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(54) **LIGHT-EMITTING MATERIALS FOR ELECTROLUMINESCENT DEVICES**

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(57) **ABSTRACT**

The present invention concerns an electroluminescent device that comprises an anode and cathode separated by intermittent layers or crystal comprising an assembly of oligo atomic metal clusters confined in molecular sieve capable of emitting electromagnetic radiation of one or more colours when a voltage is applied over the device.

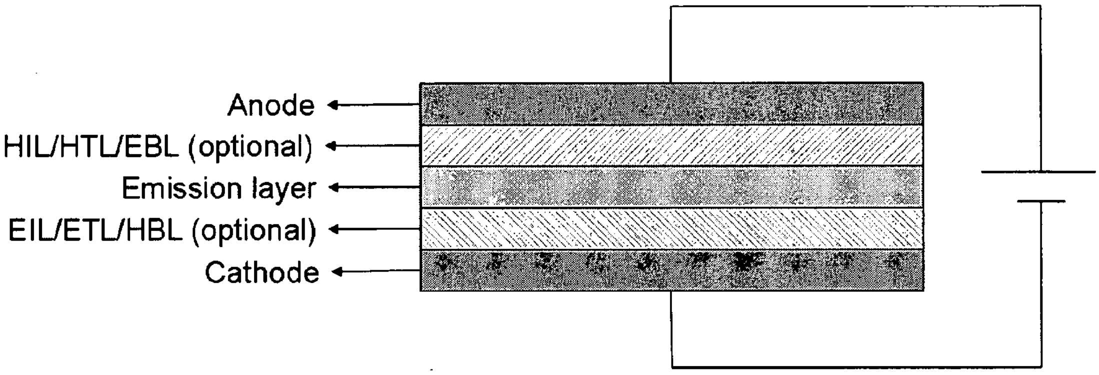


Figure 1.

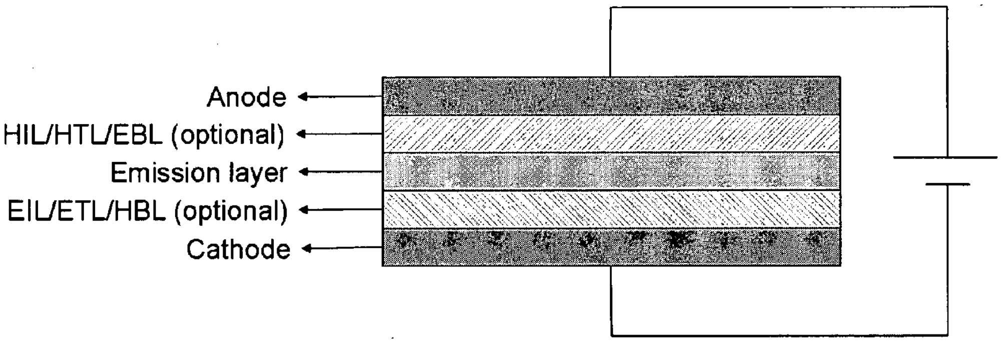


Figure 2

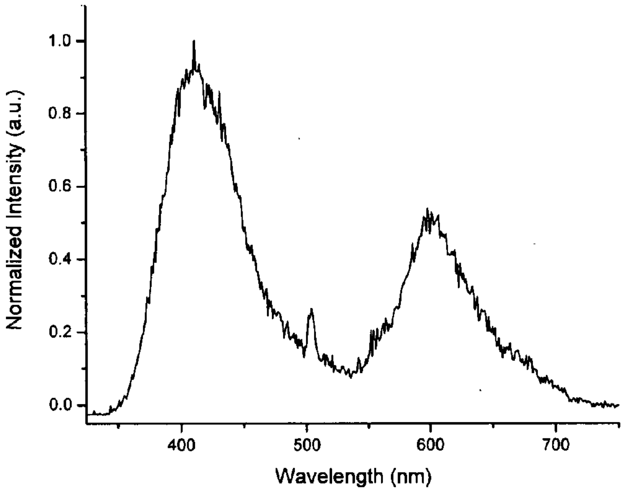
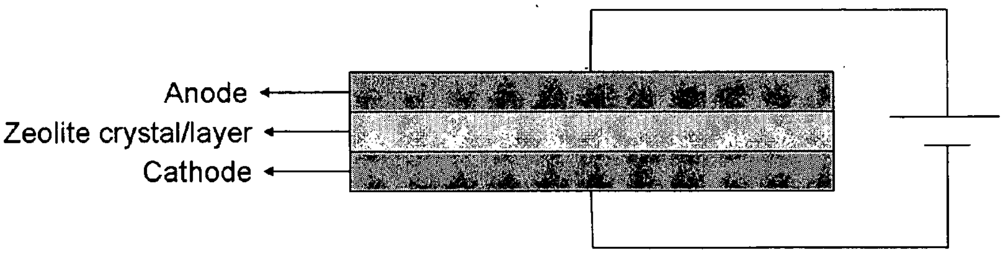


Figure 3:



LIGHT-EMITTING MATERIALS FOR ELECTROLUMINESCENT DEVICES

FIELD OF THE INVENTION

[0001] The present invention relates generally to white light and colored light emission using confined metal atomic clusters, preferably silicium, silver, copper and gold, and more particularly to the use of molecular sieves comprising oligo atomic silver clusters as luminescent materials for electroluminescence based lighting and display applications.

BACKGROUND OF THE INVENTION

[0002] The present invention concerns emissive material of confined metal oligo atomic clusters in molecular sieves, for instance zeolites, used in the emissive layer of organic light emitting devices (OLED) and light emitting diodes (LED).

