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(54) Title: POROUS, SWELLABLE, SOL-GEL DERIVED SENSOR MATERIAL AND METHOD FOR USING SAME

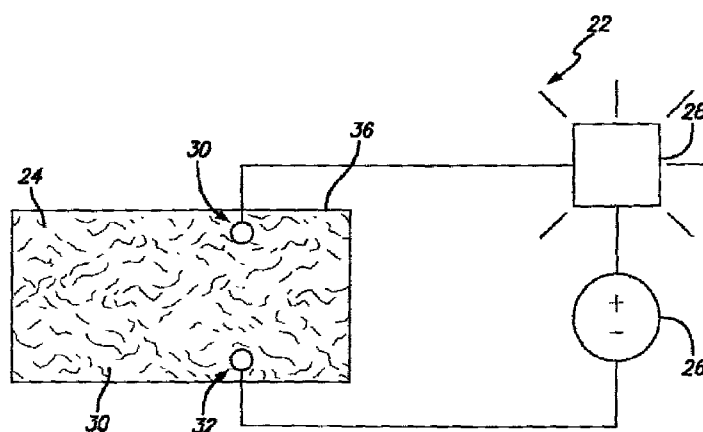


FIG. 3B

(57) Abstract: Disclosed is a sensor material for detecting a sorbate. The sensor material is formed of a swellable, sol-gel derived composition having a porous matrix and a property modifier intermixed with at least a portion of the porous matrix. The sensor material is swellable in the presence of the sorbate to be detected and has a first property value when unswollen and a second, different, property value when swollen.

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**POROUS, SWELLABLE, SOL-GEL DERIVED SENSOR MATERIAL
AND METHOD FOR USING THE SAME**

Cross Reference to Related Application

[0001] This application claims the benefit of Provisional Patent Application No. 61/293,350, filed January 8, 2010.

Statement Regarding Federally Funded Research or Development

[0002] This invention was made with Government support under National Science Foundation Grant EXP-LA CBET 0804261.

Background of the Invention

1. Field of the Invention

[0003] The present invention relates generally to the chemical arts. More particularly, the invention relates to a material for use in detecting sorbates, such as pesticides, industrial solvents, explosives, and toxic gases and a method for using the materials.

2. Discussion of the Related Art

[0004] Sol-gel synthesis is a relatively simple and versatile method to prepare chemical compositions, including porous materials with diverse morphologies (Wright, *Sol-Gel Materials: Chemistry and Applications*, Gordon and Breach Science Publ., Amsterdam (2001)). In contrast to hydrophilic polymers prepared from biomaterials which can be elastic and flexible when dried (Khalid *et al.*, *Eur. J. Pharm. Sci.* 15:425 (2002); Elvira *et al.*, *Biomaterials* 1955 (2002)), dried, hydrophilic sol-gel derived compositions formed from alkoxysilane precursors have a silicon dioxide (SiO₂) matrix that is inelastic and not prone to significant swelling when fully dried. The lack of swelling is likely due to the considerable condensation reactions that occur during the gelation and drying processes which crosslink the sol-gel derived composition (Brinker *et al.*, *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*, Academic Press (San Diego), Chapter 9 (1990)).

[0005] Due to this inherently inflexible structure of sol-gel derived siloxanes, there are few reports of swellable siloxane materials prepared via sol-gel methods. Some sol-gel derived siloxanes compositions have been formulated using amine-bridged silane precursors. The resulting materials can swell in response to changes in pH (Rao et al., J. Sol-Gel Sci. and Tech. 26:553 (2003)) or temperature (Rao et al., Adv. Mater. 13:274 (2001); Rao et al., Adv. Mater. 14:443 (2002)). These amine-bridged siloxane sol-gel derived materials, however, are only capable of very limited swelling.

[0006] Porous materials that have the ability to swell, significantly, may be useful in a variety of applications. For example, the use of certain organic compounds (*e.g.*, volatile organic compounds ("VOC's"), small molecule organic pharmaceuticals ("SMOP's") and solvents) necessitates techniques for determining the presence of such compounds. Consequently, there remains a need for improved porous materials for determining the presence of such compounds in a sample. There remains a further definite need for sensors and related methods that are reliable and inexpensive, yet have the robustness, selectivity, and sensitivity of state-of-the art instrumentation for determining the presence of such compounds. The present invention satisfies these and other needs, and provides further related advantages.

Summary of the Invention

[0007] The present invention generally relates to swellable materials and methods of use, and more particularly to a chemically-sensitive, swellable sol-gel composition for detecting a sorbate. Now in accordance with the invention there has been discovered a novel sensor material for detecting a sorbate. The sensor material includes a swellable, sol-gel derived composition having a porous matrix and a property modifier intermixed with at least a portion of the porous matrix.

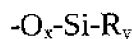
[0008] In some embodiments, the sol-gel derived composition is swellable to at least 1.5 times its volume in a sorbate.

[0009] And in some embodiments, the sol-gel derived composition is an aromatically-bridged, organosiloxane sol-gel derived composition, containing a plurality of alkyl siloxy substituents, the aromatically-bridged, organosiloxane sol-gel derived composition having a porous matrix. In some embodiments, the swellable, aromatically-bridged, organosiloxane sol-gel derived composition is derived from a trialkoxysilane corresponding to the formula:



where n and m are individually an integer from 1 to 8, Ar is a single-, fused-, or poly-aromatic ring, and each alkoxy is independently a C₁ to C₅ alkoxy. Preferred trialkoxysilanes include bis(trialkoxysilylalkyl)benzene with 1,4-bis(trimethoxysilylmethyl)benzene or bis(triethoxysilylethyl)benzene being most preferred.

[0010] In some embodiments, the alkyl siloxy substituents correspond to the formula:



where R is independently a hydrocarbon containing up to about 30 carbons, x is 1 or 2, y is 2 or 3 and the total of x and y is 4. And in some embodiments, the alkyl siloxy substituents additionally include at least one heteroatom selected from sulfur, oxygen, nitrogen, phosphorous or halogen atoms or combinations thereof.

[0011] The sensor material has a first property value when unswollen and a second property value when swollen, the first value property different than the second property value. For example, in some embodiments, the first property value and second property value are each an electrical conductivity value, an optical value, a mechanical value or a chemical value of the sensor material.

[0012] Representative property modifiers for use in embodiments where the first property value is a first electrical conductivity value and the second property value is a second electrical conductivity value include electrically conductive polymers, such as substituted and unsubstituted polyanilines, polyparaphenylenes, polyazines, polyparapheylenevinylenes, polythiophenes, polyfurans, polypyrroles, polyselenophenes, polyisothianaphenes, polyphenylene sulfides, polyacetylenes, polypyridylvinylenes or

combinations thereof; pluralities nanowires, such as a plurality of metallic nanowires, semiconducting nanowires, and graphite nanowires; carbon black; carbon nanotubes; and metallic particles. And in some such embodiments the property modifier is present in the sensor material in an amount of at least about 5% w/w.

[0013] Furthermore, some such embodiments include an electrically-insulating material such as acrylonitrile, butadiene, styrene, acetate resins, acrylic resins, beryllium oxide, ceramics, acetal resins, epoxy/fiberglass resins, glass, a polyimide films, fluoropolymers, polycarbonate resins, melamine resins laminated with woven glass, mica, neoprene, aromatic polyamide, resin, nylon, polyethylene terephthalate, copolyester resins, phenolic resins, polyolefins, polystyrene, polyurethane, polyvinylchloride, silicone, teflon, thermoplastics (*e.g.*, polysulfone, polyetherimide, polyamideimide or polyphenylene), and derivatives or combinations thereof.

[0014] Representative property modifiers for use in embodiments where the first property value is a first value for a chromatic property and the second property value is a second value for a chromatic property include Reichardt's dye. And in some such embodiments, the property modifier is present in the sensor material in an amount from about 0.001% w/w to about 1% w/w, preferably from about 0.01% w/w to about 0.1% w/w.

[0015] In some embodiments, the sensor material is a powder or a pellet. Additionally in some embodiments, the sensor material is a pellet and the sensor material further comprises a binder, such as a polymeric binder. Useful polymeric binders include microcrystalline cellulose and elastomeric polymers. Preferred elastomeric polymers have a glass transition temperature below about 150 C. Preferred elastomeric polymer binders have a glass transition temperature below about 150 C. For example, polystyrene and is a currently most preferred elastomeric polymer binder. In some such embodiments, the binder is present in an amount of at least 50% and in some such embodiments at least 95% and in some such embodiments at least 99.5% based on the weight of the sensor material.

