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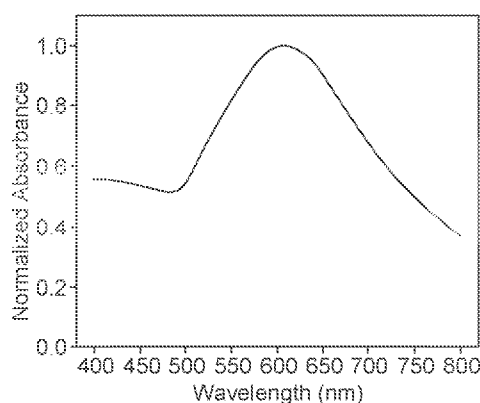


FIG. 1A

(57) Abstract: Disclosed herein are compositions and methods comprising a composition for light filtering. An example composition comprises a plurality of metal nanoparticles, at least a portion of the plurality of metal nanoparticles having an anisotropic shape; and a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of metal nanoparticles, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.



SHAPE ENGINEERING OF PARTICLES TO CREATE A NARROW SPECTRAL FILTER AGAINST A SPECIFIC PORTION OF THE LIGHT SPECTRUM

RELATED APPLICATIONS

[0001] This application claims priority to U.S. Patent Application Serial No. 17/661,105, filed April 28, 2022, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This application generally relates to optical filters. More particularly, this application relates to nanoparticles configured for filtering light.

BACKGROUND

[0003] Nanoparticle integration into hydrogels may be used in a large variety of biomedical devices, such as contact lenses, for antibacterial, sensing and therapeutic applications (Clasky et al, Acta Biomaterialia 2021).

[0004] Current commercial contact lenses may adjust the curvature of the eye and/or the refractive index to improve focusing. Preliminary research suggests that blocking specific ranges of light may facilitate the progression of myopia (Liu et al., Investig. Ophthalmology Vis. Sci., 2014; Lingham, et al., Br J Ophthalmol, 2020; Long, et al., Cutan. Ocul. Toxicol., 2009; Wang, et al., Biomed Res. Int., 2013).

[0005] A method describing the dispersion of metal nanoparticles for optical filtering in sunglasses is described in US 2007/0298242A1. Gold nanoparticles or dyes are dispersed in a polymer matrix, and the composite either acts as a lens itself or is used as a coating on one or both faces of a lens. US 2007/0298242A1 does not disclose information pertaining to the immobilization of the light blocking materials within the polymer matrix requisite for light blocking material integration into soft materials.

[0006] Another example of incorporating nanoparticles into polymer matrices is described in US20080203592A1 wherein a dry hydrogel contact lens is hydrated in a hydrating solution, wherein the hydrating solution comprises silver ions, silver nanoparticles, or combinations thereof, a lubricant or wetting agent, or combinations thereof. The silver nanoparticles and/or the lubricant or wetting agent are adsorbed onto and/or entrapped in the hydrogel contact lens during the extraction step and/or the hydrating step. While the method

described may be translatable to gold nanoparticles and/or dyes, the patent does not disclose information pertaining to light blocking materials or to the chemical embedding of these materials in the final product. The nanoparticles are added after the contact lens has been cured which has implications for nanoparticle distribution within the contact lens.

[0007] A recent publication (Salih et al, ACS Nano 2021) demonstrates nanoparticle addition to contact lens materials prior to lens curing but only uses commercially available citrate-coated gold nanoparticles that were purchased from Sigma-Aldrich and used as is. While gold nanoparticles can achieve the chemical and physical stability by virtue of their innate properties, neither versatility nor tunability were demonstrated. The publication also does not demonstrate that their light blocking material can withstand key sterilization procedures such as autoclaving.

[0008] However, improvements are needed.

SUMMARY

[0009] Disclosed herein are systems, compositions, and methods for light filtering.

[0010] One general aspect includes a composition for light filtering. The composition also includes a base material; a plurality of gold nanoparticles dispersed in the base material, at least a portion of the plurality of gold nanoparticles having an anisotropic shape; and a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of gold nanoparticles to enhance stability of at least the portion of the plurality of gold nanoparticles in the base material, where the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[0011] One general aspect includes a composition for light filtering. The composition also includes a plurality of metal nanoparticles, at least a portion of the plurality of metal nanoparticles having an anisotropic shape; and a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of metal nanoparticles, where the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[0012] One general aspect includes a composition for light filtering. The composition also includes a base material; and a plurality of nanoparticles dispersed in the base material where the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm, and where the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm 58nm.

[0013] One general aspect includes a contact lens comprising a composition for light filtering as described herein, wherein the contact lens is a free radical reaction product of a reactive mixture comprising: one or more silicone-containing components and one or more hydrophilic components, the contact lens having a water content of at least about 20 weight percent, preferably at least about 30 weight percent, and an oxygen permeability of at least about 80 barrers, preferably at least about 100 barrers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The following drawings show generally, by way of example, but not by way of limitation, various examples discussed in the present disclosure. In the drawings:

[0015] FIGS. 1A-1D depict absorbance spectra of nanosized spheres (FIG. 1A), cubes (FIG. 1B), rods (FIG. 1C) and bipyramids (FIG. 1D) blocking in the target range via Ultraviolet-Visible (UV-Vis) spectroscopy.

[0016] FIGS. 1E-1H show high-Angle Annular Dark-Field-Scanning Transmission Electron Microscopy (HAADF-STEM) micrographs of spheres (FIG. 1E), cubes (FIG. 1F), rods (FIG. 1G) and bipyramids (FIG. 1H). Scale bars: 200 nm.

[0017] FIGS. 2A-2C depict aspects of nanosized bipyramids. FIG. 2A shows absorbance spectra of bipyramids of varying sharpness. FIG. 2B displays average aspect ratio (blue circles) and volume (orange squares) for each bipyramid sample ($n=100$, error bars represent $\pm$ s.d.). FIG. 2C shows corresponding Transmission Electron Microscopy (TEM) micrographs.

[0018] FIGS. 3A-3B show the change in spectrum light filtering and intensity as a function of AgNO_3 (FIG. 3A) and seed (FIG. 3B).

DETAILED DESCRIPTION

[0019] There exists a significant need to develop light filtering materials with specificity towards certain wavelengths, versatility to tailor light filtering to different regions of the visible spectrum, resistance against thermal and mechanical stress, resistance to corrosion and oxidation, and long-term stability to UV exposure. While approaches to selective light filtering exist, there is no solution that can be tuned to different wavelengths of interest in the

red light range without changing the fundamental mechanism or composition, can withstand long-term storage, autoclaving and UV exposure, and can be readily adopted commercially.

[0020] The present disclosure relates to methods of producing gold nanoparticles (GNPs). The present disclosure further relates to methods of engineering the shape of such nanoparticles. Such shapes may comprise anisotropic shapes. Anisotropic gold nanoparticles may require additional engineering to imbue thermal stability. This may result from higher surface energies associated with sharper features of anisotropic gold nanoparticles. Such features may lead to thermal reshaping at high temperatures, which may be due to diffusion of surface atoms to lower energy configurations. The present disclosure relates to methods to provide additional engineering to imbue thermal stability. The present disclosure therefore relates to methods to overcome significant barriers to commercialization.

[0021] The present disclosure relates to methods of adding a light filtering material before contact lens curing to ensure full integration and a more uniform distribution within the final product.

[0022] The present disclosure relates to gold nanoparticles. Gold nanoparticles may comprise a specified shape. Gold nanoparticles may comprise a stabilizing mechanism. The synthesis process of a gold nanoparticle enables close control over the size and shape of a nanoparticle. Such control may enable fine-tuning of the optical properties of a nanoparticle. The intrinsic properties of a gold nanoparticle, namely the resistance to corrosion, oxidation, Ultraviolet (UV) irradiation, and UV exposure may facilitate long-term storage. The use of a stabilizing mechanism may enable nanoparticle resistance to thermal stress. Such resistance may arise from a stabilizing mechanism passivating atoms on the surface of nanoparticles. This passivation may lead to restricting the tendency of atoms on the surface of nanoparticles to revert to a sphere upon exposure to heat during processes such as autoclaving. In such a reversion, a sphere may be noted as the more thermodynamically stable morphology.

[0023] The present disclosure relates to nanoparticles such as metal nanoparticles, and more particularly to gold nanoparticles, for example. Reference made to gold nanoparticles may be applied to other nanoparticles, including metal nanoparticles. Gold nanoparticles may be configured (e.g., grown) to block light in the range of about 600nm up to about 850nm or from 600nm to 850nm including endpoints and intervening endpoints. Other ranges may be used by configuring at least a shape and/or size of the nanoparticles. The present disclosure relates to the

use of a seed-mediated gold nanoparticle synthesis (e.g., Sanchez-Iglesias et al, JACS 2017). Gold nanoparticles may be grown from a pentatwinned gold seed in a synthesis comprising the use of gold (III) chloride, hydrochloric acid, silver nitrate and L-ascorbic acid in varying amounts, though other synthesis methods may be used. Light absorbance of GNPs may depend on size and shape. As a result, parameters used to grow nanoparticles of varying sizes and shapes may be modified to tune a light filtering spectrum of a final product. The seed-mediated method of the present disclosure enables increased control over the final light blocking characteristics of a nanoparticle compared to other methods. Other such methods may comprise one-pot synthesis.

[0024] Nanoparticles such as gold nanoparticles of the present disclosure may comprise a bipyramid shape with truncated peaks on either end. Such bipyramid shape may allow more specific light filtering in the target range. This effect may result from the presence of truncated peaks disposed on opposing ends of a bipyramid. Anisotropic nanoparticles, such as rods and bipyramids, may comprise absorbance spectrum with two peaks. One such peak, a longitudinal peak, may be of particular interest in the target range. The position and magnitude of a longitudinal peak may be controlled by the sharpness of a bipyramid. There also exists a transverse peak around 530 nm. In an aspect of the present disclosure, such a transverse peak is innate to gold nanoparticles. The relative contribution of the longitudinal peak compared to the transverse peak may be modulated by the sharpness of a bipyramid. A higher contribution of the longitudinal peak compared to the transverse peak may display more specific light filtering.

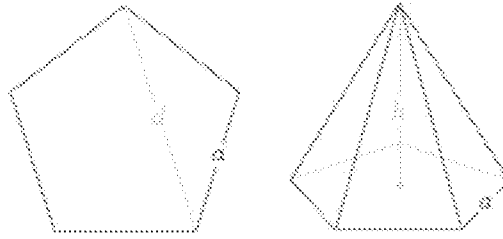
[0025] The present disclosure relates to a stabilizing mechanism. In an aspect of the present disclosure, a stabilizing mechanism may comprise 55kDa poly(vinyl pyrrolidone) (PVP) polymer chains, though other such mechanisms are known. The monomer units of PVP comprise nitrogen atoms with lone pairs of electrons. Such lone pairs of electrons may bind to the surface of gold nanoparticles. This binding may facilitate enhanced colloidal and thermal stability. PVP may be attached to nanoparticle surfaces by incubating nanoparticles in a solution comprising a high concentration of PVP overnight at 40°C. Such a solution may further comprise ethanol (>10% w/v) with a small amount of sodium dodecyl sulfate (0.6% w/v in water). PVP may enable long-term colloidal stability, thermal stability and biocompatibility. The conjugation of PVP to the surface of gold nanoparticles comprises a negligible effect on the engineered light filtering spectrum of such nanoparticles.

[0026] The present disclosure relates to methods of controlling nanoparticle morphology (e.g. size and shape geometry) through modular synthesis. In such methods, controlling nanoparticle morphology may facilitate the tuning of light filtering profiles of such nanoparticles. In an aspect of the present disclosure, multiple morphologies were examined. A specific morphology capable of targeting certain wavelengths of light was not previously known.

[0027] The present disclosure relates to a base material. Such a base material may comprise, a biomaterial, a biomaterial matrix, a hydrogel, and other such materials known in the art. The disclosure further relates to nanoparticles. Such nanoparticles may comprise gold. Gold nanoparticles may be grown from a pentatwinned gold seed, though other methods of synthesis are known in the art. Such nanoparticles may comprise shapes. Such shapes may be anisotropic. Such shapes may be bipyramids. Alternative shapes are known in the art and may comprise, but are not limited to, cubic shape, a nanorod shape, an octahedral shape, a decahedral shape, a cuboctahedral shape, a tetrahedral shape, a rhombic dodecahedral shape, a truncated ditetragonal prismatic shape, or a truncated bitetrahedral shape. The present disclosure further relates to a stabilizing mechanism. Such stabilizing mechanism may comprise a polymer. Such polymers may comprise a variety of molecular weights. Such polymer may comprise PVP. Alternative polymers are known in the art and may comprise, but are not limited to, poly(ethylene glycol) (PEG), polycarbonate, poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP), polystyrene (PS), polycaprolactone (PCL), ethylene oligomers or polyethylene (PE), polypropylene (PP), and poly(methyl methacrylate) (PMMA), as well as copolymers or blends thereof. Such polymer may comprise PVP with molecular weights of about 55kDa up to about 1300kDa. The present disclosure relates to a method of coupling a gold nanoparticle to a stabilizing mechanism. Coupling may occur through chemical conjugation. Such coupling may be selective. Such coupling may enhance colloidal and/or thermal stability of a nanoparticle, as well as biocompatibility. The present disclosure relates to a composition, wherein a base material comprising nanoparticles and a stabilizing material exhibits a peak light filtering (e.g., absorption) in the range of about 600nm up to about 850nm. Such peak light filtering may be tuned through tuning nanoparticle morphology. Morphology may be tuned by configuring an aspect ratio defined by a quotient of major and minor axes length, a volume, sharpness, and/or other related features. Aspect ratios may be tuned to about 1.9 up to about 2.9, though other

such aspect ratios may be possible. As non-limiting examples, aspect ratios may range from about 1.9 up to about 2.8, about 1.9 up to about 2.7, about 1.9 up to about 2.6, about 1.9 up to about 2.5, about 1.9 up to about 2.4, about 1.9 up to about 2.3, about 1.9 up to about 2.2, about 1.9 up to about 2.1, about 1.9 up to about 2.0, about 2.0 up to about 2.8, about 2.0 up to about 2.7, about 2.0 up to about 2.6, about 2.0 up to about 2.5, about 2.0 up to about 2.4, about 2.0 up to about 2.3, about 2.0 up to about 2.2, or about 2.0 up to about 2.1. Volumes may be tuned to about 250nm^3 up to about $30,000\text{nm}^3$, though other such volumes may be possible. As non-limiting examples, volumes may be tuned to about $1,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $2,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $3,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $4,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $5,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $6,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $7,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $8,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $9,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $10,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $11,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $12,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $13,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $14,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $15,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $16,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $17,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $18,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $19,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $20,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $21,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $22,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $23,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $24,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $25,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $26,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $27,250\text{nm}^3$ up to about $30,000\text{nm}^3$, about $28,250\text{nm}^3$ up to about $30,000\text{nm}^3$, or about $29,250\text{nm}^3$ up to about $30,000\text{nm}^3$. Such tuning may result in a Full-Width at Half Maximum (FWHM) value of about 54nm up to about 58nm . As non-limiting examples, FWHM values may range from about 54nm up to about 57nm , about 54nm up to about 56nm , about 54nm up to about 55nm , about 55nm up to about 58nm , about 56nm up to about 58nm , or about 57nm up to about 58nm .

[0028] As an example, calculating the volume of a nanobipyramids may be accomplished as a pair of pentagonal pyramids. We assume that the minor axis (L2) we measure from the images is the value of the diagonal of the pentagon, shown as d below. And we assumed the major axis (L1) was double the height (h) of a single pyramid:



[0029] The volume of one pentagonal pyramid is shown below where a is the edge length, which we can calculate from d (L2).

$$V = \frac{5}{12} \tan(54^\circ) h a^2 \quad a = \frac{2d}{1 + \sqrt{5}}$$

[0030] The simplified expression for the volume of a pair of pentagonal pyramids in terms of major (L1) and minor (L2) axes is thus:

$$V = 2 \times \frac{5}{12} \tan 54^\circ \left(\frac{L1}{2} \right) \left(\frac{2 \times L2}{1 + \sqrt{5}} \right)^2$$

$$V = \frac{5}{3} \tan 54^\circ (L1) \left(\frac{L2}{1 + \sqrt{5}} \right)^2$$

[0031] Other calculations may be used.