[0003] LED's have been around since the 1960's and have known a constant evolution, the latest developments being bright blue and white LED's. These LED's require high purity semiconductor material which usually entail high production costs. Emission of coloured LED's generally consists of narrow-spectrum light of a predefined wavelength dependant on the material used, making it difficult to tune the emission colour. The present invention provides an alternative for the current semiconductor materials at lower production cost and greater ease of tuning the emission spectrum of the LED.

[0004] OLED's are a far more recent innovation and have known an increasing interest as an alternative to current display (e.g. plasma, LCD) and lighting (e.g. fluorescent lamps) technologies because of the numerous advantages they offer, such as: low production cost, ease of manufacture, wide viewing angle, high efficiency, possibility of flexible displays, high contrast, large area, . . . However, it's development has been curbed by several factors. One of the most challenging problems is the limited lifetime of the organic materials used in the fabrication of OLED's. During the first experiments with OLED's the emission intensity halved after only 100 hours of operation (Ref Tang, C. W., Van Slyke, S. A., *Appl. Phys. Lett.,* 1987, 51, 913). Nowadays (extrapolated) lifetimes of more then 20.000 hours at 400 cd/m^2 have been reported (Ref: *Cambridge Display Technologies*, Press release, Jun. 9, 2006). Although this is sufficient for displays; lighting applications require a luminance of at least 1000 cd/m^2, resulting in far lower lifetimes. The most important causes of degradation are oxygen and moisture, therefore OLED's need to be properly sealed from the surrounding atmosphere. The use of air stable compounds can mean a strong reduction of production cost and time, and an increase in operation lifetime.

[0005] All OLED's and LED's are based on the same basic principle: one or more layers of organic or inorganic semiconductors are sandwiched between two electrodes. An electric field is applied over this layer(s) causing electrons and holes to be injected in the layer(s) from the cathode and anode. These charges recombine in the semiconductor creating an excited state. The excited state then relax back to a non-excited state by emitting a photon. The wavelength of the emitted light therefore depends on the properties of the recombination centre.

[0006] Present invention proposes the use of metal oligo atomic clusters as recombination centre. In contrast to bulk metals which are devoid of a band gap, small metal oligo atomic clusters display interesting emissive properties from discrete energy levels. This phenomenon has been demonstrated e.g., for silver smaller than 100 atoms in rare gas matrices, in aqueous solutions and on silver oxide films. Quantum chemical calculations confirm the molecular character and discrete energy states of these small silver clusters. (Ref 1. Johnston, R. L. (2002) *Atomic and Molecular Clusters* (Taylor & Francis, London and New York); Rabin, I., Schulze, W., Ertl, G., Felix, C., Sieber, C., Harbich, W., & Buttet, J. (2000) *Chemical Physics Letters* 320, 59-64; Peyser, L. A., Vinson, A. E., Bartko, A. P., & Dickson, R. M. (2001) *Science* 291, 103-106; Lee, T. -H., Gonzalez, J. I., & Dickson, R. M. (2002) *Proc. Natl. Acad. Sci. USA* 99, 10272-10275; Lee, T. H., Gonzalez, J. I., Zheng, J., & Dickson, R. M. (2005) *Accounts of Chemical Research* 38, 534-541; Bonacic-Koutecky, V., Mitric, R., Burgel, C., Noack, H., Hartmann, M., & Pittner, J. (2005) *European Physical Journal D* 34, 113-118; Lee, T. -H., Hladik, C. R., & Dickson, R. M. (2003) *Nano Letters* 3, 1561-1564; Rabin, I., Schulze, W., & Ertl, G. (1999) *Chemical Physics Letters* 312, 394-398; Felix, C., Sieber, C., Harbich, W., Buttet, J., Rabin, I., Schulze, W., & Ertl, G. (1999) *Chemical Physics Letters* 313, 105-109; Rabin, I., Schulze, W., & Ertl, G. (1998) *Crystal Research and Technology* 33, 1075-1084; Rabin, I., Schulze, W., & Ertl, G. (1998) *Journal of Chemical Physics* 108, 5137-5142; Konig, L., Rabin, I., Schulze, W., & Ertl, G. (1996) *Science* 274, 1353-1355; Zheng, J. & Dickson, R. M. (2002) *Journal of the American Chemical Society* 124, 13982-13983; Bonacic'-Koutecky, V., Veyret, V., & Mitric', R. (2001) *Journal of Chemical Physics* 115, 10450-10460; Bonacic-Koutecky, V., Pittner, J., Boiron, M., & Fantucci, P. (1999) *Journal of Chemical Physics* 110, 3876; Bonacic'-Koutecky, V., Cespiva, L., Fantucci, P., & Koutecky, J. (1993) *Journal of Chemical Physics* 98, 7981-7994; Yoon, J., Kim, K. S., & Baeck, K. K. (2000) *Journal of Chemical Physics* 112, 9335-9342; Fedrigo, S., Harbich, W., & Buttet, J. (1993) *Journal of Chemical Physics* 99, 5712-5717.

[0007] The major problem in the study and creation of small metal oligo atomic clusters is aggregation to large nanoparticles and eventually to bulk metal, with loss of emission. Here, it is demonstrated that the use of porous structures with limited pore, cavity and channel sizes, overcomes the aggregation problem enabling emissive entities, which are stable in time.

[0008] The materials of present invention, for instance zeolites containing oligo silver atom clusters exhibit remarkable stability, based on absorbance measurements in mordonites. (Ref Bogdanchikova, N. E., Petranovskii, V. P., Machorro, R., Sugi, Y., Soto, V. M., & Fuentes, S. (1999) *Applied Surface Science* 150, 58-64) Bogdanchikova et al. found that the stability of the silver clusters depends on the acid strength, which may be related to the composition, e.g., the SiO_2/Al_2O_3 molar ratio, of the molecular sieves. Silver clusters in mordenites having weak acidic sites are stable for at least 50 months, a sufficiently long period with respect to the applications in mind for use in a visible light source. Disappearance of the clusters was linked to oxidation. Reduction of the clusters or an oxygen-free or -poor device obviously can increase the stability even more. In the present invention, metal oligo atomic clusters are protected from oxidation due to encapsulation in the molecular sieves. Additionally, if necessary, an external coating of the material crystals or capping of the pore entrances can be used to further protect the occluded metal clusters.