[0016] Now in accordance with the invention, there also has been discovered a novel method for determining the presence of a sorbate. The method includes contacting the sensor material with the sorbate and then detecting any change in the property value of the sensor material, where a change in the property value indicates the presence of a sorbate in a sample. In some embodiments, the first property value and second property value are each an electrical conductivity value, an optical value, a mechanical value or a chemical value of the sensor material.

[0017] In some embodiments, the sorbate has a Snyder Index of ≤ 6.5 . Furthermore, in some embodiments, the sorbate is dissolved in an aqueous solution and the sorbate has a $\log k_{ow} > -0.32$ and a molecular weight less than 1,000,000, while in some embodiments the sorbate has a $\log k_{ow} > 1.25$ and a molecular weight less than 2,000.

[0018] Representative of the sorbates that can be detected in accordance with the inventive method are alkyl hydrocarbons, such as hexane, cyclohexane and octane; aromatic hydrocarbons, such as benzene, toluene, xylene, naphthalene, nitrobenzene; chlorinated hydrocarbons, such as dichloromethane, trichloroethylene, perchloroethylene, dichloroethylene, vinyl chloride and polychlorinated triphenylstibine; alcohols, including both aliphatic alcohols, such as lower alkyl alcohols, including methanol and ethanol, and phenols, including phenol and m-nitrophenol; naphthols; ethers, such as methyl-t-butyl ether; as well as aldehydes; epoxides; and ketones, such as acetone; organic acids, including organic species possessing at least one carboxylic acid group, at least one sulfonic acid group, at least one thiol group, or at least one enol group, sulfinic acids, protonated amines, and hydroxamic acids; and acetonitrile.

[0019] The method is additionally of use to detect pesticides, such as atrazine, 2,4-dichlorophenoxyacetic acid, malathion, and dichlorodiphenyltrichloroethane, and explosives, such as trinitrotoluene, 1,3,5-trinitroperhydro-1,3,5-triazine and triacetone triperoxide.

[0020] Now in accordance with the invention, there has further been discovered a novel swellable material. The swellable material includes a swellable, sol-gel derived composition having a porous matrix and a binder, such as a polymeric binder. Useful polymeric binders include microcrystalline cellulose and elastomeric polymers. Preferred elastomeric polymers have a glass transition temperature below about 150 C. For, example, polystyrene and is a currently most preferred elastomeric polymer binder. In some such embodiments, the binder is present in an amount of at least 50% and in some such embodiments at least 95% and in some such embodiments at least 99.5% based on the weight of the swellable material.

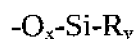
[0021] In some embodiments, the sol-gel derived composition is swellable to at least 1.5 times its volume in a sorbate.

[0022] And in some embodiments, the sol-gel derived composition is an aromatically-bridged, organosiloxane sol-gel derived composition, containing a plurality of alkyl siloxy substituents, the aromatically-bridged, organosiloxane sol-gel derived composition having a porous matrix. In some embodiments, the swellable, aromatically-bridged, organosiloxane sol-gel derived composition is preferably derived from a trialkoxysilane corresponding to the formula:



where n and m are individually an integer from 1 to 8, Ar is a single-, fused-, or poly-aromatic ring, and each alkoxy is independently a C₁ to C₅ alkoxy. Preferred trialkoxysilanes include bis(trialkoxysilylalkyl)benzene with 1,4-bis(trimethoxysilylmethyl)benzene or bis(triethoxysilylethyl)benzene being most preferred.

[0023] In some embodiments, the alkyl siloxy substituents correspond to the formula:



where R is independently a hydrocarbon containing up to about 30 carbons, x is 1 or 2, y is 2 or 3 and the total of x and y is 4. And in some embodiments, the alkyl siloxy substituents additionally include at least one heteroatom selected from sulfur, oxygen, nitrogen, phosphorous or halogen atoms or combinations thereof.

[0024] In some embodiments, the swellable material is in the form of a powder or a pellet. Additionally in some embodiments, the sensor material is in the form of a pellet and the swellable material further comprises a binder, such as a polymeric binder. Useful polymeric binders include microcrystalline cellulose and elastomeric polymers. Preferred elastomeric polymers have a glass transition temperature below about 150 C. For, example, polystyrene is a currently most preferred elastomeric polymer binder. In some such embodiments, the binder is present in an amount of at least 50% and in some such embodiments at least 95% and in some such embodiments at least 99.5% based on the weight of the sensor material.

Brief Description of the Drawings

[0025] The foregoing and other features of the present invention will become apparent to those skilled in the art to which the present invention relates upon reading the following description with reference to the accompanying drawings, in which:

[0026] Fig. 1 is a representation of exemplary derivatization reactions used during the preparation of one embodiment of the sensor material in accordance with the invention.

[0027] Fig. 2 identifies exemplary chlorosilanes used to derivatize silanols during the preparation of one embodiment of the sensor material in accordance with the invention.

[0028] Figs. 3A and B are schematic illustrations showing one embodiment of a detector in accordance with the invention, in unswollen and swollen states, respectively.

Detailed Description of the Preferred Embodiments

[0029] Particular embodiments of the invention are described below in considerable detail for the purpose of illustrating its principles and operation. However, various modifications may be made, and the scope of the invention is not limited to the exemplary embodiments described below.

[0030] Unless otherwise defined, all technical terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the present invention pertains.

[0031] As used herein, the term “sorbate” means an organic compound that is taken up by the swellable sensor materials of the present invention, whether by adsorption, absorption, or a combination thereof.

[0032] As used herein, the term “VOC” means any hydrocarbon or other organic species having a boiling point that is less than or equal to about 250 C.

[0033] As used herein, the term “SMOP” means any molecule and/or organic pharmaceutical having a molar mass of less than about 1000 grams/mole and used in the medical treatment of humans or animals.

[0034] In accordance with the invention, there has been discovered a novel porous, swellable sensor material for detecting a sorbate. The swellable sensor material is formed of a swellable sol-gel derived composition having a porous matrix and includes a property modifier, the sensor material having a first property value when unswollen and a second property value when swollen, the first property different than the second property value.

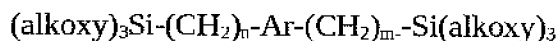
[0035] In some embodiments, the sol-gel derived composition, prior to modification, is swellable to at least 1.5 times its original volume in a sorbate. Preferred sol-gel derived compositions are swellable to at least two times their original volume, more preferably at least five times their original volume, and in some embodiments up to about eight to ten times their original volume when exposed to a sorbate.

[0036] And in some embodiments, the swellable sensor material is formed of a porous, swellable, aromatically-bridged, organosiloxane sol-gel derived composition containing a plurality of alkyl siloxy substituents. In such embodiments, the swellable sensor

material contains a plurality of flexibly tethered and interconnected organosiloxane particles having diameters on the nanometer scale. The organosiloxane nanoparticles form a disorganized porous matrix defined by a plurality of cross-linked aromatic siloxanes.

[0037] The porous, swellable, aromatically bridged, organosiloxane sol-gel derived compositions contain a plurality of polysiloxanes that include an aromatic bridging group flexibly linking the silicon atoms of the polysiloxanes. Such organosiloxane nanoparticles have a multilayer configuration comprising a hydrophilic inner layer and a hydrophobic, aromatic-rich outer layer.

[0038] The swellable sensor materials are obtained using a sol-gel reaction beginning with trialkoxysilanes containing an aromatic bridging group. Suitable trialkoxysilanes include, without limitation, trialkoxysilanes corresponding to the formula:



where n and m are individually an integer from 1 to 8, Ar is a single-, fused-, or poly-aromatic ring, and each alkoxy is independently a C₁ to C₅ alkoxy.

Bis(trialkoxysilylalkyl)benzenes are preferred and include 1,4-bis(trimethoxysilylmethyl)benzene (BTB) and bis(triethoxysilylethyl)benzene (BTEB).

[0039] The trialkoxysilanes are typically present in the reaction medium at between about 0.25M and about 1M, preferably between about 0.4M and about 0.8M, most preferably between about 0.4M and about 0.6M.

