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(54) **Title:** METHOD OF FABRICATING POROUS OLED SUBSTRATE FOR EXTRACTION

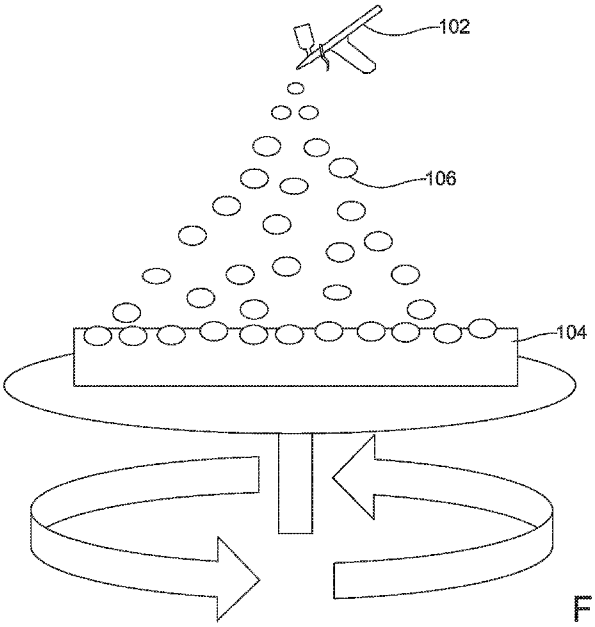

FIG. 1

(57) **Abstract:** Organic light emitting diodes (OLEDs) include: (i) a substrate including polycarbonate having a plurality of pores randomly disposed on the surface thereof; (ii) an anode layer, said anode disposed adjacent to said substrate; (iii) a phosphor layer disposed on the anode layer; and (iv) a cathode layer disposed on said phosphor layer. Methods of making the same are also described.

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METHOD OF FABRICATING POROUS OLED SUBSTRATE FOR EXTRACTION

TECHNICAL FIELD

[0001] The disclosure concerns porous substrates useful in organic light emitting diodes.

BACKGROUND

[0002] Currently, nearly 100% internal quantum efficiency in convention organic light emitting diodes (OLEDs) has been demonstrated by using phosphorescent emitting materials. However, the external quantum efficiency in conventional OLEDs is still limited due to at least surface plasmon resonance on the cathode and total internal reflection (TIR) by the difference of the refractive index at the glass substrate/air and indium tin oxide (ITO)/substrate interfaces. For at least these reasons, the light out-coupling efficiency for the OLEDs with a flat glass substrate or flexible plastic substrate is limited to about 20%. Many methods have attempted to enhance light out-coupling from OLEDs, including surface roughness scatter, photonic crystals, microlens arrays, microcavity structure and so on. In the case of microlens and photonic crystals, they have a wavelength dependency which leads to a difference of light intensity according to the viewing angle because of their periodic ordered surface pattern. However, the methods for fabricating the microlens and photonic crystal involve complicated fabrication process such as photolithography, etching, and imprinting. Moreover, additional process steps such as lamination to be applied to OLED substrate may be required. Microactivity technology is also limited in application due to complicated device structure and strong viewing angle dependency which may cause color shift according to viewing angle.

[0003] These and other shortcomings are addressed by aspects of the present disclosure.

SUMMARY

[0004] In some aspects of the disclosure, OLEDs comprise: a substrate comprising polycarbonate having a plurality of pores randomly disposed on the surface thereof; an anode layer, said anode disposed adjacent to said substrate; a phosphor layer disposed on the anode layer; and a cathode layer disposed on said phosphor layer.

[0005] In other aspects of the disclosure, a method of forming a porous polycarbonate substrate having a random pattern of pores includes (i) contacting a polycarbonate substrate with droplets of a ketone solvent, (ii) allowing said droplets to form pores in said polycarbonate substrate, and (iii) evaporating said ketone solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] **FIG. 1** presents a schematic illustration of porous polycarbonate substrate fabrication process by a spray & spin-coating method according to aspects of the disclosure (not necessarily drawn to scale).

[0007] **FIG. 2** presents a schematic illustration of porous polycarbonate substrate fabrication process by spray coating and propeller method according to aspects of the disclosure (not necessarily drawn to scale).

[0008] **FIG. 3** presents a schematic illustration of porous polycarbonate substrate fabrication process by a roll-to-roll method according to aspects of the disclosure (cross section view) (not necessarily drawn to scale).

[0009] **FIG. 4** shows the schematic of an OLED device according to aspects of the disclosure (not necessarily drawn to scale).

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0010] A conventional organic light emitting diode may include an encapsulant, a cathode, an organic layer, an electrode and a barrier substrate. Generally, in the case of a flexible OLED lighting, the barrier film substrate itself is may be provided as a film. An electrode material, such as ITO (indium tin oxide) or PEDOT-PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) polymer electrode, may be laminated or coated by vacuum process on the barrier substrate. Finally, the remaining layers are laminated together to form the OLED device. In order to extract the light lost by currently used OLED substrates, aspects of the present disclosure provide a light extraction substrate with a randomly dispersed porous structure. Because this light extraction substrate has randomly ordered pores, it can reduce total internal reflection from substrate mode and diffuse the light dispersedly by scattering effect. This scattering effect of porous substrate will not only enhance out-coupling efficiency, but also reduce viewing angle dependency of microcavity OLEDs.

[0011] Many methods, including surface roughness or random scatters, photonic crystals, microlens arrays, and microcavity have been developed to improve light out-coupling in OLEDs. These methods, however, have limited application due to distorted or shifted emission spectrum and complicated fabrication process. Therefore, a new extraction substrate, which can maintain emission spectrum and be fabricated by a simple and cost-effective fabrication process, is desired.