[0009] Silver clusters in molecular sieves are cheap and non toxic. Zeolites are currently used in large quantities in washing powder and silver despite its antimicrobial properties, has no known toxic effect on human tissue. Colloidal silver has for instance widely been marketed as a dietary supplement for protective activity against oxidative stress and reactive oxygen species formation.

[0010] In recent years, expertise has been gained in the synthesis of zeolites with desired properties by the choice of the structure directing agent (SDA), control of the synthesis conditions, and post-synthesis treatments. (Ref van Bekkum, H., Flanigen, E. M., Jacobs, P. A., Jansen, J. C. (editors) *Introduction to Zeolite Science and Practice, 2nd edition. Studies in Surface Science and Catalysis,* 2001, 137; Corma, A., *Chem. Rev.,* 1997, 97, 2373-2419; Davis, M. E., *Nature,* 2002, 417, 813-821; Davis, M. E., et al., *Chem. Mater.,* 1992, 4, 756-768; de Moor P -P. E. A. et al., *Chem. Eur. J.,* 1999, 5(7J, 2083-2088; Galo, J de A. A., et al., *Chem. Rev.,* 2002, 102, 4093-4138) At the same time, the family of ordered mesoporous materials has been greatly expanded by the use of different surfactants and synthesis conditions. (Ref Corma, A., *Chem. Rev.,* 1997, 97, 2373-2419; Davis, M. E., *Nature,* 2002, 417, 813-821; Galo, J. de A. A., et al., *Chem. Rev.,* 2002, 102, 4093-4138; Ying, J. Y., et al., *Angew. Chem. Int. Ed.,* 1999, 3S, 56-77) The use of the appropriate template enables the control of the pore size, distribution and connectivity during the zeolite synthesis. For example, use of surfactants such as cetyltrimethylammonium bromide or dodecyltrimethylammonium bromide generally results in formation of mesoporous materials. In a preferred embodiment, the molecular sieves are one or more selected from the group consisting of mordenite, ZSM-5, A-zeolite, L-zeolite, faujasite, ferrierite, chabazite type of zeolites, and mixtures of the foregoing zeolites.

[0011] The use of stable inorganic metal nanoclusters as dopant is a further improvement, as degradation will be negligible with these inorganic systems. In summary, the current state of the art has never suggested or demonstrated the conversion of an electric current to visible light, by oligo atomic metal clusters embedded in molecular sieves.

[0012] Present invention concerns the field of lighting devices, and related, comprising e.g., white light and colored luminescent materials with emission of visible white or colored light. Such devices thus comprise luminescent materials for electroluminescence based lighting generated through the action of confined metal oligo atomic clusters, more particularly oligo atomic silver clusters loaded in molecular sieves (e.g., LTA zeolites, Linde Type A zeolites).

SUMMARY OF THE INVENTION

[0013] The present invention solves problems of the related art by providing highly stable electroluminescent materials for use in display and lighting technologies.

[0014] In accordance with the purpose of the invention, as embodied and broadly described herein, the invention is broadly drawn to an illuminating device comprising one or more layers containing an electroluminescent (EL) material in contact with an anode and cathode. The anode and cathode are electrically isolated from one and other. If an electrical field or voltage is applied over the anode and cathode, the EL material will emit electromagnetic radiation. In accordance with the purpose of the invention, the invention comprises an assembly of small clusters of the noble metals of the group consisting of gold, silver, copper, platinum, palladium, silicium, rhodium, nickel, iridium and cobalt preferably Au and/or Ag clusters confined in molecular sieves, preferably zeolites, as EL material.

[0015] Under voltage such EL material can emit an electromagnetic radiation for instance in the ultraviolet to visible and infrared region of the electromagnetic spectrum. The preferred voltage to activate the EL material to emit electromagnetic radiation is a voltage of 0.05 to 100 volt, more preferably 0.1 to 50 volt, yet more preferably 0.2 to 25 volt, yet more preferably 0.5 to 15 volt and most preferably 1 to 10 volt.

[0016] The molecular sieves doped with metal clusters can be dispersed in a getter material or deposited as a single layer, or even a single crystal, between the anode and cathode. The getter material can consist of one or more conducting or non-conducting polymers or small molecule compounds. A conducting getter material can be used to achieve higher efficiency by facilitating charge transport to the metal clusters.

[0017] The illumination system can be used for the generation of white light and or specific colored light and at a predetermined color temperature.

[0018] The clusters in the illumination system of present invention are oligo atomic clusters of 1-100 atoms. The molecular sieves in this invention are selected from the group consisting of zeolites, porous oxides, silicoaluminophosphates, aluminophosphates, gallophosphates, zincophophates, titanosilicates and aluminosilicates, or mixtures thereof. In a particular embodiment of present invention the molecular sieves of present invention are selected from among large pore zeolites from the group consisting of MCM-22, ferrierite, faujastites X and Y. The molecular sieves in another embodiment of present invention are materials selected from the group consisting of zeolite 3A, Zeolite 13X, Zeolite 4A, Zeolite 5A and ZKF.

[0019] In a particular embodiment of present invention the pores of the molecular sieves containing the small clusters of, e.g., Au and/or Ag are coated with a matrix, or are closed by stopper molecules.

[0020] The light system of present invention does not require the presence of charge compensating anions, such as oxalate, hydroxide, azide, carbonate, bicarbonate, sulfate, sulfite, chlorate, perchlorate, acetate and formate to be in charge association with the noble metals, such as the small metal clusters.