[0032] Additional capabilities relating to the present disclosure exist. The present disclosure additionally relates to a variety of polymers that may be grafted to the surface of nanoparticles. The use of varying polymers may enable the integration of nanoparticles into a variety of biomaterials. Such nanoparticles, may comprise a variety of shapes. The disclosure is therefore independent of a specific biomaterial. Moreover, the disclosure relates to the incorporation of a variety of shapes of nanoparticles further comprising a variety of stabilizing mechanisms into virtually any biomaterial of interest. Non-limiting examples of biomaterials may comprise hydrogel or silicone hydrogel material suitable for use in the formation of a soft contact lens. Such materials are known in the art and include Group 1—Low Water (<50% H₂O) Nonionic Hydrogel Polymers (e.g., tefilcon, tetrafilcon A, crofilcon, helfilcon A, helfilcon B, mafilcon, polymacon, hioxifilcon B); Group 2—High Water (>50% H₂O) Nonionic Hydrogel Polymers (e.g., surfilcon A, lidofilcon A, lidofilcon B, netrafilcon A, hefilcon B, alphafilcon A, omafilcon A, omafilcon B, vasurfilcon A, hioxifilcon A, hioxifilcon D, nelfilcon

A, hilafilcon A, hilafilcon B, acofilcon A, nesofilcon A); Group 3—Low Water (<50% H₂O) Ionic Hydrogel Polymers (e.g., bufilcon A, deltafilcon A, phemfilcon); Group 4—High Water (>50% H₂O) Ionic Hydrogel Polymers (e.g., bufilcon A, perfilcon A, etafilcon A, focofilcon A, ocufilcon A, ocufilcon B, ocufilcon C, ocufilcon D, ocufilcon E, ocufilcon F, phemfilcon A, methafilcon A, methafilcon B, vilfilcon A); and Silicone Hydrogel Polymers (e.g., lotrafilcon A, lotrafilcon B, galyfilcon A, senofilcon A, senofilcon C, sifilcon A, comfilcon A, enfilcon A, balafilcon A, delefilcon A, narafilcon B, narafilcon A, stenfilcon A, somofilcon A, fanfilcon A, samfilcon A, elastofilcon).

DEFINITIONS

[0033] It is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways using the teaching herein.

[0034] With respect to the terms used in this disclosure, the following definitions are provided.

[0035] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. The polymer definitions are consistent with those disclosed in the Compendium of Polymer Terminology and Nomenclature, IUPAC Recommendations 2008, edited by: Richard G. Jones, Jaroslav Kahovec, Robert Stepto, Edward S. Wilks, Michael Hess, Tatsuki Kitayama, and W. Val Metanomski. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

[0036] As used herein, the term “(meth)” designates optional methyl substitution. Thus, a term such as “(meth)acrylates” denotes both methacrylates and acrylates.

[0037] The term “individual” includes humans and vertebrates.

[0038] The term “ophthalmic device” refers to any device that resides in or on the eye or any part of the eye, including the ocular surface. These devices can provide optical correction, cosmetic enhancement, vision enhancement, therapeutic benefit (for example as bandages) or delivery of active components such as pharmaceutical and nutraceutical components, or a combination of any of the foregoing. Examples of ophthalmic devices include

but are not limited to lenses, optical and ocular inserts, including but not limited to punctal plugs, and the like. "Lenses" include soft contact lenses, hard contact lenses, hybrid contact lenses, intraocular lenses, and overlay lenses. The ophthalmic device may comprise a contact lens.

[0039] The term "contact lens" refers to an ophthalmic device that can be placed on the cornea of an individual's eye. The contact lens may provide corrective, cosmetic, or therapeutic benefit, including wound healing, the delivery of drugs or nutraceuticals, diagnostic evaluation or monitoring, ultraviolet light filtering, visible light or glare reduction, or any combination thereof. A contact lens can be of any appropriate material known in the art and can be a soft lens, a hard lens, or a hybrid lens containing at least two distinct portions with different physical, mechanical, or optical properties, such as modulus, water content, light transmission, or combinations thereof.

[0040] The ophthalmic devices and lenses described herein may be comprised of silicone hydrogels or conventional hydrogels. Silicone hydrogels typically include at least one hydrophilic monomer and at least one silicone-containing component that are covalently bound to one another in the cured device.

[0041] As used herein, the terms "physical absorption" or "chemical absorption" refer to processes in which atoms, molecules, or particles enter the bulk phase of a gas, liquid, or solid material and are taken up within the volume. Absorption in this manner may be driven by solubility, concentration gradients, temperature, pressure, and other driving forces known in the art.

[0042] As used herein, "adsorption" is defined as the deposition of a species onto a surface. The species that gets adsorbed on a surface is known as an adsorbate, and the surface on which adsorption occurs is known as an adsorbent. Examples of adsorbents may comprise clay, silica gel, colloids, metals, nanoparticles etc. Adsorption may occur via chemical or physical adsorption. Chemical adsorption may occur when an adsorbate is held to the an adsorbent via chemical bonds, whereas physical adsorption may occur when an adsorbate is joined to an adsorbent via weak van der Waal's forces.

[0043] As used herein, "antibacterial" means intended to kill or reduce the harmful effects of bacteria.

[0044] As used herein, "colloid" refers to dispersions of wherein one substance is suspended in another. Many examples of colloids in the art contain polymers. In this aspect, polymers may be adsorbed or chemically attached to the surface of particles suspended in the colloid, or the polymers may freely move in the colloidal suspension. The presence of polymers on particles in the suspension may directly relate to "colloidal stability," wherein "colloidal stability" refers to the tendency of a colloidal suspension to undergo sedimentation. Sedimentation would result in the falling of particles out of a colloid. Polymers adsorbed or chemically attached to a particle may affect its colloidal stability.

[0045] As used herein, the term "diffusion" refers to the process wherein there is a net flow of matter from one region to another. An example of such process is "surface diffusion," wherein particles move from one area of the surface of a subject to another area of the same surface. This can be caused by thermal stress or applied pressure.

[0046] As used herein, "DNA aptamers" refer to short biomolecules like oligonucleotides and peptides that bind to specific targets with extremely high affinity based on their structural conformations. DNA aptamers have been explored in areas such as disease diagnosis, therapeutics, etc.

[0047] As used herein, a "surfactant" refers to a substance that, when added to a liquid, reduces its surface tension, thereby increasing its spreading and wetting properties. Typical surfactants may be partly hydrophilic and partly lipophilic.

[0048] As used herein, the term "wetting agent" refers to a material that allows a liquid to more easily spread on or "wet" a surface. The high surface tension of water causes problems in many industrial processes where water-based solutions are used, as the solution is not able to wet the surface it is applied to. Wetting agents are commonly used to reduce the surface tension of water and thus help the water-based solutions to spread.

[0049] "Target macromolecule" means the macromolecule being synthesized from the reactive monomer mixture comprising monomers, macromers, prepolymers, cross-linkers, initiators, additives, diluents, and the like.

[0050] The term "polymerizable compound" means a compound containing one or more polymerizable groups. The term encompasses, for instance, monomers, macromers, oligomers, prepolymers, cross-linkers, and the like.

[0051] “Polymerizable groups” are groups that can undergo chain growth polymerization, such as free radical and/or cationic polymerization, for example a carbon-carbon double bond which can polymerize when subjected to radical polymerization initiation conditions. Non-limiting examples of free radical polymerizable groups include (meth)acrylates, styrenes, vinyl ethers, (meth)acrylamides, N-vinyllactams, N-vinylamides, O-vinylcarbamates, O-vinylcarbonates, and other vinyl groups. Preferably, the free radical polymerizable groups comprise (meth)acrylate, (meth)acrylamide, N-vinyl lactam, N-vinylamide, and styryl functional groups, and mixtures of any of the foregoing. More preferably, the free radical polymerizable groups comprise (meth)acrylates, (meth)acrylamides, and mixtures thereof. The polymerizable group may be unsubstituted or substituted. For instance, the nitrogen atom in (meth)acrylamide may be bonded to a hydrogen, or the hydrogen may be replaced with alkyl or cycloalkyl (which themselves may be further substituted).

[0052] Any type of free radical polymerization may be used including but not limited to bulk, solution, suspension, and emulsion as well as any of the controlled radical polymerization methods such as stable free radical polymerization, nitroxide-mediated living polymerization, atom transfer radical polymerization, reversible addition fragmentation chain transfer polymerization, organotellurium mediated living radical polymerization, and the like.

[0053] A “monomer” is a mono-functional molecule which can undergo chain growth polymerization, and in particular, free radical polymerization, thereby creating a repeating unit in the chemical structure of the target macromolecule. Some monomers have di-functional impurities that can act as cross-linking agents. A “hydrophilic monomer” is also a monomer which yields a clear single phase solution when mixed with deionized water at 25° C. at a concentration of 5 weight percent. A “hydrophilic component” is a monomer, macromer, prepolymer, initiator, cross-linker, additive, or polymer which yields a clear single phase solution when mixed with deionized water at 25° C. at a concentration of 5 weight percent. A “hydrophobic component” is a monomer, macromer, prepolymer, initiator, cross-linker, additive, or polymer which is slightly soluble or insoluble in deionized water at 25° C.

[0054] A “macromolecule” is an organic compound having a number average molecular weight of greater than 1500, and may be reactive or non-reactive.

[0055] A “macromonomer” or “macromer” is a macromolecule that has one group that can undergo chain growth polymerization, and in particular, free radical polymerization, thereby

creating a repeating unit in the chemical structure of the target macromolecule. Typically, the chemical structure of the macromer is different than the chemical structure of the target macromolecule, that is, the repeating unit of the macromer's pendent group is different than the repeating unit of the target macromolecule or its mainchain. The difference between a monomer and a macromer is merely one of chemical structure, molecular weight, and molecular weight distribution of the pendent group. As a result, and as used herein, the patent literature occasionally defines monomers as polymerizable compounds having relatively low molecular weights of about 1,500 Daltons or less, which inherently includes some macromers. In particular, monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (molecular weight=500-1500 g/mol) (mPDMS) and mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxane (molecular weight=500-1500 g/mol) (OH-mPDMS) may be referred to as monomers or macromers. Furthermore, the patent literature occasionally defines macromers as having one or more polymerizable groups, essentially broadening the common definition of macromer to include prepolymers. As a result, and as used herein, di-functional and multi-functional macromers, prepolymers, and crosslinkers may be used interchangeably.

[0056] A “silicone-containing component” is a monomer, macromer, prepolymer, cross-linker, initiator, additive, or polymer in the reactive mixture with at least one silicon-oxygen bond, typically in the form of siloxy groups, siloxane groups, carbosiloxane groups, and mixtures thereof.

[0057] Examples of silicone-containing components which are useful in this invention may be found in U.S. Pat. Nos. 3,808,178, 4,120,570, 4,136,250, 4,153,641, 4,740,533, 5,034,461, 5,070,215, 5,244,981, 5,314,960, 5,331,067, 5,371,147, 5,760,100, 5,849,811, 5,962,548, 5,965,631, 5,998,498, 6,367,929, 6,822,016, 6,943,203, 6,951,894, 7,052,131, 7,247,692, 7,396,890, 7,461,937, 7,468,398, 7,538,146, 7,553,880, 7,572,841, 7,666,921, 7,691,916, 7,786,185, 7,825,170, 7,915,323, 7,994,356, 8,022,158, 8,163,206, 8,273,802, 8,399,538, 8,415,404, 8,420,711, 8,450,387, 8,487,058, 8,568,626, 8,937,110, 8,937,111, 8,940,812, 8,980,972, 9,056,878, 9,125,808, 9,140,825, 9,156,934, 9,170,349, 9,217,813, 9,244,196, 9,244,197, 9,260,544, 9,297,928, 9,297,929, and European Patent No. 080539. These patents are hereby incorporated by reference in their entireties.

[0058] A “polymer” is a target macromolecule composed of the repeating units of the monomers used during polymerization. Exemplary polymers may comprise poly(ethylene glycol) (PEG), polycarbonate, poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP), polystyrene (PS), polycaprolactone (PCL), ethylene oligomers or polyethylene (PE), polypropylene (PP), poly(methyl methacrylate) (PMMA), and other polymers known in the art.

[0059] As used herein, the term “thermoplastic” refers to a property of polymers, wherein the polymer may be melted, solidified, and then successfully melted and solidified again. This process may be repeated several times for thermoplastic polymers without loss of functionality.

[0060] As used herein, the term “thermoset” refers to a property of polymers, wherein a thermoset polymer forms well-defined, irreversible, chemical networks that tend to grow in three dimensional directions through the process of curing, which can either occur due to heating or through the addition of a curing agent, therefore causing a crosslinking formation between its chemical components, and giving the thermoset a strong and rigid structure that can be added to other materials to increase strength. Once a thermoset polymer has formed networks during curing, the polymer cannot be re-cured to set in a different manner.

[0061] A “homopolymer” is a polymer made from one monomer; a “copolymer” is a polymer made from two or more monomers; a “terpolymer” is a polymer made from three monomers. A “block copolymer” is composed of compositionally different blocks or segments. Diblock copolymers have two blocks. Triblock copolymers have three blocks. “Comb or graft copolymers” are made from at least one macromer.

[0062] A “repeating unit” is the smallest group of atoms in a polymer that corresponds to the polymerization of a specific monomer or macromer.

[0063] An “initiator” is a molecule that can decompose into radicals which can subsequently react with a monomer to initiate a free radical polymerization reaction. A thermal initiator decomposes at a certain rate depending on the temperature; typical examples are azo compounds such as 1,1'-azobisisobutyronitrile and 4,4'-azobis(4-cyanovaleric acid), peroxides such as benzoyl peroxide, tert-butyl peroxide, tert-butyl hydroperoxide, tert-butyl peroxybenzoate, dicumyl peroxide, and lauroyl peroxide, peracids such as peracetic acid and potassium persulfate as well as various redox systems. A photo-initiator decomposes by a photochemical process; typical examples are derivatives of benzil, benzoin, acetophenone,

benzophenone, camphorquinone, and mixtures thereof as well as various monoacyl and bisacyl phosphine oxides and combinations thereof.

[0064] A “cross-linking agent” is a di-functional or multi-functional monomer or macromer which can undergo free radical polymerization at two or more locations on the molecule, thereby creating branch points and a polymeric network. Common examples are bis(2-methacryloyl)oxyethyl disulfide (DSDMA), cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, methylene bisacrylamide, triallyl cyanurate, and the like.

[0065] A “prepolymer” is a reaction product of monomers which contains remaining polymerizable groups capable of undergoing further reaction to form a polymer.

[0066] A “polymeric network” is a cross-linked macromolecule that can swell but cannot dissolve in solvents. “Hydrogels” are polymeric networks that swell in water or aqueous solutions, typically absorbing at least 10 weight percent water. “Silicone hydrogels” are hydrogels that are made from at least one silicone-containing component with at least one hydrophilic component. Hydrophilic components may also include non-reactive polymers.

[0067] “Conventional hydrogels” refer to polymeric networks made from components without any siloxy, siloxane or carbosiloxane groups. Conventional hydrogels are prepared from reactive mixtures comprising hydrophilic monomers. Examples include 2-hydroxyethyl methacrylate (“HEMA”), N-vinyl pyrrolidone (“NVP”), N, N-dimethylacrylamide (“DMA”) or vinyl acetate. U.S. Pat. Nos. 4,436,887, 4,495,313, 4,889,664, 5,006,622, 5,039,459, 5,236,969, 5,270,418, 5,298,533, 5,824,719, 6,420,453, 6,423,761, 6,767,979, 7,934,830, 8,138,290, and 8,389,597 disclose the formation of conventional hydrogels. Commercially available conventional hydrogels include, but are not limited to, etafilcon, genfilcon, hilafilcon, lenefilcon, nesofilcon, omafilcon, polymacon, and vifilcon, including all of their variants.