[0012] The instant porous substrate process is advantageous as a simple and reliable process method for large-area and low-cost fabrication. Additionally, the porous substrate can be used as substrate for OLEDs without any additional lamination process and is suitable for reducing the total internal reflection loss at the substrate/air interface. Such porous substrates can be fabricated using a polycarbonate substrate by roll-to-roll process in order to enhance productivity and reduce manufacturing cost. Because polycarbonate has outstanding durability and high transparency, it suited for use as a flexible substrate for next generation display and lighting such as flexible OLEDs. As a result, the porous polycarbonate extraction substrate is very suitable for next generation display and lighting such as flexible OLEDs.

[0013] Because the polycarbonate substrate is easily solved by ketones such as acetone, the solvent droplets which were sprayed by spray condensed on the surface of the polycarbonate substrate forms the spherical shapes by sinking and drying. This method can only be carried out through elastic bouncing of the solvent droplets near the surface of the polycarbonate substrate.

[0014] Several similar methods for fabrication of porous polycarbonate substrate are discussed herein. In one aspect of the disclosure, condensing solvent droplets delivered via a sprayer 102 are kept apart by mixing with the rotation of substrate 104 (rotation indicated by arrows) providing a separation among the droplets 106 as shown in **FIG. 1.** In another aspect, the condensing solvent droplets 206 are kept apart by mixing with the fluttering or oscillations by propeller 208 providing a separation among the solvent droplets 206 as shown in **FIG. 2** to allow formation at the substrate 204. As long as the interaction time between the droplets is shorter than the time required for the droplets to escape the interstices, the droplets will interact elastically, in which the water droplets can maintain their forms without coalescence. Accordingly, a randomly dispersed porous structure can be easily obtained. Also, the size of spherical shape of pores was similar to solvent droplets sprayed by spray.

[0015] An aspect of a further fabrication method for mass production of porous polycarbonate substrate is shown in **FIG. 3.** **FIG. 3** shows a schematic illustration of porous polycarbonate substrate fabrication process by a roll-to-roll method. In the roll-to-roll method, the porous polycarbonate substrate can be formed through at least one roller or "rolling processing". The porous polycarbonate substrate can be used in a roll-to-roll process as known in the art given its flexibility and may be mounted as a "roll." Condensing solvent droplets 306 delivered by a spray (such as from a sprayer 302) at a rolling (or conveying) surface 312 (via one or more rollers 314, 316) may proceed to a heated portion 318 of the surface 312 to provide the porous polycarbonate substrate 310.

[0016] SEM (scanning electron microscope) images measured top view and cross section view respectively show that the resulting substrate is porous.

Substrate

[0017] In certain aspects polycarbonate is a particularly suitable material for use as the substrate as it is flexible and has good transparency. Initial thickness for base substrate may be 100 micrometers (microns, μm) to 150 μm, or about 100 μm to about 150 μm, for handling purposes. While a thin film is desired, a film that is too thin can be difficult to control.

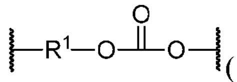
[0018] Various materials may be used to form the substrate. Accordingly, various solvents may be used to form the porous surface in the substrate. As an example, the following substrate materials and solvents may be used:

Substrate	Solvent
Polycarbonate (PC)	Ketone based solvent (Acetone, THF)
Polyvinylalcohol (PVA), Cellulose-based polymer	Water
Polyurethane (PU)	Dimethyl formamide
Polyimide (PI)	Dimethylacetamide
Polyethylene terephthalate (PET), Engineering plastic	Hexafluoroisopropanol

Polymer

[0019] The terms “polycarbonate” or “polycarbonates” as used herein includes copolycarbonates, homopolycarbonates and (co)polyester carbonates.

[0020] The term polycarbonate can be further defined as compositions have repeating structural units of the formula (1):



$$\left[-R^1-O-\overset{O}{\overset{\|}{C}}-O-\right] \quad (1),$$

in which at least 60 percent of the total number of R^1 groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. In a further aspect, each R^1 is an aromatic organic radical and, more preferably, a radical of the formula (2):

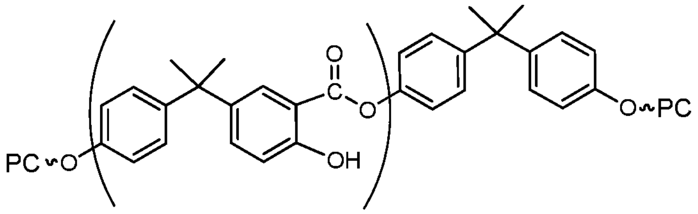
$$-A^1-Y^1-A^2- \quad (2),$$

wherein each of A^1 and A^2 is a monocyclic divalent aryl radical and Y^1 is a bridging radical having one or two atoms that separate A^1 from A^2. In various aspects, one atom separates A^1 from A^2. For example, radicals of this type include, but are not limited to, radicals such as —O—,

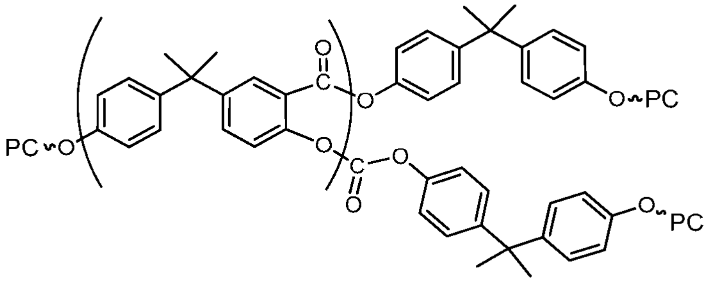
—S—, —S(O) —, —S(O$_2$) —, —C(O) —, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene. The bridging radical Y^1 is preferably a hydrocarbon group or a saturated hydrocarbon group such as methylene, cyclohexylidene, or isopropylidene. Polycarbonate materials include materials disclosed and described in U.S. Patent No. 7,786,246, which is hereby incorporated by reference in its entirety for the specific purpose of disclosing various polycarbonate compositions and methods for manufacture of same. Polycarbonate polymers can be manufactured by means known to those skilled in the art.