[0040] Conditions for sol-gel reactions are well-known in the art and include the use of acid or base catalysts in appropriate solvents. Preferred conditions employ a base catalyst in a suitable solvent. Exemplary base catalysts include, without limitation, tetrabutyl ammonium fluoride ("TBAF"), 1,5-diazabicyclo[4.3.0]non-5-ene ("DBN"), and alkylamines (*e.g.*, propyl amine), of which TBAF is preferred. Suitable solvents for use with the base catalysts include, without limitation, tetrahydrofuran ("THF"), acetone, dichloromethane/THF mixtures containing at least 15% by volume THF, and

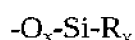
THF/acetonitrile mixtures containing at least 50% by volume THF. Of these exemplary solvents, THF is preferred.

[0041] As noted above, acid catalysts can be used to form swellable sol-gels, although acid catalysts are less preferred. Exemplary acid catalysts include, without limitation, any strong acid such as hydrochloric acid, phosphoric acid, sulfuric acid, *etc.* Suitable solvents for use with the acid catalysts include those identified above for use with base catalysts.

[0042] After gelation, the material is preferably aged for an amount of time suitable to induce syneresis, which is the shrinkage of the gel that accompanies solvent evaporation. The aging drives off much, but not necessarily all, of the solvent. While aging times vary depending upon the catalyst and solvent used to form the gel, aging is typically carried out for about 15 minutes up to about 7 days, preferably from about 1 hour up to about 4 days. Aging can be carried out at room temperature or elevated temperature (*i.e.*, from about 18 C up to about 60 C), either in open atmosphere, under reduced pressure, or in a container or oven.

[0043] Solvent and catalyst extraction (*i.e.*, rinsing) is carried out during or after the aging process. Preferred materials for extraction include, without limitation, any organic solvent of medium polarity, *e.g.*, THF, acetone, ethanol, and acetonitrile, either alone or in combination.

[0044] As shown in Fig. 1, after rinsing, the sol-gel is characterized by the presence of residual silanols. The silanol groups allow for derivatization of the gel using any reagent that includes both one or more silanol-reactive groups and one or more non-reactive alkyl groups. The derivatization process results in the end-capping of the silanol-terminated polymers present within the sol-gel with alkyl siloxy substituents having the formula:



where R is independently an aliphatic or non-aliphatic hydrocarbon containing up to about 30 carbons, with or without one or more hereto atoms (*e.g.*, sulfur, oxygen, nitrogen, phosphorous or halogen atoms), including straight-chain hydrocarbons,

branched-chain hydrocarbons, cyclic hydrocarbons, and aromatic hydrocarbons, x is 1 or 2, y is 2 or 3 and the total of x and y is 4.

[0045] One suitable class of derivatization reagents includes halosilane reagents that contain at least one halogen group and at least one alkyl group R, as defined above. The halogen group can be any halogen, preferably Cl, F, I, or Br. Preferred halosilanes or dihalosilanes include, without limitation, chlorosilanes, dichlorosilanes, fluorosilanes, difluorosilanes, bromosilanes, dibromosilanes, iodosilanes, and di-iodosilanes.

Exemplary halosilanes suitable for use as derivatization reagents include, without limitation, cyanopropyldimethyl-chlorosilane, phenyldimethylchlorosilane, chloromethyldimethylchlorosilane, (trideca-fluoro-1,1,2,2-tetrahydro-octyl)dimethylchlorosilane, n-octyldimethylchlorosilane, and n-octadecyldimethylchlorosilane. The structures of these exemplary reagents are shown in Fig. 2.

[0046] Another suitable class of derivatization reagents includes silazanes or disilazanes. Any silazane with at least one reactive group X and at least one alkyl group R, as defined above can be used. A preferred disilazane is hexamethyldisilazane.

[0047] After derivatizing, the reaction mixture is preferably rinsed in any of the rinsing agents described above, and then dried. Drying can be carried out under any suitable conditions, but preferably in an oven, *e.g.*, for about 2 hr. at about 60 C.

[0048] In some embodiments, the resulting sorbent material is swellable to at least 1.5 times and preferably at least twice its original volume when placed in contact with the media containing the sorbate. A suitable swellable sol-gel derived composition is Osorb® swellable sol-gel derived composition available from ABS Materials, Wooster, Ohio.

[0049] The porous, swellable sol-gel derived compositions include a property modifier intermixed with at least a portion of the porous matrix. Sensor materials that include a suitable property modifier have a first property value when the swellable sensor material

is unswollen and a second, different, property value when the swellable sensor material is swollen. It is an advantage of the invention that a wide variety of property modifiers can be used, including property modifiers that give rise to differing values for the electrical conductivity, optical, including chromatic, mechanical and/ or chemical properties of the sensor material.

[0050] The property modifier can be intermixed with at least a portion of the porous matrix by any suitable method. In some embodiments, the property modifier is disposed on the porous matrix, by, for example, forming a thin film on the porous, such as by sputter coating or thermal deposition or e-beam deposition or the like. In other embodiments, the property modifier is dispersed in the porous matrix. In still other embodiments, the property modifier is chemically bound to at least a portion of the polymer matrix.

[0051] In those embodiments where the first and second property values are values for electrical conductivity, suitable property modifiers include any material capable of conducting electrical energy. For example, in some embodiments, the electrically-conductive material is a plurality of nanowires, such as metallic nanowires (*e.g.*, nickel, platinum or gold nanowires) semiconducting nanowires (*e.g.*, Si, InP or GaN nanowires), or graphite nanowires intermixed with the porous matrix. Also of use are carbon black, carbon nanotubes and metallic particles, such as copper or silver.

[0052] In other embodiments, the electrically-conductive material is an electrically-conductive polymer. It is an advantage of electrically-conductive polymers that they combine the electrical properties of metals with the processing advantages of conventional polymers. Non-limiting examples of suitable electrically-conductive polymers include substituted and unsubstituted polyanilines, polyparaphenylenes, polyazines, polyparaphenylenes, polythiophenes (*e.g.*, poly(3,4-ethylenedioxythiophene)), polyfurans, polypyrroles, polyselenophenes, polyisothianaphenes, polyphenylene sulfides, polyacetylenes, polypyridylvinyls, combinations thereof, and blends thereof with other polymers and copolymers of the monomers thereof.

[0053] Some embodiments, additionally or alternatively include an electrically- insulative material intermixed with at least a portion of the porous matrix. Examples of electrically- insulative material useful in accordance with the invention include acrylonitrile, butadiene, styrene, acetate resins, acrylic resins, beryllium oxide, ceramics, acetal resins, epoxy/fiberglass resins, glass, a polyimide films, fluoropolymers, polycarbonate resins, melamine resins laminated with woven glass, mica, neoprene, aromatic polyamide, resin, nylon, polyethylene terephthalate, copolyester resins, phenolic resins, polyolefins, polystyrene, polyurethane, polyvinylchloride, silicone, teflon, thermoplastics (*e.g.*, polysulfone, polyetherimide, polyamideimide or polyphenylene), and derivatives and combinations thereof.

[0054] The amount of the electrically-conductive material included as part of the swellable sensor material varies depending upon the particular application. The amount is sufficient to cause a detectable change between first and second values of the electrical conductivity upon the swelling of the swellable sensor material and is readily determinable by one skilled in the art. For example, in some preferred embodiments, the property modifier is present in the sensor material in an amount of at least about 5% w/w. The electrically-conductive material is preferably added during synthesis of the sol-gel composition (*i.e.*, the conductor is added prior to gelation).

[0055] In those embodiments where the first and second property values are values for chromatic properties of the swellable sensor material, suitable property modifiers include any material capable of changing from a first color to a second different color upon swelling of the sensor material. For example, in some embodiments, the chromatic material is a piezochromatic material that changes from a first color to a second different color in response to a change in pressure caused by swelling of the sensor material. In other embodiments, the chromatic material is a dye, such as Reichardt's dye, that exhibits a significant degree of solvatochromism (*i.e.*, the UV-Vis spectrum values of which vary as a function of the local polarity of the environment which in turn is a function of the amount of swelling of the sensor material).

[0056] The amount of the chromatic material included as part of the swellable sensor material varies depending upon the particular application. The amount is sufficient to cause a detectable change between first and second values of a chromatic property upon the swelling of the sensor material and is readily determinable by one skilled in the art. For example, in some preferred embodiments, the property modifier is present in the sensor material in an amount from about 0.001% w/w to about 1% w/w, more preferably from about 0.01% w/w to about 0.1% w/w.