[0021] Further scope of applicability of the present invention becomes apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DETAILED DESCRIPTION

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0022] An "OLED" is a light-emitting device that can emit light, having a wavelength in the visual range, if an electric current is passed through the device. It comprises one or more layers, which can have the role of charge transport, blocking or emission layer, positioned between 2 electrodes.

[0023] An "LED" is a light-emitting device that can emit light, having a wavelength in the visual range, if an electric current is passed through the device. It comprises a crystal of EL material positioned between 2 electrodes.

[0024] Oligo atomic metal clusters include clusters ranging from 1 to 100 atoms of the following metals (sub nanometer size), Si, Cu, Ag, Au, Ni, Pd, Pt, Rh, Co and Ir or alloys thereof such as Ag/Cu, Au/Ni etc. The clusters can be neutral, positive or negatively charged. The oligo atomic metal clusters can be small oligo atomic silver- (and/or gold) molecules containing 1 to 100 atoms.

[0025] The articles "a" and "an" are used herein to refer to one or more than one (i.e., at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

[0026] The terms "comprise" and "comprising" are used in the inclusive, open sense, meaning that additional elements may be included.

[0027] The term "including" is used to mean "including but not limited to". "Including" and "including but not limited to" are used interchangeably.

[0028] The term "in particular" is used to mean "in particular but not limited to". And the term "particularly" is used to mean "particularly but not limited to"

[0029] The term "zeolite" also refers to a group, or any member of a group, of structured aluminosilicate minerals comprising cations such as sodium and calcium or, less commonly, barium, beryllium, lithium, potassium, magnesium and strontium; characterized by the ratio (Al+Si): O=approximately 1:2, an open tetrahedral framework structure capable of ion exchange, and loosely held water molecules, that allow reversible dehydration. The term "zeolite" also includes "zeolite-related materials" or "zeotypes" which are prepared by replacing Si^{4+} or Al^{3+} with other elements as in the case of aluminophosphates (e.g., MeAPO, SAPO, ElAPO, MeAPSO, and ElAPS0), gallophosphates, zincophophates, titanosilicates, etc. The zeolite can be a crystalline porous material with a frame work as described in Pure Appl. Chem., Vol. 73, No. 2, pp. 381-394,© 2001 IUPAC or provided in the Zeolite Framework Types database of the IZA structure commission where under the following structure types, as defined by the International Zeolite Association such as ABW type, ACO type, AEI type, AEL type, AEN type, AET type, AFG AFI type, AFN type, AFO type, AFR type, AFS type, AFT type, AFX type, AFY type, AHT type, ANA type, APC type, APD type, AST type, ASV type, ATN type, ATO type, ATS type, ATT type, ATV type, AWO type, AWW type, BCT type, *BEA type, BEC type, BIK type, BOG type, BPH type, BRE type, CAN type, CAS type, CDO type, CFI type, CGF type, CGS type, CHA type, —CHI type, —CLO type, CON type, CZP type, DAC type, DDR type, DFO type, DFT type, DOH type, DON type, EAB type, EDI type, EMT type, EON type, EPI type, ERI type, ESV type, ETR type, EUO type, EZT type, FAR type, FAU type, FER type, FRA type, GIS type, GIU type, GME type, GON type, GOO type, HEU type, IFR type, IHW type, IMF type, ISV type, ITE type, ITH type, ITW type, IWR type, IWV type, IWW type, JBW type, KFI type, LAU type, LEV type, LIO type, -LIT type, LOS type, LOV type, LTA type, LTL type, LTN type, MAR type, MAZ type, MEI type, MEL type, MEP type, MER type, MFI type, MFS type, MON type, MOR type, MOZ type, MSE type, MSO type, MTF type, MTN type, MTT type, MTW type, MWW type, NAB type, NAT type, NES type, NON type, NPO type, NSI type, OBW type, OFF type, OSI type, OSO type, OWE type, —PAR type, PAU type, PHI type, PON type, RHO type, —RON type, RRO type, RSN type, RTE type, RTH type, RUT type, RWR type, RWY type, SAO type, SAS type, SAT type, SAV type, SBE type, SBN type, SBS type, SBT type, SFE type, SFF type, SFG type, SFH type, SFN type, SFO type, SGT type, SIV type, SOD type, SOS type, SSF type, SSY type, STF type, STI type, *STO type, STT type, SZR type, TER type, THO type, TOL type, TON type, TSC type, TUN type, UEI type, UFI type, UOZ type, USI type, UTL type, VET type, VFI type, VNI type, VSV type, WEI type, —WEN type, YUG type and ZON type. The term "zeolite" also includes "zeolite-related materials" or "zeotypes" which are prepared by replacing Si4+ or A13+ with other elements as in the case of aluminophosphates (e.g., MeAPO, AlPO, SAPO, ElAPO, MeAPSO, and ElAPSO), gallophosphates, zincophophates, titanosilicates, etc.

[0030] The term "molecular sieves" as used herein refers to a solid with pores of the size of molecules. It includes, but is not limited to microporous and mesoporous materials. In the nomenclature of the molecular sieves the pore size of <20 Amstrong (Å) is considered microporous and 20-500 Å is considered mesoporous.

[0031] The term "microporous carrier" as used herein refers to a solid with pores the size of molecules. It includes but is not limited to microporous materials, ALPOs and (synthetic) zeolites, pillared or non-pillared clays, carbon molecular sieves, microporous titanosilicates such as ETS-10, microporous oxides. Microporous carriers can have multimodal pore size distribution, also referred to as ordered ultramicropores (typically less than 0.7 nm) and supermicropores (typically in the range of about 0.7-2 nm). A particular type of microporous carriers envisaged within the present invention, are the molecular sieve zeolites. Zeolites are the aluminosilicate members of the family of microporous carriers. The pore size of molecular sieves can further be influenced by the nature of the templating molecules in the synthesis. The addition of swelling agents to the synthesis mixture can further affect the pore size of the resulting molecular sieve. Zeolites with different pore size have been well characterized and described by Martin David Foster in "Computational Studies of the Topologies and Properties of Zeolites", The Royal Institution of Great Britain, Department of Chemistry, University College London, a thesis submitted for the degree of Doctor of Philosophy, London, January 2003.