[0021] Apart from the main polymerization reaction in polycarbonate production, there is a series of side reactions consisting of chain rearrangements of the polymer backbone that lead to branching that are often referred to as Fries rearrangement. The Fries species specifically found in bisphenol A melt polycarbonates are the ester type of structures A, B, and C.

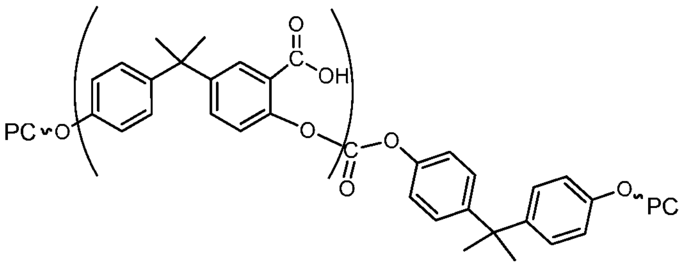
A. Linear Fries:



B. Branched Fries:



C. Acid Fries:



[0022] The Fries reaction is induced by the combined effect of basic catalysts, temperature, and residence time, which makes the melt-produced polycarbonates inherently branched as compared with the interfacial polycarbonates since their manufacturing temperatures are lower. Because high branching levels in the resin can have a negative effect on the mechanical properties of the polycarbonate (for example, on impact strength), a product with lower branched Fries product is preferred.

[0023] In certain aspects, polycarbonate produced by interfacial polymerization may be utilized. In some processes, bisphenol A and phosgene are reacted in an interfacial polymerization process. Typically, the disodium salt of bisphenol A is dissolved in water and reacted with phosgene which is typically dissolved in a solvent that not miscible with water (such as a chlorinated organic solvent like methylene chloride).

[0024] In some aspects, the polycarbonate comprises interfacial polycarbonate having a weight average molecular weight of from 10,000 Daltons to 50,000 Daltons, or from about 10,000 Daltons to about 50,000 Daltons, preferably 15,000 Daltons to 45,000 Daltons, or form about 15,000 to about 45,000 Daltons. Some interfacial polycarbonates have and endcap level of at least 90 %, or about 90 %, or preferably 95% or about 95 %.

[0025] A melt polycarbonate product may also be utilized. The melt polycarbonate process is based on continuous reaction of a dihydroxy compound and a carbonate source in a molten stage. The reaction can occur in a series of reactors where the combined effect of catalyst, temperature, vacuum, and agitation allows for monomer reaction and removal of reaction by-products to displace the reaction equilibrium and effect polymer chain growth. A common polycarbonate made in melt polymerization reactions is derived from bisphenol A (BPA) via reaction with diphenyl carbonate (DPC). This reaction can be catalyzed by, for example, tetra methyl ammonium hydroxide (TMAOH) or tetrabutyl phosphonium acetate (TBPA), which can be added in to a monomer mixture prior to being introduced to a first polymerization unit and sodium hydroxide (NaOH), which can be added to the first reactor or upstream of the first reactor and after a monomer mixer.

[0026] The melt polycarbonate may have a molecular weight (Mw) of 20,000 Daltons to 120,000 Daltons (or from about 20,000 Daltons to about 120,000 Daltons) on a polystyrene basis The melt polycarbonate product may have an endcap level of 45 % to 80 %, or about 45% to about 80%. Some polycarbonates have an endcap level of 45 % to 75 %, or about 45% to about 75%, 55 % to 75 % or about 55 % to about 75%, 60 % to 70 % or about 60% to about 70%, or 60 % to 65 % or about 60% to about 65%. Certain preferred polycarbonates have at least 200 parts per million (ppm) of hydroxide groups. Certain polycarbonates have 200-1100 ppm (or about 200 ppm to about 1100 ppm) or 950 ppm to 1050 ppm (or about 950 ppm to about 1050 ppm) hydroxide groups.

[0027] Polycarbonate polymer may contain endcapping agents. Any suitable endcapping agents can be used provided that such agents do not significantly adversely impact the desired properties of the polycarbonate composition (transparency, for example). Endcapping agents include mono-phenolic compounds, mono-carboxylic acid chlorides, and/or mono-chloroformates. Mono-phenolic endcapping agents are exemplified by monocyclic phenols such as phenol and C_1-C_{22} alkyl-substituted phenols such as p-cumyl-phenol (PCP), resorcinol monobenzoate, and p- and tertiary-butyl phenol; and monoethers of diphenols, such as p-methoxyphenol.

Pore Formation

[0028] In some aspects a porous polycarbonate substrate having a random pattern of pores is formed by a method comprising (i) contacting a polycarbonate substrate with droplets of a ketone solvent, (ii) allowing said droplets to form pores in said polycarbonate substrate, and (iii) evaporating said ketone solvent. Evaporation may be passive performed by application of one or both of heat and reduced pressure. Temperatures and pressures are selected so that the porous substrate is not damages.

[0029] While any suitable ketone solvent may be used, one particularly preferred solvent is acetone.

