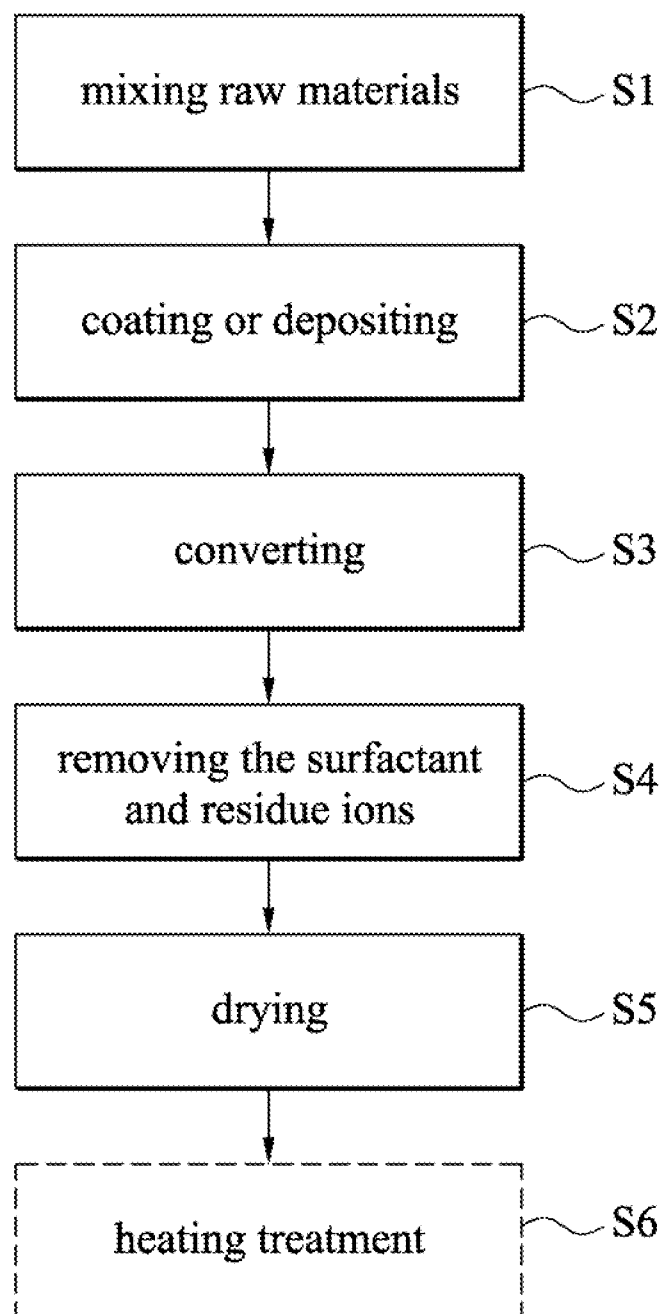


FIG. 1

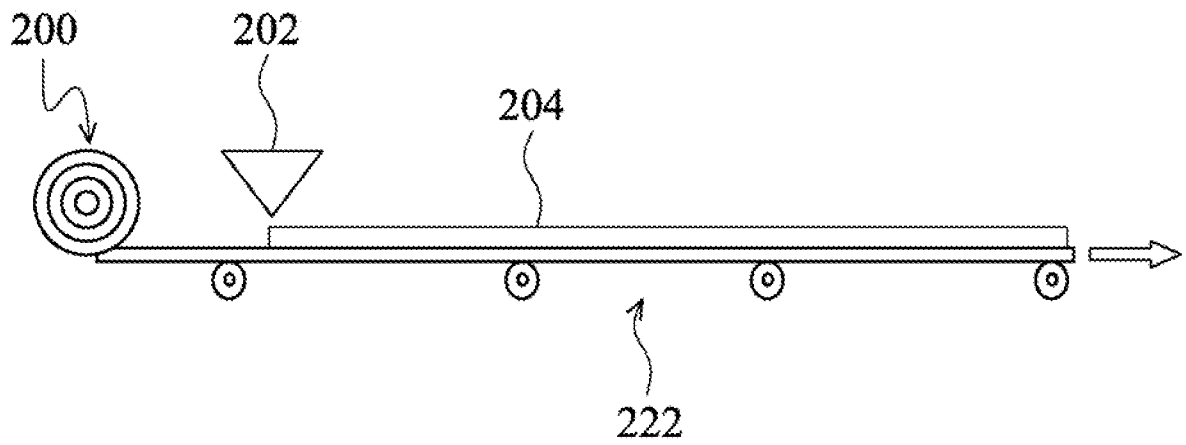


FIG. 2a

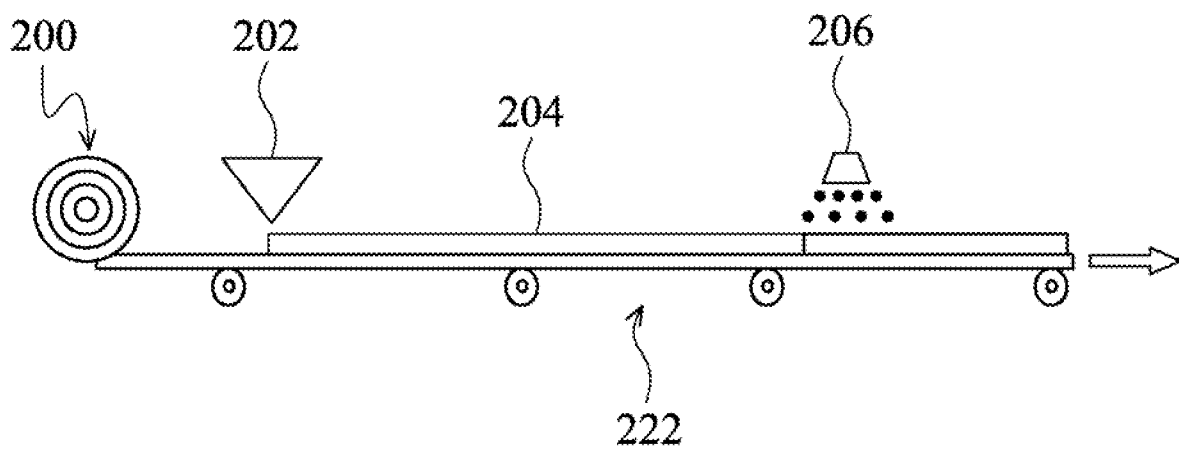


FIG. 2b

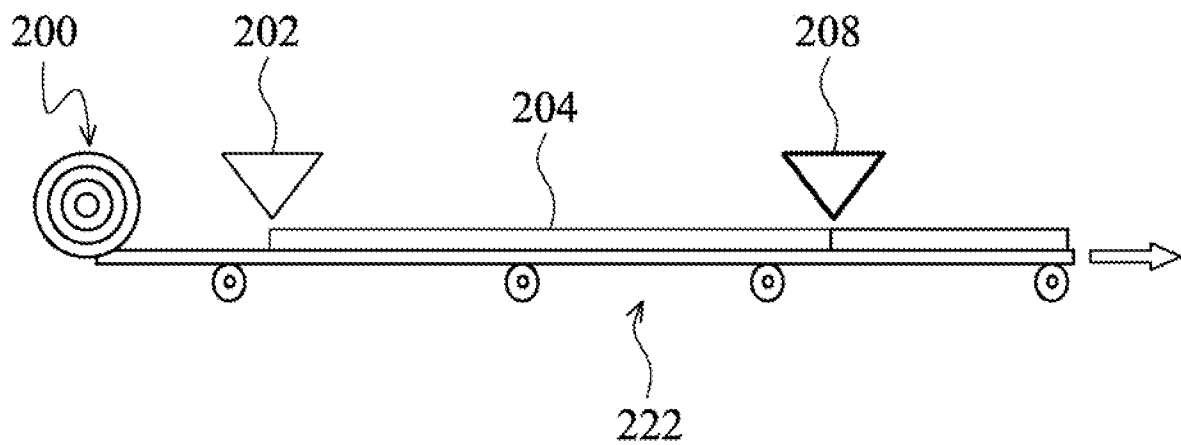


FIG. 2c

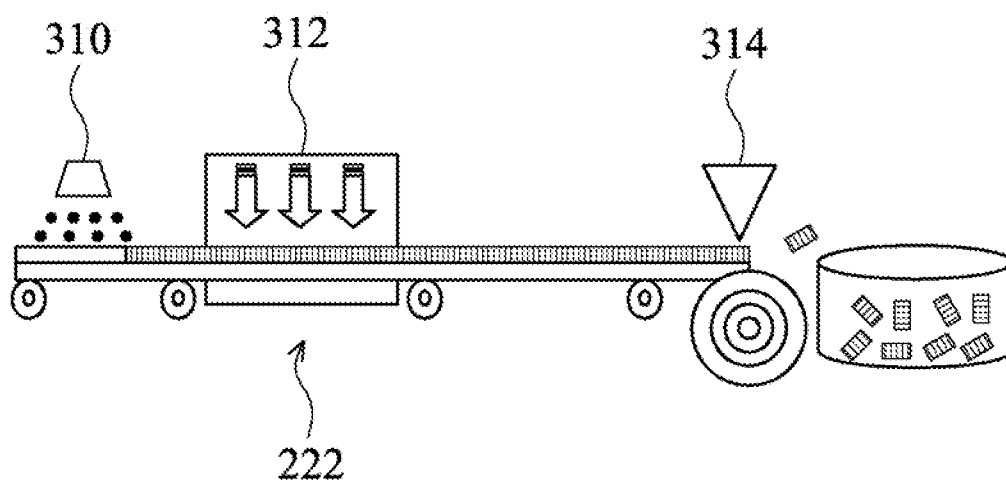


FIG. 3a