[0068] “Silicone hydrogels” refer to polymeric networks made from at least one hydrophilic component and at least one silicone-containing component. Examples of silicone hydrogels include acquafilcon, asmofilcon, balafilcon, comfilcon, delefilcon, enfilcon, falcon, fanfilcon, formofilcon, galyfilcon, lotrafilcon, narafilcon, riofilcon, samfilcon, senofilcon, somofilcon, and stenfilcon, including all of their variants, as well as silicone hydrogels as prepared in U.S. Pat. Nos. 4,659,782, 4,659,783, 5,244,981, 5,314,960, 5,331,067, 5,371,147,

5,998,498, 6,087,415, 5,760,100, 5,776,999, 5,789,461, 5,849,811, 5,965,631, 6,367,929, 6,822,016, 6,867,245, 6,943,203, 7,247,692, 7,249,848, 7,553,880, 7,666,921, 7,786,185, 7,956,131, 8,022,158, 8,273,802, 8,399,538, 8,470,906, 8,450,387, 8,487,058, 8,507,577, 8,637,621, 8,703,891, 8,937,110, 8,937,111, 8,940,812, 9,056,878, 9,057,821, 9,125,808, 9,140,825, 9,156,934, 9,170,349, 9,244,196, 9,244,197, 9,260,544, 9,297,928, 9,297,929 as well as WO 03/22321, WO 2008/061992, and US 2010/0048847. These patents are hereby incorporated by reference in their entireties.

[0069] As used herein, "gel-like" refers to a substance having properties generally relating to those associated with a gel. A "gel" may refer to a coherent mass consisting of a liquid in which particles are either dispersed or arranged in a fine network throughout the mass. A gel may be notably elastic or substantially solid and rigid (e.g. silica gel appears as a firm particle). Gels may also be seen as colloids in which the liquid medium has become viscous enough to behave more or less as a solid.

[0070] An "interpenetrating polymeric network" comprises two or more networks which are at least partially interlaced on the molecular scale but not covalently bonded to each other and which cannot be separated without breaking chemical bonds. A "semi-interpenetrating polymeric network" comprises one or more networks and one or more polymers characterized by some mixing on the molecular level between at least one network and at least one polymer. A mixture of different polymers is a "polymer blend." A semi-interpenetrating network is technically a polymer blend, but in some cases, the polymers are so entangled that they cannot be readily removed.

[0071] The terms "reactive mixture" and "reactive monomer mixture" refer to the mixture of components (both reactive and non-reactive) which are mixed together and when subjected to polymerization conditions form the conventional or silicone hydrogels of the present invention as well as contact lenses made therefrom. The reactive monomer mixture may comprise reactive components such as the monomers, macromers, prepolymers, cross-linkers, and initiators, additives such as wetting agents, release agents, polymers, dyes, light absorbing compounds such as UV absorbers, pigments, dyes and photochromic compounds, any of which may be reactive or non-reactive but are capable of being retained within the resulting biomedical device, as well as pharmaceutical and nutraceutical compounds, and any diluents. It will be appreciated that a wide range of additives may be added based upon the biomedical

device which is made and its intended use. Concentrations of components of the reactive mixture are expressed as weight percentages of all components in the reactive mixture, excluding diluent. When diluents are used, their concentrations are expressed as weight percentages based upon the amount of all components in the reactive mixture and the diluent.

[0072] “Reactive components” are the components in the reactive mixture which become part of the chemical structure of the polymeric network of the resulting hydrogel by covalent bonding, hydrogen bonding, electrostatic interactions, the formation of interpenetrating polymeric networks, or any other means.

[0073] The term “silicone hydrogel contact lens” refers to a hydrogel contact lens comprising at least one silicone containing component. Silicone hydrogel contact lenses generally have increased oxygen permeability compared to conventional hydrogels. Silicone hydrogel contact lenses use both their water and polymer content to transmit oxygen to the eye.

[0074] The term “multi-functional” refers to a component having two or more polymerizable groups. The term “mono-functional” refers to a component having one polymerizable group.

[0075] The terms “halogen” or “halo” indicate fluorine, chlorine, bromine, and iodine.

[0076] As used herein, the term “alkyl” refers to an unsubstituted or substituted linear or branched alkyl group containing the indicated number of carbon atoms. If no number is indicated, then alkyl (optionally including any substituents on alkyl) may contain 1 to 16 carbon atoms. Preferably, the alkyl group contains 1 to 10 carbon atoms, alternatively 1 to 7 carbon atoms, or alternatively 1 to 4 carbon atoms. Examples of alkyl include methyl, ethyl, propyl, isopropyl, butyl, iso-, sec- and tert-butyl, pentyl, hexyl, heptyl, 3-ethylbutyl, and the like. Examples of substituents on alkyl include 1, 2, or 3 groups independently selected from hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, amido, carbamate, carbonate, halogen, phenyl, benzyl, thiol, and combinations thereof. “Alkylene” means a divalent alkyl group, such as $\text{—CH}_2\text{—}$, $\text{—CH}_2\text{CH}_2\text{—}$, $\text{—CH}_2\text{CH}_2\text{CH}_2\text{—}$, $\text{—CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{—}$, and $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$.

[0077] “Haloalkyl” refers to an alkyl group as defined above substituted with one or more halogen atoms, where each halogen is independently F, Cl, Br or I. A preferred halogen is F. Preferred haloalkyl groups contain 1-6 carbons, more preferably 1-4 carbons, and still more

preferably 1-2 carbons. “Haloalkyl” includes perhaloalkyl groups, such as $\text{—CF}_3\text{—}$ or $\text{—CF}_2\text{CF}_3\text{—}$. “Haloalkylene” means a divalent haloalkyl group, such as $\text{—CH}_2\text{CF}_2\text{—}$.

[0078] “Cycloalkyl” refers to an unsubstituted or substituted cyclic hydrocarbon containing the indicated number of ring carbon atoms. If no number is indicated, then cycloalkyl may contain 3 to 12 ring carbon atoms. Preferred are $\text{C}_3\text{—C}_8$ cycloalkyl groups, $\text{C}_3\text{—C}_7$ cycloalkyl, more preferably $\text{C}_4\text{—C}_7$ cycloalkyl, and still more preferably $\text{C}_5\text{—C}_6$ cycloalkyl. Examples of cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. Examples of substituents on cycloalkyl include 1, 2, or 3 groups independently selected from alkyl, hydroxy, amino, amido, oxa, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, and combinations thereof. “Cycloalkylene” means a divalent cycloalkyl group, such as 1,2-cyclohexylene, 1,3-cyclohexylene, or 1,4-cyclohexylene.

[0079] “Heterocycloalkyl” refers to a cycloalkyl ring or ring system as defined above in which at least one ring carbon has been replaced with a heteroatom selected from nitrogen, oxygen, and sulfur. The heterocycloalkyl ring is optionally fused to or otherwise attached to other heterocycloalkyl rings and/or non-aromatic hydrocarbon rings and/or phenyl rings. Preferred heterocycloalkyl groups have from 5 to 7 members. More preferred heterocycloalkyl groups have 5 or 6 members. Heterocycloalkylene means a divalent heterocycloalkyl group.

[0080] “Aryl” refers to an unsubstituted or substituted aromatic hydrocarbon ring system containing at least one aromatic ring. The aryl group contains the indicated number of ring carbon atoms. If no number is indicated, then aryl may contain 6 to 14 ring carbon atoms. The aromatic ring may optionally be fused or otherwise attached to other aromatic hydrocarbon rings or non-aromatic hydrocarbon rings. Examples of aryl groups include phenyl, naphthyl, and biphenyl. Preferred examples of aryl groups include phenyl. Examples of substituents on aryl include 1, 2, or 3 groups independently selected from alkyl, hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, and combinations thereof. “Arylene” means a divalent aryl group, for example 1,2-phenylene, 1,3-phenylene, or 1,4-phenylene.

[0081] “Heteroaryl” refers to an aryl ring or ring system, as defined above, in which at least one ring carbon atom has been replaced with a heteroatom selected from nitrogen, oxygen, and sulfur. The heteroaryl ring may be fused or otherwise attached to one or more heteroaryl rings, aromatic or nonaromatic hydrocarbon rings or heterocycloalkyl rings.

Examples of heteroaryl groups include pyridyl, furyl, and thienyl. “Heteroarylene” means a divalent heteroaryl group.

[0082] “Alkoxy” refers to an alkyl group attached to the parent molecular moiety through an oxygen bridge. Examples of alkoxy groups include, for instance, methoxy, ethoxy, propoxy and isopropoxy. “Aryloxy” refers to an aryl group attached to a parent molecular moiety through an oxygen bridge. Examples include phenoxy. “Cyclic alkoxy” means a cycloalkyl group attached to the parent moiety through an oxygen bridge.

[0083] “Alkylamine” refers to an alkyl group attached to the parent molecular moiety through an —NH bridge. Alkyleneamine means a divalent alkylamine group, such as —CH₂CH₂NH—.

[0084] “Ester” refers to a class of organic compounds having the general formula RCOOR', wherein R and R' are any organic combining groups. R and R' may be selected from functional groups comprising alkyls, substituted alkyls, alkylene, haloalkyls, cycloalkyls, heterocycloalkyls, aryls, heteroaryls, alkoxys, cycloalkoxys, alkylamines, siloxanyls, silyls, alkyleneoxys, oxaalkylenes, and the like. Definitions for the above mentioned functional groups are provided herein.

[0085] As used herein, “esterification” refers to a reaction producing an ester. The reaction often involves an alcohol and a Bronsted acid (such as a carboxylic acid, sulfuric acid, or phosphoric acid). Furthermore, the term “transesterification” refers to the reaction of an alcohol molecule and a pre-existing ester molecule react to form a new ester. In some aspects, transesterification can be mediated by other compounds, such as carbonyldiimidazole.

[0086] “Siloxanyl” refers to a structure having at least one Si—O—Si bond. Thus, for example, siloxanyl group means a group having at least one Si—O—Si group (i.e. a siloxane group), and siloxanyl compound means a compound having at least one Si—O—Si group. “Siloxanyl” encompasses monomeric (e.g., Si—O—Si) as well as oligomeric/polymeric structures (e.g., —[Si—O]_n—, where n is 2 or more). Each silicon atom in the siloxanyl group is substituted with independently selected R^A groups (where R^A is as defined in formula A options (b)-(i)) to complete their valence.

[0087] “Silyl” refers to a structure of formula R₃Si— and “siloxy” refers to a structure of formula R₃Si—O—, where each R in silyl or siloxy is independently selected from

trimethylsiloxy, C₁-C₈ alkyl (preferably C₁-C₃ alkyl, more preferably ethyl or methyl), and C₃-C₈ cycloalkyl.

[0088] “Alkyleneoxy” refers to groups of the general formula $-(\text{alkylene-O})_p-$ or $-(\text{O-alkylene})_p-$, wherein alkylene is as defined above, and p is from 1 to 200, or from 1 to 100, or from 1 to 50, or from 1 to 25, or from 1 to 20, or from 1 to 10, wherein each alkylene is independently optionally substituted with one or more groups independently selected from hydroxyl, halo (e.g., fluoro), amino, amido, ether, carbonyl, carboxyl, and combinations thereof. If p is greater than 1, then each alkylene may be the same or different and the alkyleneoxy may be in block or random configuration. When alkyleneoxy forms a terminal group in a molecule, the terminal end of the alkyleneoxy may, for instance, be a hydroxy or alkoxy (e.g., HO— $[\text{CH}_2\text{CH}_2\text{O}]_p-$ or $\text{CH}_3\text{O}-[\text{CH}_2\text{CH}_2\text{O}]_p-$). Examples of alkyleneoxy include polymethyleneoxy, polyethyleneoxy, polypropyleneoxy, polybutyleneoxy, and poly(ethyleneoxy-co-propyleneoxy).

[0089] “Oxaalkylene” refers to an alkylene group as defined above where one or more non-adjacent CH₂ groups have been substituted with an oxygen atom, such as —CH₂CH₂OCH(CH₃)CH₂—. “Thiaalkylene” refers to an alkylene group as defined above where one or more non-adjacent CH₂ groups have been substituted with a sulfur atom, such as —CH₂CH₂SCH(CH₃)CH₂—.

[0090] The term “linking group” refers to a moiety that links the polymerizable group to the parent molecule. The linking group may be any moiety that does not undesirably interfere with the polymerization of the compound of which it is a part. For instance, the linking group may be a bond, or it may comprise one or more alkylene, haloalkylene, amide, amine, alkyleneamine, carbamate, carboxylate ($-\text{CO}_2-$), disulfide, arylene, heteroarylene, cycloalkylene, heterocycloalkylene, alkyleneoxy, oxaalkylene, thiaalkylene, haloalkyleneoxy (alkyleneoxy substituted with one or more halo groups, e.g., $-\text{OCF}_2-$, $-\text{OCF}_2\text{CF}_2-$, $-\text{OCF}_2\text{CH}_2-$), siloxanyl, alkylenesiloxanyl, thiol, or combinations thereof. The linking group may optionally be substituted with 1 or more substituent groups. Suitable substituent groups may include those independently selected from alkyl, halo (e.g., fluoro), hydroxyl, HO-alkyleneoxy, CH₃O-alkyleneoxy, siloxanyl, siloxy, siloxy-alkyleneoxy-, siloxy-alkylene-alkyleneoxy- (where more than one alkyleneoxy groups may be present and wherein each methylene in alkylene and alkyleneoxy is independently optionally substituted with hydroxyl),

ether, amine, carbonyl, carbamate, and combinations thereof. The linking group may also be substituted with a polymerizable group, such as (meth)acrylate (in addition to the polymerizable group to which the linking group is linked).

[0091] Preferred linking groups include C₁-C₈ alkylene (preferably C₂-C₆ alkylene) and C₁-C₈ oxaalkylene (preferably C₂-C₆ oxaalkylene), each of which is optionally substituted with 1 or 2 groups independently selected from hydroxyl and siloxy. Preferred linking groups also include carboxylate, amide, C₁-C₈ alkylene-carboxylate-C₁-C₈ alkylene, or C₁-C₈ alkylene-amide-C₁-C₈ alkylene.

[0092] When the linking group is comprised of combinations of moieties as described above (e.g., alkylene and cycloalkylene), the moieties may be present in any order. For instance, if in Formula E below, L is indicated as being -alkylene-cycloalkylene-, then Rg-L may be either Rg-alkylene-cycloalkylene-, or Rg-cycloalkylene-alkylene-. Notwithstanding this, the listing order represents the preferred order in which the moieties appear in the compound starting from the terminal polymerizable group (Rg) to which the linking group is attached. For example, if in Formula E, L and L² are indicated as both being alkylene-cycloalkylene, then Rg-L is preferably Rg-alkylene-cycloalkylene- and -L²-Rg is preferably -cycloalkylene-alkylene-Rg.

[0093] As used herein, "oxidation" refers to a chemical process by which an atom of an element gains bonds to more electronegative elements, most commonly oxygen. In this process, the oxidized element increases its oxidation state, which represents the charge of an atom. Oxidation reactions are commonly coupled with "reduction" reactions, wherein the oxidation state of the reduced atom decreases.

[0094] As used herein, "anchoring" or "anchoring mechanism" refers to the process by which nanoparticles may become embedded in a colloidal or polymeric matrix. "Anchoring" may occur either chemically via crosslinking of a nanoparticle to members of an exemplary matrix or physically via entanglement of a molecule joined to the surface of a nanoparticle with members of an exemplary matrix.

[0095] As used herein, the "visible spectrum" refers to a range of wavelengths within the electromagnetic spectrum, wherein the range spans about 380nm to 700nm. The visible spectrum may be broken up into different wavelength regions corresponding to colors including

red, orange, yellow, green, blue, indigo, and violet. Certain ranges of wavelengths falling in the visible spectrum have been known to cause damage to human eyes.

[0096] As used herein, the "ultraviolet (UV) spectrum" refers to a range of wavelengths within the electromagnetic spectrum, wherein the range spans about 10nm to 400nm.