[0032] A comprehensive list of the abbreviations utilized by organic chemists of ordinary skill in the art appears in the first issue of each volume of the Journal of Organic Chemistry; this list is typically presented in a table entitled Standard List of Abbreviations.

[0033] For purposes of this invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 67th Ed., 1986-87, inside cover. [Contemplated equivalents of the zeolitic structures, subunits and other compositions described above include such materials which otherwise correspond thereto, and which have the same general properties thereof (e.g., biocompatible), wherein one or more simple [variations of substituents are made which do not adversely affect the efficacy of such molecule to achieve its intended purpose. In general, the compounds of the present invention may be prepared by the methods illustrated in the general reaction schemes as, for [example, described below, or by modifications thereof, using readily available starting materials, reagents and conventional synthesis procedures. In these reactions, it is also possible to make use of variants which are in themselves known, but are not mentioned here.

[0034] a. "the molecular sieve matrix is selected from among microporous materials, selected from among zeolites, porous oxides, silicoaluminophosphates and aluminosilicates"

[0035] b. "zeolite selected from among the family of small pore sized zeolites such as zeolite A and ZKF, and combinations thereof"

[0036] c. "large pore zeolites such as ZSM-5, MCM-22, ferrierite, faujastites X and Y and microporous molecular sieves"

[0037] d. "The matrix can also be a molecular sieve selected from among molecular sieves MCM-41, MCM-48, HSM, SBA-15, and combinations thereof"

[0038] e. "Methods are available in the art for preparation of microporous zeolites."

[0039] f. "As used herein, microporous zeolites preferably have a pore size of about 3 angstroms to about 14 angstroms"

[0040] The term microporous materials also include amorphous microporous solids. Alternative amorphous microporous solids can be used for present invent. For instance amorphous microporous mixed oxides having, in dried form, a narrow pore size distribution (half width <±10% of the pore diameter) of micropores with diameters in the range of <3 nm and the preparation of said amorphous microporous mixed oxides have been well described in U.S. Pat. No. 6,121,187 and others have been well documented in WO0144308, U.S. Pat. No. 6,753,287, U.S. Pat. No. 6,85,5304, U.S. Pat. No. 6,977,237, WO2005097679, U.S. Pat. No. 7,055,756 and U.S. Pat. No. 7,132,093" Several documents are cited throughout the text of this specification. Each of the documents herein (including any manufacturer's specifications, instructions etc.) are hereby incorporated by reference; however, there is no admission that any document cited is indeed prior art of the present invention.

[0041] The oligo atomic metal clusters confined in molecular sieves or microporous structures can be incorporated in membranes or films for instance by embedding in transparent matrix materials such as silicone, epoxy, adhesives, polymethylmethacrylate, polycarbonate. Moreover the molecular sieves or the ordered comprising oligo atomic silver clusters of present invention can be incorporated in paints or fluids of film formers for coating on surface surfaces. Media (paints, gelling liquids, elastomers) are available and methods of manufacturing to achieve such membranes or films, for instance a filled elastomeric polymer, which comprise the oligo-atomic metal clusters confined in molecular sieves or in ordered porous oxides (microporous or mesoporous or mixed mesoporous/microporous) or porous materials with nanometer dimension (**0**.**3**-**10** nm) windows, channels and cavity architectures. Typical but not exclusive examples of such elastomeric polymers are polydimethylsiloxane (silicone rubber), polyisobutene (butyl rubber), polybutadiene, polychloroprene, polyisoprene, styrene-butadiene rubber, acrylonitrile-butadiene rubber (NBR), ethene-propene-diene-rubber (EPDM) and acrylonitrile-butadiene-styrene(ABS). Such films or membranes of the molecular sieves comprising oligo atomic silver clusters; ordered mesoporous and/or microporous oxides comprising oligo atomic silver clusters or porous materials with nanometer dimension (e.g. 0.3-10 nm) windows, channels and cavity architectures comprising oligo atomic silver clusters can be coated on a substrate. Following the ASTM (American Society for Testing and Materials) standards, 'elastomers' are defined as "macromolecular materials that return to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress". Elastomers are sometimes also referred to as 'rubbery materials'. A 'rubber' is defined as "a material that is capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent, such as benzene, toluene, methyl ethyl ketone, and ethanol/toluene azeotrope".

[0042] In the preparation of membranes with the oligo atomic metal clusters confined in the microporous structures, the microporous structures are first dispersed in an appropriate solvent. An appropriate solvent is a solvent of low ionic strength, for instance an ionic strength of a value in the range of 1 mmol/L to 0.05 mol/L, and should be able to dissolve the elastomer as well, or at least, should be partially miscible with the solvent in which the membrane forming polymer is dissolved. To improve the dispersion, ultrasonic wave treatment, high speed mixing, modification reactions, can be applied. The content of porous structures with oligo atomic metal clusters confined therein and polymer, in the dispersion, may range from 1 wt % to 80 wt %, preferably 20 wt % to 60 wt %. The dispersion is stirred for a certain time to allow (polymer/filler) interactions to establish, to improve dispersion and possibly to let a chemical reaction take place. When appropriate, the dispersion can be heated or sonicated.