[0030] In some aspects, the solvent drops are contacted with the polycarbonate film by use of a spin-coater to rotate the substrate and spray of a plurality of droplets to contact the surface of the substrate. Such a process is illustrated by **FIG. 1**.

[0031] In some aspects, the contacting of the substrate with solvent is accomplished by use of a propeller to provide a spray of a plurality of droplets. Such a process is illustrated by **FIG. 2**.

[0032] In yet other aspects, the ketone solvent is air brushed onto the substrate.

[0033] **FIG. 3** shows a schematic illustration of porous polycarbonate substrate fabrication process by a roll-to-roll method according to an aspect of the disclosure. Solvent droplets are contacted with a film as it moves from a first roll to a second roll. Heat is applied after the solvent is contacted with the substrate film to evaporate the solvent prior to the substrate film being rolled on the second roll.

[0034] Each of the afore-mentioned methods can be performed on commercially available equipment.

[0035] Optionally, the pores of the porous substrate can be at least partially filled with a liquid or with nano- or microparticles. Various liquids may be used to control a refractive index of the porous substrate. It is understood that a selection of liquid or nano-particle may be dependent on a particular application requiring a particular index of refraction. Suitable particles include titanium dioxide TiO_2, zirconium dioxide ZrO_2, or aluminum oxide Al_2O_3, or a combination thereof. Other particles or liquids may be used. The filling of the pores in the substrate provides a custom level of control over index of refraction.

[0036] In some examples, average pore size is between 1 µm and 500 µm, or about 1 µm and about 500 µm, or from 1 µm and 400 µm, or from about 1 µm and about 400 µm.

Electrode Layers

[0037] The electrode is transparent and in some aspects includes materials such as ITO, SnO_2, ZnO, iridium zinc oxide, $ZnO\text{-}Al_2O_3$ (a zinc oxide doped with aluminum), $ZnO_4Ga_2O_3$ (a zinc oxide doped with gallium), niobium Nb-doped TiO_2, tantalum Ta-doped TiO_2, metals such as gold Au and platinum Pt, and a combination thereof. In particular aspects the layer has a thickness of 50 nanometers (nm) to 1 micrometer (micron, µm) or about 50 nm to about 1µm, or from 100 nm to 1 µm, or about 100 nm to about 1µm.

[0038] In certain aspects indium tin oxide (ITO) is used as the anode material. Metals such as barium and calcium may be used for the cathode material in further aspects.

Phosphor layer

[0039] The phosphor layer (also known as phosphorescent emitting material) may comprise a phosphorescent dopant in a polymer that is transparent when the layer is formed. Different phosphorescent dopants are known in the art and can be selected based on desired color output and other properties. Such dopants include use of YAG:Ce phosphors for yellow and CASN:Eu phosphors for red. YAG is yttrium aluminum garnet ($Y_3Al_5O_{12}$). YAG:Ce is cerium-doped YAG (YAG:Ce). CASN is $CaAlSiN_3$ and CASN:Eu is europium-doped CASN.

[0040] Silicones such as polydimethylsiloxane (PDMS) or acrylic or urethane based material could be used as binder material.

Conducting Polymer Layer

[0041] In some OLEDs according to aspects of the disclosure, a conducting polymer layer resides between the anode and phosphor layers. Conductive polymers include polyaniline (PANI;PSS) and polyethylenedioxythiopene (PDOT:PSS).

Barrier layer

[0042] An optional barrier layers may comprise one or both of inorganic and organic materials. For example, the barrier layer may comprise inorganic particles in a polymer media. The layer may comprise a metal oxide such as, but not limited to, oxides of aluminum, zirconium, zinc, titanium, and silicone (such as Al_2O_3, ZrO_2, ZnO, TiO_2, TiO_x, silicone dioxide SiO_2, and SiO_x), a polymer comprising acrylate-polymer, parylene, p-xylene, or ethylene glycol, and combinations thereof. Polymer layers may be formed by molecular layer deposition (e.g., by molecular layer deposition of ethylene-glycol), plasma polymer (e.g., direct radical polymerization by plasma) or other applications known to those skilled in the art. The layer has a thickness of from 0.5 μm to 50 μm, or from about 0.5 μm to about 50 μm in some aspects.

Formation of layers within the OLED

[0043] Layers may be formed by use of one or more of ink jet printing, application of a polymer solution or slurry, roll-to-roll printing, vacuum vapor deposition operations or other techniques known to those skilled in the art. Additionally, aerosol-deposition process can be used for phosphor layer coating.

[0044] Certain layers of the OLED according to aspects of the disclosure may be laminated or connected by use of an adhesive.

Use of the Porous Substrates as Sound Insulation Materials

[0045] The porous polycarbonate material may be used as a sound insulation material. Particular end uses include, but are not limited to, home appliances and for buildings.

[0046] Home appliances include, but are not limited to, dish washers, washing machines, dryers, refrigerators, and freezers.

[0047] Building uses include, but are not limited to, positioning the films in walls, floors or ceilings to reduce sound transfer.

Definitions

[0048] It is to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term “comprising” can include the embodiments “consisting of” and “consisting essentially of.” Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined herein.

[0049] As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural equivalents unless the context clearly dictates otherwise. Thus, for example, reference to "a polycarbonate polymer" includes mixtures of two or more polycarbonate polymers.