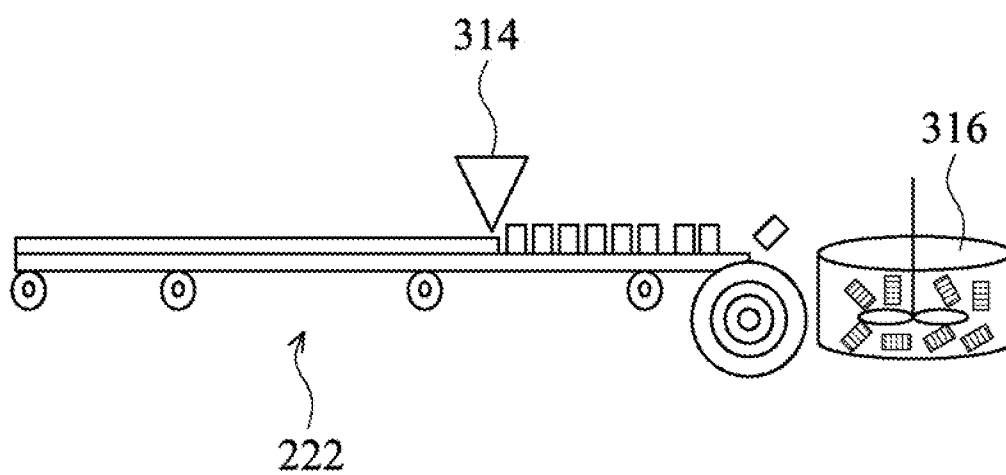


FIG. 3b

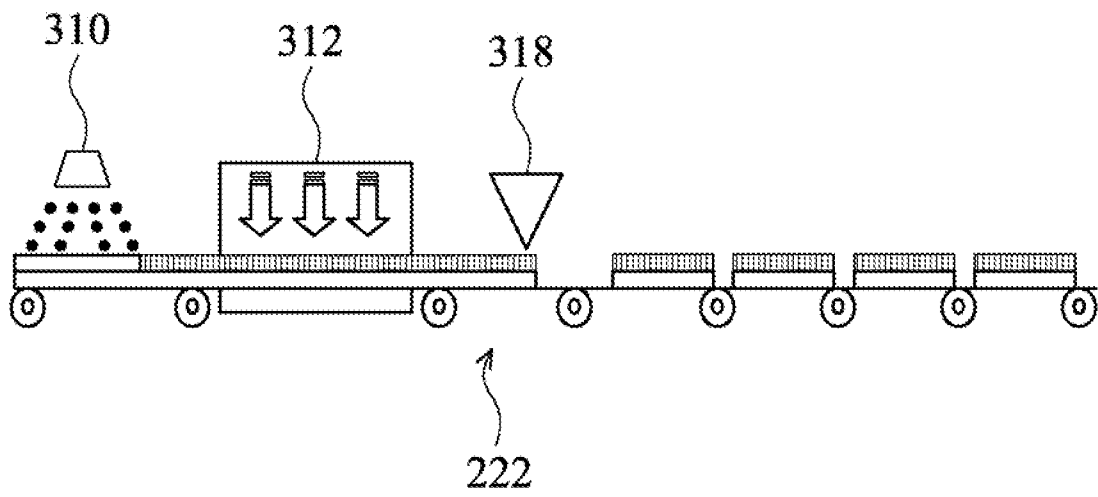


FIG. 4

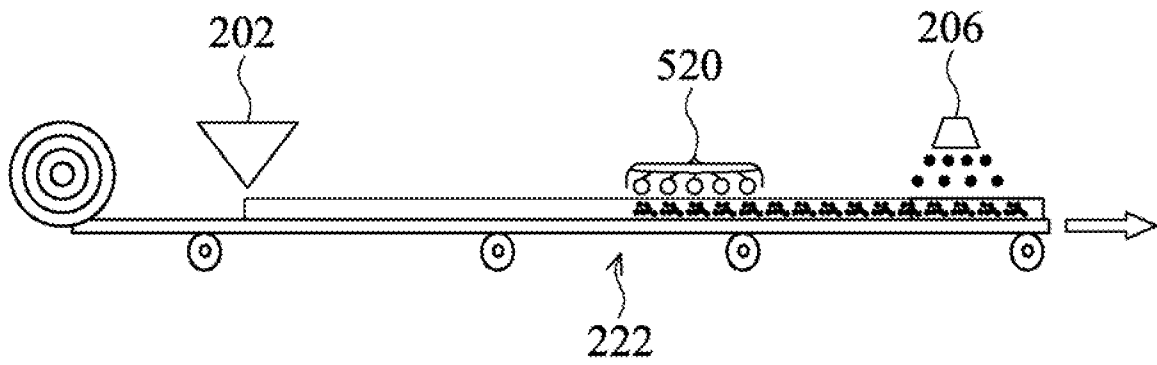


FIG. 5a

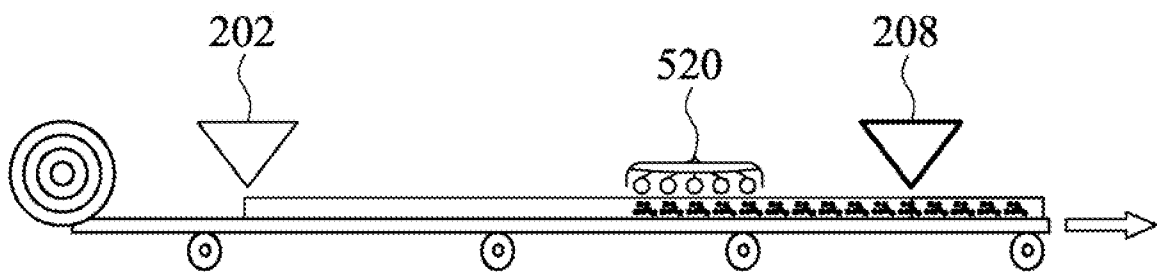


FIG. 5b

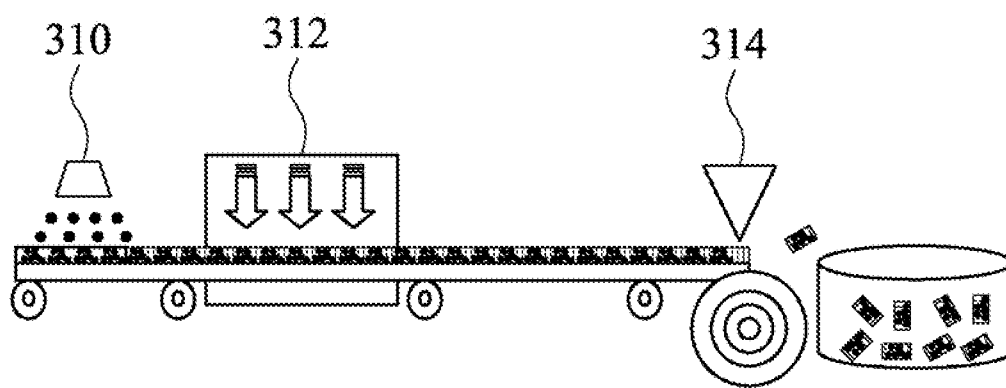


FIG. 5c

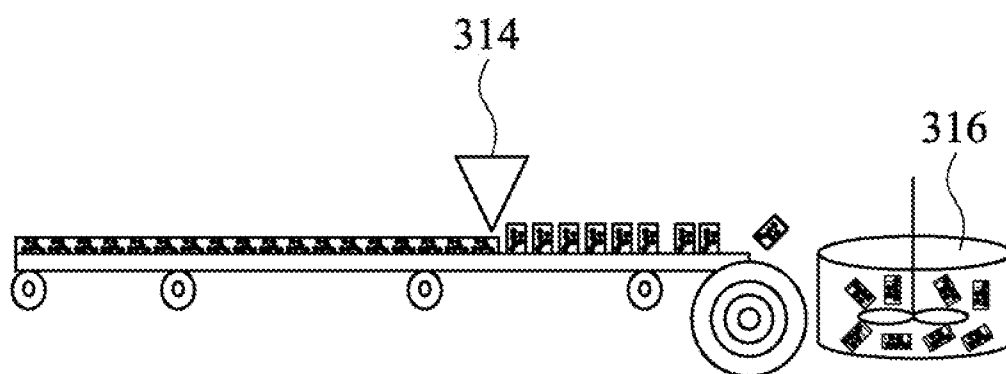


