(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 August 2017 (24.08.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/142782 A1

(51) International Patent Classification:
C09K 11/02 (2006.01) *C09K 11/70* (2006.01)
C09K 11/56 (2006.01)

(21) International Application Number:
PCT/US2017/017152

(22) International Filing Date:
9 February 2017 (09.02.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/296,289 17 February 2016 (17.02.2016) US

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: **ARMSTRONG, Paul, B.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **CHAKRABORTY, Saswata**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **PALAZZOTTO, Michael, C.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **KOKKO, Kent, S.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

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

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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

(54) Title: QUANTUM DOTS WITH STABILIZING FLUOROCHEMICAL COPOLYMERS

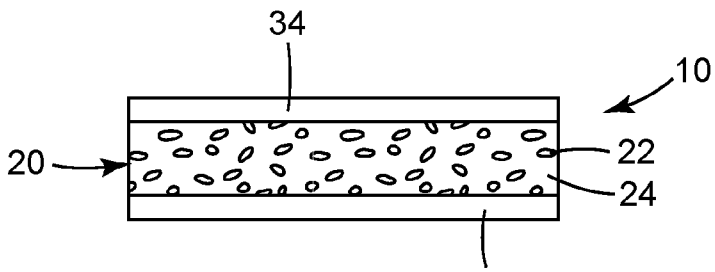


FIG. 1

(57) Abstract: Disclosed are quantum dots and quantum dot articles stabilized by a fluorochemical copolymer having pendent arsine, stibine or phosphine stabilizing groups; and pendent fluorochemical groups.

WO 2017/142782 A1

QUANTUM DOTS WITH STABILIZING FLUOROCHEMICAL COPOLYMERS

Background

Quantum Dot Enhancement Films (QDEF) are used as part of the backlight for LCD displays. Red and green quantum dots in the film down-convert light from the blue LED source to give white light. This has the advantage of improving the color gamut over the typical LCD display and keeping the energy consumption low compared to LED displays.

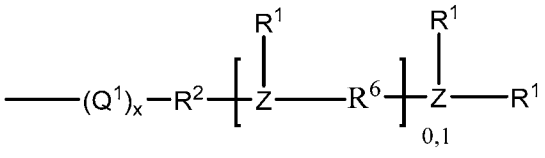
Colloidal quantum dot nanoparticles (preferably, nanocrystals) are stabilized with organic ligands and/or additives to maintain dispersion stability in a carrier fluid (or solvent). Quantum dot ligands also improve photoluminescent quantum yields by passivating surface traps, stabilize against aggregation and degradation, and influence the kinetics of nanoparticle (preferably, nanocrystal) growth during synthesis. Therefore, optimizing the organic ligand and/or additive is important for achieving optimal quantum yield, processability, and functional lifetime in QDEF.

Summary

Composite particles are provided that are capable of fluorescence and suitable for use in quantum dot enhancement films.

In one aspect, the present disclosure provides a composite particle that includes: a fluorescent semiconductor core/shell nanoparticle (preferably, nanocrystal); and a stabilizing copolymer combined with the core/shell nanoparticle, the stabilizing copolymer comprising a copolymer having pendent fluorochemical groups and pendent phosphine, arsine or stibine groups.

The copolymer has pendent stabilizing groups of the formula:



I

wherein each R^1 is a hydrocarbyl group including alkyl, aryl, alkaryl and aralkyl;

R^2 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene;

Z is P, As or Sb;

Q^1 is a functional group selected from $–CO_2$-, -O-, -S-, $-CONR^3$-, $-NH-CO-NR^3$-, and $–NR^3$-, where R^3 is H or C_1-C_4 alkyl, and subscript x is 0 or 1, and

R^6 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene.

Further, the copolymer has pendent fluorochemical groups of the formula:

$-(Q^2)_g-R^{10}-(Q^3)_h-R_f$; II

where

Q^2 is selected from a covalent bond ("-"), $–CO_2$-, $-CONR^3$-, $-NH-CO-NR^3$-, and $–NR^3$-, where R^3 is H or C_1-C_4 alkyl;

Q^3 is selected from $–CH_2-S$-, $–CH_2-O$-, $–CO_2$-, $-CONR^3$-, $-NH-CO-NR^3$-, and $–NR^3$, where R^3 is H or C_1-C_4 alkyl,

subscripts g and h are independently 0 or 1;

R^{10} is a hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene and R_f is a perfluorinated group.

In one aspect, the present disclosure provides a composite particle that includes: a fluorescent semiconductor core/shell nanoparticle (preferably, nanocrystal); and a stabilizing copolymer having 1) pendent phosphine, arsine or stibine groups, and 2) pendent fluorochemical groups, that is combined with, attached to, or associated with, the core/shell nanoparticle.

In a preferred embodiment, the fluorescent semiconductor core/shell nanoparticle includes: an InP core; an inner shell overcoating the core, wherein the inner shell includes zinc selenide and zinc sulfide; and an outer shell overcoating the inner shell, wherein the outer shell includes zinc sulfide.

As used herein

"Alkyl" means a linear or branched, cyclic or acylic, saturated monovalent hydrocarbon.

"Alkylene" means a linear or branched unsaturated divalent hydrocarbon.

"Alkenyl" means a linear or branched unsaturated hydrocarbon.

"Aryl" means a monovalent aromatic, such as phenyl, naphthyl and the like.

"Arylene" means a polyvalent, aromatic, such as phenylene, naphthalene, and the like.

"Aralkylene" means a group defined above with an aryl group attached to the alkylene, e.g., benzyl, 1-naphthylethyl, and the like.

As used herein, "(hetero)hydrocarbyl" is inclusive of hydrocarbyl alkyl, aryl, aralkyl and alkaryl groups, and heterohydrocarbyl heteroalkyl and heteroaryl groups, the later comprising one or more catenary (in-chain) heteroatoms such as ether or amino groups. Heterohydrocarbyl may optionally contain one or more catenary (in-chain) functional groups including ester, amide, urea, urethane, and carbonate functional groups. Unless otherwise indicated, the non-polymeric (hetero)hydrocarbyl groups typically contain from 1 to 60 carbon atoms. Some examples of such heterohydrocarbyls as used herein include, but are not limited to, methoxy, ethoxy, propoxy, 4-diphenylaminobutyl, 2-(2'-phenoxyethoxy)ethyl, 3,6-dioxaheptyl, 3,6-dioxahexyl-6-phenyl, in addition to those described for "alkyl", "heteroalkyl", and "aryl" *supra*.

The term "composite particle" as used herein refers to a nanoparticle, which is typically in the form of a core/shell nanoparticle (preferably, nanocrystal), having any associated organic coating or other material on the surface of the nanoparticle that is not removed from the surface by ordinary solvation. Such composite particles are useful as "quantum dots," which have a tunable emission in the near ultraviolet (UV) to far infrared (IR) range as a result of the use of a semiconductor material.

The term "nanoparticle" refers to a particle having an average particle diameter in the range of 0.1 to 1000 nanometers such as in the range of 0.1 to 100 nanometers or in the range of 1 to 100 nanometers. The term "diameter" refers not only to the diameter of substantially spherical particles but also to the distance along the smallest axis of the structure. Suitable techniques for measuring the average particle diameter include, for example, scanning tunneling microscopy, light scattering, and transmission electron microscopy.

A "core" of a nanoparticle is understood to mean a nanoparticle (preferably, a nanocrystal) to which no shell has been applied or to the inner portion of a core/shell nanoparticle. A core of a nanoparticle can have a homogenous composition or its composition can vary with depth inside the core. Many materials are known and used in core nanoparticles, and many methods are known in the art for applying one or more shells to a core nanoparticle. The core has a different composition than the one more shells. The

core typically has a different chemical composition than the shell of the core/shell nanoparticle.

Brief Description of the Drawings

FIG. 1 is a schematic side elevation view of an edge region of an illustrative film article including quantum dots.

FIG. 2 is a flow diagram of an illustrative method of forming a quantum dot film.

FIG. 3 is a schematic illustration of an embodiment of a display including a quantum dot article.

Fig. 4 illustrates the color measurement system.

Fig. 5 illustrates the change in quantum yield of InP upon light exposure.

Detailed Description

The present disclosure provides composite particles that contain fluorescent semiconductor nanoparticles that can fluoresce when excited with actinic radiation. The composite particles can be used in coatings and films for use in optical displays.

Fluorescent semiconductor nanoparticles emit a fluorescence signal when suitably excited. They fluoresce at a second wavelength of actinic radiation when excited by a first wavelength of actinic radiation that is shorter than the second wavelength. In some embodiments, the fluorescent semiconductor nanoparticles can fluoresce in the visible region of the electromagnetic spectrum when exposed to wavelengths of light in the ultraviolet region of the electromagnetic spectrum. In other embodiments, the fluorescent semiconductor nanoparticles can fluoresce in the infrared region when excited in the ultraviolet or visible regions of the electromagnetic spectrum. In still other embodiments, the fluorescent semiconductor nanoparticles can fluoresce in the ultraviolet region when excited in the ultraviolet region by a shorter wavelength of light, can fluoresce in the visible region when excited by a shorter wavelength of light in the visible region, or can fluoresce in the infrared region when excited by a shorter wavelength of light in the infrared region. The fluorescent semiconductor nanoparticles are often capable of fluorescing in a wavelength range such as, for example, at a wavelength up to 1200 nanometers (nm), or up to 1000 nm, up to 900 nm, or up to 800 nm. For example, the

fluorescent semiconductor nanoparticles are often capable of fluorescence in the range of 400 to 800 nanometers.

The nanoparticles have an average particle diameter of at least 0.1 nanometer (nm), or at least 0.5 nm, or at least 1 nm. The nanoparticles have an average particle diameter of up to 1000 nm, or up to 500 nm, or up to 200 nm, or up to 100 nm, or up to 50 nm, or up to 20 nm, or up to 10 nm. Semiconductor nanoparticles, particularly with sizes on the scale of 1-10 nm, have emerged as a category of the most promising advanced materials for cutting-edge technologies.

Semiconductor materials include elements or complexes of Group 2-Group 16, Group 12-Group 16, Group 13-Group 15, Group 14-Group 16, and Group 14 semiconductors of the Periodic Table (using the modern group numbering system of 1-18). Some suitable quantum dots include a metal phosphide, a metal selenide, a metal telluride, or a metal sulfide. Exemplary semiconductor materials include, but are not limited to, Si, Ge, Sn, BN, BP, BAs, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, lnAs, InSb, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, BeS, BeSe, BeTe, MgS, MgSe, MgTe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, CuF, CuCI, CuBr, CuI, Si_3N_4, Ge_3N_4, $A1_2O_3$, $(Ga,In)_2(S,Se,Te)_3$, Al_2CO, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, and an appropriate combination of two or more such semiconductors. These semiconductor materials can be used for the core, the one or more shell layers, or both.

In certain embodiments, exemplary metal phosphide quantum dots include indium phosphide and gallium phosphide, exemplary metal selenide quantum dots include cadmium selenide, lead selenide, and zinc selenide, exemplary metal sulfide quantum dots include cadmium sulfide, lead sulfide, and zinc sulfide, and exemplary metal telluride quantum dots include cadmium telluride, lead telluride, and zinc telluride. Other suitable quantum dots include gallium arsenide and indium gallium phosphide. Exemplary semiconductor materials are commercially available from Evident Thermoelectrics (Troy, NY), and from Nanosys Inc., Milpitas, CA.

Nanocrystals (or other nanostructures) for use in the present invention can be produced using any method known to those skilled in the art. Suitable methods are disclosed in U.S. Patent Application No. 10/796,832, filed March 10, 2004, U.S. Patent No. 6,949,206 (Whiteford) and U.S. Provisional Patent Application No. 60/578,236, filed

June 8, 2004, the disclosures of each of which are incorporated by reference herein in their entireties. The nanocrystals (or other nanostructures) for use in the present invention can be produced from any suitable material, suitably an inorganic material, and more suitably an inorganic conductive or semiconductive material. Suitable semiconductor materials include those disclosed in U.S. patent application Ser. No. 10/796,832 and include any type of semiconductor, including group 12-16, group 13-15, group 14-16 and group 14 semiconductors.

Suitable semiconductor materials include, but are not limited to, Si, Ge, Sn, Se, Te, B, C (including diamond), P, BN, BP, BAs, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, AlN, AlP, As, AlSb, GaN, GaP, GaAs, GaSb, ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, BeS, BeSe, BeTe, MgS, MgSe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, CuF, CuCl, CuBr, CuI, Si_3N_4, Ge_3N_4, Al_2O_3, $(Ga, In)_2(S, Se, Te)_3$, Al_2CO, and an appropriate combination of two or more such semiconductors.

In certain aspects, the semiconductor nanocrystals or other nanostructures may comprise a dopant from the group consisting of: a p-type dopant or an n-type dopant. The nanocrystals (or other nanostructures) useful in the present invention can also comprise Group 12-Group 16 or Group 13-Group 15 semiconductors. Examples of Group 12-Group 16 or Group 13-Group 15 semiconductor nanocrystals and nanostructures include any combination of an element from Group 12, such as Zn, Cd and Hg, with any element from Group 16, such as S, Se, Te, Po, of the Periodic Table; and any combination of an element from Group 13, such as B, Al, Ga, In, and Tl, with any element from Group 15, such as N, P, As, Sb and Bi, of the Periodic Table.

Other suitable inorganic nanostructures include metal nanostructures. Suitable metals include, but are not limited to, Ru, Pd, Pt, Ni, W, Ta, Co, Mo, Ir, Re, Rh, Hf, Nb, Au, Ag, Ti, Sn, Zn, Fe, FePt, and the like.

While any known method can be used to create nanocrystal phosphors, suitably, a solution-phase colloidal method for controlled growth of inorganic nanomaterial phosphors is used. See Alivisatos, A. P., "Semiconductor clusters, nanocrystals, and quantum dots," Science 271:933 (1996); X. Peng, M. Schlamp, A. Kadavanich, A. P. Alivisatos, "Epitaxial growth of highly luminescent CdSe/CdS Core/Shell nanocrystals with photostability and electronic accessibility," J. Am. Chem. Soc. 30:7019-7029 (1997);

and C. B. Murray, D. J. Norris, M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E=sulfur, selenium, tellurium) semiconductor nanocrystallites," J. Am. Chem. Soc. 115:8706 (1993). This manufacturing process technology leverages low cost proccessability without the need for clean rooms and expensive manufacturing equipment. In these methods, metal precursors that undergo pyrolysis at high temperature are rapidly injected into a hot solution of organic surfactant molecules. These precursors break apart at elevated temperatures and react to nucleate nanocrystals. After this initial nucleation phase, a growth phase begins by the addition of monomers to the growing crystal. The result is freestanding crystalline nanoparticles in solution that have an organic surfactant molecule coating their surface.

Utilizing this approach, synthesis occurs as an initial nucleation event that takes place over seconds, followed by crystal growth at elevated temperature for several minutes. Parameters such as the temperature, types of surfactants present, precursor materials, and ratios of surfactants to monomers can be modified so as to change the nature and progress of the reaction. The temperature controls the structural phase of the nucleation event, rate of decomposition of precursors, and rate of growth. The organic surfactant molecules mediate both solubility and control of the nanocrystal shape.