[0057] The chromatic material can be intermixed with the porous matrix during the formation of the swellable sensor material (*i.e.*, prior to gelation). Typically, the chromatic material is added in an organic solvent and the resultant composition then gelled (as described above). For example, to form a swellable sensor material containing Reichardt's dye, about 2 mg of Reichardt's dye is added to about 20 mL of ethanol. The resultant solution is then added to the swellable, sol-gel derived composition and the mixture then completely gelled.

[0058] The swellable sensor materials can be used in any suitable form, including in powder or pellet forms. Powdered forms of the sensor materials are characterized by a high surface area, for example, in the range of about 800 m²/g, which allows for rapid and effective uptake of the non-polar sorbate. Depending upon the manner in which grinding of the sensor material is carried out to obtain the powdered form, the particle sizes may vary widely. Preferred powdered forms will have a high surface area (*e.g.*, about 800 m²/g) and an average particle size that is less than about 250 μm, for example, between about 50 to about 250 μm.

[0059] In some embodiments and in particular those embodiments where the sensor material is in pellet form, the porous swellable sol-gel derived composition and the property modifier are combined with a binder. Useful polymeric binders include microcrystalline cellulose and elastomeric polymers. Preferred elastomeric polymers have a glass transition temperature below about 150 C, the temperature at which the sensor material begins to decompose. For, example, polystyrene is a currently most preferred elastomeric polymer binder. Other suitable thermoplastic elastomers are

described in U.S. Patent Nos. 7,834,093, 7,799,873, 7,799,868, 7,799,869, 7,790,805, 7,786,206, 7,776,968, 7,771,627, 7,744,781, 7,737,206, 7,655,719, 7,462,309, 6,596,792, 6,162,849, 5,194,480, 7,837,901, 7,815,998, 7,645,399, 7,608,342, 7,550,097, 7,402,616, 6,720,369, 4,634,730, 7,834,093, 7,799,873, 7,799,868, 7,799,869, 7,790,805, 7,786,206, 7,776,968, 7,771,627, 7,744,781, 7,737,206 which patents are herein incorporated by reference.

[0060] The amount of binder will depend on the particular application and will be readily determinable by one skilled in the art. Typically, the binder is present in an amount of at least 50% and in some embodiments at least 95% and in some embodiments at least 99.5% based on the weight of the sensor material.

[0061] Pellets can be formed in any desired shape and size suitable for their desired application. For example, in some embodiments, a sol-gel solution is poured into a silicone mold before gellation. The solution is then gelled in the mold to produce a pellet having the desired dimensions.

[0062] In other embodiments, pellets are prepared by casting the sol-gel derived material in a die having a desired internal configuration and dimension, which will result in a polymerized sol-gel conforming to the desired size and shape. In such embodiments, the components of the ingredients of the sensor material are combined using any suitable means, such as by combining in a ball mill. The ingredients are then feed into a die using any suitable means, such as by using a screw feeder or a gravity feeder. Screw feeders provide the advantage that they crush infeed particles to achieve a more favorable size consistency before compacting. In some cases, heat generated by the screw feeding process may be beneficial, for example, by softening a thermoplastic polymer binder prior to casting.

[0063] The ingredients are then compressed at a sufficient force, typically from about 1-8 tonnes, for a sufficient time, typically from about five to about ten minutes, to form a pellet. In some embodiments where the binder is a thermoplastic polymer, the die is

preheated to a temperature less than the decomposition temperature of the sol-gel derived composition, typically less than about 150 C.

[0064] The swellable sensor materials are useful in a method for detecting a fluid sorbate, *i.e.*, a sorbate in either a gaseous or liquid phase. It is a distinct advantage that the method is useful with a wide variety of sorbates, in the liquid phase, including both neat sorbates and sorbates contained in aqueous samples. For example, the method is useful with samples of neat sorbates having a Snyder Index of ≤ 6.5 .

[0065] The inventive method is also of use with sorbates dissolved in aqueous solutions, where the sorbates have a $\log k_{ow} > -0.32$ and is of especial use where the sorbates have a $\log k_{ow} > 1.25$. Sorbates detectable in accordance with the inventive method include SMOP's having a molecular weight less than 1,000,000 and VOC's having molecular weight less than 2,000.

[0066] Examples of sorbates that can be detected in accordance with the inventive method include alkyl hydrocarbons, such as hexane, cyclohexane and octane; aromatic hydrocarbons, such as benzene, toluene, xylene, naphthalene, nitrobenzene; chlorinated hydrocarbons, such as dichloromethane, trichloroethylene, perchloroethylene, dichloroethylene, vinyl chloride and polychlorinated triphenylstibine; alcohols, including both aliphatic alcohols, such as lower alkyl alcohols, including methanol and ethanol, and phenols, including phenol and m-nitrophenol; naphthols; ethers, such as methyl-*t*-butyl ether; as well as aldehydes; epoxides; and ketones, such as acetone; organic acids, including organic species possessing at least one carboxylic acid group, at least one sulfonic acid group, at least one thiol group, or at least one enol group, sulfinic acids, protonated amines, and hydroxamic acids; and acetonitrile.

[0067] The method is additionally of use to detect pesticides, such as atrazine, 2,4-dichlorophenoxyacetic acid, malathion, and dichlorodiphenyltrichloroethane, and explosives, such as trinitrotoluene, 1,3,5-trinitroperhydro-1,3,5-triazine and triacetone triperoxide.

[0068] In accordance with the inventive method, a swellable sensor material, as described above, is contacted with a sample. Any suitable method can be used to make the contact.

[0069] Any change in a property of the swellable sensor material is then determined, where a change in the property indicates the presence of the sorbate in the sample. Any suitable detector can be used to determine the property. For example, the detector can respond to electrical, optical, physical, mechanical signal, and/or chemical signals to indicate the changes in the swellable sensor material.

[0070] Figs. 3A and B illustrate one embodiment of a detector in accordance with the invention, in unswollen and swollen states, respectively. In the embodiment shown in Figs. 3A and B, the sensor device is formed of a detector 22 for detecting a change in the electrical conductivity of a swellable sensor material 24. The detector is operably connected to a swellable sensor material, the sensor material including at least one property modifier, the sensor material having a first property value when unswollen and a second property value when swollen, the first property value different than the second property value.

[0071] The detector 22 includes an electrical circuit that has a voltage source 26, a signal source 28, a first electrical contact 30, and a second electrical contact 32, all of which are operably connected to one another and with the swellable sensor material 24. Suitable voltage sources include any device or system for producing an electromotive force or deriving a secondary voltage from a primary source of the electromotive force. Suitable signal sources include an alarm that sounds or an LED display that changes color upon the change from a first property value to a second, different property value when the sensor material changes from an unswollen to a swollen state. Suitable first and second electrical contacts include electrodes capable of transporting a charge to and/or from the voltage source. The first and second electrical contacts can be made of any known conductive material (*e.g.*, a metal or metal alloy), and have any desired 2-dimensional or 3-dimensional shape (*e.g.*, discrete lines, pads, planes, spheres, cylinders, *etc.*).

[0072] In the embodiment shown in Figs. 3A and B, the property modifier 34 is a conductive polymer, such as polyaniline, for detecting a change in the electrical conductivity of the sensor material. As shown in Fig. 3A, the close proximity of the polyaniline polymers in the sensor material 24 in the unswollen state provides conductive pathways through the swellable sensor material when the sensor material is unswollen. However, as shown in Fig. 3B, the pathways are disrupted when the sensor material swells, thus changing the electrical conductivity of the sensor material from a first property value to a second, property value when the sensor material is swollen, the change being indicated by the signal source 28.

[0073] In one example of the present invention, the detector is used to detect the presence of a sorbate, such as hexane, in a stream of water. A preferred embodiment of a device useful for detecting a sorbate in a stream of water has a housing having a perforated portion, (not shown) a voltage source 26, a signal source 28, for example an LED display, and first and second electrical contacts 30 and 32, all of which are operably connected to one another. When placed in a stream, the swellable sensor material remains unswollen for so long as there is no sorbate in the stream entering the sensor device through the perforated housing. In this non-swollen state, electricity continuously flows through the swellable sensor material. However, when hexane is present in the stream and comes into contact with the swellable material, the sensor material becomes swollen and the distance between the polyaniline polymers increases thereby decreasing the electrical conductivity of the sensor material. As a result, the electrical circuit is disrupted causing the LED display to display a color signal indicating the presence of hexane in the stream.

[0074] The following examples are for the purpose of illustration only and are not intended to limit the scope of the claims, which are appended hereto.