[0050] Ranges can be expressed herein as from one particular value to another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent 'about,' it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0051] As used herein, the terms "about" and "at or about" mean that the amount or value in question can be the value designated some other value approximately or about the same. It is generally understood, as used herein, that it is the nominal value indicated ±5% variation unless otherwise indicated or inferred. The term is intended to convey that similar values promote equivalent results or effects recited in the claims. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but can be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about" or "approximate" whether or not expressly stated to be such. It is understood that where "about" is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0052] Disclosed are the components to be used to prepare the compositions of the disclosure as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the disclosure. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific aspect or combination of aspects of the methods of the disclosure.

[0053] When a layer is denoted as disposed on a second layer, it is understood that an intervening layer or layers may reside between the two layers.

[0054] As used herein, the term “transparent” means that the level of transmittance for a disclosed composition is greater than 50%. It is preferred that the transmittance be at least 60%, 70%, 80%, 85%, 90%, or 95%, or any range of transmittance values derived from the above exemplified values. In the definition of “transparent”, the term “transmittance” refers to the amount of incident light that passes through a sample measured in accordance with ASTM D1003 at a thickness of 3.2 millimeters.

[0055] The term “adhesive” as used herein refers to a sticky, gluey or tacky substance capable of adhering two films together. It is preferred that the adhesive be transparent. In the adhesive, desiccant material can be added for improving WVTR property. And UV or thermal energy may be necessary for curing adhesive layer.

[0056] “UV” stands for ultraviolet.

[0057] The abbreviation “nm” stands for nanometer(s).

[0058] The abbreviation “μm” stands for micrometer(s).

[0059] The terms “random” and “randomly” refer to an arrangement where the pores do not have a defined pattern.

[0060] Unless otherwise stated to the contrary herein, all test standards are the most recent standard in effect at the time of filing this application.

Aspects

[0061] The present disclosure comprises at least the following aspects.

[0062] Aspect 1. An OLED comprising: a substrate comprising polycarbonate having a plurality of pores randomly disposed on the surface thereof; an anode layer, said anode disposed adjacent to said substrate; a phosphor layer disposed on the anode layer; and a cathode layer disposed on said phosphor layer.

[0063] Aspect 2. An OLED consisting essentially of: a substrate comprising polycarbonate having a plurality of pores randomly disposed on the surface thereof; an anode layer, said anode disposed adjacent to said substrate; a phosphor layer disposed on the anode layer; and a cathode layer disposed on said phosphor layer.

[0064] Aspect 3. An OLED consisting of: a substrate comprising polycarbonate having a plurality of pores randomly disposed on the surface thereof; an anode layer, said anode disposed adjacent to said substrate; a phosphor layer disposed on the anode layer; and a cathode layer disposed on said phosphor layer.

[0065] Aspect 4. The OLED of any of Aspects 1-3, wherein said pores are at least partially filled with a liquid.

[0066] Aspect 5. The OLED of any of Aspects 1-4, wherein said pores are at least partially filled with nano- or microparticles.

[0067] Aspect 6. The OLED of any of Aspects 1-5, wherein said nano- or microparticles comprise TiO_2, ZrO_2, or Al_2O_3, or a combination thereof.

[0068] Aspect 7. A method of forming a porous polycarbonate substrate having a random pattern of pores, said method comprising (i) contacting a polycarbonate substrate with droplets of a ketone solvent, (ii) allowing said droplets to form pores in said polycarbonate substrate, and (iii) evaporating said ketone solvent.

[0069] Aspect 8. The method of Aspect 7, wherein the evaporating is passive.

[0070] Aspect 9. The method of Aspect 7, wherein the evaporating is performed by application of one or both of heat and reduced pressure.

[0071] Aspect 10. The method of any one of Aspects 7-9, wherein said ketone solvent is acetone.

[0072] Aspect 11. The method of any one of Aspects 7-10, wherein said contacting is accomplished by use of a spin-coater to provide a spray of a plurality of droplets.

[0073] Aspect 12. The method of any one of Aspects 7-11, wherein said contacting is accomplished by use of a propeller to provide a spray of a plurality of droplets.

[0074] Aspect 13. The method of any one of Aspects 7-12, wherein said polycarbonate substrate is rotated while being sprayed with a plurality of droplets of said ketone solvent.

[0075] Aspect 14. The method of any one of Aspects 7-13, wherein said ketone solvent is air brushed onto said polycarbonate substrate.

[0076] Aspect 15. The method of any one of Aspects 7-14, wherein said pores are at least partially filled with a liquid.

[0077] Aspect 16. The method of any one of Aspects 7-15, wherein said pores are at least partially filled with nano- or microparticles.

[0078] Aspect 17. The method of Aspect 16, wherein said nano- or microparticles comprise TiO_2, ZrO_2, or Al_2O_3, or a combination thereof.

[0079] Aspect 18. The method of any one of Aspects 7-14, wherein said porous polycarbonate substrate is suitable for use as a light extraction substrate in an OLED.

[0080] Aspect 19. The method of any one of Aspects 7-14, wherein said porous polycarbonate substrate is suitable for use as a sound insulation layer.

[0081] Aspect 20. The method of Aspect 19, wherein the sound insulation layer is used in a home appliance.

[0082] Aspect 21. The method of Aspect 19, wherein the sound insulation layer is used in the insulation of a building.

[0083] Aspect 22. The method of any one of Aspects 7-21, wherein the average size of the pores is between about 1 μm and about 500 μm.

[0084] Aspect 23. The method of any one of Aspects 7-21, wherein the average size of the pores is between 1 μm and 500 μm.

[0085] Aspect 24. The method of any one of Aspects 7-22, wherein said substrate exhibits a haze value between 30% and 95%, or between about 30 % and about 95 %, due at least in part to the pores formed therein according to ASTM D1003.