In semiconductor nanocrystals, photo-induced emission arises from the band edge states of the nanocrystal. The band-edge emission from nanocrystals competes with radiative and non-radiative decay channels originating from surface electronic states. X. Peng, et al., J. Am. Chem. Soc. 30:7019-7029 (1997). As a result, the presence of surface defects such as dangling bonds provide non-radiative recombination centers and contribute to lowered emission efficiency. An efficient and permanent method to passivate and remove the surface trap states is to epitaxially grow an inorganic shell material on the surface of the nanocrystal. X. Peng, et al., J. Am. Chem. Soc. 30:7019-7029 (1997). The shell material can be chosen such that the electronic levels are type I with respect to the core material (e.g., with a larger bandgap to provide a potential step localizing the electron and hole to the core). As a result, the probability of non-radiative recombination can be reduced.

Core-shell structures are obtained by adding organometallic precursors containing the shell materials to a reaction mixture containing the core nanocrystal. In this case, rather than a nucleation-event followed by growth, the cores act as the nuclei, and the

shells grow from their surface. The temperature of the reaction is kept low to favor the addition of shell material monomers to the core surface, while preventing independent nucleation of nanocrystals of the shell materials. Surfactants in the reaction mixture are present to direct the controlled growth of shell material and ensure solubility. A uniform and epitaxially grown shell is obtained when there is a low lattice mismatch between the two materials. Additionally, the spherical shape acts to minimize interfacial strain energy from the large radius of curvature, thereby preventing the formation of dislocations that could degrade the optical properties of the nanocrystal system.

In suitable embodiments, ZnS can be used as the shell material using known synthetic processes, resulting in a high-quality emission. As above, if necessary, this material can be easily substituted, e.g., if the core material is modified. Additional exemplary core and shell materials are described herein and/or known in the art.

For many applications of quantum dots, two factors are typically considered in selecting a material. The first factor is the ability to absorb and emit visible light. This consideration makes InP a highly desirable base material. The second factor is the material's photoluminescence efficiency (quantum yield). Generally, Group 12-16 quantum dots (such as cadmium selenide) have higher quantum yield than Group 13-15 quantum dots (such as InP). The quantum yield of InP cores produced previously has been very low (<1 %), and therefore the production of a core/shell structure with InP as the core and another semiconductor compound with higher bandgap (e.g., ZnS) as the shell has been pursued in attempts to improve the quantum yield.

Thus, the fluorescent semiconductor nanoparticles (i.e., quantum dots) of the present disclosure include a core and a shell at least partially surrounding the core. The core/shell nanoparticles can have two distinct layers, a semiconductor or metallic core and a shell surrounding the core of an insulating or semiconductor material. The core often contains a first semiconductor material and the shell often contains a second semiconductor material that is different than the first semiconductor material. For example, a first Group 12-16 (e.g., CdSe) semiconductor material can be present in the core and a second Group 12-16 (e.g., ZnS) semiconductor material can be present in the shell.

In certain embodiments of the present disclosure, the core includes a metal phosphide (e.g., indium phosphide (InP), gallium phosphide (GaP), aluminum phosphide

(AlP)), a metal selenide (e.g., cadmium selenide (CdSe), zinc selenide (ZnSe), magnesium selenide (MgSe)), or a metal telluride (e.g., cadmium telluride (CdTe), zinc telluride (ZnTe)). In certain embodiments, the core includes a metal phosphide (e.g., indium phosphide) or a metal selenide (e.g., cadmium selenide). In certain preferred embodiments of the present disclosure, the core includes a metal phosphide (e.g., indium phosphide).

The shell can be a single layer or multilayered. In some embodiments, the shell is a multilayered shell. The shell can include any of the core materials described herein. In certain embodiments, the shell material can be a semiconductor material having a higher bandgap energy than the semiconductor core. In other embodiments, suitable shell materials can have good conduction and valence band offset with respect to the semiconductor core, and in some embodiments, the conduction band can be higher and the valence band can be lower than those of the core. For example, in certain embodiments, semiconductor cores that emit energy in the visible region such as, for example, CdS, CdSe, CdTe, ZnSe, ZnTe, GaP, InP, or GaAs, or near IR region such as, for example, InP, InAs, InSb, PbS, or PbSe may be coated with a shell material having a bandgap energy in the ultraviolet regions such as, for example, ZnS, GaN, and magnesium chalcogenides such as MgS, MgSe, and MgTe. In other embodiments, semiconductor cores that emit in the near IR region can be coated with a material having a bandgap energy in the visible region such as CdS or ZnSe.

Formation of the core/shell nanoparticles may be carried out by a variety of methods. Suitable core and shell precursors useful for preparing semiconductor cores are known in the art and can include Group 2 elements, Group 12 elements, Group l3 elements, Group 14 elements, Group 15 elements, Group 16 elements, and salt forms thereof. For example, a first precursor may include metal salt (M+X-) including a metal atom (M+) such as, for example, Zn, Cd, Hg, Mg, Ca, Sr, Ba, Ga, In, Al, Pb, Ge, Si, or in salts and a counter ion (X-), or organometallic species such as, for example, dialkyl metal complexes. The preparation of a coated semiconductor nanocrystal core and core/shell nanocrystals can be found in, for example, Dabbousi et al. (1997) *J. Phys. Chem. B* 101:9463, Hines et al. (1996) *J. Phys.Chem.* 100: 468-471, and Peng et al. (1997) *J. Amer. Chem. Soc.* 119:7019-7029, as well as in U.S. Pat. No. 8,283,412 (Liu et al.) and International Publication No. WO 2010/039897 (Tulsky et al.).

In certain preferred embodiments of the present disclosure, the shell includes a metal sulfide (e.g., zinc sulfide or cadmium sulfide). In certain embodiments, the shell includes a zinc-containing compound (e.g., zinc sulfide or zinc selenide). In certain embodiments, a multilayered shell includes an inner shell overcoating the core, wherein the inner shell includes zinc selenide and zinc sulfide. In certain embodiments, a multilayered shell includes an outer shell overcoating the inner shell, wherein the outer shell includes zinc sulfide.

In some embodiments, the core of the shell/core nanoparticle contains a metal phosphide such as indium phosphide, gallium phosphide, or aluminum phosphide. The shell contains zinc sulfide, zinc selenide, or a combination thereof. In some more particular embodiments, the core contains indium phosphide and the shell is multilayered with the inner shell containing both zinc selenide and zinc sulfide and the outer shell containing zinc sulfide.

The thickness of the shell(s) may vary among embodiments and can affect fluorescence wavelength, quantum yield, fluorescence stability, and other photostability characteristics of the nanocrystal. The skilled artisan can select the appropriate thickness to achieve desired properties and may modify the method of making the core/shell nanoparticles to achieve the appropriate thickness of the shell(s).

The diameter of the fluorescent semiconductor nanoparticles (i.e., quantum dots) of the present disclosure can affect the fluorescence wavelength. The diameter of the quantum dot is often directly related to the fluorescence wavelength. For example, cadmium selenide quantum dots having an average particle diameter of about 2 to 3 nanometers tend to fluoresce in the blue or green regions of the visible spectrum while cadmium selenide quantum dots having an average particle diameter of about 8 to 10 nanometers tend to fluoresce in the red region of the visible spectrum.

Since InP may be purified by bonding with dodecylsuccinic acid (DDSA) and lauric acid (LA) first, following by precipitation from ethanol, the precipitated quantum dots may have some of the acid functional ligands attached thereto, prior to dispersing in the fluid carrier. Similarly, CdSe quantum dots may be functionalized with amine-functional ligands as result of their preparation, prior to functionalization with the instant ligands. As result, the quantum dots may be functionalized with those surface modifying additives or ligands resulting from the original synthesis of the nanoparticles.

As result, the quantum dots may be surface modified with ligands of Formula III:

R^5-$R^{12}(X)_n$ III

wherein

R^5 is (hetero)hydrocarbyl group having C_2 to C_{30} carbon atoms;

R^{12} is a hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene;

n is at least one;

X is a ligand group, including -CO_2H, -SO_3H, -$P(O)(OH)_2$, -OP(O)(OH), -OH and -NH_2.

In addition to, or in lieu of, the ligands of Formula III, the nanoparticles may be surface modified with fluorochemical ligands of the formula:

R_f^1-$[X^{21}$-R^{22}-X^{22}-$R^{23}(L)_v]_w$ IV

wherein

R_f^1 is a perfluoroalkyl, perfluoroether or perfluoropolyether group of valence w,

R^{22} is a divalent hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene;

R^{23} is a divalent hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene;

X^{21} is –CH_2-O-, -O-, -S-, -CO_2-, -$CONR^1$-, or -SO_2NR^1- where R^1 is H or C_1-C_4 alkyl;

X^{22} is a covalent bond, –S-, -O- or -NR^1-, -CO_2-, -$CONR^1$-, or -SO_2NR^1- where R^1 is H or C_1-C_4 alkyl;

v at least one;

w is 1 or 2;

L is an ligand group selected from –CO_2H, -SH, -$P(O)(OH)_2$, -P(O)OH, -NH_2 -OH, and -SO_3H. Such fluorochemical ligands are described in Applicant's copending application US 62/269711, filed 18 December 2015 and incorporated herein by reference.

When using a perfluorinated carrier fluid, it is preferred that the nanoparticles are ligand functionalized with the compounds of Formula IV to improve the compatibility of the phases.

Such additional surface modifying ligands may be added when the functionalizing with the stabilizing copolymer (as described herein and of Formula V), or may be attached to the nanoparticles as result of the synthesis. Such additional surface modifying agents are present in amounts less than or equal to the weight of the instant stabilizing copolymer, preferably 10wt.% or less, relative to the amount of the stabilizing copolymer.

Various methods can be used to surface modify the fluorescent semiconductor nanoparticles with the ligand compounds. In some embodiments, procedures similar to

those described in U.S. 7160613 (Bawendi et al.) and 8,283,412 (Liu et al.) can be used to add the surface modifying agent. For example, the ligand compound and the fluorescent semiconductor nanoparticles can be heated at an elevated temperature (e.g., at least 50°C, at least 60°C, at least 80°C, or at least 90°C) for an extended period of time (e.g., at least 1 hour, at least 5 hours, at least 10 hours, at least 15 hours, or at least 20 hours).

If desired, any by-product of the synthesis process or any solvent used in surface-modification process can be removed, for example, by distillation, rotary evaporation, or by precipitation of the nanoparticles and centrifugation of the mixture followed by decanting the liquid and leaving behind the surface-modified nanoparticles. In some embodiments, the surface-modified fluorescent semiconductor nanoparticles are dried to a powder after surface-modification. In other embodiments, the solvent used for the surface modification is compatible (i.e., miscible) with any carrier fluids used in compositions in which the nanoparticles are included. In these embodiments, at least a portion of the solvent used for the surface-modification reaction can be included in the carrier fluid in which the surface-modified, fluorescent semiconductor nanoparticles are dispersed.

The fluorescent semiconductor nanoparticles are stabilized using a copolymer having 1) pendent phosphine, stibine or arsine groups and 2) pendent fluorochemical groups. The stabilizing copolymer improves the stability of the quantum dots for their use in quantum dot articles. In particular, the instant stabilizing copolymer renders the quantum dots stable in the dispersion of fluorochemical carrier fluids, droplets of which are dispersed in the polymeric matrix. The combination of the stabilizing copolymers with the quantum dots may prevent the quantum dot particles from photodegradation.

More particularly, the stabilizing copolymer is of the formula:

$$\sim[M^{stab}]_d\text{-}[M^{FC}]_e\sim, \qquad V$$

where

$[M^{stab}]$ represents monomer units having pendent phosphine, arsine or stibine groups and subscript d parts by weight; and

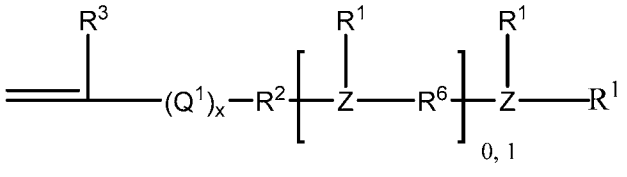
$[M^{FC}]$ represents fluorochemical-functional monomer units having subscript e parts by weight.

The copolymer generally is at least 50, preferably >60, more preferably greater than 70 parts by weight of M^{FC} monomer units and less than 50, preferably less than 40, more preferably less than 30 parts by weight of M^{stab} monomer units.

It is generally preferred that the number of monomer units of the copolymer is ≥ 8. With reference to Formula V subscripts a+b ≥ 8. It is further preferred that the number of monomer units in the copolymer is ≤ 30, preferably ≤ 25. The molecular weight of the copolymer may be controlled by the addition of chain transfer agents during free radical polymerization of the monomers, as is known in the art.

A chain transfer agent may also be used during synthesis of the copolymer to control the molecular weight. Chain transfer agents which may be used are mercapto compounds such as dodecylmercaptan, and halogen compounds such as carbon tetrabromide. For simplicity, the copolymeric copolymers illustrated herein do not show the residue of the chain transfer agent.

The monomer units represented by M^{stab} may derived from monomers of the formula:



, VI

wherein

each R^1 is a hydrocarbyl group including alkyl, aryl, alkaryl and aralkyl;

R^2 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene;

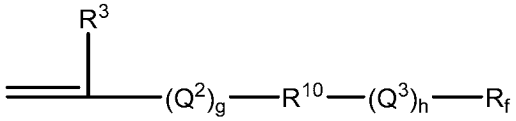
Z is P, As or Sb;

Q^1 is a functional group selected from $–CO_2$-, -O-, -S-, $-CONR^3$-, $-NH-CO-NR^3$-, and $–NR^3$-, where R^3 is H or C_1-C_4 alkyl, and subscript x is 0 or 1, and

R^6 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene.

Preferably at least one of the R^1 groups is an aryl group, and all of the R^1 groups are aryl groups. In some preferred embodiments R^2 comprises are aryl group, an alkaryl group or an aralkyl group.

The copolymer further comprises monomer units derived from monomers of the formula:



VII

wherein

Q^2 is selected from a covalent bond ("-"), $-CO_2-$, $-CONR^3-$, $-NH-CO-NR^3-$, and $-NR^3-$, where R^3 is H or C_1-C_4 alkyl;

Q^3 is selected from $-CH_2-S-$, $-CH_2-O-$, $-CO_2-$, $-CONR^3-$, $-NH-CO-NR^3-$, and $-NR^3$, where R^3 is H or C_1-C_4 alkyl,

subscripts g and h are independently 0 or 1;

R^{10} is a hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene and R_f is a perfluorinated group.

The perfluorinated R_f group may be a perfluoroalkyl, a perfluoroether, or a perfluoropolyether. The R_f groups can be linear, branched and are of the formula:

$C_aF_{2a+1}-(O-C_bF_{2b})_c-$,

where a is at least 1, preferably 1-10, more preferably 2-6;

b is at least 1, preferably 1-10, more preferably 2-6, and c may be a number from 0 to 50, preferably 1 to 30, more preferably 1 to 10. As can be seen, when subscript c is zero, the R_f group is a perfluoroalkyl, and a perfluoroether or perfluoropolyether when subscript c is non-zero.