[0097] As used herein, "ultraviolet (UV) irradiation" refers to exposure to electromagnetic waves falling in the ultraviolet spectrum of wavelengths, wherein UV irradiation uses selected times and intensity of exposure to achieve its effects, such as curing. UV irradiation can result in chemical (photo-crosslinking, photo-oxidation, or photochemical reactions) or physical (surface morphology, etc.) changes. Photochemical reactions caused by UV irradiation can be surface-limited or can take place deep inside the bulk (unlike plasma) of a material. Some exemplary sources of UV irradiation may comprise continuous wave (CW) UV-lamps with a moderate light and pulsed lasers.

[0098] As used herein, "light absorption" is defined as the phenomenon wherein electrons absorb the energy of incoming light waves (i.e. photons) and change their energy state. In order for this to occur, the incoming light waves must be at or near the energy levels of the electrons. The resultant absorption patterns characteristic to a given material may be displayed using an "absorption spectrum", wherein an "absorption spectrum" shows the change in absorbance of a sample as a function of the wavelength of incident light and may be measured using a spectrophotometer. A "filtering spectrum" includes an "absorption spectrum" and comprises is an "absorption peak" or "filtering peak", wherein the frequency or wavelength of a given sample exhibits the maximum or the highest spectral value of light absorption. With regards to light absorption of wavelengths of light corresponding to the visible spectrum, a material or matter absorbing light waves of certain wavelengths of the visible spectrum may cause an observer to not see these wavelengths in the reflected light.

[0099] As used herein, "Full Width at Half Maximum (FWHM)" refers to a parameter commonly used to describe the width of a portion of a curve or function and may be used in relation to absorbance spectra. It is given by the distance between points on the independent axis of a curve at which the function reaches half its maximum value on the dependent axis.

[00100] "Light filtering" may include absorbing, scattering, and/or extinguishing incident light. Light filtering may include the terms "light-blocking material", Light blocking

may refer to a material with the ability to absorb, scatter, and/or extinguish incident light within a given region of the electromagnetic spectrum. Thus, the term "light-blocking material" or "lighting filtering material" encompasses particles that absorb, scatter, and/or extinguish incident light within a given region of the electromagnetic spectrum. The particles can be incorporated in varying quantities within an optically transparent substrate to achieve an optically transparent material which exhibits a desired level of light blocking at one or more wavelengths or a range of wavelengths within the electromagnetic spectrum. The percent blocking at a particular wavelength can be determined from the material's transmission spectrum, where $\text{blocking} = 100 - \text{percent transmission (\% T)}$.

[00101] As used herein, the term "light-blocking profile" or "light-blocking spectrum" refers to the absorption, scattering, and/or extinguishing spectrum of a light-blocking material.

[00102] The terms "red-light blocking" or "red-light absorbing" or "red-light filtering" refer to the ability of certain particles to absorb, scatter, and/or extinguish incident light within the red region of the visible spectrum (e.g., between 620 and 750nm or between about 600 nm up to about 850 nm). Thus, the terms "red-light blocking" or "red-light absorbing" encompass particles that absorb, scatter, and/or extinguish incident light within the red region of the visible spectrum. The particles can be incorporated in varying quantities within an optically transparent substrate to achieve an optically transparent material which exhibits a desired level of red-light blocking at one or more wavelengths or a range of wavelengths within a spectral region.

[00103] "Nanoparticle (NP)" as used herein refers to a particle having at least one dimension that is less than 100 nm. In some cases, nanoparticles can have at least one dimension less than 50 nm. NP's may have a variety of shapes. In some instances, NP's may have a cubic shape, spherical shape, rod shape, bipyramidal shape, an octahedral shape, a decahedral shape, a cuboctahedral shape, a tetrahedral shape, a rhombic dodecahedral shape, a truncated ditetragonal prismatic shape, or a truncated bitetrahedral shape. "Plasmonic nanoparticle" as used herein refers to a metal nanoparticle that has unique optical properties due to local surface plasmon resonance that allow them to interact with light waves. These properties are tunable by changing the shape, size, composition or medium surrounding the nanoparticle's surface. It will be appreciated that the term includes all plasmonic nanoparticles of various shapes that gives rise to a surface plasmon absorption and scattering spectrum

[00104] As used herein, a "shape-directing agent" is a surfactant or reagent used to grow nanoparticles into specific morphologies. By utilizing specific shape-directing agents, specific morphologies may be selected, allowing for the optical properties of the resultant nanoparticles to be tuned. Exemplary shape-directing agents may include, but are not limited to, AgNO₃, CTAB, CTAC, and other such agents known in the art.

[00105] As used herein, "anisotropic" describes a material wherein a given property of said material depends on the direction in which it is measured. Moreover, something that is "anisotropic" changes in size or in its physical properties according to the direction in which it is measured. Examples of anisotropic materials may comprise graphite, carbon fiber, nanoparticles, etc.

[00106] As used herein, "isotropic" describes a material wherein a given property of said material does not depend on the direction in which it is measured. Moreover, something that is "isotropic" remains constant in size or in its physical properties according to the direction in which it is measured.

[00107] As used herein, "surface energy" may refer to the excess energy (i.e., the difference in the energy between a nanoparticle and the same number of atoms in an infinitely extended solid). More broadly, the surface energy of a particle may define its stability given its morphology and directly relates to the thermodynamics of a given nanoparticle.

[00108] As used herein, "surface plasmon resonance (SPR)" refers to a phenomenon wherein the conduction electrons in the surface layer of a metal may become excited by photons of incident light with a certain angle of incidence, causing the excited conduction electrons to then propagate parallel to the metal surface in resonant oscillations (Zeng et al., 2017). With a constant light source wavelength and a thin metal surface layer, the certain angle that triggers SPR is dependent on the refractive index of the material near the metal surface. As used herein, "localized surface plasmon resonance (LSPR)" refers to an optical phenomena generated by light when it interacts with conductive nanoparticles that are smaller than the incident wavelength. As in surface plasmon resonance, the electric field of incident light can be deposited to collectively excite electrons of a conduction band, with the result being coherent localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, dielectric environment and separation distance of NP's.

[00109] As used herein, a "localized surface plasmon resonance (LSPR) peak" refers to the frequency or wavelength of incident light that exhibits the maximum or the highest spectral value of localized surface plasmon resonance. With regards to LSPR peaks, there are frequently two distinct peaks observed: a "longitudinal peak" and a "transverse peak". The former relates to the shape of the nanoparticle utilized, whereas the latter is a result of the innate properties of the material used. Gold, for instance, has an inherent transverse peak around 530nm, though the longitudinal peak of a gold NP can be tuned by adjusting its morphology.

[00110] As used herein, "plasmonic light blocker" refers to a material with the ability to absorb, scatter, and/or extinguish incident light within a given region of the electromagnetic spectrum due to surface plasmonic resonance (SPR) or localized surface plasmonic resonance (LSPR), wherein the wavelength or range of wavelengths blocked correspond to the wavelength of incident light that induces the SPR or LSPR. Thus, the term "plasmonic light blocker" encompasses particles that absorb, scatter, and/or extinguish incident light within a given region of the electromagnetic spectrum due to SPR or LSPR. The particles can be incorporated in varying quantities within an optically transparent substrate to achieve an optically transparent material which exhibits a desired level of light filtering at one or more wavelengths or a range of wavelengths within the electromagnetic spectrum. The percent blocking at a particular wavelength can be determined from the material's transmission spectrum, where $\text{blocking} = 100 - \text{percent transmission (\% T)}$. As used herein, "ligand" refers to an ion or neutral molecule that bonds to a central metal atom or ion. Exemplary ligands may comprise PVP, PVA, DSDMA, and other molecules capable of bonding to a central metal atom. Metal atoms may comprise a variety of metals including, but not limited to, noble metals such as gold. Ligands have at least one donor with an electron pair used to form covalent bonds with the metal central atom.

[00111] As used herein, an "intermediate ligand" refers to a ligand temporarily conjugated to a metal atom that is further exchanged to allow the conjugation of an alternate ligand.

[00112] The term "biocompatible", as used herein is intended to describe materials that do not elicit a substantial detrimental response in vivo. In certain embodiments, the materials are "biocompatible" if they are not toxic to cells. In certain embodiments, materials are "biocompatible" if their addition to cells in vitro results in less than or equal to 20% cell

death, and/or their administration in vivo does not induce inflammation or other such adverse effects.

[00113] The term “static concentration”, as used herein, refers to a concentration of the trigger, which may vary from about 1% to about 10%. For example, the static concentration may vary by $\pm 10\%$, $\pm 5\%$, $\pm 2\%$, or $\pm 1\%$.

[00114] Unless otherwise indicated, ratios, percentages, parts, and the like are by weight.

[00115] Unless otherwise indicated, numeric ranges, for instance as in “from 2 to 10,” are inclusive of the numbers defining the range (e.g., 2 and 10).

[00116] Devices

[00117] The resulting optically transparent materials can be used to form a variety of different articles, including optical lenses (e.g., eyeglass lenses, camera lenses, contact lenses, etc.), ophthalmic devices (e.g., contact lenses, corneal onlays, corneal inlays, intraocular lenses, overlay lenses, etc.), screen covers (e.g., a transparent sheet configured to cover a computer monitor, tablet screen, or cell phone screen), and housings for electronic devices having LED displays. Accordingly, also provided are optical lenses (e.g., eyeglass lenses, camera lenses, contact lenses, etc.), ophthalmic devices (e.g., contact lenses, corneal onlays, corneal inlays, intraocular lenses, overlay lenses, etc.), screen covers (e.g., a transparent sheet configured to cover a computer monitor, tablet screen, or cell phone screen), and housings for electronic devices having LED displays which are formed at whole or in part from the optically transparent materials described herein.

[00118] A variety of ophthalmic devices containing the nanoparticles described herein may be prepared, including hard contact lenses, soft contact lenses, corneal onlays, corneal inlays, intraocular lenses, or overlay lenses. Preferably, the ophthalmic device is a soft contact lens, which may be made from conventional or silicone hydrogel formulations.

[00119] Ophthalmic devices may be prepared by polymerizing a reactive mixture containing a population of the nanoparticles described herein, one or more monomers suitable for making the desired ophthalmic device, and optional components. In some cases, the reactive mixture may include, in addition to a population of the nanoparticles described above, one or more of: hydrophilic components, hydrophobic components, silicone-containing components,

wetting agents such as polyamides, crosslinking agents, and further components such as diluents and initiators.

[00120] Silicone-Containing Components

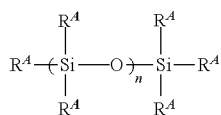
[00121] Silicone-containing components suitable for use comprise one or more polymerizable compounds, where each compound independently comprises at least one polymerizable group, at least one siloxane group, and one or more linking groups connecting the polymerizable group(s) to the siloxane group(s). The silicone-containing components may, for instance, contain from 1 to 220 siloxane repeat units, such as the groups defined below. The silicone-containing component may also contain at least one fluorine atom.

[00122] The silicone-containing component may comprise: one or more polymerizable groups as defined above; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units. The silicone-containing component may comprise: one or more polymerizable groups that are independently a (meth)acrylate, a styryl, a vinyl ether, a (meth)acrylamide, an N-vinyl lactam, an N-vinylamide, an O-vinylcarbamate, an O-vinylcarbonate, a vinyl group, or mixtures of the foregoing; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units.

[00123] The silicone-containing component may comprise: one or more polymerizable groups that are independently a (meth)acrylate, a (meth)acrylamide, an N-vinyl lactam, an N-vinylamide, a styryl, or mixtures of the foregoing; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units.

[00124] The silicone-containing component may comprise: one or more polymerizable groups that are independently a (meth)acrylate, a (meth)acrylamide, or mixtures of the foregoing; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units.

[00125] Formula A. The silicone-containing component may comprise one or more polymerizable compounds of Formula A:



Formula A

wherein:

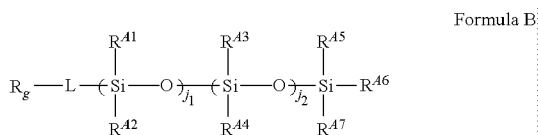
[00126] at least one R^A is a group of formula R_g-L- wherein R_g is a polymerizable group and L is a linking group, and the remaining R^A are each independently:

- (a) R_g-L- ,
- (b) C_1-C_{16} alkyl optionally substituted with one or more hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, or combinations thereof,
- (c) C_3-C_{12} cycloalkyl optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, or combinations thereof,
- (d) a C_6-C_{14} aryl group optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, or combinations thereof,
- (e) halo,
- (f) alkoxy, cyclic alkoxy, or aryloxy,
- (g) siloxy,
- (h) alkyleneoxy-alkyl or alkoxy-alkyleneoxy-alkyl, such as polyethyleneoxyalkyl, polypropyleneoxyalkyl, or poly(ethyleneoxy-co-propyleneoxyalkyl), or
- (i) a monovalent siloxane chain comprising from 1 to 100 siloxane repeat units optionally substituted with alkyl, alkoxy, hydroxy, amino, oxa, carboxy, alkyl carboxy, alkoxy, amido, carbamate, halo or combinations thereof; and

[00127] n is from 0 to 500 or from 0 to 200, or from 0 to 100, or from 0 to 20, where it is understood that when n is other than 0, n is a distribution having a mode equal to a stated value. When n is 2 or more, the SiO units may carry the same or different R^A substituents and if different R^A substituents are present, the n groups may be in random or block configuration.

[00128] In Formula A, three R^A may each comprise a polymerizable group, alternatively two R^A may each comprise a polymerizable group, or alternatively one R^A may comprise a polymerizable group.

[00129] Formula B. The silicone-containing component of formula A may be a mono-functional polymerizable compound of formula B:



wherein:

[00130] R_g is a polymerizable group;

[00131] L is a linking group;

[00132] j₁ and j₂ are each independently whole numbers from 0 to 220, provided that the sum of j₁ and j₂ is from 1 to 220;

[00133] R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5}, and R^{A7} are independently at each occurrence C₁-C₆ alkyl, C₃-C₁₂ cycloalkyl, C₁-C₆ alkoxy, C₄-C₁₂ cyclic alkoxy, alkoxy-alkyleneoxy-alkyl, aryl (e.g., phenyl), aryl-alkyl (e.g., benzyl), haloalkyl (e.g., partially or fully fluorinated alkyl), siloxy, fluoro, or combinations thereof, wherein each alkyl in the foregoing groups is optionally substituted with one or more hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, carbamate, carbonate, halo, phenyl, or benzyl, each cycloalkyl is optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carbonyl, alkoxy, carbamate, carbonate, halo, phenyl, or benzyl and each aryl is optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, carbamate, carbonate, halo, phenyl, or benzyl; and

[00134] R^{A6} is siloxy, C₁-C₈ alkyl (e.g., C₁-C₄ alkyl, or butyl, or methyl), or aryl (e.g., phenyl), wherein alkyl and aryl may optionally be substituted with one or more fluorine atoms.

[00135] Formula B-1. Compounds of formula B may include compounds of formula B-1, which are compounds of formula B wherein j₁ is zero and j₂ is from 1 to 220, or j₂ is from 1 to 100, or j₂ is from 1 to 50, or j₂ is from 1 to 20, or j₂ is from 1 to 5, or j₂ is 1.

[00136] B-2. Compounds of formula B may include compounds of formula B-2, which are compounds of formula B wherein j₁ and j₂ are independently from 4 to 100, or from 4 to 20, or from 4 to 10, or from 24 to 100, or from 10 to 100.

[00137] B-3. Compounds of formulae B, B-1, and B-2 may include compounds of formula B-3, which are compounds of formula B, B-1, or B-2 wherein R^{A1}, R^{A2}, R^{A3}, and R^{A4} are independently at each occurrence C₁-C₆ alkyl or siloxy. Preferred alkyl are C₁-C₃ alkyl, or more preferably, methyl. Preferred siloxy is trimethylsiloxy.

[00138] B-4. Compounds of formulae B, B-1, B-2, and B-3 may include compounds of formula B-4, which are compounds of formula B, B-1, B-2, or B-3 wherein R^{A5} and R^{A7} are independently alkoxy-alkyleneoxy-alkyl, preferably they are independently a methoxy capped polyethyleneoxyalkyl of formula $CH_3O-[CH_2CH_2O]_p-CH_2CH_2CH_2$, wherein p is a whole number from 1 to 50.