Example 1

Addition of an Electrically-Conductive Polymer to a Swellable Sol-Gel Derived Composition Powder

[0075] Osorb® swellable sol-gel derived composition was blended with polyaniline (emeraldine salt) in a mixed dispersion of 1:5 polyaniline:sol-gel derived composition

weight ratio in THF. Visible light microscopy indicated that a bulk of the polyaniline was not dissolved into the swellable sol-gel derived composition and, rather, coated the outside surface of the sol-gel particles. The mixture was then dried to produce a sensor material.

[0076] The non-swollen (dry) sensor material was conductive, having a conductivity of $3 \times 10^{-3} \text{ S}\cdot\text{m}$. However, as the sensor material swelled, there was a greater than 200 times drop in its conductivity.

Example 2

Addition of a Chromatic Material Property Modifier to a Swellable Sol-Gel Derived Composition

[0077] Reichardt's dye solution was prepared by dissolving 2 mg of the Reichardt's dye in 20 mL of ethanol. The resultant solution was added to Osorb® swellable sol-gel derived composition to fully swell the composition. The solvent was then evaporated, leaving the dye entrapped within the organosilica matrix. The color of the dye changed as the sensor material swelled upon absorption of different sorbates, including methanol, toluene, acetonitrile, and hexane different polarity.

Example 3

Addition of an Electrically-Conductive Metallic Powder to a Swellable Sol-Gel Derived Composition Pellet

[0078] Copper powder (200 mesh) and Osorb® swellable sol-gel derived composition powder, in a 10:1 portion by mass, were mixed together in a ball mill (30Hz). 0.1 g of the resulting composite powder was poured into a 13mm diameter cylindrical anvil press, manufactured by International Crystal Laboratories, Garfield New Jersey, and compressed with 8 tonnes of force by a hydraulic jack to produce a sensor pellet. As the Osorb component expands upon absorption of compounds the internal network of metal particle contacts is broken leading to an decrease in conductivity (inncrease in resistance) across the sensor pellet.

[0079] The sensor pellet was was clamped to two electrodes, and the resistance across the pellet was measured as it was exposed to a mixture of 50% toluene vapor 50% dry air. The resistance of the sensor pellet increased with exposure, by $2M\Omega$ (10^6 ohm).

Example 4

Formation of an Electrically-Conductive Metallic Film on a Swellable Sol-Gel Derived Composition Pellet

[0080] An Osorb® swellable sol-gel derived composition pellet was formed by pouring a sol-gel solution into a silicone mold before gellation. The Osorb® then gelled in the mold, and a cylindrical pellet approximately 1/8" in diameter and 1/8" long was produced. A 10nm thick platinum film was then deposited on the pellet using a sputter coater.

[0081] The thus coated sensor pellet was then placed over two electrodes in such a way that the coating was barely in contact with the electrodes resulting in high contact resistance, about $250k\Omega$. A backstop was used to hold the pellet in place. The sensor pellet was then contacted with a mixture of approximately 50% toluene vapor and 50% hydrocarbon-free air. When the pellet absorbed the toluene and expanded, it pushed against the plastic and forced itself into better contact with the electrodes, causing the resistance between the electrodes and film to diminish to about $11k\Omega$. When the pellet was exposed to hydrocarbon-free air only, the toluene evaporated out of the pellet which then shrank, and the contact resistance between the electrodes and thin film increased. This process was reversible and repeatable.

Example 5

Electical Switched Formed with a Swellable Sol-Gel Derived Composition Pellet having an Electrically-Conductive Metallic Film

[0082] An Osorb® swellable sol-gel derived composition pellet was formed as described in Example 4. The Osorb® pellet was placed on a electrically conductive third class lever and held in place with a backstop. The Osorb® pellet was then contacted with a

mixture of approximately 50% toluene vapor and 50% hydrocarbon-free air. When the Osorb® pellet absorbed the toluene vapor and expanded, it pushed against the plastic and forced the lever into contact with an electrode, closing an electrical switch. The closed switch completed a circuit and turned on a LED. In this way single pole single throw (SPST) and single pole double throw (SPDT) switches can be operated with swellable sol-gel derived composition pellets.

[0083] From the above description of the invention, those skilled in the art will perceive improvements, changes and modifications. For example, one skilled in the art will appreciate that other agents and materials, such as charged organic polymers (e.g., polyethyleneimine) and/or organosilica nanoparticles having different surface chemistries can be included in the sensor material to facilitate detection of sorbates. Such improvements, changes, and modifications are within the skill of the art and are intended to be covered by the appended claims.

I claim:

1. A sensor material for detecting a sorbate, the sensor material comprising:
a swellable, sol-gel derived composition having a porous matrix, the sol-gel derived composition swellable to at least 1.5 times its volume in a sorbate, and
a property modifier intermixed with at least a portion of the porous matrix, the sensor material swellable in the presence of the sorbate to be detected and the sensor material having a first property value when unswollen and a second property value when swollen, the first value property different than the second property value.
2. The sensor material of claim 1, wherein the first property value and second property value are each an electrical conductivity value, an optical value, a mechanical value or a chemical value of the sensor material.
3. The sensor material of claim 1, wherein the first property value is a first electrical conductivity value and the second property value is a second electrical conductivity value.
4. The sensor material of claim 3, wherein the property modifier is an electrically conductive polymer, a plurality of nanowires, carbon black, carbon nanotubes or metallic particles.
5. The sensor material of claim 4, wherein the property modifier is an electrically conductive polymer selected from substituted and unsubstituted polyanilines, polyparaphenylenes, polyazines, polyparapheylenevinylenes, polythiophenes, polyfurans, polypyrroles, polyselenophenes, polyisothianaphthenes, polyphenylene sulfides, polyacetylenes, polypyridylvinylenes or combinations thereof.
6. The sensor material of claim 3, wherein the property modifier is a plurality of nanowires selected from metallic nanowires, semiconducting nanowires, or graphite nanowires.

7. The sensor material of claim 3, wherein the property modifier is present in the sensor material in an amount of at least about 5% w/w.

8. The sensor material of claim 6, further comprising an electrically-insulative material.

9. The sensor material of claim 8, wherein the electrically-insulative material is acrylonitrile, butadiene, styrene, acetate resins, acrylic resins, beryllium oxide, ceramics, acetal resins, epoxy/fiberglass resins, glass, a polyimide films, fluoropolymers, polycarbonate resins, melamine resins laminated with woven glass, mica, neoprene, aromatic polyamide, resin, nylon, polyethylene terephthalate, copolyester resins, phenolic resins, polyolefins, polystyrene, polyurethane, polyvinylchloride, silicone, teflon, polysulfone, polyetherimide, polyamideimide or polyphenylene.

10. The sensor material of claim 1 wherein, the first property value is a first value for a chromatic property and the second property value is a second value for a chromatic property.

11. The sensor material of claim 10, wherein the property modifier is Reichardt's dye.

12. The sensor material of claim 10, wherein the property modifier is present in the sensor material in an amount from about 0.001% w/w to about 1% w/w.

13. The sensor material of claim 10, wherein the property modifier is present in the sensor material in an amount from about 0.01% w/w to about 0.1% w/w.

14. The sensor material of claim 1, where the sensor material is a powder or a pellet.

15. The sensor material of claim 14, wherein the sensor material is a pellet and the sensor material further comprises a binder.

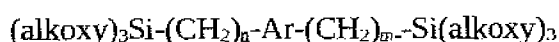
16. The sensor material of claim 15, wherein the binder is microcrystalline cellulose or an elastomeric polymer having a glass transition temperature below about 150 C.

17. The sensor material of claim 16, wherein the binder is present in an amount of at least 50% based on the weight of the sensor material.

18. The sensor material of claim 16, wherein the binder is present in an amount of at least 95% based on the weight of the sensor material.

19. A sensor material for detecting a sorbate, the sensor material comprising:
a swellable, aromatically-bridged, organosiloxane sol-gel derived composition, containing a plurality of alkyl siloxy substituents, the swellable, aromatically-bridged, organosiloxane sol-gel derived composition having a porous matrix and
a property modifier intermixed with at least a portion of the porous matrix, the sensor material having a first property value when unswollen and a second property value when swollen, the first value property different than the second property value.

20. The sensor material of claim 19, wherein the swellable, aromatically-bridged, organosiloxane sol-gel derived composition is derived from a trialkoxysilane corresponding to the formula:

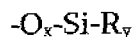


where n and m are individually an integer from 1 to 8, Ar is a single-, fused-, or poly-aromatic ring, and each alkoxy is independently a C₁ to C₅ alkoxy.