In preferred embodiments, the R_f has at least one catenated (in-chain) oxygen heteroatoms, i.e. R_f is a perfluoroether or perfluoropolyether.

Exemplary perfluoropolyethers include, but are not limited to, those that have perfluorinated repeating units selected from the group of $-(C_pF_{2p})-$, $-(C_pF_{2p}O)-$, $-(CF(R_f^2))-$, $-(CF(R_f^2)O)-$, $-(CF(R_f^2)C_pF_{2p}O)-$, $-(C_pF_{2p}CF(R_f^2)O)-$, $-(CF_2CF(R_f^2)O)-$, or combinations thereof. In these repeating units, p is typically an integer of 1 to 10. In some embodiments, p is an integer of 1 to 8, 1 to 6, 1 to 4, 1 to 3, or 1 to 2. The group R_f^2 is a fluorine atom, perfluoroalkyl group, perfluoroether group, nitrogen-containing perfluoroalkyl group, perfluoropolyether, or a perfluoroalkoxy group, all of which can be linear, branched, or cyclic. The R_f^2 group typically has no more than 12 carbon atoms, no more than 10 carbon atoms, or no more than 9 carbon atoms, no more than 4 carbon atoms, no more than 3 carbon atoms, no more than 2 carbon atoms, or no more than 1 carbon atom. In some embodiments, the R_f^2 group can have no more than 4, no more than 3, no more than 2, no more than 1, or no oxygen atoms. In these perfluoropolyether structures, the different repeat units can be distributed randomly along the chain.

Suitable structures for R_f groups include, but are not limited to,

R_f'-$CF_2O(CF_2O)_q(C_2F_4O)_rCF_2$-, R_f'-$(CF_2)_3O(C_4F_8O)_r(CF_2)_3$-, R_f'-$CF_2O(C_2F_4O)_rCF_2$-, and R_f'-$CF(CF_3)(OCF_2CF(CF_3))_sOC_tF_{2t}O(CF(CF_3)CF_2O)_sCF(CF_3)$-, wherein R_f' is F or a perfluoroalkyl group; q has an average value of 0 to 50, 1 to 50, 3 to 30, 3 to 15, or 3 to 10; r has an average value of 0 to 50, 3 to 30, 3 to 15, or 3 to 10; s has an average value of 0 to 50, 1 to 50, 3 to 30, 3 to 15, or 3 to 10; the sum (r + s) has an average value of 1 to 50 or 4 to 40; the sum (q + r) is greater than 0; and t is an integer of 2 to 6.

As synthesized, compounds typically include a mixture of R_f groups. The average structure is the structure averaged over the mixture components. The values of q, r, and s in these average structures can vary, as long as the compound has a number average molecular weight of at least about 300. Useful compounds often have a molecular weight (number average) of 400 to 5000, 800 to 4000, or 1000 to 5000.

Preferably, R_f is the oligomer of hexafluoropropylene oxide (HFPO) with a number average molecular weight at least 1,000.

The ligands may be prepared from a perfluoroether ester, such as R_f-CO_2CH_3. The ester can be reacted with a hydroxy amine followed by further functionalization to provide the polymerizable group:

R_f-CO_2CH_3 + H_2N-R^{10}-OH → R_f-CO-NH-R^{10}-OH

R_f-CO-NH-R^{10}-OH + X-C(R^3)=CH_2 → VII

An ester of a perfluorinated acid can be reduced to a –CH_2-OH group, facilitating preparation of compounds having a -CH_2-OH "Q^3" group. This in turn may be reacted with a vinyl halide, such as allyl bromide to provide a terminal allyl unsaturation. Alternatively, the nucleophilic –CH_2-OH terminal group with a compound having an electrophilic group to provide the requisite unsaturation.

R_f-CO_2CH_3 → R_f-CH_2-OH → R_f-CH_2-O-CH_2CH=CH_2.

R_f-CH_2-OH + E-R^{10}-$(Q^2)_g$-C(R^3)=CH_2 → VII, where E is an electrophilic functional group including ester, acid halide, isocyanate, aziridine, and other known in the art.

The –CH_2-O- "Q^3" group can be converted to a –CH_2-S- group by reacting with a perfluorosulfonyl fluoride, displacement with a thioester, followed by hydrolysis. The -CH_2-SH may be used in displacement and condensation reaction, or in ene reactions to provide the requisite unsaturation. Longer chain thiols may be prepared by reacting compounds of the formula R_f-CH_2OH with an allyl halide to provide a terminal allyl group, followed by an ene reaction with a thioester, and hydrolysis.

R_f-CH_2OH → R_f-CH_2OSO_2-C_4F_9 → R_f-CH_2-S-CO-CH_3 → R_f-CH_2-SH.

R_f-CH_2OCH2-CH=$CH2$ → R_f-$CH_2CH_2CH_2$-S-CO-CH_3 → R_f-$CH_2CH_2CH_2$-SH

Alternatively, a perfluorinated acid fluoride may be reacted with fluoride ion to produce an intermediate having a nucleophilic $-CF_2-O^-$ group as shown. Similarly, perfluoroketones may be reacted with fluoride ion to produce a secondary perfluoroalkoxide nucleophile. The intermediate may be functionalized with a terminal olefin, such as with allyl bromide, or reacted with a compound of the formula $Y-R^{10}-Q^2-C(R^3)=CH_2$, where Y is a leaving group, such as halide or tosylate:

R_f-CO-F → R_f-CF_2-O^- → R_f-CF_2-O-$CH_2CH=CH_2$ →

R_f-CF_2-O-CH_2CH_2-CH_2-S-C_3H_6-$(Q^2)_g$-$C(R^3)=CH_2$,

or

R_f-CF_2-O^- + $Y-R^{10}$-$(Q^2)_g$-$C(R^3)=CH_2$ → R_f-CF_2-O-R^{10}-$(Q^2)_g$-$C(R^3)=CH_2$

A dispersion of the copolymer stabilized nanoparticles composition may also include a fluorinated carrier fluid. Preferably the dispersion comprises a fluorinated carrier fluid. The fluorinated carrier fluid are typically selected to be compatible (i.e., miscible) with the stabilizing copolymer added to the fluorescent semiconductor nanoparticles. The copolymer stabilized nanoparticles and fluorinated carrier fluid form a coating that is transparent when viewed with the human eye. Likewise, any precursors of the polymeric materials that are included in the dispersion composition are soluble in a fluorinated carrier fluid and form a coating that is transparent when viewed with the unaided human eye. The term transparent means transmitting at least 85% of incident light in the visible spectrum (about 400-700 nm wavelength).

The optional fluorinated carrier fluids are inert, liquid at 25°C and have a boiling point ≥100°C, preferably ≥150°C; and can be one or a mixture of perfluorinated or highly fluorinated liquid compounds having, in some embodiments, at least 8 carbon atoms or more, and optionally containing one or more catenary heteroatoms, such as divalent oxygen, hexavalent sulfur, or trivalent nitrogen and having a hydrogen content of less than 5 percent by weight or less than 1 percent by weight. Higher boiling points are preferred so that the carrier fluids remain when organic solvents used in the preparation are removed.

Suitable fluorinated, inert fluids useful of the present disclosure include, for example, perfluoroalkanes or perfluorocycloalkanes, such as, perfluorooctane, perfluorononane, perfluorodecane, perfluorotetradecahydrophenanthrene, perfluorodecalin, and perfluoromethyldecalin; perfluoroamines, such as, perfluorotripentyl amine, perfluorotributyl amine, perfluorotripropyl amine, perfluorotriamyl amine, and perfluoro-N-isopropyl morpholine; perfluoroethers, such as $HCF_2(OCF(CF_3)CF_2)_sOCF_2CF_2H$, $HCF_2(OCF(CF_3)CF_2)_s$-$(OCF_2)_q$-OCF_2H, (where subscripts s and q are as defined for the fluorinated ligand compounds), perfluorobutyl tetrahydrofuran, perfluorodibutyl ether, perfluorobutoxyethoxy formal, perfluorohexyl formal, and perfluorooctyl formal; perfluoropolyethers; hydrofluorocarbons, such as pentadecafluorohydroheptane, 1, 1,2,2- tetrafluorocyclobutane, 1 -trifluoromethyl- 1,2,2-trifluorocyclobutane and 2-hydro-3- oxaheptadecafluorooctane.

In some embodiments, the copolymer stabilized quantum dots are added to the fluid carrier in amounts such that the optical density is at least 10, optical density defined as the absorbance at 440nm for a cell with a path length of 1 cm solution.

The stabilized fluorescent semiconductor nanoparticles may be dispersed in a solution, suspension or dispersion that contains (a) a fluorinated carrier fluid and (b) a polymeric binder, a precursor of the polymeric binder, or combinations thereof. The ligand functionalized nanoparticles may be dispersed in the carrier fluid, which is then dispersed in the polymeric binder, forming droplets of the nanoparticles in the carrier, fluid, which in turn are dispersed in the polymeric binder. Preferably, the nanoparticles may be surface-modified by the fluorochemical ligands of Formula V.

The polymeric binders desirably provide barrier properties to exclude oxygen and moisture. If water and/or oxygen enter the quantum dot article, the quantum dots can degrade and ultimately fail to emit light when excited by ultraviolet or blue light irradiation. Slowing or eliminating quantum dot degradation along the laminate edges is particularly important to extend the service life of the displays in smaller electronic devices such as those utilized in, for example, handheld devices and tablets.

The polymeric binders or resins desirably provide barrier properties to exclude oxygen and moisture when cured. If water and/or oxygen enter the quantum dot article, the quantum dots can degrade and ultimately fail to emit light when excited by ultraviolet or blue light irradiation. Slowing or eliminating quantum dot degradation along the

laminate edges is particularly important to extend the service life of the displays in smaller electronic devices such as those utilized in, for example, handheld devices and tablets.

Exemplary polymeric binders include, but are not limited to, polysiloxanes, fluoroelastomers, polyamides, polyimides, polycarolactones, polycaprolactams, polyurethanes, polyethers, polyvinyl chlorides, polyvinyl acetates, polyesters, polycarbonates, polyacrylates, polymethacrylates, polyacrylamides, and polymethacrylamides.

Suitable precursors of the polymeric binder or resin include any precursor materials used to prepare the polymeric materials listed above. Exemplary precursor materials include acrylates that can be polymerized to polyacrylates, methacrylates that can be polymerized to form polymethacrylates, acrylamides that can be polymerized to form polyacrylamides, methacrylamides that can be polymerized to form polymethacrylamides, epoxy resins and dicarboxylic acids that can be polymerized to form polyesters, diepoxides that can be polymerized to form polyethers, isocyanates and polyols that can be polymerized to form polyurethanes, or polyols and dicarboxylic acids that can be polymerized to form polyesters.

In some embodiments, such as CdSe, the polymeric binder is a thermally curable epoxy-amine composition optionally further comprising a radiation-curable acrylate as described in Applicant's copending WO 2015095296 (Eckert et al.); Thiol-epoxy resins as described in US 62/148219 (Qiu et al., filed 16 April 2015), thiol-alkene-epoxy resins as described in US 62148212 (Qui et al. filed 16 April 2015); thiol-alkene resins as described in US 62/080488 (Qui et al., filed 17 November 2014), and thiol silicones as described in US 61/950281 (Qiu et al., filed 10 march 2014).

In some preferred embodiments the polymeric binder is a radiation curable oligomer having the general formula

R^{Olig}-(L^1-Z^1)$_d$, wherein

R^{Olig} groups include urethanes, polyurethanes, esters, polyesters, polyethers, polyolefins, polybutadienes and epoxies;

L^1 is a linking group;

Z^1 is a pendent, free-radically polymerizable group such as (meth)acryloyl, vinyl or alkynyl and is preferably a (meth)acrylate, and

d is greater than 1, preferably at least 2.

The linking group L^1 between the oligomer segment and ethylenically unsaturated end group includes a divalent or higher valency group selected from an alkylene, arylene, heteroalkylene, or combinations thereof and an optional divalent group selected from carbonyl, ester, amide, sulfonamide, or combinations thereof. L^1 can be unsubstituted or substituted with an alkyl, aryl, halo, or combinations thereof. The L^1 group typically has no more than 30 carbon atoms. In some compounds, the L^1 group has no more than 20 carbon atoms, no more than 10 carbon atoms, no more than 6 carbon atoms, or no more than 4 carbon atoms. For example, L^1 can be an alkylene, an alkylene substituted with an aryl group, or an alkylene in combination with an arylene or an alkyl ether or alkyl thioether linking group.

The pendent, free radically polymerizable functional groups Z^1 may be selected from the group consisting of vinyl, vinyl ether, ethynyl, and (meth)acyroyl which includes acrylate, methacrylate, acrylamide and methacrylamide groups.

The oligomeric group R^{olig} may be selected from poly(meth)acrylate, polyurethane, polyepoxide, polyester, polyether, polysulfide, polybutadiene, hydrogenated polyolefins (including hydrogenated polybutadienes, isoprenes and ethylene/propylene copolymers, and polycarbonate oligomeric chains.

As used herein, "(meth)acrylated oligomer" means a polymer molecule having at least two pendent (meth)acryloyl groups and a weight average molecular weight (M_w) as determined by Gel Permeation Chromatography of at least 1,000 g/mole and typically less than 50,000 g/mole.

(Meth)acryloyl epoxy oligomers are multifunctional (meth)acrylate esters and amides of epoxy resins, such as the (meth)acrylated esters of bisphenol-A epoxy resin. Examples of commercially available (meth)acrylated epoxies include those known by the trade designations EBECRYL 600 (bisphenol A epoxy diacrylate of 525 molecular weight), EBECRYL 605 (EBECRYL 600 with 25% tripropylene glycol diacrylate), EBECRYL 3700 (bisphenol-A diacrylate of 524 molecular weight) and EBECRYL 3720H (bisphenol A diacrylate of 524 molecular weight with 20% hexanediol diacrylate) available from Cytec Industries, Inc., Woodland Park, NJ; and PHOTOMER 3016 (bisphenol A epoxy acrylate), PHOTOMER 3016-40R (epoxy acrylate and 40% tripropylene glycol diacrylate blend), and PHOTOMER 3072 (modified bisphenol A

acrylate, etc.) available from BASF Corp., Cincinnati, OH, and Ebecryl 3708 (modified bisphenol A epoxy diacrylate) available from Cytec Industries, Inc., Woodland Park, NJ..

(Meth)acrylated urethanes are multifunctional (meth)acrylate esters of hydroxy terminated isocyanate extended polyols, polyesters or polyethers. (Meth)acrylated urethane oligomers can be synthesized, for example, by reacting a diisocyanate or other polyvalent isocyanate compound with a polyvalent polyol (including polyether and polyester polyols) to yield an isocyanate terminated urethane prepolymer. A polyester polyol can be formed by reacting a polybasic acid (e.g., terephthalic acid or maleic acid) with a polyhydric alcohol (e.g., ethylene glycol or 1,6-hexanediol). A polyether polyol useful for making the acrylate functionalized urethane oligomer can be chosen from, for example, polyethylene glycol, polypropylene glycol, poly(tetrahydrofuran), poly(2-methyl-tetrahydrofuran), poly(3-methyl-tetrahydrofuran) and the like. Alternatively, the polyol linkage of an acrylated urethane oligomer can be a polycarbonate polyol.