[00139] B-5. Compounds of formulae B, B-1, B-2, and B-3 may include compounds of formula B-5, which are compounds of formula B, B-1, B-2, or B-3 wherein R^{A5} and R^{A7} are independently siloxy, such as trimethylsiloxy.

[00140] B-6. Compounds of formulae B, B-1, B-2, and B-3 may include compounds of formula B-6, which are compounds of formula B, B-1, B-2, or B-3 wherein R^{A5} and R^{A7} are independently C_1 - C_6 alkyl, alternatively C_1 - C_4 alkyl, or alternatively, butyl or methyl.

[00141] B-7. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, and B-6 may include compounds of formula B-7, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, or B-6 wherein R^{A6} is C_1 - C_8 alkyl, preferably C_1 - C_6 alkyl, more preferably C_1 - C_4 alkyl (for example methyl, ethyl, n-propyl, or n-butyl). More preferably R^{A6} is n-butyl.

[00142] B-8. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, and B-7, may include compounds of formula B-8, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, or B-7 wherein R_g comprises styryl, vinyl carbonate, vinyl ether, vinyl carbamate, N-vinyl lactam, N-vinylamide, (meth)acrylate, or (meth)acrylamide. Preferably, R_g comprises (meth)acrylate, (meth)acrylamide, or styryl. More preferably, R_g comprises (meth)acrylate or (meth)acrylamide.

[00143] When R_g is (meth)acrylamide, the nitrogen group may be substituted with R^{A9} , wherein R^{A9} is H, C_1 - C_8 alkyl (preferably C_1 - C_4 alkyl, such as n-butyl, n-propyl, methyl or ethyl), or C_3 - C_8 cycloalkyl (preferably C_5 - C_6 cycloalkyl), wherein alkyl and cycloalkyl are optionally substituted with one or more groups independently selected from hydroxyl, amide, ether, silyl (e.g., trimethylsilyl), siloxy (e.g., trimethylsiloxy), alkyl-siloxanyl (where alkyl is itself optionally substituted with fluoro), aryl-siloxanyl (where aryl is itself optionally substituted with fluoro), and silyl-oxaalkylene- (where the oxaalkylene is itself optionally substituted with hydroxyl).

[00144] B-9. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, and B-8 may include compounds of formula B-9, which are compounds of formula B, B-1, B-2, B-3, B-

4, B-5, B-6, B-7, or B-8 wherein the linking group comprises alkylene (preferably C₁-C₄ alkylene), cycloalkylene (preferably C₅-C₆ cycloalkylene), alkyleneoxy (preferably ethyleneoxy), haloalkyleneoxy (preferably haloethyleneoxy), amide, oxaalkylene (preferably containing 3 to 6 carbon atoms), siloxanyl, alkylenesiloxanyl, carbamate, alkyleneamine (preferably C₁-C₆ alkyleneamine), or combinations of two or more thereof, wherein the linking group is optionally substituted with one or more substituents independently selected from alkyl, hydroxyl, ether, amine, carbonyl, siloxy, and carbamate.

[00145] B-10. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-10, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-siloxanyl-alkylene-alkyleneoxy-, or alkylene-siloxanyl-alkylene-[alkyleneoxy-alkylene-siloxanyl]_q-alkyleneoxy-, where q is from 1 to 50.

[00146] B-11. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-11, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is C₁-C₆ alkylene, preferably C₁-C₃ alkylene, more preferably n-propylene.

[00147] B-12. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-12, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-carbamate-oxaalkylene. Preferably, the linking group is CH₂CH₂N(H)—C(=O)—O—CH₂CH₂—O—CH₂CH₂CH₂.

[00148] B-13. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-13, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is oxaalkylene. Preferably, the linking group is CH₂CH₂—O—CH₂CH₂CH₂.

[00149] B-14. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-14, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-[siloxanyl-alkylene]_q-, where q is from 1 to 50. An example of such a linking group is: —(CH₂)₃—[Si(CH₃)₂—O—Si(CH₃)₂—(CH₂)₂]_q—.

[00150] B-15. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-15, which are compounds of formula B, B-1, B-2, B-

3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkyleneoxy-carbamate-alkylene-cycloalkylene-carbamate-oxaalkylene, wherein cycloalkylene is optionally substituted with or 1, 2, or 3 independently selected alkyl groups (preferably C₁-C₃ alkyl, more preferably methyl). An example of such a linking group is $\text{—[OCH}_2\text{CH}_2\text{]}_q\text{—OC(=O)—NH—CH}_2\text{—[1,3-cyclohexylene]—NHC(=O)O—CH}_2\text{CH}_2\text{—O—CH}_2\text{CH}_2\text{—}$, wherein the cyclohexylene is substituted at the 1 and 5 positions with 3 methyl groups.

[00151] B-16. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-16, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein R_g comprises styryl and the linking group is alkyleneoxy wherein each alkylene in alkyleneoxy is independently optionally substituted with hydroxyl. An example of such a linking group is $\text{—O—(CH}_2\text{)}_3\text{—}$. Another example of such a linking group is $\text{—O—CH}_2\text{CH(OH)CH}_2\text{—O—(CH}_2\text{)}_3\text{—}$.

[00152] B-17. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-17, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein R_g comprises styryl and the linking group is alkyleneamine. An example of such a linking group is $\text{—NH—(CH}_2\text{)}_3\text{—}$.

[00153] B-18. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-18, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is oxaalkylene optionally substituted with hydroxyl, siloxy, or silyl-alkyleneoxy (where the alkyleneoxy is itself optionally substituted with hydroxyl). An example of such a linking group is $\text{—CH}_2\text{CH(G)CH}_2\text{—O—(CH}_2\text{)}_3\text{—}$, wherein G is hydroxyl. In another example, G is R₃SiO— wherein two R groups are trimethylsiloxy and the third is C₁-C₈ alkyl (preferably C₁-C₃ alkyl, more preferably methyl) or the third is C₃-C₈ cycloalkyl. In a further example, G is R₃Si—(CH₂)₃—O—CH₂CH(OH)CH₂—O—, wherein two R groups are trimethylsiloxy and the third is C₁-C₈ alkyl (preferably C₁-C₃ alkyl, more preferably methyl) or C₃-C₈ cycloalkyl. In a still further example, G is a polymerizable group, such as (meth)acrylate. Such compounds may function as crosslinkers.

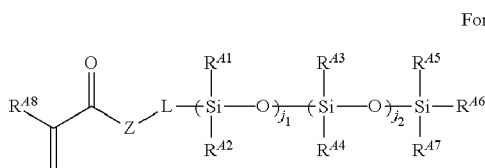
[00154] B-19. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-19, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein R_g comprises styryl and the linking group is amine-

oxaalkylene optionally substituted with hydroxyl. An example of such a linking group is —NH—CH₂CH(OH)CH₂—O—(CH₂)₃—.

[00155] B-20. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-20, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein R_g comprises styryl and the linking group is alkyleneoxy-carbamate-oxaalkylene. An example of such a linking group is —O—(CH₂)₂—N(H)C(=O)O—(CH₂)₂—O—(CH₂)₃—.

[00156] B-21. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-21, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-carbamate-oxaalkylene. An example of such a linking group is —(CH₂)₂—N(H)C(=O)O—(CH₂)₂—O—(CH₂)₃—.

[00157] Formula C. Silicone-containing components of formulae A, B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, B-9, B-10, B-11, B-12, B-13, B-14, B-15, B-18, and B-21 may include compounds of formula C, which are compounds of formula A, B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, B-9, B-10, B-11, B-12, B-13, B-14, B-15, B-18, or B-21 having the structure:



wherein

[00158] R^{A8} is hydrogen or methyl;

[00159] Z is O, S, or N(R^{A9}); and

[00160] L, j₁, j₂, R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5}, R^{A6}, R^{A7}, and R^{A9} are as defined in formula B or its various sub-formulae (e.g., B-1, B-2, etc.).

[00161] C-1. Compounds of formula C may include (meth)acrylates of formula C-1, which are compounds of formula C wherein Z is O.

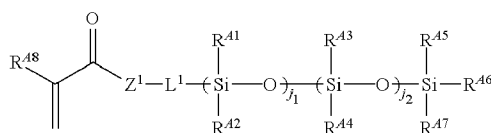
[00162] C-2. Compounds of formula C may include (meth)acrylamides of formula C-2, which are compounds of formula C wherein Z is N(R^{A9}), and R^{A9} is H.

[00163] C-3. Compounds of formulae C may include (meth)acrylamides of formula C-3, which are compounds of formula C wherein Z is N(R^{A9}), and R^{A9} is C₁-C₈ alkyl that is unsubstituted or is optionally substituted as indicated above. Examples of R^{A9} include CH₃, —

$\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH})$, $-(\text{CH}_2)_3\text{-siloxanyl}$, $-(\text{CH}_2)_3\text{-SiR}_3$, and $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{-O-}(\text{CH}_2)_3\text{-SiR}_3$ where each R in the foregoing groups is independently selected from trimethylsiloxy, $\text{C}_1\text{-C}_8$ alkyl (preferably $\text{C}_1\text{-C}_3$ alkyl, more preferably methyl), and $\text{C}_3\text{-C}_8$ cycloalkyl. Further examples of $\text{R}^{\text{A}9}$ include: $-(\text{CH}_2)_3\text{-Si}(\text{Me})(\text{SiMe}_3)_2$, and $-(\text{CH}_2)_3\text{-Si}(\text{Me}_2)\text{-[O-SiMe}_2\text{]}_{1-10}\text{-CH}_3$.

[00164] Formula D. Compounds of formula C may include compounds of formula D:

Formula D



wherein

[00165] $\text{R}^{\text{A}8}$ is hydrogen or methyl;

[00166] Z^1 is O or $\text{N}(\text{R}^{\text{A}9})$;

[00167] L^1 is alkylene containing 1 to 8 carbon atoms, or oxaalkylene containing 3 to 10 carbon atoms, wherein L^1 is optionally substituted with hydroxyl; and

[00168] j_2 , $\text{R}^{\text{A}3}$, $\text{R}^{\text{A}4}$, $\text{R}^{\text{A}5}$, $\text{R}^{\text{A}6}$, $\text{R}^{\text{A}7}$, and $\text{R}^{\text{A}9}$ are as defined above in formula B or its various sub-formulae (e.g., B-1, B-2, etc.).

[00169] D-1. Compounds of formula D may include compounds of formula D-1, which are compounds of formula D wherein L^1 is $\text{C}_2\text{-C}_5$ alkylene optionally substituted with hydroxyl. Preferably L^1 is n-propylene optionally substituted with hydroxyl.

[00170] D-2. Compounds of formula D may include compounds of formula D-2, which are compounds of formula D wherein L^1 is oxaalkylene containing 4 to 8 carbon atoms optionally substituted with hydroxyl. Preferably L^1 is oxaalkylene containing five or six carbon atoms optionally substituted with hydroxyl. Examples include $-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{-}$, and $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{-O-}(\text{CH}_2)_3\text{-}$.

[00171] D-3. Compounds of formulae D, D-1, and D-2 may include compounds of formula D-3, which are compounds of formula D, D-1, or D-2 wherein Z^1 is O.

[00172] D-4. Compounds of formulae D, D-1, and D-2 may include compounds of formula D-4, which are compounds of formula D, D-1, or D-2 wherein Z^1 is $\text{N}(\text{R}^{\text{A}9})$, and $\text{R}^{\text{A}9}$ is H.

[00173] D-5. Compounds of formulae D, D-1, and D-2 may include compounds of formula D-5, which are compounds of formula D, D-1, or D-2 wherein Z^1 is $\text{N}(\text{R}^{\text{A}9})$, and $\text{R}^{\text{A}9}$ is

C₁-C₄ alkyl optionally substituted with 1 or 2 substituents selected from hydroxyl, siloxy, and C₁-C₆ alkyl-siloxanyl-.

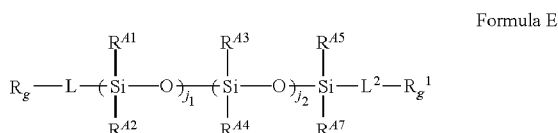
[00174] D-6. Compounds of formulae D, D-1, D-2, D-3, D-4, and D-5 may include compounds of formula D-6, which are compounds of formula D, D-1, D-2, D-3, D-4, or D-5 wherein j₂ is 1.

[00175] D-7. Compounds of formulae D, D-1, D-2, D-3, D-4, and D-5 may include compounds of formula D-7, which are compounds of formula D, D-1, D-2, D-3, D-4, or D-5 wherein j₂ is from 2 to 220, or from 2 to 100, or from 10 to 100, or from 24 to 100, or from 4 to 20, or from 4 to 10.

[00176] D-8. Compounds of formulae D, D-1, D-2, D-3, D-4, D-5, D-6, and D-7 may include compounds of formula D-8, which are compounds of formula D, D-1, D-2, D-3, D-4, D-5, D-6, or D-7 wherein R^{A3}, R^{A4}, R^{A5}, R^{A6}, and R^{A7} are independently C₁-C₆ alkyl or siloxy. Preferably R^{A3}, R^{A4}, R^{A5}, R^{A6}, and R^{A7} are independently selected from methyl, ethyl, n-propyl, n-butyl, and trimethylsiloxy. More preferably, R^{A3}, R^{A4}, R^{A5}, R^{A6}, and R^{A7} are independently selected from methyl, n-butyl, and trimethylsiloxy.

[00177] D-9. Compounds of formulae D, D-1, D-2, D-3, D-4, D-5, D-6, and D-7 may include compounds of formula D-9, which are compounds of formula D, D-1, D-2, D-3, D-4, D-5, D-6, or D-7 wherein R^{A3} and R^{A4} are independently C₁-C₆ alkyl (e.g., methyl or ethyl) or siloxy (e.g., trimethylsiloxy), and R^{A5}, R^{A6}, and R^{A7} are independently C₁-C₆ alkyl (e.g., methyl, ethyl, n-propyl, or n-butyl).

[00178] Formula E. The silicone-containing component may comprise a multi-functional silicone-containing component. Thus, for example, the silicone-containing component of formula A may comprise a bifunctional material of formula E:



wherein

[00179] R_g, L, j₁, j₂, R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5}, and R^{A7} are as defined above for formula B or its various sub-formulae (e.g., B-1, B-2, etc.);

[00180] L² is a linking group; and

[00181] R_g¹ is a polymerizable group.

[00182] E-1. Compounds of formula E may include compounds of formula E-1, which are compounds of formula E wherein R_g and R_g¹ are each a vinyl carbonate of structure CH₂=CH—O—C(=O)—O— or structure CH₂=C(CH₃)—O—C(=O)—O—.

[00183] E-2. Compounds of formula E may include compounds of formula E-2, which are compounds of formula E wherein R_g and R_g¹ are each (meth)acrylate.

[00184] E-3. Compounds of formula E may include compounds of formula E-3, which are compounds of formula E wherein R_g and R_g¹ are each (meth)acrylamide, wherein the nitrogen group may be substituted with R^{A9} (wherein R^{A9} is as defined above).

[00185] E-4. Suitable compounds of formulae E, E-1, E-2, and E-3 include compounds of formula E-4, which are compounds of formula E, E-1, E-2, or E-3 wherein j₁ is zero and j₂ is from 1 to 220, or j₂ is from 1 to 100, or j₂ is from 1 to 50, or j₂ is from 1 to 20.

[00186] E-5. Suitable compounds of formulae E, E-1, E-2, and E-3 include compounds of formula E-5, which are compounds of formula E, E-1, E-2, or E-3, wherein j₁ and j₂ are independently from 4 to 100.

[00187] E-6. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, and E-5 include compounds of formula E-6, which are compounds of formula E, E-1, E-2, E-3, E-4, or E-5 wherein R^{A1}, R^{A2}, R^{A3}, R^{A4}, and R^{A5} are independently at each occurrence C₁-C₆ alkyl, preferably they are independently C₁-C₃ alkyl, or preferably, each is methyl.