21. The sensor material of claim 20, wherein the trialkoxysilane is a bis(trialkoxysilylalkyl)benzene.

22. The sensor material of claim 19, wherein the bis(trialkoxysilylalkyl)benzene is 1,4-bis(trimethoxysilylmethyl)benzene or bis(triethoxysilylethyl)benzene.

23. The sensor material of claim 19, wherein the alkyl siloxy substituents correspond to the formula:



where R is independently a hydrocarbon containing up to about 30 carbons, x is 1 or 2, y is 2 or 3 and the total of x and y is 4.

24. The sensor material of claim 23, wherein the alkyl siloxy substituents include at least one heteroatom selected from sulfur, oxygen, nitrogen, phosphorous or halogen atoms or combinations thereof.

25. The sensor material of claim 19, wherein the first property value and second property value are each an electrical conductivity value, an optical value, a mechanical value or a chemical value of the sensor material.

26. The sensor material of claim 25, wherein the first property value is a first electrical conductivity value and the second property value is a second electrical conductivity value.

27. The sensor material of claim 26, wherein the property modifier is an electrically conductive polymer, a plurality of nanowires, carbon black, carbon nanotubes or metallic particles.

28. The sensor material of claim 27, wherein the property modifier is an electrically conductive polymer selected from substituted and unsubstituted polyanilines, polyparaphenylenes, polyazines, polyparapheylenevinylenes, polythiophenes (e.g., poly(3,4-ethylenedioxythiophene)), polyfurans, polypyrroles, polyselenophenes, polyisothianaphenes, polyphenylene sulfides, polyacetylenes, polypyridylvinylenes or combinations thereof.

29. The sensor material of claim 27, wherein the property modifier is a plurality of nanowires selected from metallic nanowires, semiconducting nanowires or graphite nanowires.

30. The sensor material of claim 27, wherein the property modifier is present in the sensor material in an amount at least about 5% w/w.

31. The sensor material of claim 27, further comprising an electrically-insulative material.

32. The sensor material of claim 31, wherein the electrically-insulative material is acrylonitrile, butadiene, styrene, acetate resins, acrylic resins, beryllium oxide, ceramics, acetal resins, epoxy/fiberglass resins, glass, a polyimide films, fluoropolymers, polycarbonate resins, melamine resins laminated with woven glass, mica, neoprene, aromatic polyamide, resin, nylon, polyethylene terephthalate, copolyester resins, phenolic resins, polyolefins, polystyrene, polyurethane, polyvinylchloride, silicone, teflon, polysulfone, polyetherimide, polyamideimide or polyphenylene.

33. The sensor material of claim 19, wherein the first property value is a first value for a chromatic property and the second property value is a second value for a chromatic property.

34. The sensor material of claim 33, wherein the property modifier is Reichardt's dye.

35. The sensor material of claim 33, wherein the property modifier is present in the sensor material in an amount from about 0.001% w/w to about 1% w/w.

36. The sensor material of claim 33, wherein the property modifier is present in the sensor material in an amount from about 0.01% w/w to about 0.1% w/w.

37. The sensor material of claim 19, wherein the sensor material is a powder or a pellet.

38. The sensor material of claim 19, further comprising a binder.

39. The sensor material of claim 38, wherein the binder is microcrystalline cellulose or an elastomeric polymer having a glass transition temperature below about 150 C.

40. The sensor material of claim 38, wherein the binder is present in an amount of at least 50% based on the weight of the sensor material.

41. A method for determining the presence of a sorbate, the method comprising the steps of:

contacting a sensor material with the sorbate,

the sensor material comprising:

a porous, swellable sol-gel derived composition, the porous swellable sol-gel derived composition swellable to at least 1.5 times its volume in the presence of the sorbate and

a property modifier intermixed with at least a portion of the porous matrix, the sensor material having a first property value when unswollen and a second property value when swollen, the first value property different than the second property value and then

detecting any change in the property value of the sensor material, a change in the property value indicating the presence of a sorbate in a sample.

42. The method of claim 41, wherein the first property value and second property value are each an electrical conductivity value, an optical value, a mechanical value or a chemical value of the sensor material.

43. The method of claim 42, wherein the first property value is a first electrical conductivity value and the second property value is a second electrical conductivity value.

44. The method of claim 43, wherein the property modifier is an electrically conductive polymer, a plurality of nanowires, carbon black, carbon nanotubes or metallic particles.

45. The method of claim 44, wherein the property modifier is an electrically conductive polymer selected from substituted and unsubstituted polyanilines, polyparaphenylenes, polyazines, polyparaphenylenevinylenes, polythiophenes (e.g., poly(3,4-ethylenedioxythiophene), polyfurans, polypyrroles, polyselenophenes, polyisothianaphenes, polyphenylene sulfides, polyacetylenes, polypyridylvinylenes or combinations thereof.

46. The method of claim 44, wherein the property modifier is a plurality of nanowires selected from metallic nanowires, semiconducting nanowires or graphite nanowires.

47. The method of claim 43, wherein the property modifier is present in the sensor material in an amount at least about 5% w/w.

48. The method of claim 44, further comprising an electrically-insulative material.

49. The method of claim 48, wherein the electrically-insulative material is acrylonitrile, butadiene, styrene, acetate resins, acrylic resins, beryllium oxide, ceramics, acetal resins, epoxy/fiberglass resins, glass, a polyimide films, fluoropolymers, polycarbonate resins, melamine resins laminated with woven glass, mica, neoprene, aromatic polyamide, resin, nylon, polyethylene terephthalate, copolyester resins, phenolic resins, polyolefins, polystyrene, polyurethane, polyvinylchloride, silicone, teflon, polysulfone, polyetherimide, polyamideimide or polyphenylene.

50. The method of claim 42, wherein the first property value is a first value for a chromatic property and the second property value is a second value for a chromatic property.

51. The method of claim 50, wherein the property modifier is Reichardt's dye.

52. The method of claim 41, wherein the sensor material is a powder or a pellet.

53. The method of claim 41, wherein the sensor material is a pellet and the sensor material further comprises a binder.

54. The method of claim of claim 53, wherein the binder is microcrystalline cellulose or an elastomeric polymer having a glass transition temperature below about 150 C.

55. The method of claim 53, wherein the binder is present in an amount of at least 50% based on the weight of the sensor material.

56. The method of claim 41, wherein the sorbate has a Snyder Index of ≤ 6.5 .

57. The method of claim 41, wherein the sorbate is dissolved in an aqueous solution.

58. The method of claim 57, wherein the sorbate has a $\log k_{ow} > -0.32$.

59. The method of claim 57, wherein the sorbate has a $\log k_{ow} > 1.25$.

60. The method of claim 58, wherein the sorbate has a molecular weight less than 1,000,000.

61. The method of claim 59, wherein the sorbate has a molecular weight less than 2,000.

62. The method of claim 41, wherein the sorbate is an alkyl hydrocarbon, an aromatic hydrocarbon, a chlorinated hydrocarbon, an alcohol, an ether, an aldehyde, an epoxide, a ketone, an organic acid or acetonitrile.

63. The method of claim 62, wherein the sorbate is hexane, cyclohexane, octane, benzene, toluene, xylene, naphthalene, nitrobenzene, dichloromethane, trichloroethylene, perchloroethylene, dichloroethylene, vinyl chloride, a polychlorinated biphenyl, methanol, ethanol, phenol, m-nitrophenol, acetone, a naphthol or methyl-t-butyl.

64. The method of claim 62, wherein the sorbate is atrazine, 2,4-dichlorophenoxyacetic acid, malathion, dichlorodiphenyltrichloroethane, trinitrotoluene, 1,3,5-trinitroperhydro-1,3,5-triazine or triacetone triperoxide.

65. A method for determining the presence of a sorbate, the method comprising the steps of:

contacting a sensor material with the sample,

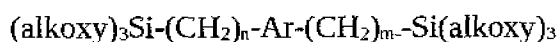
the sensor material comprising:

a swellable, aromatically-bridged, organosiloxane sol-gel derived composition, containing a plurality of alkyl siloxy substituents, the swellable, aromatically-bridged, organosiloxane sol-gel derived composition having a porous matrix and

a property modifier intermixed with at least a portion of the porous matrix, the sensor material having a first property value when unswollen and a second property value when swollen, the first value property different than the second property value and then

detecting any change in the property value of the sensor material, a change in the property value indicating the presence of a sorbate in a sample.