Subsequently, (meth)acrylates having a hydroxyl group can then be reacted with the terminal isocyanate groups of the prepolymer. Both aromatic and the preferred aliphatic isocyanates can be used to react with the urethane to obtain the oligomer. Examples of diisocyanates useful for making the (meth)acrylated oligomers are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate and the like. Examples of hydroxy terminated acrylates useful for making the acrylated oligomers include, but are not limited to, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, α-hydroxybutyl acrylate, polyethylene glycol (meth)acrylate and the like.

A (meth)acrylated urethane oligomer can be, for example, any urethane oligomer having at least two acrylate functionalities and generally less than about six functionalities. Suitable (meth)acrylated urethane oligomers are also commercially available such as, for example, those known by the trade designations PHOTOMER 6008, 6019, 6184 (aliphatic urethane triacrylates) available from Henkel Corp.; EBECRYL 220 (hexafunctional aromatic urethane acrylate of 1000 molecular weight), EBECRYL 284 (aliphatic urethane diacrylate of 1200 molecular weight diluted with 12% of 1 ,6- hexanediol diacrylate), EBECRYL 4830 (aliphatic urethane diacrylate of 1200 molecular weight diluted with 10% of tetraethylene glycol diacrylate), and EBECRYL 6602 (trifunctional aromatic urethane acrylate of 1300 molecular weight diluted with 40% of trimethylolpropane ethoxy

triacrylate), available from UCB Chemical; and SARTOMER CN1963, 963E75, 945A60, 963B80, 968, and 983) available from Sartomer Co., Exton, PA.

Properties of these materials may be varied depending upon selection of the type of isocyanate, the type of polyol modifier, the reactive functionality and molecular weight. Diisocyanates are widely used in urethane acrylate synthesis and can be divided into aromatic and aliphatic diisocyanates. Aromatic diisocyanates are used for manufacture of aromatic urethane acrylates which have significantly lower cost than aliphatic urethane acrylates but tend to noticeably yellow on white or light colored substrates. Aliphatic urethane acrylates include aliphatic diisocyanates that exhibit slightly more flexibility than aromatic urethane acrylates that include the same functionality, a similar polyol modifier and at similar molecular weight.

The curable composition may comprise a functionalized poly(meth)acrylate oligomer, which may be obtained from the reaction product of: (a) from 50 to 99 parts by weight of (meth)acrylate ester monomer units that are homo- or co-polymerizable to a polymer (b) from 1 to 50 parts by weight of monomer units having a pendent, free-radically polymerizable functional group. Examples of such materials are available from Lucite International (Cordova, TN) under the trade designations of Elvacite 1010, Elvacite 4026, and Elvacite 4059.

The (meth)acrylated poly(meth)acrylate oligomer may comprise a blend of an acrylic or hydrocarbon polymer with multifunctional (meth)acrylate diluents. Suitable polymer/diluent blends include, for example, commercially available products such as EBECRYL 303, 745 and 1710 all of which are available from Cytec Industries, Inc., Woodland Park, NJ.

The curable composition may comprise a (meth)acrylated polybutadiene oligomer, which may be obtained from a carboxyl- or hydroxyl- functionalized polybutadiene. By carboxyl or hydroxy functionalised polybutadiene is meant to designate a polybutadiene comprising free –OH or —COOH groups. Carboxyl functionalized polybutadienes are known, they have for example been described in U.S. 3,705,208 (Nakamuta et al.) and are commercially available under the trade name of Nisso PB C-1000 (Nisso America, New York, NY). Carboxyl functionalized polybutadienes can also be obtained by the reaction of a hydroxyl functionalized polybutadiene (that is a polybutadiene having free hydroxyl

groups) with a cyclic anhydride such as for example has been described in U.S. 5,587,433 (Boeckeler), U.S. 4,857,434 (Klinger) and U.S. 5,462,835 (Mirle).

Carboxyl and hydroxyl functionalized polybutadienes suitable for being used in the process according to the present invention contain besides the carboxyl and/or hydroxyl groups, units derived from the polymerization of butadiene. The polybutadiene (PDB) generally comprises 1-4 cis units/1-4 trans units/1-2 units in a ratio a/b/c where a, b and c range from 0 to 1 with a+b+c=1. The number average molecular weight (M_n) of the functionalized polybutadiene is preferably from 200 to 10000 Da. The M_n is more preferably at least 1000. The M_n more preferably does not exceed 5000 Da. The —COOH or -OH functionality is generally from 1.5 to 9, preferably from 1.8 to 6.

Exemplary hydroxyl and carboxyl polybutadienes include without limitation Poly BD R-20LM (hydroxyl functionalized PDB, a=0.2, b=0.6, c=0.2, M_n 1230) and Poly BD R45-HT (hydroxyl functionalized PDB, a=0.2, b=0.6, c=0.2, M_n 2800) commercialized by Atofina, Nisso-PB G-1000 (hydroxyl functionalized PDB, a=0, b<0.15, c>0.85, M_n 1250-1650), Nisso-PB G-2000 (hydroxyl functionalized PDB, a=0, b<0.15, c>0.85, M_n 1800-2200), Nisso-PB G-3000 (hydroxyl functionalized PDB, a=0, b<0.10, c>0.90, M_n 2600-3200), Nisso-PB C-1000 (carboxyl functionalized PDB, a=0, b<0.15, c>0.85, Mn 1200-1550) obtainable from Nisso America, New York, NY.

When carboxyl functionalized polybutadienes obtained from the reaction of a hydroxyl functionalized polybutadiene with a cyclic anhydride are used, this cyclic anhydride preferably include phthalic anhydride, hexahydrophthalic anhydride, glutaric anhydride, succinic anhydride, dodecenylsuccinic anhydride, maleic anhydride, trimellitic anhydride, pyromellitic anhydride. Mixtures of anhydrides can also be used. The amount of anhydride used for the preparation of a carboxyl functionalized polybutadiene from a hydroxyl functionalized polybutadiene is generally at least 0.8 molar, preferably at least 0.9 molar and more preferably at least 0.95 molar equivalent per molar equivalents of —OH groups present in the polybutadiene.

A (meth)acrylated polybutadiene oligomer, which is the reaction product of a carboxyl functionalized polybutadiene, may be prepared with a (meth)acrylated monoepoxide. (Meth)acrylated mono-epoxides are known. Examples of (meth)acrylated mono-epoxides that can be used are glycidyl (meth)acrylate esters, such as glycidylacrylate, glycidylmethacrylate, 4-hydroxybutylacrylate glycidylether, bisphenol-A

diglycidylether monoacrylate. The (meth)acrylated mono-epoxides are preferably chosen from glycidylacrylate and glycidylmethacrylate. Alternatively, a (meth)acrylated polybutadiene oligomer which is the reaction product of a hydroxyl functionalized polybutadiene may be prepared with a (meth)acrylate ester, or halide.

Some (meth)acrylated polybutadienes that can be used, for example, include Ricacryl 3100 and Ricacryl 3500, manufactured by Sartomer Company, Exton, PA., USA, and Nisso TE-2000 available from Nisso America, New York, NY. Alternatively, other methacrylated polybutadienes can be used. These include dimethacrylates of liquid polybutadiene resins composed of modified, esterified liquid polybutadiene diols. These are available under the tradename CN301 and CN303, and CN307, manufactured by Sartomer Company, Exton, PA., USA. Regardless which methacrylated polybutadiene is used with embodiments of the invention, the methacrylated polybutadiene can include a number of methacrylate groups per chain from about 2 to about 20.

Alternatively, the acrylate functionalized oligomers can be polyester acrylate oligomers, acrylated acrylic oligomers, acrylated epoxy oligomers, polycarbonate acrylate oligomers or polyether acrylate oligomers. Useful epoxy acrylate oligomers include CN2003B from Sartomer Co. (Exton, PA). Useful polyester acrylate oligomers include CN293, CN294, and CN2250, 2281, 2900 from Sartomer Co. (Exton, PA) and EBECRYL 80, 657, 830, and 1810 from UCB Chemicals (Smyrna, GA). Suitable polyether acrylate oligomers include CN501, 502, and 551 from Sartomer Co. (Exton, PA). Useful polycarbonate acrylate oligomers can be prepared according to U.S. 6,451,958 (Sartomer Technology Company Inc., Wilmington, DE).

In each embodiment comprising a (meth)acrylated oligomer, the curable binder composition optionally, yet preferably, comprises diluent monomer in an amount sufficient to reduce the viscosity of the curable composition such that it may be coated on a substrate. In some embodiments, the composition may comprise up to about 70 wt-% diluent monomers to reduce the viscosity of the oligomeric component to less than 10000 centipoise and to improve the processability.

Useful monomers are desirably soluble or miscible in the (meth)acrylated oligomer, highly polymerizable therewith. Useful diluents are mono- and polyethylenically unsaturated monomers such as (meth)acrylates or (meth)acrylamides. Suitable monomers typically have a number average molecular weight no greater than 450

g/mole. The diluent monomer desirably has minimal absorbance at the wavelength of the radiation used to cure the composition. Such diluent monomers may include, for example, n-butyl acrylate, isobutyl acrylate, hexyl acrylate, 2-ethyl-hexylacrylate, isooctylacrylate, caprolactoneacrylate, isodecylacrylate, tridecylacrylate, laurylmethacrylate, methoxy-polyethylenglycol-monomethacrylate, laurylacrylate, tetrahydrofurfuryl-acrylate, ethoxy-ethoxyethyl acrylate and ethoxylated-nonylacrylate. Especially preferred are 2-ethyl-hexylacrylate, ethoxy-ethoxyethyl acrylate, tridecylacrylate and ethoxylated nonylacrylate. High T_g monomers having one ethylenically unsaturated group and a glass transition temperature of the corresponding homopolymer of 50°C. or more which are suitable in the present invention, include, for example, N-vinylpyrrolidone, N-vinyl caprolactam, isobornyl acrylate, acryloylmorpholine, isobornylmethacrylate, phenoxyethylacrylate, phenoxyethylmethacrylate, methylmethacrylate and acrylamide.

Furthermore, the diluent monomers may contain an average of two or more free-radically polymerizable groups. A diluent having three or more of such reactive groups can be present as well. Examples of such monomers include: C_2-C_{18} alkylenedioldi(meth)acrylates, C_3-C_{18} alkylenetrioltri(meth)acrylates, the polyether analogues thereof, and the like, such as 1,6-hexanedioldi(meth)acrylate, trimethylolpropanetri(meth)acrylate, triethyleneglycoldi(meth)acrylate, pentaeritritoltri(meth)acrylate, and tripropyleneglycol di(meth)acrylate, and di-trimethylolpropane tetraacrylate.

Suitable preferred diluent monomers include for example benzyl (meth)acrylate, phenoxyethyl (meth)acrylate; phenoxy-2-methylethyl (meth)acrylate; phenoxyethoxyethyl (meth)acrylate, 1-naphthyloxy ethyl acrylate; 2-naphthyloxy ethyl acrylate; phenoxy 2-methylethyl acrylate; phenoxyethoxyethyl acrylate; 2-phenylphenoxy ethyl acrylate; 4-phenylphenoxy ethyl acrylate; and phenyl acrylate .

Preferred diluent monomers includes phenoxyethyl (meth)acrylate, benzyl (meth)acrylate, and tricyclodecane dimethanol diacrylate. Phenoxyethyl acrylate is commercially available from Sartomer under the trade designation "SR339"; from Eternal Chemical Co. Ltd. under the trade designation "Etermer 210"; and from Toagosei Co. Ltd under the trade designation "TO-1166". Benzyl acrylate is commercially available from Osaka Organic Chemical, Osaka City, Japan. Tricyclodecane dimethanol diacrylate is commercially available from Sartomer under the trade designation “SR833”.

Such optional monomer(s) may be present in the polymerizable composition in amount of at least about 5 wt-%. The optional monomer(s) typically total no more than about 70 wt-% of the curable composition. The some embodiments the total amount of diluent monomer ranges from about 10 wt-% to about 50-%.

When using a free-radically curable polymeric binder, the curable composition further comprises photoinitiators, in an amount between the range of about 0.1% and about 5% by weight.

Useful photoinitiators include those known as useful for photocuring free-radically polyfunctional (meth)acrylates. Exemplary photoinitiators include benzoin and its derivatives such as alpha-methylbenzoin; alpha-phenylbenzoin; alpha-allylbenzoin; alpha-benzylbenzoin; benzoin ethers such as benzil dimethyl ketal (e.g., "IRGACURE 651" from BASF, Florham Park, NJ), benzoin methyl ether, benzoin ethyl ether, benzoin n-butyl ether; acetophenone and its derivatives such as 2-hydroxy-2-methyl-1-phenyl-1-propanone (e.g., "DAROCUR 1173" from BASF, Florham Park, NJ) and 1-hydroxycyclohexyl phenyl ketone (e.g., "IRGACURE 184" from BASF, Florham Park, NJ); 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (e.g., "IRGACURE 907" from BASF, Florham Park, NJ); 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (e.g., "IRGACURE 369" from BASF, Florham Park, NJ) and phosphine oxide derivatives such as ethyl-2,4,6-trimethylbenzoylphenylphoshinate (e.g. “TPO-L” from BASF, Florham Park, NJ), and IRGACURE 819 (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide) available from BASF, Florham Park, NJ..

Other useful photoinitiators include, for example, pivaloin ethyl ether, anisoin ethyl ether, anthraquinones (e.g., anthraquinone, 2-ethylanthraquinone, 1-chloroanthraquinone, 1,4-dimethylanthraquinone, 1-methoxyanthraquinone, or benzanthraquinone), halomethyltriazines, benzophenone and its derivatives, iodonium salts and sulfonium salts, titanium complexes such as bis(eta5-2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl) phenyl]titanium (e.g., "CGI 784DC" from BASF, Florham Park, NJ); halomethyl-nitrobenzenes (e.g., 4-bromomethylnitrobenzene), mono- and bis-acylphosphines (e.g., "IRGACURE 1700", "IRGACURE 1800", "IRGACURE 1850", and "DAROCUR 4265").