FIG. 5d

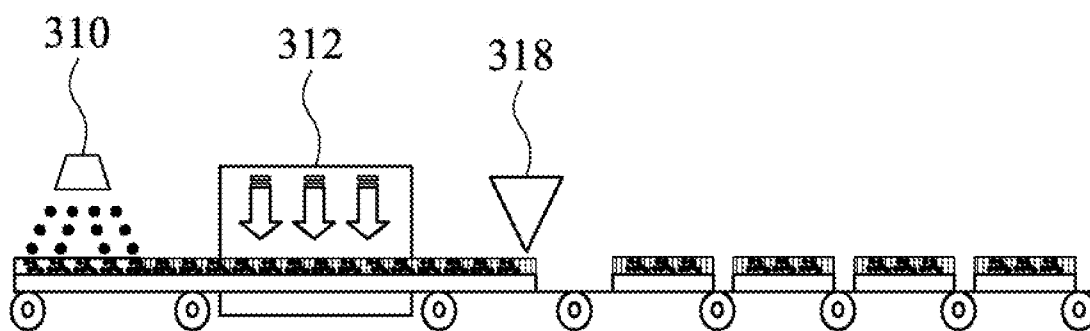


FIG. 5e

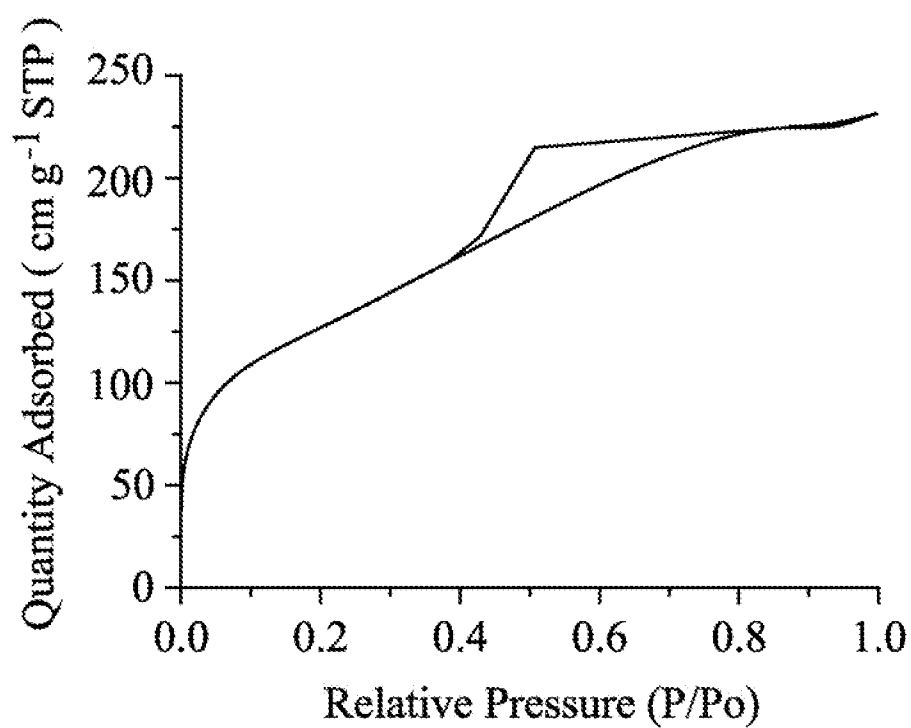


FIG. 6a

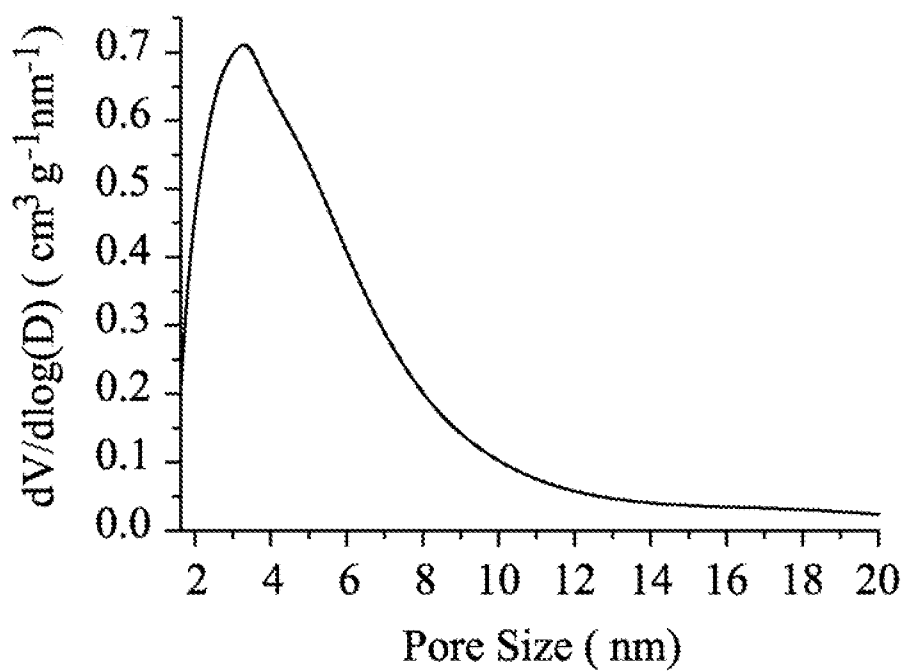


FIG. 6b

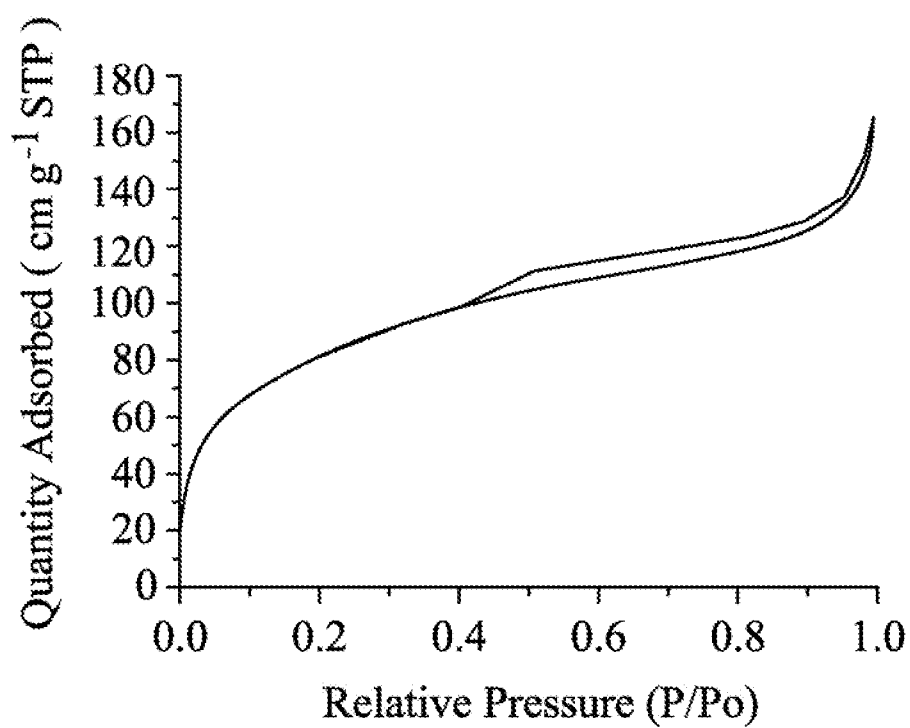


FIG. 7a

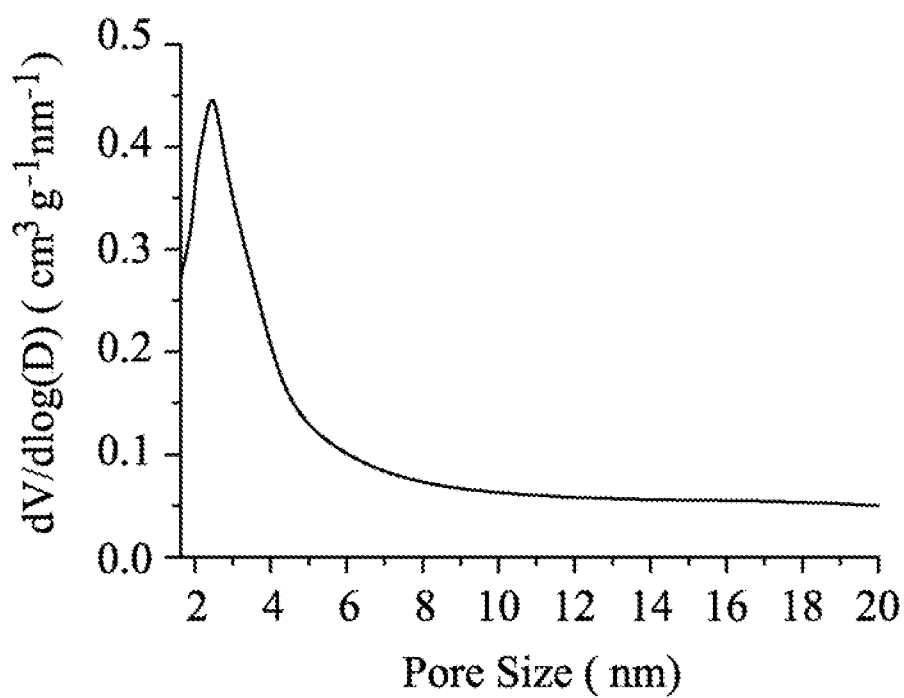


FIG. 7b

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/078026

## A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: H01G C01G

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, EPODOC, CNPAT, CNKI: surfactant, precursor, liquid crystal, porous, coating, depositing, continuous, phase, electrode, nickel, hydroxide, silver halide, developing agent, reducing agent, illumination

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------|-----------------------|
| A         | CN1770401A (UNIV QINGHUA) 10 May 2006(10.05.2006) claim 1                            | 1-37                  |
| A         | CN101563483A (NANOTECHTURE LTD) 21 Oct. 2009(21.10.2009) the whole document          | 1-37                  |
| A         | WO2009106837A1 (NANOTECHTURE LTD et al.) 03 Sep. 2009(03.09.2009) the whole document | 1-37                  |
| A         | US2007141854A1 (IND TECHNOLOGY RES INST) 21 Jun. 2007(21.06.2007) the whole document | 1-37                  |
| A         | WO2010046629A1 (QINETIQ LTD et al.) 29 Apr. 2010(29.04.2010) the whole document      | 1-37                  |