66. The method of claim 65, wherein the swellable, aromatically- bridged, organosiloxane sol-gel derived composition is derived from a trialkoxysilane corresponding to the formula:

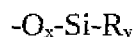


where n and m are individually an integer from 1 to 8, Ar is a single-, fused-, or poly-aromatic ring, and each alkoxy is independently a C₁ to C₅ alkoxy.

67. The method of claim 66, wherein the trialkoxysilane is a bis(trialkoxysilylalkyl)benzene.

68. The method of claim 67, wherein the bis(trialkoxysilylalkyl)benzene is 1,4-bis(trimethoxysilylmethyl)benzene or bis(triethoxysilylethyl)benzene.

69. The method of claim 65, wherein the alkyl siloxy substituents correspond to the formula:



where R is independently a hydrocarbon containing up to about 30 carbons, x is 1 or 2, y is 2 or 3 and the total of x and y is 4.

70. The method of claim of claim 69, wherein the alkyl siloxy substituents include at least one heteroatom selected from sulfur, oxygen, nitrogen, phosphorous, halogen atoms or combinations thereof.

71. The method of claim 65, wherein the first property value and second property value are each an electrical conductivity value, an optical value, a mechanical value or a chemical value of the sensor material.

72. The method of claim 71, wherein the first property value is a first electrical conductivity value and the second property value is a second electrical conductivity value.

73. The method of claim 72, wherein the property modifier is an electrically conductive polymer, a plurality of nanowires, carbon black, carbon nanotubes or metallic particles.

74. The method of claim 73, wherein the property modifier is an electrically conductive polymer selected from substituted and unsubstituted polyanilines, polyparaphenylenes, polyazines, polyparaphylenevinyls, polythiophenes, polyfurans, polypyrroles, polyselenophenes, polyisothianaphenes, polyphenylene sulfides, polyacetylenes, polypyridylvinyls or combinations thereof.

75. The method of claim 73, wherein the property modifier is a plurality of nanowires selected from metallic nanowires, semiconducting nanowires or graphite nanowires.

76. The method of claim 72, wherein the property modifier is present in the sensor material in an amount at least about 5% w/w.

77. The method of claim 73, further comprising an electrically-insulative material.

78. The method of claim 77, wherein the electrically-insulative material is acrylonitrile, butadiene, styrene, acetate resins, acrylic resins, beryllium oxide, ceramics, acetal resins, epoxy/fiberglass resins, glass, a polyimide films, fluoropolymers, polycarbonate resins, melamine resins laminated with woven glass, mica, neoprene, aromatic polyamide, resin, nylon, polyethylene terephthalate, copolyester resins, phenolic resins, polyolefins, polystyrene, polyurethane, polyvinylchloride, silicone, teflon, polysulfone, polyetherimide, polyamideimide or polyphenylene.

79. The method of claim 65, wherein the first property value is a first value for a chromatic property and the second property value is a second value for a chromatic property.

80. The method of claim 79, wherein the property modifier is Reichardt's dye.

81. The method of claim 65, wherein the sensor material is a powder or a pellet.

82. The method of claim 81, wherein the sensor material is a pellet and the sensor material further comprises a binder.

83. The method of claim of claim 81, wherein the binder is microcrystalline cellulose or an elastomeric polymer having a glass transition temperature below about 150 C.

84. The method of claim 82, wherein the binder is present in an amount of at least 50% based on the weight of the sensor material.

85. The method of claim 65, wherein the sample contains a neat sorbate and the sorbate has a Snyder Index of ≤ 6.5 .

86. The method of claim, 65 wherein the sorbate is dissolved in an aqueous solution.

87. The method of claim 86, wherein the sorbate has a $\log k_{ow} > -0.32$.

88. The method of claim 86, wherein the sorbate has a $\log k_{ow} > 1.25$.

89. The method of claim 87, wherein the sorbate has a molecular weight less than 1,000,000.

90. The method of claim 87, wherein the sorbate has a molecular weight less than 2,000.

91. The method of claim 65 wherein the sorbate is an alkyl hydrocarbon, an aromatic hydrocarbon, a chlorinated hydrocarbon, an alcohol, an ether, an aldehyde, an epoxide, a ketone, an organic acid or acetonitrile.

92. The method of claim 91, wherein the sorbate is hexane, cyclohexane, octane, benzene, toluene, xylene, naphthalene, nitrobenzene, dichloromethane, trichloroethylene, perchloroethylene, dichloroethylene, vinyl chloride, a polychlorinated biphenyl, methanol, ethanol, phenol, m-nitrophenol, acetone, a naphthol or methyl-t-butyl.

93. The method of claim 65, wherein the sorbate is atrazine, 2,4-dichlorophenoxyacetic acid, malathion, dichlorodiphenyltrichloroethane, trinitrotoluene, 1,3,5-Trinitroperhydro-1,3,5-triazine or triacetone triperoxide.

94. A swellable material comprising:
a swellable, sol-gel derived composition having a porous matrix, the sol-gel derived composition swellable to at least 1.5 times its volume in a sorbate, and a binder.

95. The swellable material of claim 94, wherein the swellable material is in the form of a powder or a pellet.

96. The swellable material of claim 95, wherein the binder is microcrystalline cellulose or an elastomeric polymer having a glass transition temperature below about 150 C.

97. The swellable material of claim 96, wherein the binder is present in an amount of at least 50% based on the weight of the sensor material.

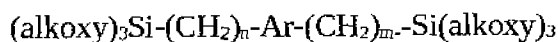
98. The swellable material of claim 96, wherein the binder is present in an amount of at least 5% based on the weight of the sensor material.

99. The swellable material of claim 96, wherein the binder is present in an amount of at least 0.5% based on the weight of the sensor material.

100. A swellable material for detecting a sorbate, the sensor material comprising:

a swellable, aromatically-bridged, organosiloxane sol-gel derived composition, containing a plurality of alkyl siloxy substituents, the swellable, aromatically-bridged, organosiloxane sol-gel derived composition having a porous matrix and a binder.

101. The swellable material of claim 100, wherein the swellable, aromatically-bridged, organosiloxane sol-gel derived composition is derived from a trialkoxysilane corresponding to the formula:

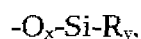


where n and m are individually an integer from 1 to 8, Ar is a single-, fused-, or poly-aromatic ring, and each alkoxy is independently a C₁ to C₅ alkoxy.

102. The swellable material of claim 101, wherein the trialkoxysilane is a bis(trialkoxysilylalkyl)benzene.

103. The swellable material of claim 100, wherein the bis(trialkoxysilylalkyl)benzene is 1,4-bis(trimethoxysilylmethyl)benzene or bis(triethoxysilylethyl)benzene.

104. The swellable material of claim 100, wherein the alkyl siloxy substituents correspond to the formula:



where R is independently a hydrocarbon containing up to about 30 carbons, x is 1 or 2, y is 2 or 3 and the total of x and y is 4.

105. The swellable material of claim 104, wherein the alkyl siloxy substituents include at least one heteroatom selected from sulfur, oxygen, nitrogen, phosphorous, halogen atoms or combinations thereof.

106. The swellable material of claim 104, wherein the swellable material is in the form of a powder or a pellet.

107. The swellable material of claim 106, wherein the binder is microcrystalline cellulose or an elastomeric polymer having a glass transition temperature below about 150 C.

108. The swellable material of claim 107, wherein the binder is present in an amount of at least 50% based on the weight of the sensor material.

109. The swellable material of claim 107, wherein the binder is present in an amount of at least 5% based on the weight of the sensor material.

110. The swellable material of claim 97, wherein the binder is present in an amount of at least 0.5% based on the weight of the sensor material.