In some embodiments, the polymeric binder is an epoxy compound that can be cured or polymerized by the processes that are those known to undergo cationic

polymerization and include 1,2-, 1,3-, and 1,4-cyclic ethers (also designated as 1,2-, 1,3-, and 1,4-epoxides). Suitable epoxy binders can include, for example, those epoxy binders described in U.S. Patent No. 6,777,460. In particular, cyclic ethers that are useful include the cycloaliphatic epoxies such as cyclohexene oxide and the ERL™ and UVR™ series type of binders available from Dow Chemical, Midland, MI, such as vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl-3, 4-epoxycyclohexane carboxylate, bis- (3,4-epoxycyclohexyl) adipate and 2- (3, 4-epoxycylclohexyl-5, 5-spiro-3,4-epoxy) cyclohexene-meta-dioxane; also included are the glycidyl ether type epoxy binders such as propylene oxide, epichlorohydrin, styrene oxide, glycidol, the EPON, EPONEX, and HELOXY series type of epoxy binders available from Resolution Performance Products, Houston, TX, including the diglycidyl either of bisphenol A and chain extended versions of this material such as EPON 828, EPON 1001, EPON 1004, EPON 1007, EPON 1009 and EPON 2002 or their equivalent from other manufacturers, EPONEX 1510, the hydrogenated diglycidyl either of bisphenol A, HELOXY 67, diglycidyl ether of 1,4- butanediol, HELOXY™ 107, diglycidyl ether of cyclohexane dimethanol, or their equivalent from other manufacturers, dicyclopentadiene dioxide, epoxidized vegetable oils such as epoxidized linseed and soybean oils available as VIKOLOX and VIKOFLEX binders from Atofina, Philadelphia, PA, epoxidized KRATON LIQUID POLYMERS, such as L-207 available from Kraton Polymers, Houston, TX, epoxidized polybutadienes such as the POLY BD binders from Atofina, Philadelphia, PA, 1,4-butanediol diglycidyl ether, polyglycidyl ether of phenolformaldehyde, and for example DENTM epoxidized phenolic novolac binders such as DEN 431 and DEN 438 available from Dow Chemical Co., Midland MI, epoxidized cresol novolac binders such as ARALDITE ECN 1299 available from Vantico AG, Basel, Switzerland, resorcinol diglycidyl ether, and epoxidized polystyrene/polybutadiene blends such as the Epofriendz binders such as EPOFRIEND A1010 available from Daicel USA Inc., Fort Lee, NJ, and resorcinol diglycidyl ether.

Higher molecular weight polyols include the polyethylene and polypropylene oxide polymers in the molecular weight (Mn) range of 200 to 20,000 such as the CARBOWAX polyethyleneoxide materials available from Dow Chemical Co., Midland, MI, caprolactone polyols in the molecular weight range of 200 to 5,000 such as the TONE polyol materials available from Dow, polytetramethylene ether glycol in the molecular

weight range of 200 to 4,000, such as the TERATHANE materials available from DuPont and POLYTHF 250 from BASF, polyethylene glycol, such as PEG™ 200 available from Dow, hydroxyl-terminated polybutadiene binders such as the POLY BD materials available from Atofina, Philadelphia, PA., phenoxy binders such as those commercially available from Phenoxy Associates, Rock Hill, S. C., or equivalent materials supplied by other manufacturers.

It is also within the scope of this invention to include one or more epoxy binders which can be blended together. It is also within the scope of this invention to include one or more mono or poly-alcohols which can be blended together. The different kinds of binders and alcohols can be present in any proportion.

It is within the scope of this invention to use vinyl ether monomers as the cationically curable material. Vinyl ether-containing monomers can be methyl vinyl ether, ethyl vinyl ether, tert-butyl vinyl ether, isobutyl vinyl ether, triethyleneglycol divinyl ether (RAPT-CURE DVE-3, available from International Specialty Products, Wayne, NJ), 1,4-cyclohexanedimethanol divinyl ether (RAPI-CURE CHVE, International Specialty Products), trimetylolpropane trivinyl ether (available from BASF Corp. , Mount Olive, NJ) and the VECTOMER divinyl ether binders from Morflex, Greensboro, N. C. , such as VECTOMER 2010, VECTOMER 2020, VECTOMER 4010, and VECTOMER 4020, or their equivalent from other manufacturers. It is within the scope of this invention to use a blend of more than one vinyl ether binder.

It is also within the scope of this invention to use one or more epoxy binders blended with one or more vinyl ether binders. The different kinds of binders can be present in any proportion.

The preferred epoxy binders include the ERL and the UVR type of binders especially 3,4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate, bis- (3,4-epoxycyclohexyl) adipate and 2- (3, 4-epoxycylclohexyl-5,5-spiro-3, 4-epoxy) cyclohexene-meta-dioxane and the bisphenol A EPON type binders including 2,2-bis- p-(2, 3-epoxypropoxy) phenylpropane and chain extended versions of this material and, binders of the type EPONEX 1510 and HELOXY 107 and 68. Also useful in the present invention are purified versions of these epoxies as described in U. S. Published Patent Application 2002/0022709 published 21 Feb 2002.

When preparing compositions containing epoxy monomers, hydroxy-functional materials can be added. The hydroxyl-functional component can be present as a mixture or a blend of materials and can contain mono-and polyhydroxyl containing materials. Preferably, the hydroxy-functional material is at least a diol. When used, the hydroxyl-functional material can aid in chain extension and in preventing excess crosslinking of the epoxy during curing, e. g., increasing the toughness of the cured composition.

When present, useful hydroxyl-functional materials include aliphatic, cycloaliphatic or alkanol-substituted arene mono-or poly-alcohols having from about 2 to about 18 carbon atoms and two to five, preferably two to four hydroxy groups, or combinations thereof. Useful mono-alcohols can include methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol, 1-butanol, 2-butanol, 1-pentanol, neopentyl alcohol, 3-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 2-phenoxyethanol, cyclopentanol, cyclohexanol, cyclohexylmethanol, 3-cyclohexyl-l-propanol, 2-norbornanemethanol and tetrahydrofurfuryl alcohol.

Polyols useful in the present invention include aliphatic, cycloaliphatic, or alkanol-substituted arene polyols, or mixtures thereof having from about 2 to about 18 carbon atoms and two to five, preferably two to four hydroxyl groups. Examples of useful polyols include 1,2-ethanediol, 1,2-propanediol, 1,3- propanediol, 1,4-butanediol, 1,3-butanediol, 2-methyl-1, 3-propanediol, 2, 2-dimethyl-1, 3- propanediol, 2-ethyl-1, 6-hexanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, glycerol, trimethylolpropane, 1,2, 6-hexanetriol, trimethylolethane, pentaerythritol, quinitol, mannitol, sorbitol, diethylene glycol, triethylene glycol, tetraethylene glycol, glycerine, 2-ethyl-2- (hydroxymethyl)-1, 3-propanediol, 2-ethyl-1, 3- pentanediol, 1,4-cyclohexanedimethanol, 1,4-benzene-dimethanol and polyalkoxylated bisphenol A derivatives. Other examples of useful polyols are disclosed in U. S. Pat. No. 4,503, 211.

Bi-functional monomers having both cationically polymerizable and free-radically polymerizable moieties in the same monomer are useful in the present invention, such as, for example, glycidyl methacrylate, or 2-hydroxyethyl acrylate.

It is also within the scope of this invention to add a free radically polymerizable monomer, such as an acrylate or methacrylate. The addition of such a monomer broadens the scope of obtainable physical properties and processing options. When two or more polymerizable monomers are present, they can be present in any proportion.

Suitable cationic photoinitiators are selected from organic onium cations, for example those described in photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2'~d Edition, J. V. Crivello & K. Dietliker, John Wiley and Sons, 1998, pp. 275 to 298, and U.S. Pat. Nos. 4,250,311, 3,708,296, 4,069,055, 4,216,288, 5,084,586 and 5,124,417 and such descriptions incorporated herein by reference, including aliphatic or aromatic Group IVA—VIIA (CAS version) centered onium salts, preferably I-, S-, P- and C-centered onium salts, such as those selected from sulfoxonium, diaryliodonium, triarylsulfonium, carbonium and phosphonium, and most preferably I-, and S-centered onium salts, such as those selected from sulfoxonium, diaryliodonium, and triarylsulfonium, wherein "aryl" means an unsubstituted or substituted aromatic moiety having up to four independently selected substituents.

The quantum dot layer can have any useful amount of quantum dots, and in some embodiments the quantum dot layer can include from 0.1 to 10 wt.%, preferably 0.1 to 1 wt.%, quantum dots, based on the total weight of the quantum dot layer (dots, optional liquid carrier and polymeric binder). The dispersion composition can also contain a surfactant (i.e., leveling agent), a polymerization initiator, and other additives, as known in the art.

Generally, the stabilized quantum dots, the stabilizing copolymer, the polymeric binder, fluorinated carrier fluid and surface modifying ligand of Formula IV are combined and subject to high shear mixing to produce a dispersion of the ligand functional quantum dots in the polymer matrix. The matrix is chosen such there is limited compatibility and the quantum dots form a separate, non-aggregating phase in the matrix. As the quantum dots are often prepared and ligand-functionalized in an organic solvent, the fluorinated carrier fluid enables separation and removal of any organic solvent.

The dispersion, comprising droplets of stabilized nanoparticle and optional fluorochemical carrier fluid, are dispersed in the binder resin, is then coated and cured either thermally, free-radically, or both to lock in the dispersed structure and exclude oxygen and water from the dispersed quantum dots.

When using a free-radically curable polymeric binder, the curable composition further comprises photoinitiators, in an amount between the range of about 0.1% and about 5% by weight.

Useful photoinitiators include those known as useful for photocuring free-radically polyfunctional (meth)acrylates. Exemplary photoinitiators include benzoin and its derivatives such as alpha-methylbenzoin; alpha-phenylbenzoin; alpha-allylbenzoin; alpha-benzylbenzoin; benzoin ethers such as benzil dimethyl ketal (e.g., "IRGACURE 651" from BASF, Florham Park, NJ), benzoin methyl ether, benzoin ethyl ether, benzoin n-butyl ether; acetophenone and its derivatives such as 2-hydroxy-2-methyl-1-phenyl-1-propanone (e.g., "DAROCUR 1173" from BASF, Florham Park, NJ) and 1-hydroxycyclohexyl phenyl ketone (e.g., "IRGACURE 184" from BASF, Florham Park, NJ); 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (e.g., "IRGACURE 907" from BASF, Florham Park, NJ); 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (e.g., "IRGACURE 369" from BASF, Florham Park, NJ) and phosphine oxide derivatives such as Ethyl-2,4,6-trimethylbenzoylphenylphoshinate (e.g. "TPO-L" from BASF, Florham Park, NJ), and Irgacure 819 (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide) available from BASF, Florham Park, NJ..

Other useful photoinitiators include, for example, pivaloin ethyl ether, anisoin ethyl ether, anthraquinones (e.g., anthraquinone, 2-ethylanthraquinone, 1-chloroanthraquinone, 1,4-dimethylanthraquinone, 1-methoxyanthraquinone, or benzanthraquinone), halomethyltriazines, benzophenone and its derivatives, iodonium salts and sulfonium salts, titanium complexes such as bis(eta5-2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl) phenyl]titanium (e.g., "CGI 784DC" from BASF, Florham Park, NJ); halomethyl-nitrobenzenes (e.g., 4-bromomethylnitrobenzene), mono- and bis-acylphosphines (e.g., "IRGACURE 1700", "IRGACURE 1800", "IRGACURE 1850", and "DAROCUR 4265").

The curable composition may be irradiated with activating UV or visible radiation to polymerize the components preferably in the wavelengths of 250 to 500 nanometers. UV light sources can be of two types: 1) relatively low light intensity sources such as blacklights that provide generally 10 mW/cm^2 or less (as measured in accordance with procedures approved by the United States National Institute of Standards and Technology as, for example, with a UVIMAP™ UM 365 L-S radiometer manufactured by Electronic Instrumentation & Technology, Inc., in Sterling, VA) over a wavelength range of 280 to 400 nanometers and 2) relatively high light intensity sources such as medium- and high-pressure mercury arc lamps, electrodeless mercury lamps, light emitting diodes, mercury-

xenon lamps, lasers and the like, which provide intensities generally between 10 and 5000 mW/cm^2 in the wavelength rages of 320-390nm (as measured in accordance with procedures approved by the United States National Institute of Standards and Technology as, for example, with a PowerPuck™ radiometer manufactured by Electronic Instrumentation & Technology, Inc., in Sterling, VA).

Referring to FIG. 1, quantum dot article 10 includes a first barrier layer 32, a second barrier layer 34, and a quantum dot layer 20 between the first barrier layer 32 and the second barrier layer 34. The quantum dot layer 20 includes a plurality of quantum dots 22 dispersed in a matrix 24.

The barrier layers 32, 34 can be formed of any useful material that can protect the quantum dots 22 from exposure to environmental contaminates such as, for example, oxygen, water, and water vapor. Suitable barrier layers 32, 34 include, but are not limited to, films of polymers, glass and dielectric materials. In some embodiments, suitable materials for the barrier layers 32, 34 include, for example, polymers such as polyethylene terephthalate (PET); oxides such as silicon oxide, titanium oxide, or aluminum oxide (e.g., SiO_2, Si_2O_3, TiO_2, or Al_2O_3); and suitable combinations thereof.

More particularly, barrier films can be selected from a variety of constructions. Barrier films are typically selected such that they have oxygen and water transmission rates at a specified level as required by the application. In some embodiments, the barrier film has a water vapor transmission rate (WVTR) less than about 0.005 g/m^2/day at 38°C. and 100% relative humidity; in some embodiments, less than about 0.0005 g/m^2/day at 38°C. and 100% relative humidity; and in some embodiments, less than about 0.00005 g/m^2/day at 38°C and 100% relative humidity. In some embodiments, the flexible barrier film has a WVTR of less than about 0.05, 0.005, 0.0005, or 0.00005 g/m^2/day at 50 °C and 100% relative humidity or even less than about 0.005, 0.0005, 0.00005 g/m^2/day at 85 °C and 100% relative humidity. In some embodiments, the barrier film has an oxygen transmission rate of less than about 0.005 g/m^2/day at 23°C and 90% relative humidity; in some embodiments, less than about 0.0005 g/m^2/day at 23 °C and 90% relative humidity; and in some embodiments, less than about 0.00005 g/m^2/day at 23 °C and 90% relative humidity.

Exemplary useful barrier films include inorganic films prepared by atomic layer deposition, thermal evaporation, sputtering, and chemical vapor deposition. Useful barrier

films are typically flexible and transparent. In some embodiments, useful barrier films comprise inorganic/organic. Flexible ultra-barrier films comprising inorganic/organic multilayers are described, for example, in U.S. 7,018,713 (Padiyath et al.). Such flexible ultra-barrier films may have a first polymer layer disposed on polymeric film substrate that is overcoated with two or more inorganic barrier layers separated by at least one second polymer layer. In some embodiments, the barrier film comprises one inorganic barrier layer interposed between the first polymer layer disposed on the polymeric film substrate and a second polymer layer 224.

In some embodiments, each barrier layer 32, 34 of the quantum dot article 10 includes at least two sub-layers of different materials or compositions. In some embodiments, such a multi-layered barrier construction can more effectively reduce or eliminate pinhole defect alignment in the barrier layers 32, 34, providing a more effective shield against oxygen and moisture penetration into the matrix 24. The quantum dot article 10 can include any suitable material or combination of barrier materials and any suitable number of barrier layers or sub-layers on either or both sides of the quantum dot layer 20. The materials, thickness, and number of barrier layers and sub-layers will depend on the particular application, and will suitably be chosen to maximize barrier protection and brightness of the quantum dots 22 while minimizing the thickness of the quantum dot article 10. In some embodiments each barrier layer 32, 34 is itself a laminate film, such as a dual laminate film, where each barrier film layer is sufficiently thick to eliminate wrinkling in roll-to-roll or laminate manufacturing processes. In one illustrative embodiment, the barrier layers 32, 34 are polyester films (e.g., PET) having an oxide layer on an exposed surface thereof.