[0043] The metal clusters in microporous materials are in molecular sieves or microporous structures, may be incorporated in paints or printing inks (e.g. printable matrix printing ink or printable paints, varnishes (e.g. overprinting varnishes) and paints for depositing, spraying, printing or painting a layer or a coating on a substrate. Printing inks or paints of the art which are suitable for comprising the emitting materials of present invention are for instance hard resins, colophony-modified phenol resins, maleate resins, hydrogenated mineral oil cuts, synthetic aromatic oils, alkyd resins in particular hydrocarbon resins and/or a colophony resin ester and dialkyl ether such as di-n-dodecyl ether, di-n-undecyl ether, allyl-n-octyl ether, n-hexyl-n-undecyl ether as a vehicle. Particular suitable solvents are the resin(s) water-insoluble fatty acid esters of polyvalent alcohols or ethinols. Suitable printing inks in the art are described in U.S. Pat. No. 4,028,291, U.S. Pat. No. 4,169,821, U.S. Pat. No. 4,196,033, U.S. Pat. No. 4,253,397, U.S. Pat. No. 4,262,936, U.S. Pat. No. 4,357,164, U.S. Pat. No. 5,075,699, U.S. Pat. No. 5,286,287, U.S. Pat. No. 5,431,721, U.S. Pat. No. 5,886,066, U.S. Pat. No. 5,891,943, U.S. Pat. No. 6,613,813 and U.S. Pat. No. 5,965,633. Such emitting material of present invention may be painted, printed or coated on the substrate.

[0044] Solvent casting or coating is used as the membrane preparation process.

[0045] A particular method of coating is solution-depositing of the molecular sieves comprising oligo atomic silver clusters comprises spray-coating, dip-casting, drop-casting, evaporating, blade-casting, or spin-coating the molecular sieves comprising oligo atomic silver clusters; ordered mesoporous and/or microporous oxides comprising oligo atomic silver clusters or porous materials with nanometer dimension (e.g. 0.3-10 nm) windows, channels and cavity architectures with an assembly of oligo atomic metal clusters confined in such structures (hereinafter the porous structures with oligo atomic metal clusters confined therein) onto a substrate.

[0046] The (polymer/porous structures with oligo atomic metal clusters confined therein) dispersion can be cast on a non-porous support from which it is released afterwards to form a self-supporting film. One way tot realise this is by soaking it previously with a solvent, which has a low affinity for the dispersion. Also, the support can be treated with adhesion promoters.

[0047] After casting or coating, the solvent is evaporated and, if necessary, a heat treatment can be applied to finish the cross-linking reactions. The heat treatment can possibly occur under vacuum conditions to remove the remaining solvent. The resulting supported membranes be a filled elastomer with the thickness of this selective layer in a range from 0.01 μm to 500 μm, preferably from 0.1 to 250 μm and yet more preferably from 10 to 150 μm.

[0048] The most important elastomers are polyisoprene (natural or synthetic rubber (IR)), polychloroprene (chloroprene rubber (CR)), butyl rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), ethene-propene-diene-rubber (EPDM), acrylonitrile-butadiene-styrene (ABS), chlorosulfonated polyethylene (CSM), I polyacrylate (polyacrylic rubber), polyurethane elastomers, polydimethylsiloxane (PDMS, sometimes more generally referred to as silicone rubber), fluorosilicones and polysulfides. Polystyrene is a thermoplastic polymer that particularly resistant to irradiation.

[0049] The films with the porous structures of present invention may need particular characteristics according to its environment of use. A variety of alternatives polymers that provide design freedom which preparation protocols are available in the art to design complex shapes, to consolidate parts into fewer components, simplify production, to produce transparent and precolored components, to reduce part weight, to reduce noise when the porous structures with oligo atomic metal clusters is moving, to have a reliable performance at elevated temperature, to have chemical resistance in harsh climates, to have the desired stiffness, strength and toughness, to have hydrolytic stability over time, to have electrical properties to have a desired physical appearance.

[0050] Polymers that are suitable for incorporation of the porous structures of present invention are for instance Spire™ family of ultra polymers such as 1) KetaSpire® polyetheretherketone (PEEK) which is easy-to-mold ultra polymer offering outstanding chemical resistance and mechanical performance up to 300° C. (570° F.) or AvaSpire® modified PEEK, a PEEK-based formulations or 2) PrimoSpire® self-reinforced polyphenylene (SRP) known to be designable in a very stiff, strong unreinforced polymer with a remarkable combination of surface hardness, chemical resistance and inherent flame-retardant properties or 3) EpiSpire™, an high-temperature sulfone (HTS) known to be a transparent amorphous polymer with excellent creep resistance at temperatures up to 265° C. (510° F.) or 4) Torlon® polyamide-imide (PAI) with higher strength and stiffness that most thermoplastic up to 275° C. (525° F.) combined with superior resistance to chemicals, creep and wear. Other polymers that are suitable for incorporation of the porous structures with oligo atomic metal clusters confined therein of present invention are the family of amorphous sulfone polymers such as 1) Udel® PSU known to be designable into tough, transparent plastic with exceptional chemical resistance, good hydrolytic stability and an HDT of 345° F. (174° C.) or the 2) Mindel® modified polysulfone with superior electrical properties or 3) the Radel® R (PPSU) known to deliver a super-tough transparent plastic with an HDT of 405° F. (207° C.), excellent chemical resistance and the unique ability to be steam sterilized without significant loss of properties or 4) the Radel® A (PES) know to deliver a transparent plastic with a high HDT of 400° F. (204° C.) and good chemical resistance or the Acudel® modified PPSU. Other polymers that are suitable for incorporation of the porous structures with oligo atomic metal clusters confined therein of present invention are for instance the semi-crystalline aromatic polyamides such as for instance the Amodel® polyphthalamide (PPA) known to deliver a high-temperature nylon with exceptional mechanical properties, an HDT of 535° F. (280° C.), excellent chemical resistance and low moisture uptake or the Ixef® polyarylamide (PA MXD6) known to deliver aesthetic, structural specialty nylon that combines outstanding stiffness with exceptional surface appearance, plus low and slow water uptake, and great flow properties. Other polymers that are suitable for incorporation of the porous structures with oligo atomic metal clusters confined therein of present invention are for instance semi-crystalline polymers such as the Primef® polyphenylene sulfide (PPS) which delivers a high-flow, structural plastic with good temperature and chemical resistance as well as inherent flame retardant properties or the Xydar® liquid crystal polymer (LCP) known to deliver high-flow, high-temperature plastic with an HDT of 570° F. (300° C.), and extremely high chemical resistance. These are available with design and processing guides form Solvay Advanced Polymers.