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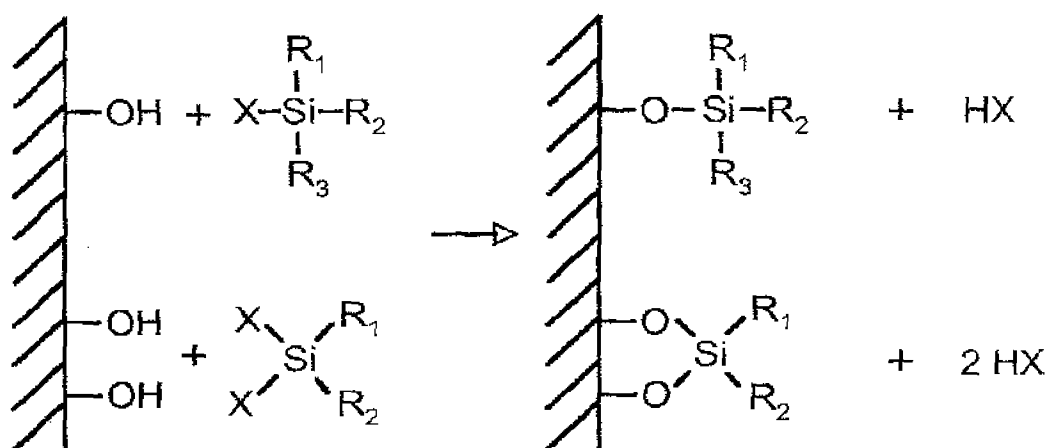


FIG. 1

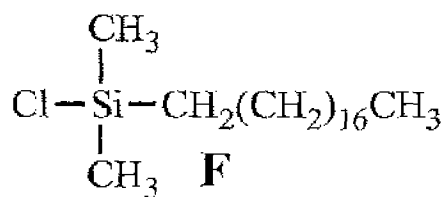
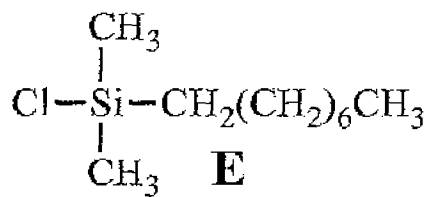
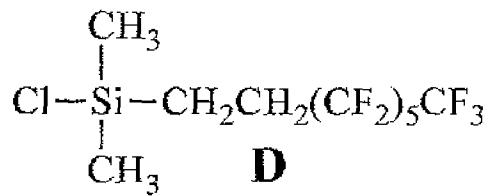
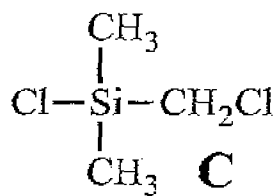
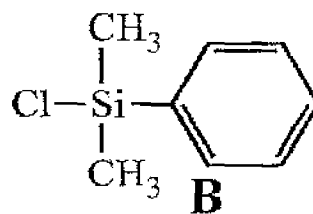
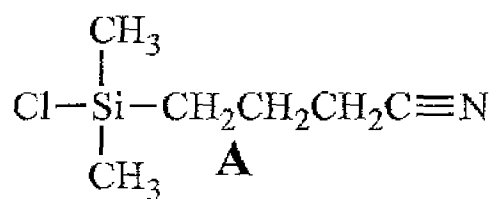


FIG. 2

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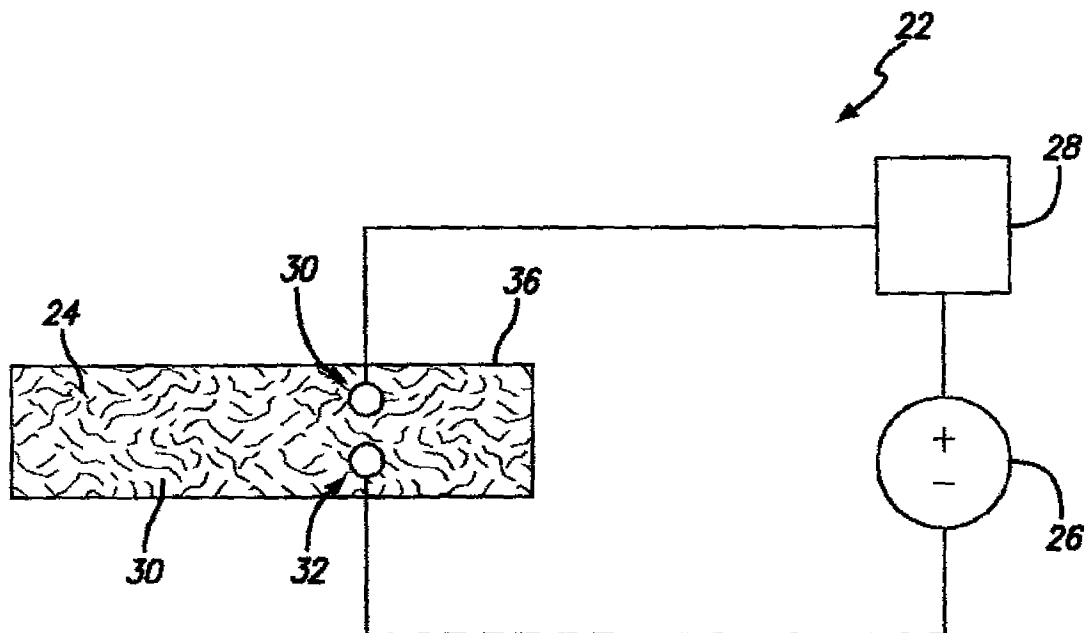


FIG. 3A

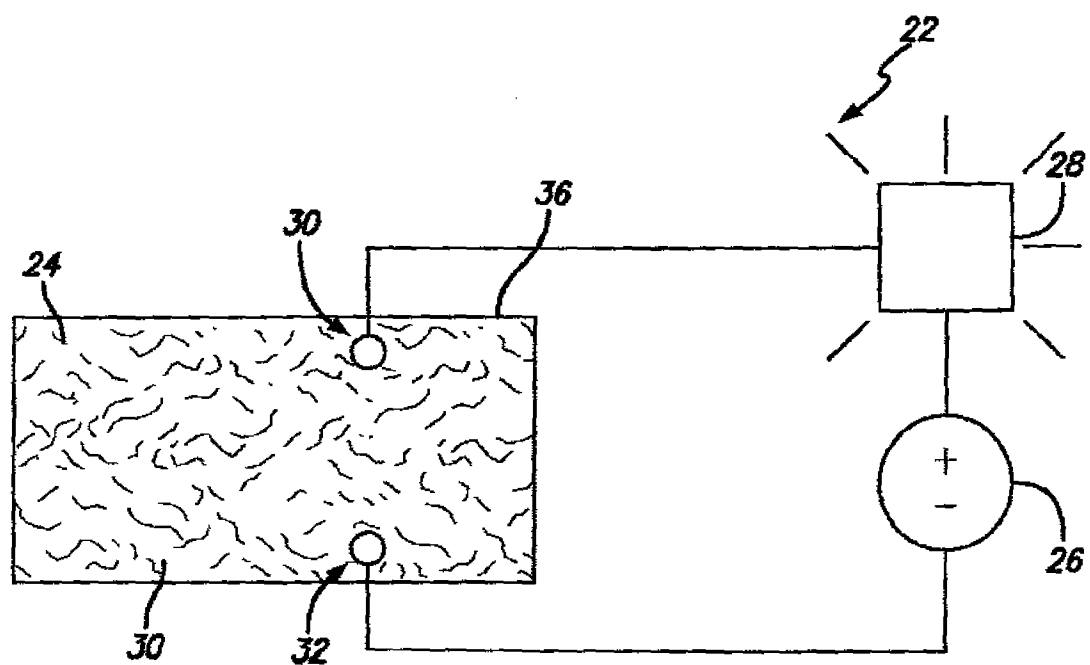


FIG. 3B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/020562

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/12 C08G77/48 B01J20/28
ADD.

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)

G01N C08G B01J

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007/112242 A1 (EDMISTON PAUL L [US]) 17 May 2007 (2007-05-17) paragraph [0026] - paragraph [0028] paragraph [0044] - paragraph [0045] -----	1-110
Y	US 2006/292033 A1 (BLOK EDWARD J [US] ET AL) 28 December 2006 (2006-12-28) paragraph [0004] - paragraph [0009] paragraph [0030] - paragraph [0036] figures ----- -/-	1-110



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

17 May 2011

Date of mailing of the international search report

23/05/2011

Name and mailing address of the ISA/

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Authorized officer

Savage, John

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/020562

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>ZOU ET AL: "Glucose biosensor based on electrodeposition of platinum nanoparticles onto carbon nanotubes and immobilizing enzyme with chitosan-SiO₂ sol-gel", BIOSENSORS AND BIOELECTRONICS, ELSEVIER BV, NL, vol. 23, no. 7, 25 October 2007 (2007-10-25), pages 1010-1016, XP022440004, ISSN: 0956-5663, DOI: DOI:10.1016/J.PHYSC.2007.11.010 the whole document -----</p>	1-110

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/020562

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007112242 A1	17-05-2007	US 2010254856 A1	07-10-2010
US 2006292033 A1	28-12-2006	NONE	