[00188] E-7. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, E-5, and E-6 include compounds of formula E-7, which are compounds of formula E, E-1, E-2, E-3, E-4, E-5, or E-6 wherein R^{A7} is alkoxy-alkyleneoxy-alkyl, preferably it is a methoxy capped polyethyleneoxyalkyl of formula CH₃O—[CH₂CH₂O]_p—CH₂CH₂CH₂, wherein p is a whole number from 1 to 50, or from 1 to 30, or from 1 to 10, or from 6 to 10.

[00189] E-8. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, E-5, E-6, and E-7 include compounds of formula E-8, which are compounds of formula E, E-1, E-2, E-3, E-4, E-5, E-6, or E-7 wherein L comprises alkylene, carbamate, siloxanyl, cycloalkylene, amide, haloalkyleneoxy, oxaalkylene, or combinations of two or more thereof, wherein the linking group is optionally substituted with one or more substituents independently selected from alkyl, hydroxyl, ether, amine, carbonyl, and carbamate.

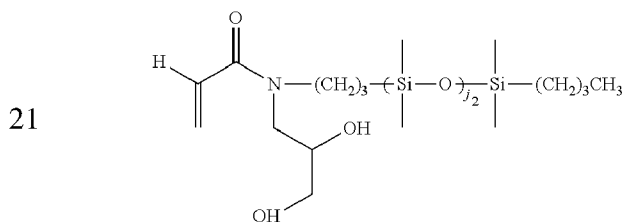
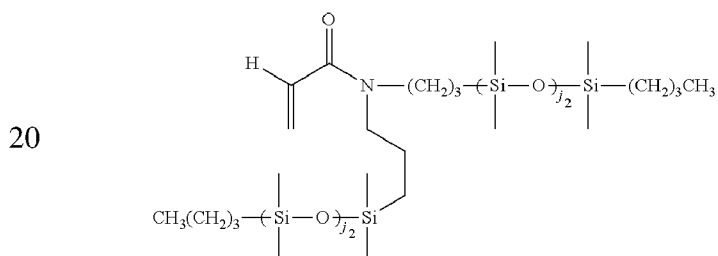
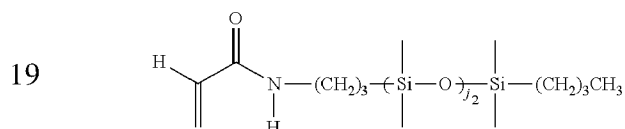
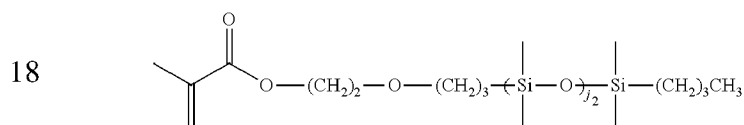
[00190] E-9. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, E-5, E-6, E-7, and E-8 include compounds of formula E-9, which are compounds of formula E, E-1, E-2, E-3,

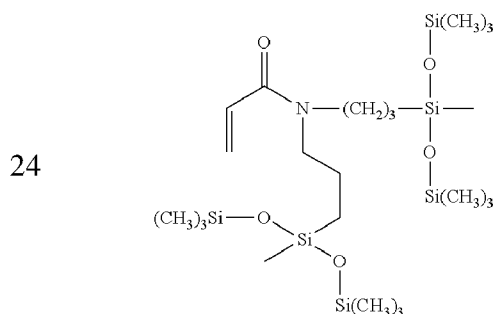
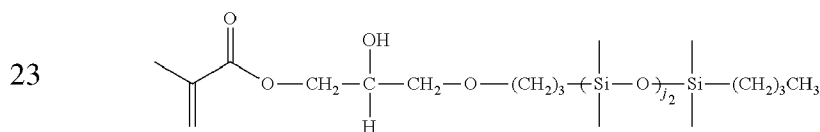
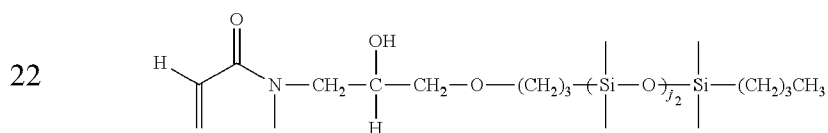
E-4, E-5, E-6, E-7, or E-8 wherein L^2 comprises alkylene, carbamate, siloxanyl, cycloalkylene, amide, haloalkyleneoxy, oxaalkylene, or combinations of two or more thereof, wherein the linking group is optionally substituted with one or more substituents independently selected from alkyl, hydroxyl, ether, amine, carbonyl, and carbamate.

[00191] Examples of silicone-containing components suitable for use in the invention include, but are not limited to, compounds listed in the table below. Where the compounds in the table below include polysiloxane groups, the number of Si repeat units in such compounds, unless otherwise indicated, is preferably from 3 to 100, more preferably from 3 to 40, or still more preferably from 3 to 20.

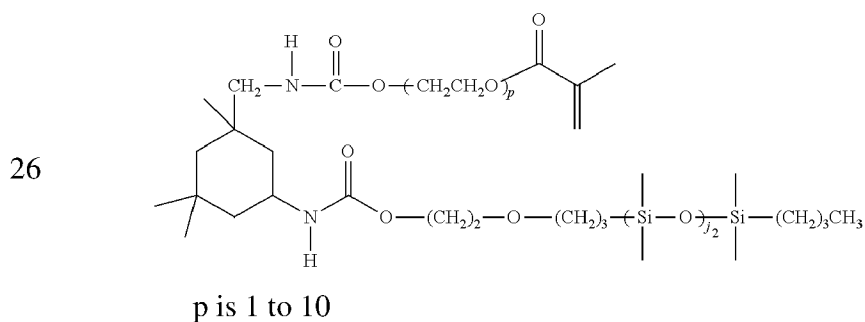
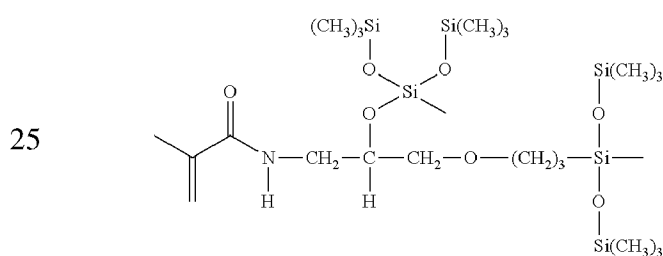
1	mono-methacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxanes (mPDMS) (preferably containing from 3 to 15 SiO repeating units)
2	mono-acryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane
3	mono(meth)acryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane
4	mono(meth)acryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane
5	mono(meth)acryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane
6	mono(meth)acrylamidoalkylpolydialkylsiloxanes
7	mono(meth)acryloxyalkyl terminated mono-alkyl polydiarylsiloxanes
8	3-methacryloxypropyltris(trimethylsiloxy)silane (TRIS)
9	3-methacryloxypropylbis(trimethylsiloxy)methylsilane
10	3-methacryloxypropylpentamethyl disiloxane
11	mono(meth)acrylamidoalkylpolydialkylsiloxanes
12	mono(meth)acrylamidoalkyl polydimethylsiloxanes

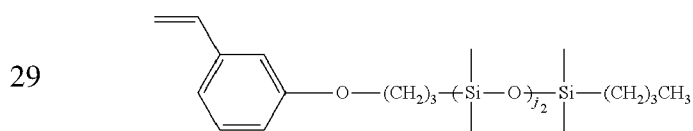
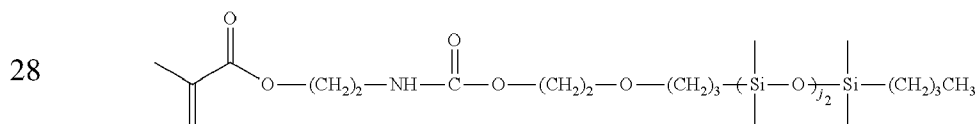
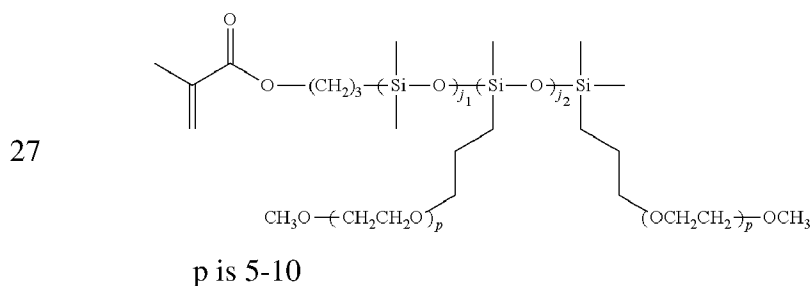
- 13 N-(2,3-dihydroxypropane)-N' -(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide
- 14 N-[3-tris(trimethylsiloxy)silyl]-propyl acrylamide (TRIS-Am)
- 15 2-hydroxy-3-[3-methyl-3,3-di(trimethylsiloxy)silylpropoxy]-propyl methacrylate (SiMAA)
- 16 2-hydroxy-3-methacryloxypropyloxypropyl-tris(trimethylsiloxy)silane mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxanes (OH-mPDMS) (containing from 4 to 30, or from 10 to 20, or from 4 to 8 SiO repeat units)





[00192] Additional non-limiting examples of suitable silicone-containing components are listed in the table below. Unless otherwise indicated, j_2 where applicable is preferably from 1 to 100, more preferably from 3 to 40, or still more preferably from 3 to 15. In compounds containing j_1 and j_2 , the sum of j_1 and j_2 is preferably from 2 to 100, more preferably from 3 to 40, or still more preferably from 3 to 15.





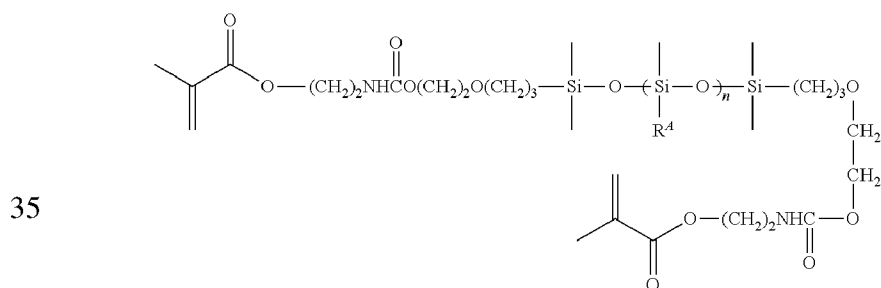
30 1,3-bis[4-(vinylloxycarbonyloxy)but-1-yl][tris(trimethylsiloxy)silyl]tetramethyl-disiloxane

31 3-(vinylloxycarbonylthio) propyl-(trimethylsiloxy)silane

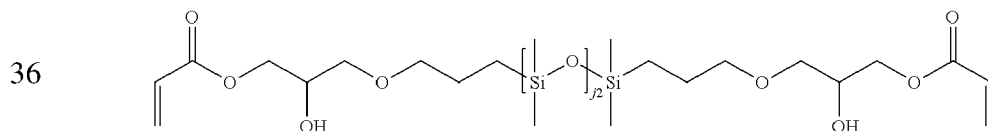
32 3-[tris(trimethylsiloxy)silyl] propyl allyl carbamate

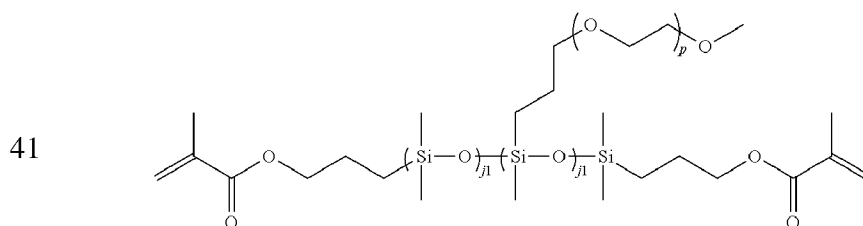
33 3-[tris(trimethylsiloxy)silyl] propyl vinyl carbamate

34 tris(trimethylsiloxy)silylstyrene (Styryl-TRIS)



$\text{R}^A = \text{CH}_3$ (a) or $\text{CH}_2\text{CH}_2\text{CF}_3$ (b) or $\text{CH}_2-(\text{CH}_2)_2-[\text{OCH}_2\text{CH}_2]_{1-10}-\text{OCH}_3$ (c); $a + b + c = n$





The chemical structure shows a fluorinated polyether-polyimide copolymer. It features a central siloxane block, $[-Si-O-]_p$, flanked by polyether segments, $[-O-CH_2-CH_2-O-]_{1-2}$. The structure is terminated with fluorinated polyether groups, $[-O-CF_2-CF_2-O-]_m$ and $[-O-CF_2-CF_2-CF_2-CF_2-O-]_n$, which are connected to a polyimide backbone. The polyimide backbone consists of a central benzene ring and two phthalimide rings, with the terminal groups being $-CO-NH-$ and $-NH-CO-$ groups. The structure is also terminated with a vinyl group, $-CH=CH_2$.

The image displays two chemical structures, labeled 1 and 2, representing polyether-siloxane copolymers. Both structures consist of a central siloxane chain with various functional groups attached.

Structure 1 (top) features a central siloxane chain with the following components from left to right: a methyl methacrylate (MMA) group, a polyether chain, a siloxane unit with subscript y , another polyether chain, a second siloxane unit with subscript x , and a final polyether chain. The MMA group is attached to the first polyether chain via an ester linkage.

Structure 2 (bottom) is similar to Structure 1 but includes a different functional group. It features a central siloxane chain with the following components from left to right: a MMA group, a polyether chain, a siloxane unit with subscript y , another polyether chain, a siloxane unit with subscript x , and a final polyether chain. The MMA group is attached to the first polyether chain via an ester linkage.

IEM-PDMS(Mn $\approx$ 3000)-IPDI-PDMS(Mn $\approx$ 2000)-IPDI-PDMS(Mn $\approx$ 3000)-IEM (see WO2016100457)

[00193] Silicone-containing components may have an average molecular weight of from about 400 to about 4000 daltons.

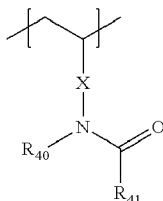
[00194] The silicone containing component(s) may be present in amounts up to about 95 weight %, or from about 10 to about 80 weight %, or from about 20 to about 70 weight %, based upon all reactive components of the reactive mixture (excluding diluents).

[00195] Polyamides

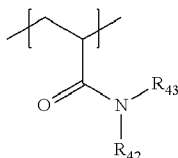
[00196] The reactive monomer mixture may include at least one polyamide. As used herein, the term “polyamide” refers to polymers and copolymers comprising repeating units containing amide groups. The polyamide may comprise cyclic amide groups, acyclic amide groups and combinations thereof and may be any polyamide known to those of skill in the art. Acyclic polyamides comprise pendant acyclic amide groups and are capable of association with hydroxyl groups. Cyclic polyamides comprise cyclic amide groups and are capable of association with hydroxyl groups.

[00197] Examples of suitable acyclic polyamides include polymers and copolymers comprising repeating units of Formulae G1 and G2:

Formula G1



Formula G2



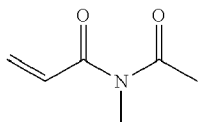
[00198] wherein X is a direct bond, —(CO)—, or —(CONHR₄₄)—, wherein R₄₄ is a C₁ to C₃ alkyl group; R₄₀ is selected from H, straight or branched, substituted or unsubstituted C₁ to C₄ alkyl groups; R₄₁ is selected from H, straight or branched, substituted or unsubstituted C₁ to C₄ alkyl groups, amino groups having up to two carbon atoms, amide groups having up to four carbon atoms, and alkoxy groups having up to two carbon groups; R₄₂ is selected from H, straight or branched, substituted or unsubstituted C₁ to C₄ alkyl groups; or methyl, ethoxy,

hydroxyethyl, and hydroxymethyl; R_{43} is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups; or methyl, ethoxy, hydroxyethyl, and hydroxymethyl; wherein the number of carbon atoms in R_{40} and R_{41} taken together is 8 or less, including 7, 6, 5, 4, 3, or less; and wherein the number of carbon atoms in R_{42} and R_{43} taken together is 8 or less, including 7, 6, 5, 4, 3, or less. The number of carbon atoms in R_{40} and R_{41} taken together may be 6 or less or 4 or less. The number of carbon atoms in R_{42} and R_{43} taken together may be 6 or less. As used herein substituted alkyl groups include alkyl groups substituted with an amine, amide, ether, hydroxyl, carbonyl or carboxy groups or combinations thereof.