The quantum dot layer 20 can include one or more populations of quantum dots or quantum dot materials 22. Exemplary quantum dots or quantum dot materials 22 emit green light and red light upon down-conversion of blue primary light from a blue LED to secondary light emitted by the quantum dots. The respective portions of red, green, and blue light can be controlled to achieve a desired white point for the white light emitted by a display device incorporating the quantum dot article 10. Exemplary quantum dots 22 for use in the quantum dot articles 10 include, but are not limited to, CdSe with ZnS shells. Suitable quantum dots for use in quantum dot articles described herein include, but are not limited to, core/shell luminescent nanocrystals including CdSe/ZnS, InP/ZnS, PbSe/PbS,

CdSe/CdS, CdTe/CdS or CdTe/ZnS. In exemplary embodiments, the luminescent nanocrystals include an outer ligand coating and are dispersed in a polymeric matrix. Quantum dot and quantum dot materials 22 are commercially available from, for example, Nanosys Inc., Milpitas, CA. The quantum dot layer 20 can have any useful amount of quantum dots 22, and in some embodiments the quantum dot layer 20 can include from 0.1 wt% to 1 wt% quantum dots, based on the total weight of the quantum dot layer 20.

In some embodiments, the quantum dot materials can include quantum dots dispersed in a liquid carrier. For example, the liquid carrier can include an oil such as an amino-silicone oil.

In one or more embodiments the quantum dot layer 20 can optionally include scattering beads or particles. These scattering beads or particles have a refractive index that differs from the refractive index of the matrix material 24 by at least 0.05, or by at least 0.1. These scattering beads or particles can include, for example, polymers such as silicone, acrylic, nylon, and the like, or inorganic materials such as TiO_2, SiO_x, AlO_x, and the like, and combinations thereof. In some embodiments, including scattering particles in the quantum dot layer 20 can increase the optical path length through the quantum dot layer 20 and improve quantum dot absorption and efficiency. In many embodiments, the scattering beads or particles have an average particle size from 1 to 10 micrometers, or from 2 to 6 micrometers. In some embodiments, the quantum dot material 20 can optionally include fillers such fumed silica.

In some preferred embodiments, the scattering beads or particles are Tospearl^{tm} 120A, 130A, 145A and 2000B spherical silicone resins available in 2.0, 3.0, 4.5 and 6.0 micron particle sizes respectively from Momentive Specialty Chemicals Inc., Columbus, Ohio.

The matrix 24 of the quantum dot layer 20 can be formed from an polymeric binder or binder precursor that adheres to the materials forming the barrier layers 32, 34 to form a laminate construction, and also forms a protective matrix for the quantum dots 22. In one embodiment, the matrix 24 is formed by curing or hardening an adhesive composition including an epoxy amine polymer and an optional radiation-curable methacrylate compound.

Referring to FIG. 2, in another aspect, the present disclosure is directed to a method of forming a quantum dot film article 100 including coating a polymeric binder

composition including quantum dots on a first barrier layer 102 and disposing a second barrier layer on the quantum dot material 104. In some embodiments, the method 100 includes polymerizing (e.g., radiation curing) a radiation curable polymeric binder to form a fully- or partially cured quantum dot material 106 and optionally thermally polymerizing the binder composition to form a cured polymeric binder 108. For thermally curable polymeric binders, step 106 is omitted.

In some embodiments, the binder composition can be cured or hardened by heating. In other embodiments, the binder composition may also be cured or hardened by applying radiation such as, for example, ultraviolet (UV) light. Curing or hardening steps may include UV curing, heating, or both. In some example embodiments that are not intended to be limiting, UV cure conditions can include applying about 10 mJ/cm^2 to about 4000 mJ/cm^2 of UVA, more preferably about 10mJ/cm^2 to about 1000 mJ/cm^2 of UVA. Heating and UV light may also be applied alone or in combination to increase the viscosity of the binder composition, which can allow easier handling on coating and processing lines.

In some embodiments, the binder composition may be cured after lamination between the overlying barrier films 32, 34. Thus, the increase in viscosity of the binder composition locks in the coating quality right after lamination. By curing right after coating or laminating, in some embodiments the cured binder increases in viscosity to a point that the binder composition acts as a pressure sensitive adhesive (PSA) to hold the laminate together during the cure and greatly reduces defects during the cure. In some embodiments, the radiation cure of the binder provides greater control over coating, curing and web handling as compared to traditional thermal curing.

Once at least partially cured, the binder composition forms polymer network that provides a protective supporting matrix 24 for the quantum dots 22.

Ingress, including edge ingress, is defined by a loss in quantum dot performance due to ingress of moisture and/or oxygen into the matrix 24. In various embodiments, the edge ingress of moisture and oxygen into the cured matrix 24 is less than about 1.25 mm after 1 week at 85°C, or about less than 0.75 mm after 1 week at 85°C, or less than about 0.5 mm after 1 week at 85°C. In various embodiments, oxygen permeation into the cured matrix is less than about 80 (cc.mil)/(m^2day), or less than about 50 (cc.mil)/(m^2day). In

various embodiments, the water vapor transmission rate of the cured matrix should be less than about 15 ($20g/m^2$.mil.day), or less than about 10 ($20g/m^2$.mil.day).

In various embodiments, the thickness of the quantum dot layer 20 is about 80 microns to about 250 microns.

FIG. 3 is a schematic illustration of an embodiment of a display device 200 including the quantum dot articles described herein. This illustration is merely provided as an example and is not intended to be limiting. The display device 200 includes a backlight 202 with a light source 204 such as, for example, a light emitting diode (LED). The light source 204 emits light along an emission axis 235. The light source 204 (for example, a LED light source) emits light through an input edge 208 into a hollow light recycling cavity 210 having a back reflector 212 thereon. The back reflector 212 can be predominately specular, diffuse or a combination thereof, and is preferably highly reflective. The backlight 202 further includes a quantum dot article 220, which includes a protective matrix 224 having dispersed therein quantum dots 222. The protective matrix 224 is bounded on both surfaces by polymeric barrier films 226, 228, which may include a single layer or multiple layers.

The display device 200 further includes a front reflector 230 that includes multiple directional recycling films or layers, which are optical films with a surface structure that redirects off-axis light in a direction closer to the axis of the display, which can increase the amount of light propagating on-axis through the display device, this increasing the brightness and contrast of the image seen by a viewer. The front reflector 230 can also include other types of optical films such as polarizers. In one non-limiting example, the front reflector 230 can include one or more prismatic films 232 and/or gain diffusers. The prismatic films 232 may have prisms elongated along an axis, which may be oriented parallel or perpendicular to an emission axis 235 of the light source 204. In some embodiments, the prism axes of the prismatic films may be crossed. The front reflector 230 may further include one or more polarizing films 234, which may include multilayer optical polarizing films, diffusely reflecting polarizing films, and the like. The light emitted by the front reflector 230 enters a liquid crystal (LC) panel 280. Numerous examples of backlighting structures and films may be found in, for example, U.S. 8848132 (O'Neill et al.).

Examples

Table 1: Materials

Material	Description
Quantum Dots	InP core/ZnS shell quantum dots were obtained from Nanosys, Inc (Milpitas, CA). "Green growth solution" describes a dispersion of green-emitting InP quantum dots with a zinc sulfide shell dispersed in octadecene with an optical density (optical density, OD, is defined as the absorbance at 440 nm with a 1 cm cell path length) of 10. "Red growth solution" describes a similar dispersion of red-emitting quantum dots, also with an OD of 10. The quantum dot dispersions were stored and handled in an inert atmosphere glove box.
FC-70	A high-boiling perfluorinated fluid available from 3M (St. Paul, MN) under trade designation "FLUORINERT ELECTRONIC LIQUID FC-70." This material was deoxygenated with bubbling N_2 gas and stored in an inert atmosphere glove box.
poly(HFPO) methacrylate	An oligomer of hexafluoropropylene oxide with an approximate M_n of 1400 Da end-functionalized with a single methacrylate group. Obtained from 3M Company, (St. Paul, MN).
4-(diphenylphosphino)styrene	Obtained from Sigma Aldrich Chemical Company (St.Louis, MO).
PF-5052	a fully perfluorinated solvent available from 3M Company (St. Paul, MN) under trade designation "PERFORMANCE FLUID PF-5052".
VAZO-67	A solid thermal radical initiator available from DuPont (Wilmington, DE) under trade designation "VAZO-67".
CN2003B	modified epoxy acrylate available from Sartomer USA, LLC (Exton, PA) under trade designation "CN2003B"

SR833 S	tricyclodecane dimethanol diacrylate available from Sartomer USA, LLC (Exton, PA) under trade designation "SR833".
IRGACURE 819	Photoinitiator obtained from BASF America (Florham Park, NJ) under trade designation "IRGACURE 819".
UV Barrier film	2 mil (50 micrometer) barrier film obtained as FTB-M-50 from 3M Company (St. Paul, MN).

Reagents and solvents not listed in Table 1, above were obtained from standard chemical suppliers such as Sigma Aldrich (St Louis, MO) and were used as received.

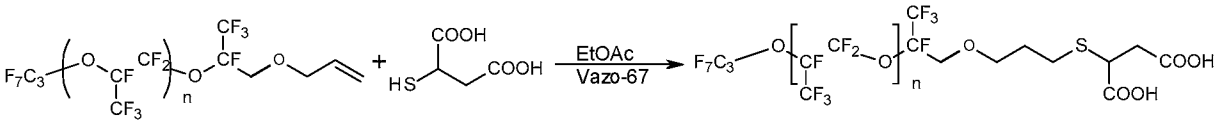
Preparative Example 1: Preparation of HFPO-Derived Methyl Ester

The methyl ester $F(CF(CF_3)CF_2O)_aCF(CF_3)C(O)OCH_3$, wherein the variable a has an average value of about 6, was prepared by metal fluoride-initiated oligomerization of hexafluoropropylene oxide (HFPO) in diglyme solvent according to the method described in U.S. Patent No. 3,250,808 (Moore et al.), the description of which is incorporated herein by reference. The product was purified by distillation to remove low-boiling components.

Preparative Example 2: Preparation of HFPO-Derived Allyl Ether

The allyl ether $F(CF(CF_3)CF_2O)_aCF(CF_3)CH_2OCH_2CHCH_2$, wherein the variable a has an average value of about 6, was prepared from the methyl ester of Preparative Example 1 by sodium borohydride reduction to the alcohol followed by allylation with allyl bromide according to the method described in US Patent Publication 20140287248 (Flynn et. al.), the description of which is incorporated herein by reference.

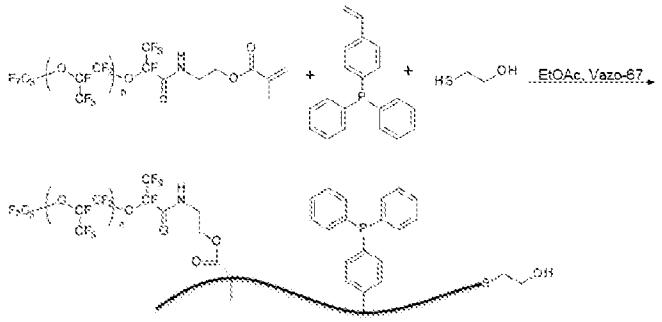
Example 1: Preparation of HFPO-derived ether succinic acid



A flask with condenser attached was charged with the polymer of Preparative Example 2 (5.0 g, 3.5 mmol), ethyl acetate (20 mL), mercaptosuccinic acid (0.79 g, 5.3

mmol), and VAZO-67 (100 mg, 0.53 mmol). The mixture was deoxygenated by bubbling N_2 through the liquid for 15 min. The solution was then heated to reflux and stirred overnight. The solvent was removed by rotary evaporation at reduced pressure, and the product was dissolved in 50 mL of PF-5052. The solution was washed three times with 70 mL of a 5:2 isopropanol:water mixture (by volume). The solvent was removed by rotary evaporation at reduced pressure to yield 4.5 g of clear viscous oil.

Example 2: Synthesis of a triphenylphosphine/poly(HFPO) stabilizing copolymer



A flask with condenser attached was charged with poly(HFPO) methacrylate (5.0g, 3.6 mmol), 4-(diphenylphosphino)styrene (1.0g, 3.6 mmol), 2-mercaptoethanol (70 mg, 0.9 mmol), VAZO-67 (34 mg, 0.18 mmol), and ethyl acetate (20 mL). This mixture was degassed by bubbling nitrogen through the suspension while stirring with a mechanical stir bar for 10 minutes. The solution was then heated to reflux and stirred overnight. After cooling to room temperature, the solvent was removed by rotary evaporation at reduced pressure. The remaining solid was dissolved in PF-5052 (50 mL) and washed twice with 50 mL portions of isopropanol. The fluorinated layer was concentrated by rotary evaporation at reduced pressure yielding a white solid (4.5 g).

Example 3: Preparation of a green InP/ZnS dispersion in FC-70.

A mixture of 20g of the polymer of Example 1 and 40g of FC-70 was degassed using bubbling nitrogen and then placed in an inert atmosphere glovebox. A 250 mL round bottomed flask was charged with 15 mL of the above solution and 120 mL of green growth solution. The flask was fitted with an overhead stirrer and placed on a hot plate held at 80 °C. The mixture was stirred vigorously for 1 hour, after which it was allowed to cool and separate into 2 layers. The colorless top layer was removed, and the bottom fluorinated layer was washed twice with 30 mL of heptane, stirring for 5 minutes during

each washing. Residual heptane was removed under low pressure, yielding a haze-free orange-green oil with an OD of approximately 80.

Example 4: Preparation of a red InP/ZnS dispersion in FC-70.

A mixture of 20g of the polymer of Example 1 and 40g of FC-70 was degassed using bubbling nitrogen and then placed in an inert atmosphere glovebox. A 100 mL round bottomed flask was charged with 10 mL of the above solution and 40 mL of red growth solution. The flask was fitted with an overhead stirrer and placed on a hot plate held at 80 °C. The mixture was stirred vigorously for 1 hour, after which it was allowed to cool and separate into 2 layers overnight. The colorless top layer was removed, and the bottom fluorinated layer was washed twice with 20 mL of heptane, stirring for 5 minutes during each washing. Residual heptane was removed under low pressure, yielding a slightly hazy red oil with an OD of approximately 40.

Examples 5-8: Preparation of Mixed Red and Green InP Quantum Dot Concentrates.

A 25% solution of PPh_3 copolymer in FC-70 was prepared by heating a mixture of the polymer of Example 2 (1.0 g) and FC-70 (3.0 g) with stirring on a hot plate held at 80 °C for 1 hour. The three solutions were then mixed with FC-70 and the quantum dot dispersions of Examples 3 and 4 in the amounts shown in table 2 below to create the InP dot concentrates at OD=20 used in subsequent experiments.