[0051] A particular example of manufacturing emitting film based on the porous structures oligo atomic metal clusters confined therein of present invention and a polymer is for instance the use of polydimethylsiloxane (PDMS), RTV-615 A and B (density 1.02 g/ml) and the adhesion promoter (SS 4155) which are obtainable from General Electric Corp. (USA). Component A is a prepolymer with vinyl groups. Component B has hydride groups and acts as cross-linker and EPDM (Keltan 578 from DSM) and porous structures with oligo atomic metal clusters confined therein of present invention which are well dried before use.

[0052] Such can be produced by preparing dispersing a powder of the porous structures with oligo atomic metal clusters confined therein of present invention (for instance a zeolite comprising oligo atomic silver clusters) in hexane adding the cross-linker (RTV 615 B) to the dispersion of porous structures with oligo atomic metal clusters confined therein of present invention and stirring this this mixture at 40° C. for two hours to allow sufficient time to establish strong interactions between both phases. Adding the prepolymer (RTV 615 A) and stirring the mixture for another hour at 60° C. to induce prepolymerisation. Pouring the (PDMS/ZSM-5 CBV 3002) in a petri dish and allowing the solvent to evaporate for several hours and the resulting film was cured at 100° C. The content of the solid components (i.e. PDMS and filler) in the casting solution was 18.5 wt %. The RTV 615 A/B ratio for optimal polymer curing was 7 in order compensate for the loss of hydride groups due to their reaction with the surface silanol groups on the zeolite (normally it is in a 10/1 ratio, as proposed by the manufacturer to be the ratio for optimal curing).

[0053] For flexible substrates thermoplastics (e.g., Polyethylene naphthalate (PEN), Polyethersulfone (PES), Polycarbonate (PC), Polyethylene terephthalate (PET), Polypropylene (PP), oriented polypropylene (OPP), etc.), and glass (e.g., borosilicate) substrates may be used for these applications. Low liquidus temperature material, which typically has a low liquidus temperature (or in specific embodiments a low glass transition temperature can be used form a barrier layer on a flexible substrate and can be can be deposited onto the flexible substrate by, for example, sputtering, co-evaporation, laser ablation, flash evaporation, spraying, pouring, frit-deposition, vapor-deposition, dip-coating, painting or rolling, spin-coating, or any combination thereof. The porous structures with oligo atomic metal clusters confined therein can be incorporated into the low liquidus temperature materials. Such low liquidus temperature material includes, but is not limited to, tin fluorophosphate glass, chalcogenide glass, tellurite glass and borate glass.

Examples

Example 1

Preparation of the Emissive Materials

[0054] Various methods for the production of metal ion exchanged molecular sieves are available in the art. A method similar as described by Jacobs et al. (Jacobs, P. A. & Uytterhoeven, J. B., 1979, Journal of the Chemical Society-Faraday Transactions I 75, 56-64) was used for incorporating silver ions in molecular sieves and creating silver clusters. However lots of parameters like loading percentage of the zeolites, exchange time, length of temperature treatment, initial, gradient and final temperature of the temperature treatment, presence of gasses during the temperature treatment (e.g. in vacuum, in presence of oxygen, in presence of oxygen and nitrogen, in presence of hydrogen, in presence of CO and/or CO_2 gas) and the presence of moisture in the air influences the finally formed types of clusters, oxidation state of the clusters and distribution and polydispersity of the types of clusters formed.

Example 2

Emission

[0055] It was demonstrated that metal cluster especially silver in confined molecular sieves have a distinct and tunable emission throughout the VIS and NIR part of the electromagnetic spectrum. Thanks to the host matrix the confined metal clusters are prevented from aggregation with each other to form bigger non emissive nanoparticles. Also they can be shielded from the outside environment (e.g. oxygen) if required by adding a silicon coating around the molecular sieves.

Example 3

Modified OLED Building Scheme

[0056] The molecular sieve materials and mixtures thereof can be used as emissive material in OLED's either as dopant in a matrix layer or as a pure layer. This layer then emits visible (white) light. The materials now currently used in OLED's as dopants in the emission layer can be replaced by the present invention; molecular sieves containing metal clusters. FIG. **1** shows a schematic drawing of a possible design. By mixing metal cluster containing molecular sieves with different sized clusters, a variety of spectral properties can be generated. By changing the ratios of the mixed materials a whole range of light colors can be generated, including white light. If one however wants light of a particular color, one can select molecular sieves with uniform sized metal clusters.

[0057] For the preparation of an OLED a 3A zeolite was exchanged with silver (10% weight) and then thermally treated (24 hours at 450° C.) resulting in a partial reduction and formation of small silver clusters in the host matrix. 0.4 mg of these silver loaded zeolites were added to 1 ml of a 20 mg/ml PVK (poly-N-vinylcarbazole) in chlorobenzene solution. From this solution a film was spincoated on a ITO covered glass substrate. Ytterbium was then evaporated through a patterning mask on the spincoated film as a second electrode. After applying an electric field over this device, in which ITO functioned as anode and ytterbium as cathode, red electroluminescence was observed. The emission spectrum of this electroluminescence is shown in FIG. **2**. The synthesis of the oligo metal clusters with the desired emissive properties can be tuned by changing the synthesis parameters.