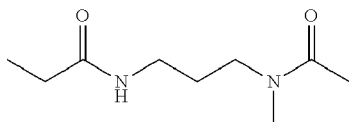
[00199] R_{40} and R_{41} may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. X may be a direct bond, and R_{40} and R_{41} may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. R_{42} and R_{43} can be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups, methyl, ethoxy, hydroxyethyl, and hydroxymethyl.

[00200] The acyclic polyamides of the present invention may comprise a majority of the repeating units of Formula LV or Formula LVI, or the acyclic polyamides can comprise at least 50 mole percent of the repeating unit of Formula G or Formula G1, including at least 70 mole percent, and at least 80 mole percent. Specific examples of repeating units of Formula G and Formula G1 include repeating units derived from N-vinyl-N-methylacetamide, N-vinylacetamide, N-vinyl-N-methylpropionamide, N-vinyl-N-methyl-2-methylpropionamide, N-vinyl-2-methyl-propionamide, N-vinyl-N,N'-dimethylurea, N, N-dimethylacrylamide, methacrylamide, and acyclic amides of Formulae G2 and G3:

Formula G2

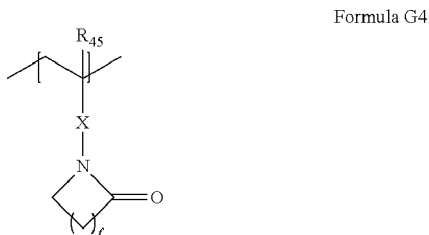


Formula G3



[00201] Examples of suitable cyclic amides that can be used to form the cyclic polyamides of include α -lactam, β -lactam, γ -lactam, δ -lactam, and ϵ -lactam. Examples of

suitable cyclic polyamides include polymers and copolymers comprising repeating units of Formula G4:



[00202] wherein R_{45} is a hydrogen atom or methyl group; wherein f is a number from 1 to 10; wherein X is a direct bond, $-(CO)-$, or $-(CONHR_{46})-$, wherein R_{46} is a C_1 to C_3 alkyl group. In Formula LIX, f may be 8 or less, including 7, 6, 5, 4, 3, 2, or 1. In Formula G4, f may be 6 or less, including 5, 4, 3, 2, or 1. In Formula G4, f may be from 2 to 8, including 2, 3, 4, 5, 6, 7, or 8. In Formula LIX, f may be 2 or 3. When X is a direct bond, f may be 2. In such instances, the cyclic polyamide may be polyvinylpyrrolidone (PVP).

[00203] Cyclic polyamides may comprise 50 mole percent or more of the repeating unit of Formula G4, or the cyclic polyamides can comprise at least 50 mole percent of the repeating unit of Formula G4, including at least 70 mole percent, and at least 80 mole percent.

[00204] The polyamides may also be copolymers comprising repeating units of both cyclic and acyclic amides. Additional repeating units may be formed from monomers selected from hydroxyalkyl(meth)acrylates, alkyl(meth)acrylates, other hydrophilic monomers and siloxane substituted (meth)acrylates. Any of the monomers listed as suitable hydrophilic monomers may be used as comonomers to form the additional repeating units. Specific examples of additional monomers which may be used to form polyamides include 2-hydroxyethyl (meth)acrylate, vinyl acetate, acrylonitrile, hydroxypropyl (meth)acrylate, methyl (meth)acrylate and hydroxybutyl (meth)acrylate, dihydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, and the like and mixtures thereof. Ionic monomers may also be included. Examples of ionic monomers include (meth)acrylic acid, N -[(ethenyloxy)carbonyl]- β -alanine (VINAL, CAS #148969-96-4), 3-acrylamidopropanoic acid (ACA1), 5-acrylamidopentanoic acid (ACA2), 3-acrylamido-3-methylbutanoic acid (AMBA), 2-(methacryloyloxy)ethyl trimethylammonium chloride (Q Salt or METAC), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 1-propanaminium, N -(2-carboxyethyl)- N,N -dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt (CBT), 1-propanaminium, N,N -dimethyl- N -[3-[(1-

oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt (SBT), 3,5-Dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI) (PBT), 2-methacryloyloxyethyl phosphorylcholine, 3-(dimethyl(4-vinylbenzyl)ammonio)propane-1-sulfonate (DMVBAPS), 3-((3-acrylamidopropyl)dimethylammonio)propane-1-sulfonate (AMPDAPS), 3-((3-methacrylamidopropyl)dimethylammonio)propane-1-sulfonate (MAMPDAPS), 3-((3-(acryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (APDAPS), 3-((3-(methacryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (MAPDAPS).

[00205] The reactive monomer mixture may comprise both an acyclic polyamide and a cyclic polyamide or copolymers thereof. The acyclic polyamide can be any of those acyclic polyamides described herein or copolymers thereof, and the cyclic polyamide can be any of those cyclic polyamides described herein or copolymers thereof. The polyamide may be selected from the group polyvinylpyrrolidone (PVP), polyvinylmethylacetamide (PVMA), polydimethylacrylamide (PDMA), polyvinylacetamide (PNVA), poly hydroxyethyl (meth)acrylamide, polyacrylamide, and copolymers and mixtures thereof.

[00206] The total amount of all polyamides in the reactive mixture may be in the range of between 1 weight percent and about 35 weight percent, including in the range of about 1 weight percent to about 15 weight percent, and in the range of about 5 weight percent to about 15 weight percent, in all cases, based on the total weight of the reactive components of the reactive monomer mixture.

[00207] Without intending to be bound by theory, when used with a silicone hydrogel, the polyamide functions as an internal wetting agent. The polyamides may be non-polymerizable, and in this case, are incorporated into the silicone hydrogels as semi-interpenetrating networks. The polyamides are entrapped or physically retained within the silicone hydrogels. Alternatively, the polyamides may be polymerizable, for example as polyamide macromers or prepolymers, and in this case, are covalently incorporated into the silicone hydrogels. Mixtures of polymerizable and non-polymerizable polyamides may also be used.

[00208] When the polyamides are incorporated into the reactive monomer mixture they may have a weight average molecular weight of at least 100,000 daltons; greater than about 150,000; between about 150,000 to about 2,000,000 daltons; between about 300,000 to about

1,800,000 daltons. Higher molecular weight polyamides may be used if they are compatible with the reactive monomer mixture.

[00209] Cross-linking Agents

[00210] It is generally desirable to add one or more cross-linking agents, also referred to as cross-linking monomers, multi-functional macromers, and prepolymers, to the reactive mixture. The cross-linking agents may be selected from bifunctional crosslinkers, trifunctional crosslinkers, tetrafunctional crosslinkers, and mixtures thereof, including silicone-containing and non-silicone containing cross-linking agents. Non-silicone-containing cross-linking agents include ethylene glycol dimethacrylate (EGDMA), tetraethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC), glycerol trimethacrylate, methacryloxyethyl vinylcarbonate (HEMAVc), allyl methacrylate, methylene bisacrylamide (MBA), and polyethylene glycol dimethacrylate wherein the polyethylene glycol has a molecular weight up to about 5000 Daltons. The cross-linking agents are used in the usual amounts, e.g., from about 0.000415 to about 0.0156 mole per 100 grams of reactive Formulas in the reactive mixture. Alternatively, if the hydrophilic monomers and/or the silicone-containing components are multifunctional by molecular design or because of impurities, the addition of a cross-linking agent to the reactive mixture is optional. Examples of hydrophilic monomers and macromers which can act as the cross-linking agents and when present do not require the addition of an additional cross-linking agent to the reactive mixture include (meth)acrylate and (meth)acrylamide endcapped polyethers. Other cross-linking agents will be known to one skilled in the art and may be used to make the silicone hydrogel of the present invention.

[00211] It may be desirable to select crosslinking agents with similar reactivity to one or more of the other reactive components in the formulation. In some cases, it may be desirable to select a mixture of crosslinking agents with different reactivity in order to control some physical, mechanical or biological property of the resulting silicone hydrogel. The structure and morphology of the silicone hydrogel may also be influenced by the diluent(s) and cure conditions used.

[00212] Multifunctional silicone-containing components, including macromers, cross-linking agents, and prepolymers, may also be included to further increase the modulus and retain tensile strength. The silicone containing cross-linking agents may be used alone or in combination with other cross-linking agents. An example of a silicone containing component

which can act as a cross-linking agent and, when present, does not require the addition of a crosslinking monomer to the reactive mixture includes α , ω -bismethacryloxypropyl polydimethylsiloxane.

[00213] Cross-linking agents that have rigid chemical structures and polymerizable groups that undergo free radical polymerization may also be used. Non-limiting examples of suitable rigid structures include cross-linking agents comprising phenyl and benzyl moieties, such as 1,4-phenylene diacrylate, 1,4-phenylene dimethacrylate, 2,2-bis(4-methacryloxyphenyl)-propane, 2,2-bis[4-(2-acryloxyethoxy)phenyl]propane, 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl]propane, and 4-vinylbenzyl methacrylate, and combinations thereof. Rigid crosslinking agents may be included in amounts between about 0.5 and about 15, or 2-10, 3-7 based upon the total weight of all of the reactive components. The physical and mechanical properties of the silicone hydrogels of the present invention may be optimized for a particular use by adjusting the components in the reactive mixture.

[00214] Non-limiting examples of silicone cross-linking agents also include the multi-functional silicone-containing components described above, such as compounds of Formula E (and its sub-formulae) and the multi-functional compounds shown in the tables above.

[00215] When the compositions described herein are used in silicone hydrogel contact lenses, the lens may preferably exhibit the following properties. All values are prefaced by "about," and the lens may have any combination of the listed properties. The properties may be determined by methods known to those skilled in the art, for instance as described in United States pre-grant publication US20180037690, which is incorporated herein by reference.

[00216] Water content weight %: at least 20 %, at least 25 %, at least about 30 %, or at least about 35 %, and up to 80 % or up to 70 %

[00217] Haze: 30 % or less, or 10 % or less

[00218] Advancing dynamic contact angle (Wilhelmy plate method): 100° or less, or 80° or less; or 50° or less

[00219] Tensile Modulus (psi): 120 or less, or 80 to 120

[00220] Oxygen permeability (Dk, barrers): at least 80, or at least 100, or at least 150, or at least 200

[00221] Elongation to Break: at least 100

[00222] For ionic silicon hydrogels, the following properties may also be preferred (in addition to those recited above):

[00223] Lysozyme uptake ($\mu\text{g}/\text{lens}$): at least 100, or at least 150, or at least 500, or at least 700

[00224] Polyquaternium 1 (PQ1) uptake (%): 15 or less, or 10 or less, or 5 or less

EXAMPLES

[00225] The present disclosure comprises at least the following examples. The examples below are intended to further illustrate certain aspects of the materials and methods described herein, and is not intended to limit the scope of the claims.

[00226] Aspect 1: A composition for light filtering, the composition comprising: a base material; a plurality of gold nanoparticles dispersed in the base material, at least a portion of the plurality of gold nanoparticles having an anisotropic shape; and a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of gold nanoparticles to enhance stability of at least the portion of the plurality of gold nanoparticles in the base material, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[00227] Aspect 2: The composition of aspect 1, wherein the anisotropic shape is tuned such that the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[00228] Aspect 3: The composition of any one of aspects 1-2, wherein the anisotropic shape is tuned such that the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

[00229] Aspect 4: The composition of any one of aspects 1-3, wherein the anisotropic shape is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

[00230] Aspect 5: The composition of any one of aspects 1-4, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.

[00231] Aspect 6: The composition of any one of aspects 1-5, wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00232] Aspect 7: The composition of any one of aspects 1-6, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00233] Aspect 8: The composition of any one of aspects 1-7, wherein the base material comprises a biomaterial.

[00234] Aspect 9: The composition of any one of aspects 1-7, wherein the base material comprises a biomaterial matrix.

[00235] Aspect 10: The composition of any one of aspects 1-7, wherein the base material comprises hydrogel.

[00236] Aspect 11: The composition of any one of aspects 1-7, wherein the base material comprises silicone-based hydrogel.

[00237] Aspect 12: The composition of any one of aspects 1-11, wherein at least a portion of the plurality of gold nanoparticles are grown from a pentatwinned gold seed.

[00238] Aspect 13: The composition of any one of aspects 1-12, wherein the anisotropic shape comprises a bipyramid shape.

[00239] Aspect 14: The composition of aspect 13, wherein the bipyramid shape comprises a longitudinal peak and a transverse peak, and wherein a sharpness of the bipyramid shape relative to the longitudinal peak and the transverse peak is tuned such that the composition exhibits a peak light filtering in the range of about 600nm to about 850nm.

[00240] Aspect 15: The composition of any one of aspects 1-14, wherein the anisotropic shape comprises a bipyramid shape with each a pair of opposing truncated peaks disposed on opposing ends.

[00241] Aspect 16: The composition of aspect 15, wherein a sharpness of the bipyramid shape is tuned such that the composition exhibits a peak light filtering in the range of about 600nm to about 850nm.

[00242] Aspect 17: The composition of any one of aspects 1-16, wherein the stabilizing mechanism enhances colloidal stability, thermal stability, or both of at least the portion of the plurality of gold nanoparticles in the base material

[00243] Aspect 18: The composition of any one of aspects 1-17, wherein the stabilizing mechanism enhances biocompatibility of at least the portion of the plurality of gold nanoparticles in the base material

[00244] Aspect 19: The composition of any one of aspects 1-18, wherein the stabilizing mechanism comprises poly(vinyl pyrrolidone).

[00245] Aspect 20: The composition of any one of aspects 1-18, wherein the stabilizing mechanism comprises 55kDa poly(vinyl pyrrolidone).

[00246] Aspect 21: The composition of any one of aspects 1-18, wherein the stabilizing mechanism comprises one or more of 10kDa poly(vinyl pyrrolidone), 55kDa poly(vinyl pyrrolidone), 360kDa poly(vinyl pyrrolidone), 1300kDa poly(vinyl pyrrolidone).

[00247] Aspect 22: The composition of any one of aspects 1-21, wherein the stabilizing mechanism chemically binds with at least a portion of the plurality of gold nanoparticless to enhance colloidal stability of at least the portion of the plurality of gold nanoparticles in the base material.

[00248] Aspect 23: A method of making the composition of any one of aspects 1-22.

[00249] Aspect 24: The method of claim 23, wherein at least a portion of the plurality of gold nanoparticles are grown from a pentatwinned gold seed.

[00250] Aspect 25: A composition for light filtering, the composition comprising: a plurality of metal nanoparticles, at least a portion of the plurality of metal nanoparticles having an anisotropic shape; and a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of metal nanoparticles, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[00251] Aspect 26: The composition of aspect 25, wherein the anisotropic shape is tuned such that the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

[00252] Aspect 27: The composition of any one of aspects 25-26, wherein the anisotropic shape is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

[00253] Aspect 28: The composition of any one of aspects 25-27, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.

[00254] Aspect 29: The composition of any one of aspects 25-28, wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00255] Aspect 30: The composition of any one of aspects 25-29, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00256] Aspect 31: The composition of any one of aspects 25-30, wherein the anisotropic shape comprises a bipyramid shape.

[00257] Aspect 32: The composition of aspect 31, wherein the bipyramid shape comprises a longitudinal peak and a transverse peak, and wherein a sharpness of the bipyramid shape relative to the longitudinal peak and the transverse peak is tuned to exhibit a peak light filtering in the range of about 600nm to about 850nm.

[00258] Aspect 33: The composition of any one of aspects 25-32, wherein the anisotropic shape comprises a bipyramid shape with each a pair of opposing truncated peaks disposed on opposing ends.

[00259] Aspect 34: The composition of aspect 33, wherein a sharpness of the bipyramid shape is tuned such that the composition exhibits a peak light filtering in the range of about 600nm to about 850nm.