Table 2: InP Concentrate Formulations

Example#	Description	Green InP Concentrate (Example 3)	Red InP Concentrate (Example 4)	25% PPh_3 copolymer solution	FC-70
5	2:1 Green:Red control	0.3 mL	0.3 mL	0 mL	1.2 mL
6	~4% PPh_3 copolymer	0.3 mL	0.3 mL	0.3 mL	0.9 mL
7	~8% PPh_3 copolymer	0.3 mL	0.3 mL	0.6 mL	0.6 mL
8	~17% PPh_3 copolymer	0.3 mL	0.3 mL	1.2 mL	0 mL

Example 9: Stability to light exposure of InP concentrate dispersions

The quantum dot concentrate dispersions of Examples 5-8 (300 µL each) were placed in septum-capped quartz cuvettes with a cell of width 1 cm and length 0.1 cm. These cells were placed in a lamp between two 15 watt Phillips TLD fluorescent bulbs with a spectral output in the blue range. The lamp was covered with reflective foil and turned on. At specified times, 12 µL aliquots of concentrate were removed from the cuvettes and diluted with 4 mL of FC-70. Quantum yields of these dilute dispersions were measured using an absolute PL Quantum Yield Spectrometer C11347 (Hamamatsu Corporation, Middlesex, New Jersey). The results are shown in Figure 5.

Example 10: Preparation of an acrylate binder

To prepare an acrylate binder formulation, the components shown in Table 3 were added together and mixed until uniform.

Table 3: Acrylate binder

Material	Weight %
CN2003B	49.68%
SR833 S	49.68%
IRGACURE 819	0.66%
Sum	100.02%

Examples 11-14: Preparation of quantum dot dispersions with and without stabilizing copolymer

The following dispersions of quantum dots in fluoropolymer were prepared by mixing the components in the amounts shown in Table 4 until uniform.

Table 4: InP Dispersions for QDEF Coating

Example	**Green InP Concentrate (Example 3)**	**Red InP Concentrate (Example 4)**	**25% PPh_3 copolymer solution**	**FC-70**
11	3 mL	0	2 mL	0
12	0	3 mL	1 mL	1 mL
13	3 mL	0	0	2 mL
14	0	3 mL	0	2 mL

Example 15. Preparation of a QDEF with stabilizing copolymer

The formulation, preparation, coating, and curing was carried out inside a VAC-Atmosphere glove box. The quantum dot dispersion of Example 11 (1.37 g) and the dispersion of example 12 (0.79 g) were added to the acrylate polymeric binder of example 10 (20 g). The solution of dot concentrate and binder was mixed with a cowles-blade mixer for 3 minutes at 1400 rpm. This mixture was coated between two 2 mil (~ 51 μm) barrier films at a thickness of 100 μm using a knife coater. The coatings were then cured with ultraviolet (UV) radiation using a CLEARSTONE UV LED lamp at 385 nm for 60 seconds.

Example 16: Preparation of a QDEF without stabilizing copolymer

The formulation preparation, coating, and curing was carried out inside a VAC-Atmosphere glove box. The quantum dot dispersion of Example 13 (1.37 g) and the dispersion of example 14 (0.79 g) were added to the acrylate polymeric binder of example 10 (20 g). The solution of dot concentrate and binder was mixed with a cowles-blade mixer for 3 minutes at 1400 rpm. This mixture was coated between two 2 mil (~ 51 μm) barrier films at a thickness of 100 μm using a knife coater. The coatings were then cured with ultraviolet (UV) radiation using a CLEARSTONE UV LED lamp at 385 nm for 60 seconds.

Example 17: Accelerated Aging Studies of QDEF

Coatings were tested initially, after 1 week of aging at 85 °C, and after 1 week of aging in a lifetime screening box (aged at a temperature of 85 °C and under illumination with a light intensity of 152 watts/steradian/m^2). Initial results are shown in Table 5. Table 6 shows aging results after 1 week 85 °C. Lifetime screening box results are shown in Table 7.

Transmission was measured using a Byk HazeGuard Plus (Columbia, Maryland).

Color, luminance, and %efficiency were quantified by placing the constructed QDEF film into a recycling system (Figure 4) and measuring with a colorimeter 302 available from Photo Research, Inc. (Chatsworth, CA) under the trade designation PR650. The QDEF under investigation was placed on a gain cube 304 with a blue LED light. A micro-replicated brightness enhancement film available from 3M (St. Paul, MN) under the trade designation VIKUITI BEF was placed over the QDEF. A white point was achieved in this recycling system.

Table 5: Optical Characterization of QDEF Coatings

Example	%transmission	Luminance (cd/m^2)	X	Y	% Efficiency
15	74.0	227.8	0.2103	0.1754	35.5
16 (Comparative)	66.1	244.9	0.2154	0.1925	37.2

Table 6: Performance Change of QDEF Coatings After Aging for 1 Week at 85 °C

Example	%Luminance Change	Δ X,Y	Edge Ingress (mm)
15	8.1	0.004	0.00
16 (Comparative)	5.5	0.003	0.00

Table 7: Performance Change After Accelerated Aging in the Lifetime Screening Box

Example	%Luminance Change	Δ x	Δ y	Δ x,y
15	1.08	0.006	-0.005	0.008
16 (Comparative)	-12.54	-0.003	-0.021	0.021

What is claimed is:

1. A composite particle comprising a fluorescent core/shell nanoparticle and a stabilizing copolymer having pendent arsine, stibine or phosphine stabilizing groups; and pendent fluorochemical groups.

2. The composite particle of claim 1 where the pendent fluorochemical groups are perfluoroalkyl groups.

3. The composite particle of claim 1 where the pendent fluorochemical groups are perfluoroether groups.

4. The composite particle of claim 1 where the pendent fluorochemical groups are perfluoropolyether groups.

5. The composite particle of claim 1 wherein the pendent fluorochemical groups are of the formula:

$-(Q^2)_g-R^{10}-(Q^3)_h-R_f$;

where

Q^2 is selected from a covalent bond ("-"), $-CO_2-$, $-CONR^3-$, $-NH-CO-NR^3-$, and $-NR^3-$, where R^3 is H or C_1-C_4 alkyl;

Q^3 is selected from $-CH_2-S-$, $-CH_2-O-$, $-CO_2-$, $-CONR^3-$, $-NH-CO-NR^3-$, and $-NR^3$, where R^3 is H or C_1-C_4 alkyl,

subscripts g and h are independently 0 or 1;

R^{10} is a hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene and

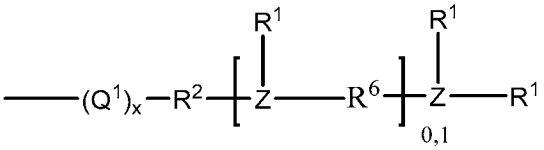
R_f is a perfluorinated group.

6. The composite particle of claim 5 wherein R_f is of the formula $C_aF_{2a+1}-(O-C_bF_{2b})_c-$, where a is at least 1, b is at least 1 and c is from 0 to 50.

7. The composite particle of claim 6 wherein each of subscripts a and b are 1 to 6.

8. The composite particle of claim 5 wherein R_f is a perfluoropolyether having perfluorinated repeating units selected from the group of -(C_pF_{2p})-, -($C_pF_{2p}O$)-, -($CF(R_f^2)$)-, -($CF(R_f^2)O$)-, -($CF(R_f^2)C_pF_{2p}O$)-, -($C_pF_{2p}CF(R_f^2)O$)-, -($CF_2CF(R_f^2)O$)-, where p is an integer of 1 to 10 and R_f^2 is a fluorine atom, perfluoroalkyl group, perfluoroether group, nitrogen-containing perfluoroalkyl group, perfluoropolyether, or a perfluoroalkoxy group.

9. The composite particle of any of the previous claims wherein the pendent stabilizing groups are of the formula:



wherein each R^1 is a hydrocarbyl group including alkyl, aryl, alkaryl and aralkyl;
R^2 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene;
Z is P, As or Sb;
Q^1 is a functional group selected from $–CO_2$-, -O-, -S-, -$CONR^3$-, -NH-CO-NR^3-, and –NR^3-, where R^3 is H or C_1-C_4 alkyl, and subscript x is 0 or 1, and
R^6 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene.

10. The composite particle of any of the previous claims wherein the copolymer is of the formula:
~[M^{stab}]$_d$-[M^{FC}]$_e$~, where
[M^{stab}] represents monomer units having pendent phosphine, arsine or stibine groups and subscript d parts by weight; and
[M^{FC}] represents fluorochemical-functional monomer units having subscript e parts by weight.

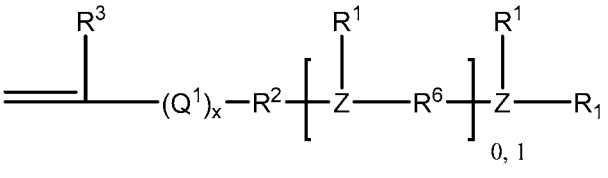
11. The composite particle of claim 10 wherein subscript d of [M^{stab}] is <50 parts by weight, and subscript e of [M^{FC}] is > 50 parts by weight, the sum being 100 parts by weight.

12. The composite particle of claim 10 wherein subscript d of [M^{stab}] is <40 parts by weight, and subscript e of [M^{FC}] is > 60 parts by weight, the sum being 100 parts by weight.

13. The composite particle of claim 10 wherein subscript d of [M^{stab}] is <30 parts by weight, and subscript e of [M^{FC}] is > 70 parts by weight, the sum being 100 parts by weight.

14. The composite particle of claim 10 wherein d+e ≥ 8.

15. The copolymer of claim 10 wherein the copolymer is derived from monomers of the formula:



, wherein

wherein each R^1 is a hydrocarbyl group including alkyl, aryl, alkaryl and aralkyl;

R^2 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene;

Z is P, As or Sb;

Q^1 is a functional group selected from $–CO_2$-, -O-, -S-, -$CONR^3$-, -NH-CO-NR^3-, and –NR^3-, where R^3 is H or C_1-C_4 alkyl, and subscript x is 0 or 1, and

R^6 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene.

and subscript x is 0 or 1.

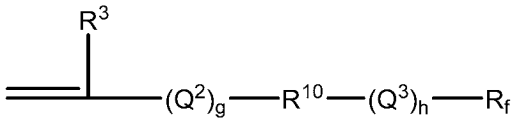
16. The composite particle of claim 15 wherein at least one of said R^1 groups is an aryl or alkaryl group.

17. The composite particle of claim 16 wherein two of said R^1 groups are an aryl or alkaryl group.

18. The composite particle of claim 16 wherein R^1 is phenyl.

19. The composite particle of claim 16 wherein R^2 is phenylene.

20. The copolymer of claim 10 wherein the copolymer is derived from monomers of the formula:



21. The composite particle of any of the previous claims further comprising a surface modifying ligand bound to the surface of the nanoparticle of the formula:

R_f^1-[X^{21}-R^{22}-X^{22}-$R^{23}(L)_v$]$_w$

wherein

R_f^1 is a perfluoroalkyl, perfluoroether or perfluoropolyether group of valence w,

R^{22} is a divalent hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene;

R^{23} is a divalent hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene;

X^{21} is $–CH_2$-O-, -O-, -S-, $-CO_2$-, $-CONR^1$-, or $-SO_2NR^{1-}$ where R^1 is H or C_1-C_4 alkyl;

X^{22} is a covalent bond, –S-, -O- or $-NR^1$-, $-CO_2$-, $-CONR^1$-, or $-SO_2NR^{1-}$ where R^1 is H or C_1-C_4 alkyl;

v at least one;

w is 1 or 2;

L is an ligand group selected from $–CO_2H$, -SH, $-P(O)(OH)_2$, -P(O)OH, $-NH_2$ -OH, and $-SO_3H$.

22. The composite particle of any of the previous claims further comprising a surface modifying ligand bound to the surface of the nanoparticle of the formula:

R^5-$R^2(X)_n$

wherein

R^5 is (hetero)hydrocarbyl group having C_2 to C_{30} carbon atoms;

R^2 is a a hydrocarbyl group including alkylene, arylene, alkarylene and aralkylene;

n is at least one;

X is a ligand group.

23. The composite particle of any of the previous claims wherein the core comprises InP, CdS or CdSe.

24. The composite particle of any of the previous claims wherein the shell comprises a magnesium or zinc-containing compound.

25. The composite particle of claim 24 wherein the shell is a multilayered shell.

26. The composite particle of claim 25 wherein the multilayered shell comprises an inner shell overcoating the core, wherein the inner shell comprises zinc selenide and zinc sulfide.

27. The composite particle of claim 25 wherein the multilayered shell comprises an outer shell overcoating the inner shell, wherein the outer shell comprises zinc sulfide or MgS.

28. The composite particle comprising:
a fluorescent semiconductor core/shell nanoparticle comprising:
an InP core;
an inner shell overcoating the core, wherein the inner shell comprises zinc selenide and zinc sulfide; and
an outer shell overcoating the inner shell, wherein the outer shell comprises zinc sulfide; and
a stabilizing copolymer having pendent arsine, stibine or phosphine stabilizing groups; and pendent fluorochemical groups.

29. A composition comprising the composite particle of any of claims 1-28 further comprising a fluorochemical carrier fluid.

30. A composition comprising the composite particle of claim 29 dispersed in droplets of the stabilizing copolymer and fluorochemical carrier fluid and fluorochemical surface-modifying agent (Formula IV), said droplets dispersed in a polymeric binder.

31. The composition of claims 29-30 wherein the polymeric binder comprises polysiloxanes, fluoroelastomers, polyamides, polyimides, polycaprolactones, polycaprolactams, polyurethanes, polyvinyl alcohols, polyvinyl chlorides, polyvinyl acetates, polyesters, polycarbonates, polyacrylates, polymethacrylates, polyacrylamides, epoxy resins and polymethacrylamides

32. An article comprising the composite particle of any of claims 1-28 dispersed in the cured polymeric binder between two barrier films.

33. A quantum dot film article comprising:

a first barrier layer;

a second barrier layer; and

a quantum dot layer between the first barrier layer and the second barrier layer, the quantum dot layer comprising the composite particles of claim 1-28, the composite particles dispersed in a polymeric binder.

34. The quantum dot film article of claim 33 wherein the quantum dot layer comprises dispersed droplets of composite particles in the stabilizing copolymer, surface modifying ligand, and fluorochemical carrier fluid.

35. The composite particle of any of claims 1-28 wherein the copolymer contains between 8 and 25 repeat units.

36. Copolymers of the formula:

~$[M^{stab}]_d$-$[M^{FC}]_e$~, where

$[M^{stab}]$ represents monomer units having pendent phosphine, arsine or stibine groups and subscript d parts by weight; and

$[M^{FC}]$ represents fluorochemical-functional monomer units having subscript e parts by weight.

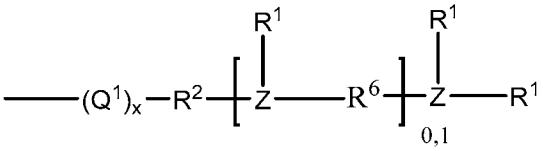
37. The copolymers of claim 36 wherein subscript d of [M^{stab}] is <50 parts by weight, and subscript e of [M^{FC}] is > 50 parts by weight, the sum being 100 parts by weight.

38. The copolymers of claim 36 wherein subscript d of [M^{stab}] is <40 parts by weight, and subscript e of [M^{FC}] is > 60 parts by weight, the sum being 100 parts by weight.

39. The copolymers of claim 36 wherein subscript d of [M^{stab}] is <30 parts by weight, and subscript e of [M^{FC}] is > 70 parts by weight, the sum being 100 parts by weight.