[0086] Aspect 25. The OLED of any one of Aspects 1-6, wherein the average size of the pores is between about 1 μm and about 400 μm.

[0087] Aspect 26. The OLED of any one of Aspects 1-6, wherein the average size of the pores is between 1 μm and 400 μm.

[0088] Aspect 27. The OLED of any one of Aspects 1-6 or 25-26, wherein said substrate exhibits a haze value between 30% and 95%, or between about 30 % and about 95 %, due at least in part to the pores formed therein according to ASTM D1003.

Examples

[0089] The disclosure is illustrated by the following non-limiting examples. Although reference is made to polycarbonate films, it is understood that other materials may be used in a similar fashion. It is further understood that other mechanism for creating a random formation of pores in a substrate may be used without departing form the spirit of the present disclosure.

Example 1

[0090] A porous polycarbonate film is made by the spray and spin method depicted in **Fig. 2**. As an example, a polycarbonate film may be rotated beneath a spray application of a solvent to ensure a random formation of pores within the polycarbonate film. In certain aspects, separation of the solvent spray into spaced apart droplets of the solvent is desirable to form random pores in the film. Random may mean that no etching paste or deliberate limitation is provided to the formation of the pores in the substrate. Random may mean that each portion of the substrate has an equal chance of receiving the solvent and forming a pore therein.

Example 2

[0091] A porous polycarbonate film is made by the spray coating and propeller method depicted in **Fig. 3**. As an example, a polycarbonate film may exposed to a spray application of a solvent, whereby the solvent spray is subjected to fluid dynamics created by a propeller or fan. Such an application may create turbulent fluid flow in a fluid (e.g., air) above the polycarbonate film to ensure a random formation of pores within the polycarbonate film. In other aspects, the fluid flow caused by the propeller may cause the solvent to evaporate from the film surface in a random manner. Random may mean that no etching paste or deliberate limitation is provided to the formation of the pores in the substrate. Random may mean that each portion of the substrate has an equal chance of receiving the solvent and forming a pore therein.

Example 3

[0092] A porous polycarbonate film is made by the roll to roll method depicted in **Fig. 3**. As an example, a polycarbonate film may be disposed on a conveyor and subjected to a spray application of a solvent. The conveyor may translate the film from the spray application to a heater area, where solvent may be caused to evaporate in a random manner to ensure a random formation of pores within the polycarbonate film. Random may mean that no etching paste or deliberate limitation is provided to the formation of the pores in the substrate. Random may mean that each portion of the substrate has an equal chance of receiving the solvent and forming a pore therein.

Example 4

[0093] An OLED may be made in a construction according to **FIG. 4** using the porous polycarbonate films as a substrate. The OLED may include an encapsulant, a cathode, an organic layer, an electrode and a barrier substrate. The porous polycarbonate film can be used as a light extraction substrate.

What is Claimed:

1. An organic light emitting diode (OLED) comprising:

-- a substrate comprising polycarbonate having a plurality of pores randomly disposed on the surface thereof;

-- an anode layer, said anode disposed adjacent to said substrate;

-- a phosphor layer disposed on the anode layer; and

-- a cathode layer disposed on said phosphor layer.

2. The OLED of claim 1, wherein said pores are at least partially filled with a liquid.

3. The OLED of claim 1, wherein said pores are at least partially filled with nano- or microparticles.

4. The OLED of claim 3, wherein said nano- or microparticles comprise titanium oxide, zirconium dioxide, aluminum oxide or a combination thereof.

5. The OLED of any of claims 1-4, wherein said pores have an average size between about 1 micrometer (μm) and about 400 μm.

6. A method of forming a porous polycarbonate substrate having a random pattern of pores, said method comprising (i) contacting a polycarbonate substrate with droplets of a ketone solvent, (ii) allowing said droplets to form pores in said polycarbonate substrate, and (iii) evaporating said ketone solvent.

7. The method of claim 6, wherein the evaporating is passive.

8. The method of claim 6, wherein the evaporating is performed by application of one or both of heat and reduced pressure.

9. The method of any one of claims 6-8, wherein said ketone solvent is acetone.

10. The method of any one of claims 6-9, wherein said contacting is accomplished by use of a spin-coater to provide a spray of a plurality of droplets.

11. The method of any one of claims 6-9, wherein said contacting is accomplished by use of a propeller to provide a spray of a plurality of droplets.

12. The method of any one of claims 6-9, wherein said polycarbonate substrate is rotated while being sprayed with a plurality of droplets of said ketone solvent.

13. The method of any one of claims 6-9, wherein said ketone solvent is air brushed onto said polycarbonate substrate.

14. The method of any one of claims 6-13, wherein said pores are at least partially filled with a liquid.

15. The method of any one of claims 6-13, wherein said pores are at least partially filled with nano- or microparticles.

16. The method of any one of claims 6-14, wherein said substrate exhibits a haze value between 30% and 95% due at least in part to the pores formed therein according to ASTM D1003.

17. The method of any one of claims 6-16, wherein said porous polycarbonate substrate is suitable for use as a light extraction substrate in an OLED.

18. The method of any one of claims 6-16, wherein said porous polycarbonate substrate is suitable for use as a sound insulation layer.