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

|                                                                                                                                                                          |                                                                                                                                                                                                                                                  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * Special categories of cited documents:                                                                                                                                 | "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                                              |
| "A" document defining the general state of the art which is not considered to be of particular relevance                                                                 | "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                                                                     |
| "E" earlier application or patent but published on or after the international filing date                                                                                | "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 |
| "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) | "&" document member of the same patent family                                                                                                                                                                                                    |
| "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                                                                   |                                                                                                                                                                                                                                                  |

|                                                                                                                                                                                                              |                                                                                        |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Date of the actual completion of the international search<br>17 Oct. 2011(17.10.2011)                                                                                                                        | Date of mailing of the international search report<br><b>10 Nov. 2011 (10.11.2011)</b> |
| Name and mailing address of the ISA/CN<br>The State Intellectual Property Office, the P.R.China<br>6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China<br>100088<br>Facsimile No. 86-10-62019451 | Authorized officer<br><b>GUO, Yanhua</b><br>Telephone No. (86-10)62084842              |

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/078026

### 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:

I: Claims 1-32 direct to a continuous process for manufacturing a porous material or an electrode;

II: Claims 33-37 also direct to a continuous process for manufacturing a porous material or an electrode.

The same or corresponding technical features among the inventions above are "mixing a surfactant with a precursor of a predetermined material to form a mixture"; "coating or depositing the mixture onto a flexible substrate" and "converting the precursor of the predetermined material", which do not make a contribution over the prior art and can not be considered as special technical features within the meaning of Rule 13.2 PCT. The application, hence does not meet the requirements of unity of invention as defined in Rules 13.1 PCT.

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 an additional fee, this Authority did not invite payment of additional fee.
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.

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/CN2011/078026

| Patent Documents referred<br>in the Report | Publication Date | Patent Family     | Publication Date |
|--------------------------------------------|------------------|-------------------|------------------|
| CN1770401A                                 | 10.05.2006       | CN100386849C      | 07.05.2008       |
| CN101563483A                               | 21.10.2009       | GB2441531A        | 12.03.2008       |
|                                            |                  | WO2008029160A2    | 13.03.2008       |
|                                            |                  | WO2008029160A3    | 09.10.2008       |
|                                            |                  | TW200827497A      | 01.07.2008       |
|                                            |                  | EP2059629A2       | 20.05.2009       |
|                                            |                  | KR20090063247A    | 17.06.2009       |
|                                            |                  | INDELNP200901538E | 29.05.2009       |
|                                            |                  | AU2007293317A1    | 13.03.2008       |
|                                            |                  | JP2010502839T     | 28.01.2010       |
|                                            |                  | US2010044240A1    | 25.02.2010       |
|                                            |                  | CA2662714         | 13.03.2008       |
|                                            |                  | CN101563483B      | 27.07.2011       |
| WO2009106837A1                             | 03.09.2009       | GB2457952A        | 02.09.2009       |
|                                            |                  | TW200940454A      | 01.10.2009       |
|                                            |                  | AU2009219915A1    | 03.09.2009       |
|                                            |                  | KR20100128313A    | 07.12.2010       |
|                                            |                  | EP2271791A1       | 12.01.2011       |
|                                            |                  | CA2717113A1       | 03.09.2009       |
|                                            |                  | CN101978099A      | 16.02.2011       |
|                                            |                  | US2011086270A1    | 14.04.2011       |
|                                            |                  | INDELNP201005987E | 25.03.2011       |
|                                            |                  | JP2011518742A     | 30.06.2011       |
| US2007141854A1                             | 21.06.2007       | US7598595B2       | 06.10.2009       |
|                                            |                  | TWI264557B        | 21.10.2006       |
| WO2010046629A1                             | 29.04.2010       | US2011171095A     | 14.07.2011       |
|                                            |                  | EP2356069A        | 17.08.2011       |

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/078026

Continuation of: **A. CLASSIFICATION OF SUBJECT MATTER**

H01G 4/01 (2006.01) i

C01G 53/04 (2006.01) i