Example 4

Modified LED Building Scheme

[0058] A LED can be constructed by placing a single zeolite crystal or layer loaded with metal clusters in between two electrodes as shown in FIG. **3**. This material can provide considerable advantages for white LED's in reference to the current state of the art by making it possible to generate an emission spectrum similar to that of black body emission. Currently the white emission is mostly realized by a blue emitter surrounded by a yellow emitting phosphor. The resulting emission approaches white, but gives a rather cold and grey impression due to the fact that the emission spectrum consists of two emission spikes rather then a broad band. By using a zeolite crystal loaded with metal clusters of different sizes, it is possible to generate an emission which covers the whole visual range. Using zeolite crystals with metal clusters of the same size, single color LED's can be made as well.

Example 5

Modified Organic Lasers

[0059] Electrically pumped organic lasers as yet have not been realized. One of the reasons for this is the high current densities necessary for lasing at which most organic materials disintegrate and device breakdown occurs. The inorganic system proposed here will provide an interesting alternative due to its higher stability at high current densities. The structure of such a laser system will be comparable to that of an OLED with the major difference being the presence of a lasing cavity in which the emission layer will be present. Such a cavity can simply be the space between anode and cathode, where one of the two will be highly reflective and the other will allow a small percentage of the light to be transmitted while the rest will reflect back in the cavity.

DRAWING DESCRIPTION

BRIEF DESCRIPTION OF THE DRAWINGS

[0060] The present invention will become more fully understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

[0061] FIG. **1**: Scheme of an OLED containing several layers. The basic structure consists of the anode, cathode and emission layer. Other layers to facilitate or optimize the device such as a hole blocking (HBL), electron injecting (EIL), electron transport (ETL), hole injecting (HIL), hole transporting (HTL) or electron blocking layer (EBL) can be added to optimize the efficiency. In the device presented here the emission layer can consist of a pure metal cluster loaded zeolite film or a dispersion of metal cluster loaded zeolites in a polymer or low molecular matrix.

[0062] FIG. **2**: Emission spectrum of the detected electroluminescence of the OLED presented in example **3**. PVK emission band is centered around 425 nm, oligo metal cluster emission is centered around 600 nm.

[0063] FIG. **3**: Scheme of a LED containing a crystal or layer of microporous oligo metal clusters containing material, contacted by two electrodes.

1-15. (canceled)

16. A light-emitting device comprising: an anode, a cathode and at least one layer or crystal comprising an assembly of oligo atomic metal clusters confined in microporous molecular sieves, the metal clusters being capable of emitting electromagnetic radiation in response to an electrical voltage applied through the anode and cathode, wherein said microporous molecular sieves are selected from the group consisting of zeolites, porous oxides, silicoaluminophosphates, aluminophosphates, gallophosphates, zincophosphates, titanosilicates and aluminosilicates, or mixtures thereof.

17. The light-emitting device according to claim **16**, wherein the anode, the cathode and the layers in between the electrodes comprising the electroluminescent (EL) material comprise layers on a substantially transparent substrate.

18. The light-emitting device according to claim **16**, wherein the anode or cathode is transparent or partially transparent.

19. The light-emitting device according to claim **16** wherein one single crystal of molecular sieves comprising an assembly of oligo atomic metal clusters is disposed in between an anode and cathode.

20. The light-emitting device according to claim **16**, wherein the emission layer comprises an assembly of oligo atomic metal clusters confined in molecular sieves dispersed in a conductive polymer.

21. The light-emitting device according to claim **16**, wherein the emission layer comprises an assembly of oligo atomic metal clusters confined in molecular sieves dispersed in a non-conductive polymer.

22. The light-emitting device according to claim **16**, wherein the emission layer comprises a deposited layer of an assembly of oligo atomic metal clusters confined in molecular sieves.

23. The light-emitting device according to claim **16**, wherein the device is encapsulated from the surrounding atmosphere.

24. The light-emitting device according to claim **16**, wherein the emission layer is part of a cavity in order to achieve lasing.

25. The light-emitting device according to claim **16** used for the generation of white light and or specific colored light.

26. The light-emitting device according to claim **16** comprising an assembly of different small Au and/or Ag clusters confined in one or a combination of multiple molecular sieves to create light at a predetermined color temperature.

27. The light-emitting device according to claim **16**, wherein the molecular sieves are selected from among microporous materials selected from the group consisting of zeolites, porous oxides, silicoaluminophosphates and aluminosilicates.

28. The light-emitting device according to claim **16**, wherein the molecular sieves are zeolites selected from the small pore zeolites among zeolite A like materials such as zeolite 3A, Zeolite 13X, Zeolite 4A and Zeolite 5A, and ZKF, and combinations thereof.

29. The light-emitting device according to claim **16**, wherein the molecular sieves are large pore zeolites selected from the group consisting of Mordenite, ZSM-5, MCM-22, Ferrierite, Faujasites X and Y.

30. The light-emitting device according to claim **16**, wherein the pores of the molecular sieves containing the small clusters of Au and/or Ag are coated with a coating matrix.

* * * * *

专利名称(译)	用于电致发光器件的发光材料		
公开(公告)号	US20100194265A1	公开(公告)日	2010-08-05
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[标]申请(专利权)人(译)	天主教鲁汶大学		
申请(专利权)人(译)	鲁汶大学		
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摘要(译)

本发明涉及一种电致发光器件，其包括由间歇层或晶体隔开的阳极和阴极，所述晶体包括限制在分子筛中的低聚原子金属簇的组件，当在器件上施加电压时能够发射一种或多种颜色的电磁辐射。