40. The copolymers of claim 36 wherein d+e $\geq$ 8.

41. The copolymer of claim 36 wherein [M^{Stab}] comprises pendent stabilizing groups of the formula:



wherein each R^1 is a hydrocarbyl group including alkyl, aryl, alkaryl and aralkyl;

R^2 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene;

Z is P, As or Sb;

Q^1 is a functional group selected from $–CO_2$-, -O-, -S-, -$CONR^3$-, -NH-CO-NR^3-, and –NR^3-, where R^3 is H or C_1-C_4 alkyl, and subscript x is 0 or 1, and

R^6 is a divalent hydrocarbyl group selected from alkylene, arylene, alkarylene and aralkylene.

42. A composition comprising

a. 1 to 10 parts by weight of fluorescent nanoparticles,

b. 1 to 40 parts by weight of a copolymer the formula:

~[M^{stab}]$_d$-[M^{FC}]$_e$~, where

[M^{stab}] represents monomer units having pendent phosphine, arsine or stibine groups and subscript d parts by weight; and

[M^{FC}] represents fluorochemical-functional monomer units having subscript e parts by weight, and

c. 5 to 50 parts by weight of a perfluorinated carrier fluid.

43. The composition of claim 42 further comprising:

d. 5 to 30 parts by weight of the surface modifying ligand.

44. The composition of claim 42 dispersed in a polymeric binder.

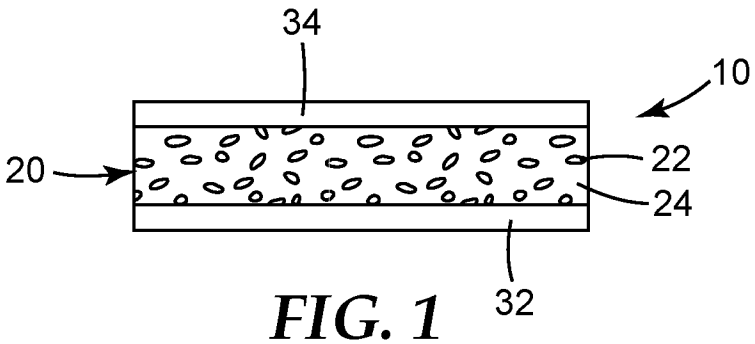

34
10
20
22
24
32

FIG. 1

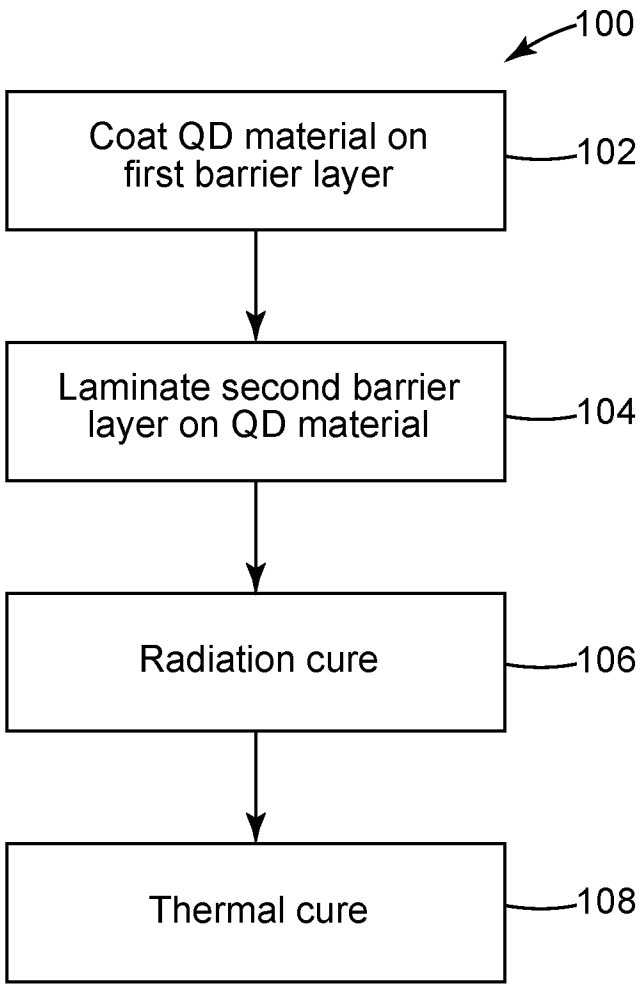

100
Coat QD material on first barrier layer
102
Laminate second barrier layer on QD material
104
Radiation cure
106
Thermal cure
108

FIG. 2

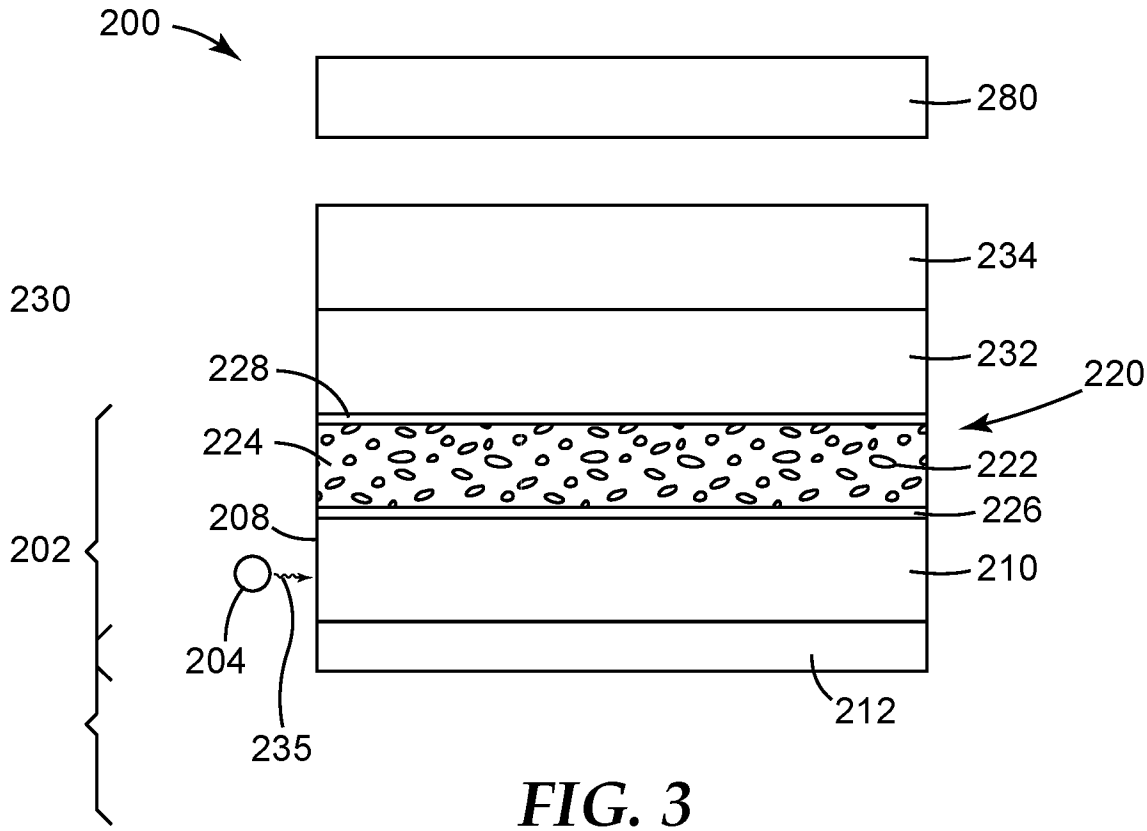

200
280
234
230
232
228
220
224
222
208
226
202
210
204
212
235

FIG. 3

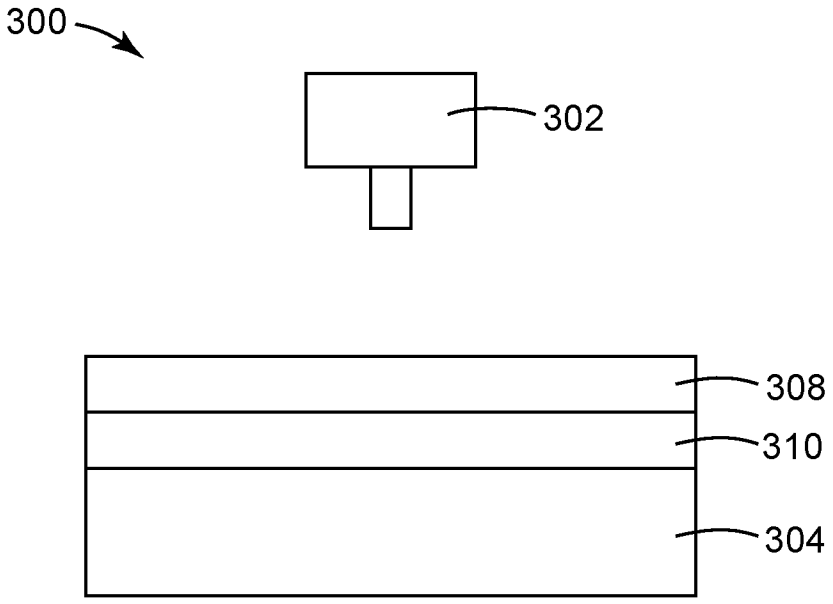

300
302
308
310
304

FIG. 4

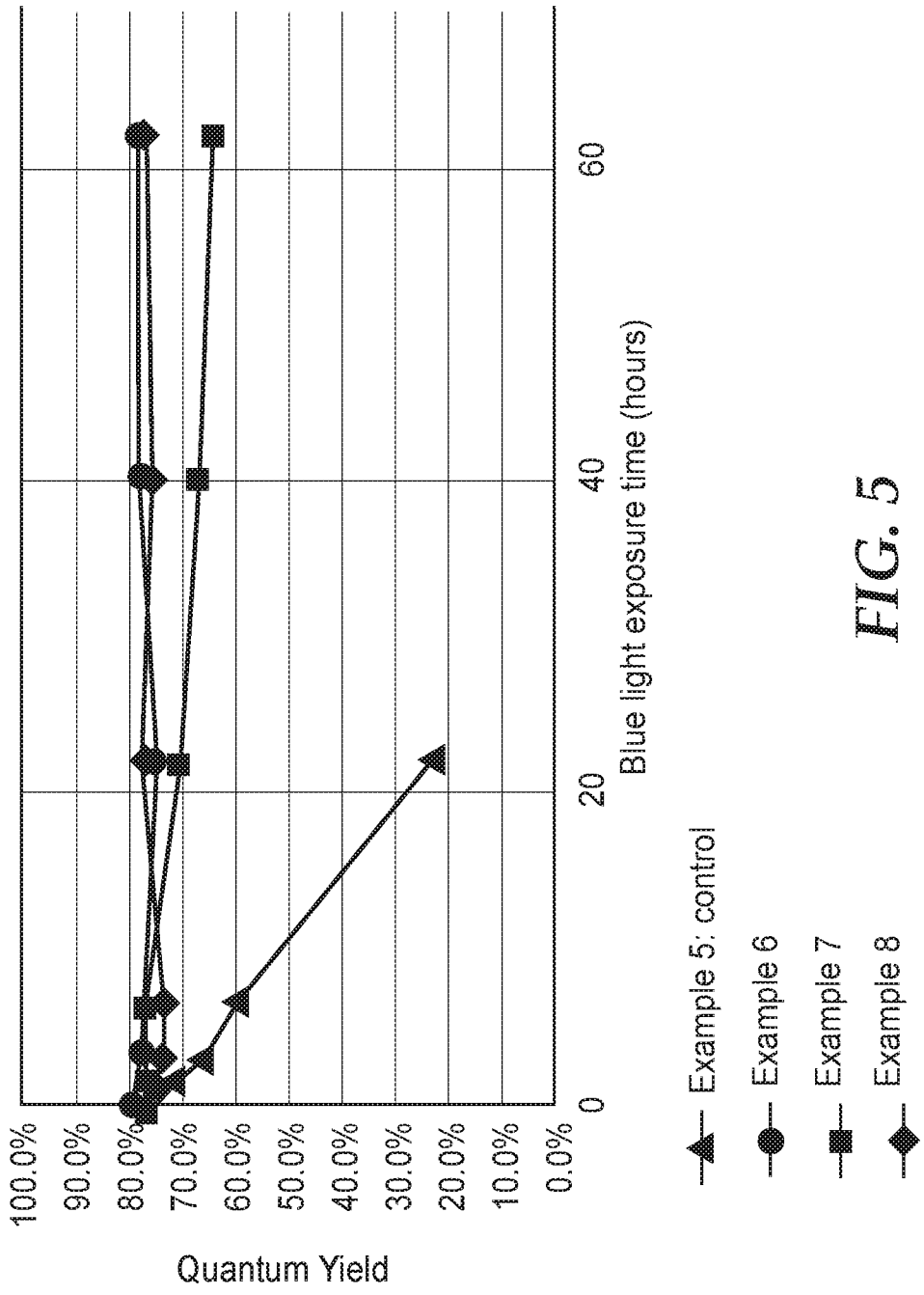

100.0%
90.0%
80.0%
70.0%
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
Quantum Yield
0
20
40
60
Blue light exposure time (hours)
Example 5: control
Example 6
Example 7
Example 8

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/017152

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/02 C09K11/56 C09K11/70
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)
C09K C08F

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, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2015/307776 A1 (CASEY JAMES ALLEN [US] ET AL) 29 October 2015 (2015-10-29) claims 1-20; example 3	1-44
A	US 2014/027711 A1 (BREEN CRAIG [US] ET AL) 30 January 2014 (2014-01-30) claims 1-25; figure 2	1-44
X	JP H05 59172 A (TOKUYAMA SODA KK) 9 March 1993 (1993-03-09) page 9	36-41

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 May 2017	01/06/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Mehdaoui, Imed

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YULAI HU ET AL: "Fast and unprecedented chemoselective hydroformylation of acrylates with a fluoropolymer ligand in supercritical CO2", CHEMICAL COMMUNICATIONS - CHEMCOM., no. 7, 13 March 2002 (2002-03-13), pages 788-789, XP055375487, ISSN: 1359-7345, DOI: 10.1039/b201166b compound 1	36-41
X	KANI I ET AL: "Homogeneous catalysis in supercritical carbon dioxide with rhodium catalysts tethering fluoroacrylate polymer ligands", TETRAHE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 58, no. 20, 13 May 2002 (2002-05-13), pages 3923-3928, XP004353767, ISSN: 0040-4020, DOI: 10.1016/S0040-4020(02)00219-3 Scheme 2; compound V	36-41
A	CHEN W ET AL: "New approaches to fluorinated ligands and their application in catalysis", TETRAHE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 58, no. 20, 13 May 2002 (2002-05-13), pages 3889-3899, XP004353764, ISSN: 0040-4020, DOI: 10.1016/S0040-4020(02)00213-2 Scheme 6; compounds 16, 17	36-41

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/017152

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015307776 A1	29-10-2015	NONE	
US 2014027711 A1	30-01-2014	US 2014027711 A1	30-01-2014
		WO 2012134629 A1	04-10-2012
JP H0559172 A	09-03-1993	NONE	