19. The method of claim 18, wherein the sound insulation layer is used in a home appliance.

20. The method of claim 18, wherein the sound insulation layer is used in the insulation of a building.

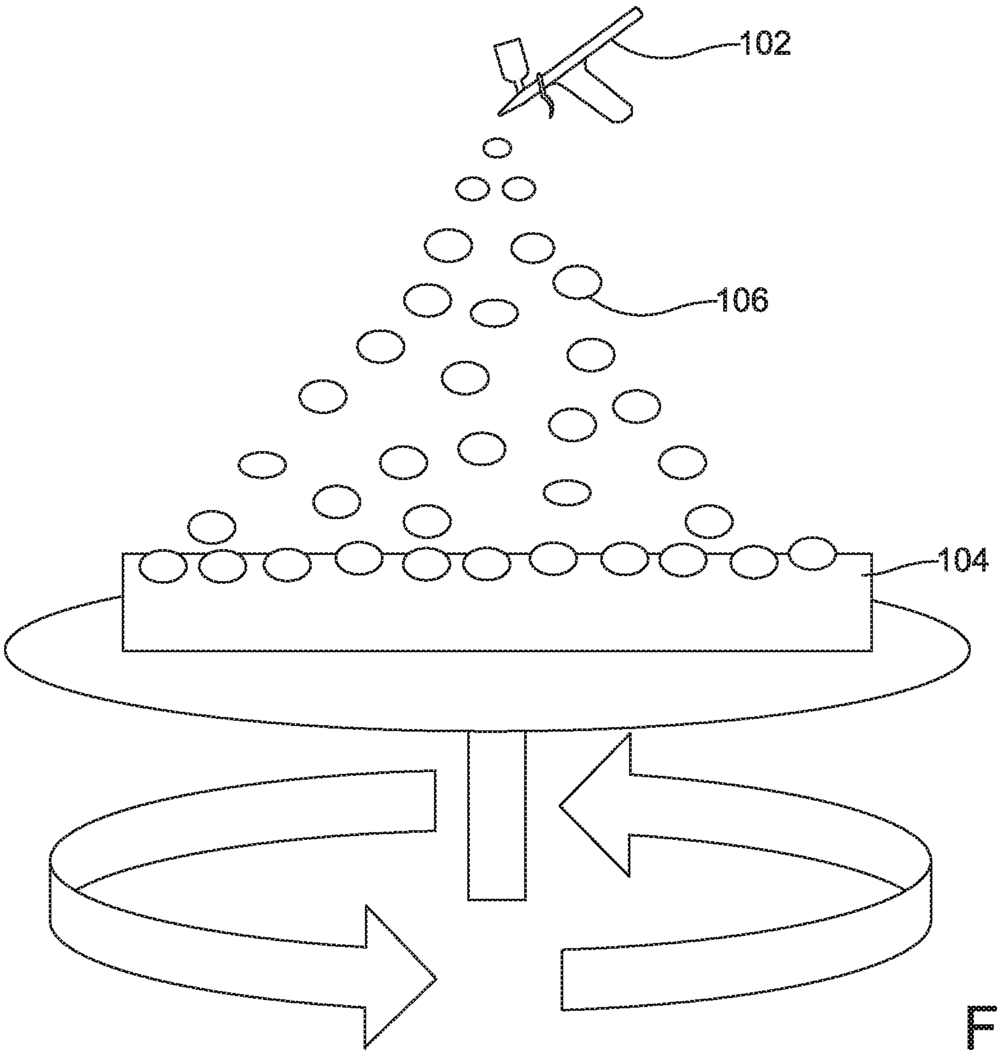


FIG. 1

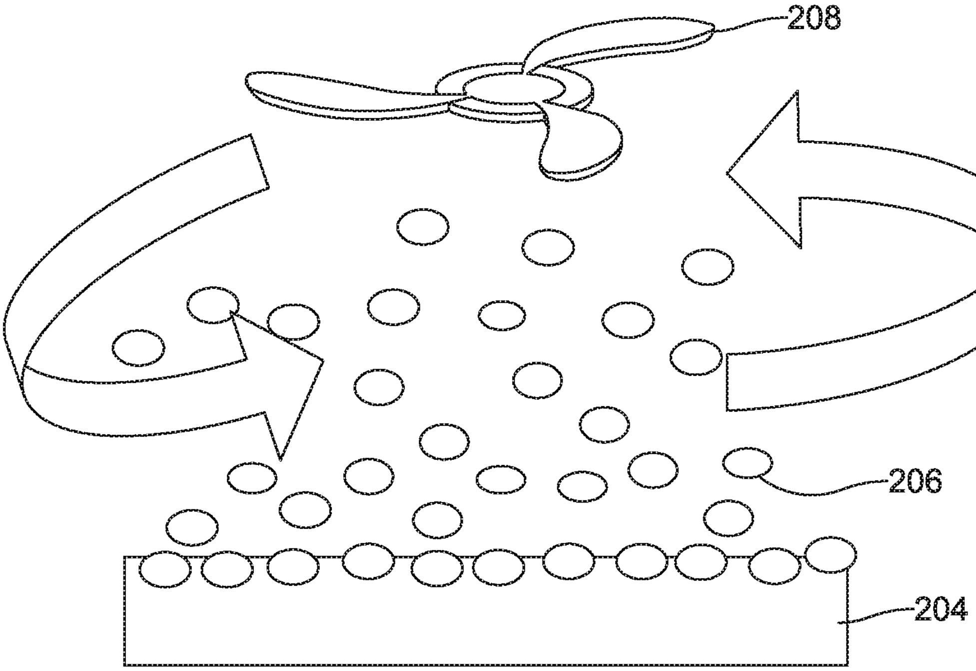


FIG. 2

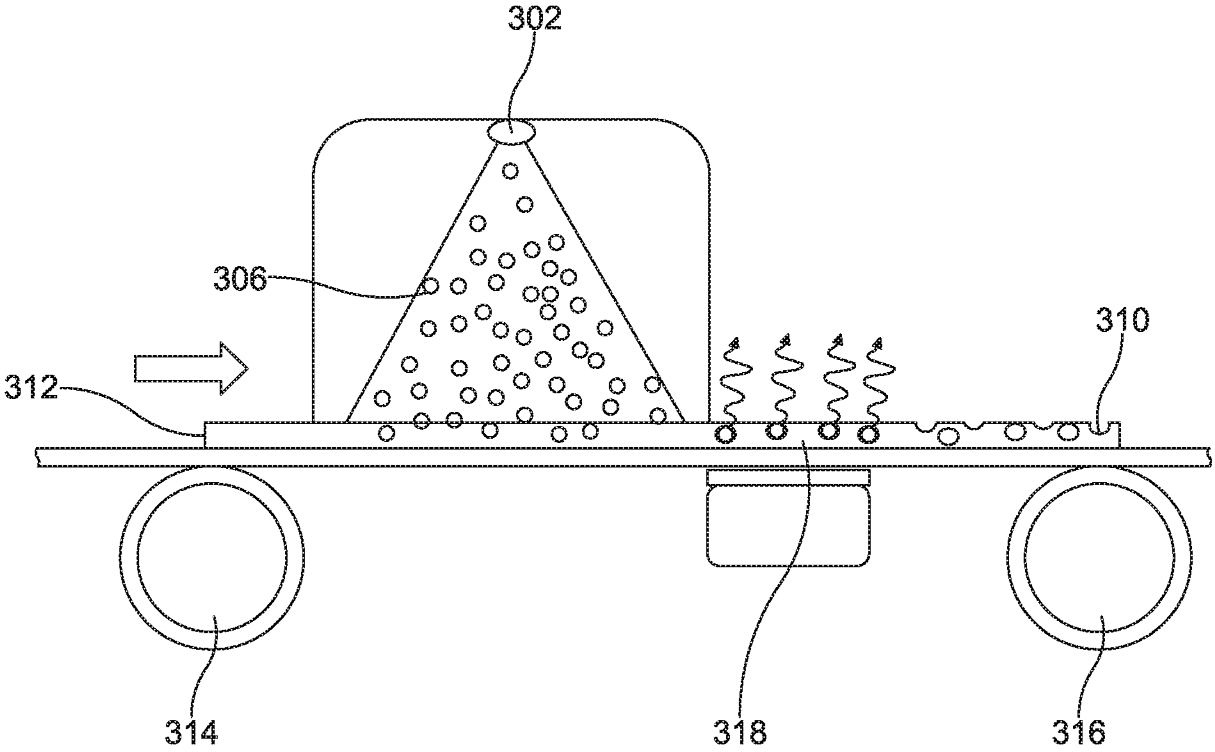

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FIG. 3

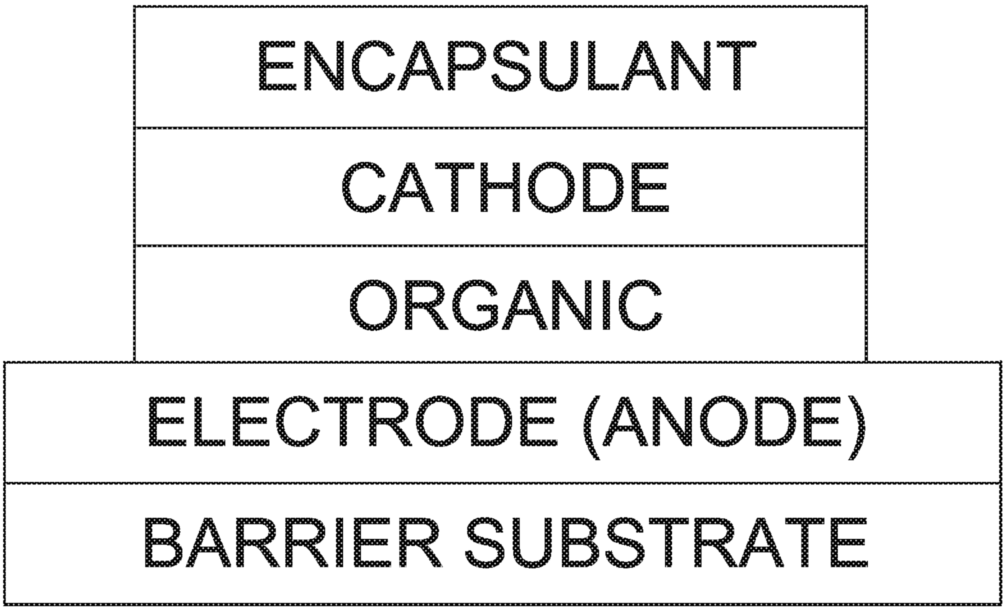
ENCAPSULANT
CATHODE
ORGANIC
ELECTRODE (ANODE)
BARRIER SUBSTRATE

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/052412

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/52 C08J9/00 B60R13/08 B32B5/18 C08J7/02
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)
H01L C08J B60R B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/181242 A1 (CHO DOO-HEE [KR]) 18 July 2013 (2013-07-18) page 6, paragraph 105; claims 1-15; figures 9, 12, 13 -----	1-20
X	KR 2016 0026774 A (LG CHEMICAL LTD [KR]) 9 March 2016 (2016-03-09) claims 1, 5, 9, 20; figures 1-4 -----	1,3,4
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A	CN 101 384 425 A (DAICEL CHEM [JP]) 11 March 2009 (2009-03-11) the whole document -----	1-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 7 July 2017	Date of mailing of the international search report 20/07/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Parashkov, Radoslav

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2017/052412

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