[00260] Aspect 35: The composition of any one of aspects 25-34, wherein the stabilizing mechanism comprises poly(vinyl pyrrolidone).

[00261] Aspect 36: The composition of any one of aspects 25-35, wherein the stabilizing mechanism comprises 55kDa poly(vinyl pyrrolidone).

[00262] Aspect 37: The composition of any one of aspects 25-36, wherein the stabilizing mechanism comprises one or more of 10kDa poly(vinyl pyrrolidone), 55kDa poly(vinyl pyrrolidone), 360kDa poly(vinyl pyrrolidone), 1300kDa poly(vinyl pyrrolidone).

[00263] Aspect 38: The composition of any one of aspects 25-37, wherein the stabilizing mechanism chemically binds with at least a portion of the plurality of metal nanoparticles to enhance colloidal stability of at least the portion of the plurality of metal nanoparticles.

[00264] Aspect 39: A method of making the composition of any one of aspects 25-38.

[00265] Aspect 40: The method of aspect 39, wherein at least a portion of the plurality of metal nanoparticles are grown from a pentatwinned metal seed.

[00266] Aspect 41: A composition for light filtering, the composition comprising: a base material; and a plurality of nanoparticles dispersed in the base material, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm, and wherein the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

[00267] Aspect 42: The composition of aspect 41, wherein a shape of at least a portion of the nanoparticles is tuned such that the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[00268] Aspect 43: The composition of any one of aspects 41-42, wherein a shape of at least a portion of the nanoparticles is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

[00269] Aspect 44: The composition of any one of aspects 41-43, wherein a shape of at least a portion of the nanoparticles is tuned such that the composition exhibits an filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

[00270] Aspect 45: The composition of aspect 44, wherein a shape of at least a portion of the nanoparticles is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

[00271] Aspect 46: The composition of any one of aspects 41-45, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.

[00272] Aspect 47: The composition of any one of aspects 41-46, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00273] Aspect 48: The composition of any one of aspects 41-47, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00274] Aspect 49: The composition of any one of aspects 41-48, wherein the base material comprises a biomaterial.

[00275] Aspect 50: The composition of any one of aspects 41-48, wherein the base material comprises a biomaterial matrix.

[00276] Aspect 51: The composition of any one of aspects 41-48, wherein the base material comprises hydrogel.

[00277] Aspect 52: The composition of any one of aspects 41-48, wherein the base material comprises silicone-based hydrogel.

[00278] Aspect 53: The composition of any one of aspects 41-48, wherein the nanoparticles comprise plasmonic nanoparticles.

[00279] Aspect 54: The composition of any one of aspects 41-48, wherein the nanoparticles comprise metal nanoparticles.

[00280] Aspect 55: The composition of any one of aspects 41-48, wherein the nanoparticles comprise gold nanoparticles.

[00281] Aspect 56: A composition for light filtering, the composition comprising: a base material; and a plurality of nanoparticles dispersed in the base material, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm, and wherein the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

[00282] Aspect 57: The composition of aspect 56, wherein a shape of at least a portion of the nanoparticles is tuned such that the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

[00283] Aspect 58: The composition of aspect 57, wherein a shape of at least a portion of the nanoparticles is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

[00284] Aspect 59: The composition of aspect 56, wherein a shape of at least a portion of the nanoparticles is tuned such that the composition exhibits an filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

[00285] Aspect 60: The composition of aspect 59, wherein a shape of at least a portion of the nanoparticles is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

[00286] Aspect 61: The composition of aspect 56, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.

[00287] Aspect 62: The composition of aspect 56, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00288] Aspect 63: The composition of aspect 56, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.

[00289] Aspect 64: The composition of aspect 56, wherein the base material comprises a biomaterial.

[00290] Aspect 65: The composition of aspect 56, wherein the base material comprises a biomaterial matrix.

[00291] Aspect 66: The composition of aspect 56, wherein the base material comprises hydrogel.

[00292] Aspect 67: The composition of aspect 56, wherein the base material comprises silicone-based hydrogel.

[00293] Aspect 68: The composition of aspect 56, wherein the nanoparticles comprise plasmonic nanoparticles.

[00294] Aspect 69: The composition of aspect 56, wherein the nanoparticles comprise metal nanoparticles.

[00295] Aspect 70: The composition of aspect 56, wherein the nanoparticles comprise gold nanoparticles.

[00296] As an illustrative example, FIGS. 1A-1D show representative morphologies of gold nanoparticles and their associated absorbance spectra. FIGS. 1E-1H display Transmission Electron Microscopy (TEM) micrographs of the representative morphologies of FIGS. 1A-1D. Large spherical nanoparticles (NPs) of about 170 nm up to about 200 nm are shown to block in the lower end of the target range (about 600 nm up to about 650 nm). However, large spherical NP's are shown to lose peak specificity at larger sizes, significantly limiting the dynamic range. Cubic NPs are similarly limited with comparably large FWHM values. Nanorods may likely be the most obvious strategy due to myriad synthesis pathways and

the very broad dynamic range of the longitudinal peak. However, the Full Width at Half Maximum (FWHM) of 83 nm of nanorods may be larger than that of bipyramids (typically, 56 nm). The tapered ends of bipyramids were shown to improve the overall absorbance profile of nanoparticles, and the dynamic range may be readily tuned by varying synthesis conditions. For bipyramids, a method was adapted from methods which use a seed-mediated growth strategy and produced pentatwinned bipyramids in high yield. Other bipyramid syntheses exist but may produce bipyramids with low yield and/or require extensive purification methods.

[00297] In preparing nanoseeds, solutions of 55.5 mM CTAC (16.2 ml) and 20 mM citric acid were prepared separately in 20 ml scintillation vials and heated at 45°C to dissolve. In a 20 ml scintillation vial, 2.5 mM HAuCl₄ (1.8 ml) and 20 mM citric acid (4.5 ml) were added to a solution of 55.5 mM CTAC (16.2 ml), followed by the rapid addition of ice-cold 25 mM NaBH₄ (0.45 ml). Samples were stirred at room temperature for 2 min at 2000 rpm then placed in an oil bath at 80°C for 90 min. In order to maximize repeatability, care was taken to produce a uniform vortex in the center of the vial with as few bubbles as possible. Addition of NaBH₄ produced a dark brown color, indicating nucleation, and the samples were red upon reaction completion.

[00298] In preparing nanobipyramids, 10 mM HAuCl₄, 1 M HCl, 10 mM AgNO₃, 100 mM L-AA and the previously prepared nanoseed solution were added sequentially to a solution of 111 mM CTAB in a 20 ml scintillation vial and stirred at 30°C for 2 h at 700 rpm. Volumes of each reagent for different target peak wavelengths are listed in Table 1 below.

Table 1. Nanobipyramid light blocker formulations.

Peak wavelength (nm)	HAuCl ₄ (μl)	HCl (μl)	AgNO ₃ (μl)	L-AA (μl)	Seed (ml)	CTAB (ml)
647	833	666	83	133	3	15
669	833	666	83	133	2.5	15
697	833	666	83	133	2	15
717	833	666	166	133	2	15
726	833	666	83	133	1.5	15
739	833	666	166	133	1.5	15

770	833	666	166	133	1	15
800	833	666	166	133	0.5	15

[00299] Using bipyramids as the basis of a plasmonic light blocker, the controllability and repeatability of the designed synthesis method was tested. Seed-mediated growth is a common strategy employed in nanomaterial synthesis since the separation of nucleation and growth enables more control over the final product. The growth of bipyramids was shown to be highly repeatable. For the same seed, a repeatable peak of 631 ± 1.7 nm, FWHM 56.3 ± 1.5 nm with a consistent peak ratio of 1.9 (n=6) was achieved (Table 2). Repeatability may depend on seed production, requiring a high proportion of pentatwinned NPs. Seed repeatability may increase through the use of high stirring rates (2000 rpm), aqua regia-cleaned stir bars, and fresh, ice-cold sodium borohydride. Seed production should be tightly controlled before proceeding to growth steps, as the absorbance (and thus size) of the seeds relates directly to the final bipyramid products.

Table 2. Repeatability of Au Bipyramid Growth

Sample	Peak (nm)	FWHM (nm)	Peak ratio
1	632	56	1.9
2	632	56	1.9
3	630	58	1.9
4	632	58	1.9
5	628	56	1.9
6	632	54	1.9

[00300] The amount of AgNO_3 used in synthesis and the amount of gold seeds added to the growth solution may vary. Such variation may produce bipyramids capable of blocking selective bands along the red light spectrum (FIGS. 2A, 3A, and 3B). AgNO_3 may be used as a shape-directing agent, directly influencing the sharpness of bipyramids. The amount of seed may determine the number of nucleation points present in the growth solution. Samples may be labeled as “BP” for “bipyramids”, with numbers indicating the longitudinal peak wavelength in nm (e.g. BP-647, BP-669, etc). As expected, the peak wavelength (nm) of the NPs increases as both the aspect ratio (quotient of major and minor axes) and volumes of the NPs increase (FIG.

2B). The longitudinal axis may be used as the major axis while the thickest latitudinal axis (e.g. through the middle of a nanoparticle) may be used as the minor axis. The FWHM may remain relatively consistent across all samples, though the ratio between the longitudinal and transverse peaks increased as spectra red-shifted. TEM images confirm the bipyramidal shape of the nanoparticles, though may also show that samples had varying degrees of sphere- and rod-shaped impurities. The pentatwinning efficiency of the seeds may be a determinant of both the morphology and monodispersity of the final nanoparticles.

[00301] The systems, methods, compositions, and devices of the appended claims are not limited in scope by the specific materials and devices described herein, which are intended as illustrations of a few aspects of the claims. Any systems, methods, compositions, and devices that are functionally equivalent are intended to fall within the scope of the claims. Various modifications of the systems, methods, compositions, and devices in addition to those shown and described herein are intended to fall within the scope of the appended claims. Further, while only certain representative systems, methods, compositions, and devices disclosed herein are specifically described, other combinations of the systems, methods, compositions, and devices are also intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of elements, components, or constituents may be explicitly mentioned herein or less, however, other combinations of elements, components, and constituents are included, even though not explicitly stated.

[00302] The term “comprising” and variations thereof as used herein is used synonymously with the term “including” and variations thereof and are open, non-limiting terms. Although the terms “comprising” and “including” have been used herein to describe various embodiments, the terms “consisting essentially of” and “consisting of” can be used in place of “comprising” and “including” to provide for more specific embodiments of the invention and are also disclosed. Other than where noted, all numbers expressing geometries, dimensions, and so forth used in the specification and claims are to be understood at the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, to be construed in light of the number of significant digits and ordinary rounding approaches.

[00303] Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed

invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

Claims

What is claimed is:

1. A composition for light filtering, the composition comprising:
a base material;
a plurality of gold nanoparticles dispersed in the base material, at least a portion of the plurality of gold nanoparticles having an anisotropic shape; and
a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of gold nanoparticles to enhance stability of at least the portion of the plurality of gold nanoparticles in the base material,
wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.
2. The composition of claim 1, wherein the anisotropic shape is tuned such that the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.
3. The composition of claim 1, wherein the anisotropic shape is tuned such that the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm – 58nm.
4. The composition of claim 1, wherein the anisotropic shape is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.
5. The composition of claim 1, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.
6. The composition of claim 1, wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.
7. The composition of claim 1, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.
8. The composition of claim 1, wherein the base material comprises a biomaterial.
9. The composition of claim 1, wherein the base material comprises a biomaterial matrix.

10. The composition of claim 1, wherein the base material comprises hydrogel.
11. The composition of claim 1, wherein the base material comprises silicone-based hydrogel.
12. The composition of claim 1, wherein at least a portion of the plurality of gold nanoparticles are grown from a pentatwinned gold seed.
13. The composition of claim 1, wherein the anisotropic shape comprises a bipyramid shape.
14. The composition of claim 13, wherein the bipyramid shape comprises a longitudinal peak and a transverse peak, and wherein a sharpness of the bipyramid shape relative to the longitudinal peak and the transverse peak is tuned such that the composition exhibits a peak light filtering in the range of about 600nm to about 850nm.
15. The composition of claim 1, wherein the anisotropic shape comprises a bipyramid shape with each a pair of opposing truncated peaks disposed on opposing ends.
16. The composition of claim 15, wherein a sharpness of the bipyramid shape is tuned such that the composition exhibits a peak light filtering in the range of about 600nm to about 850nm.
17. The composition of claim 1, wherein the stabilizing mechanism enhances colloidal stability, thermal stability, or both of at least the portion of the plurality of gold nanoparticles in the base material
18. The composition of claim 1, wherein the stabilizing mechanism enhances biocompatibility of at least the portion of the plurality of gold nanoparticles in the base material
19. The composition of claim 1, wherein the stabilizing mechanism comprises poly(vinyl pyrrolidone).
20. The composition of claim 1, wherein the stabilizing mechanism comprises 55kDa poly(vinyl pyrrolidone).
21. The composition of claim 1, wherein the stabilizing mechanism comprises one or more of 10kDa poly(vinyl pyrrolidone), 55kDa poly(vinyl pyrrolidone), 360kDa poly(vinyl pyrrolidone), 1300kDa poly(vinyl pyrrolidone).
22. The composition of claim 1, wherein the stabilizing mechanism chemically binds with at least a portion of the plurality of gold nanoparticles to enhance colloidal stability of at least the portion of the plurality of gold nanoparticles in the base material.

23. A method of making the composition of claim 1.
24. The method of claim 23, wherein at least a portion of the plurality of gold nanoparticles are grown from a pentatwinned gold seed.
25. A composition for light filtering, the composition comprising:
a plurality of metal nanoparticles, at least a portion of the plurality of metal nanoparticles having an anisotropic shape; and
a stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of metal nanoparticles,
wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.
26. The composition of claim 25, wherein the anisotropic shape is tuned such that the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm – 58nm.
27. The composition of claim 25, wherein the anisotropic shape is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.
28. The composition of claim 25, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.
29. The composition of claim 25, wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.
30. The composition of claim 25, wherein the anisotropic shape is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about 1,250nm³ up to about 30,000nm³.
31. The composition of claim 25, wherein the anisotropic shape comprises a bipyramid shape.
32. The composition of claim 31, wherein the bipyramid shape comprises a longitudinal peak and a transverse peak, and wherein a sharpness of the bipyramid shape relative to the longitudinal peak and the transverse peak is tuned to exhibit a peak light filtering in the range of about 600nm to about 850nm.

33. The composition of claim 25, wherein the anisotropic shape comprises a bipyramid shape with each a pair of opposing truncated peaks disposed on opposing ends.
34. The composition of claim 33, wherein a sharpness of the bipyramid shape is tuned such that the composition exhibits a peak light filtering in the range of about 600nm to about 850nm.
35. The composition of claim 25, wherein the stabilizing mechanism comprises poly(vinyl pyrrolidone).
36. The composition of claim 25, wherein the stabilizing mechanism comprises 55kDa poly(vinyl pyrrolidone).
37. The composition of claim 25, wherein the stabilizing mechanism comprises one or more of 10kDa poly(vinyl pyrrolidone), 55kDa poly(vinyl pyrrolidone), 360kDa poly(vinyl pyrrolidone), 1300kDa poly(vinyl pyrrolidone).
38. The composition of claim 25, wherein the stabilizing mechanism chemically binds with at least a portion of the plurality of metal nanoparticles to enhance colloidal stability of at least the portion of the plurality of metal nanoparticles.
39. A method of making the composition of claim 1.
40. The method of claim 39, wherein at least a portion of the plurality of metal nanoparticles are grown from a pentatwinned metal seed.
41. A contact lens comprising a composition for light filtering, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm, and wherein the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm - 58nm, wherein the contact lens is a free radical reaction product of a reactive mixture comprising: one or more silicone-containing components and one or more hydrophilic components; the contact lens having a water content of at least about 20 weight percent and an oxygen permeability of at least about 80 barrers.
42. The contact lens of claim 41 wherein the composition comprises a plurality of nanoparticles dispersed in the contact lens.
43. The contact lens of claim 42, wherein a shape of at least a portion of the nanoparticles is tuned such that the composition exhibits a peak light filtering value in the range of about

600nm to about 850nm.

44. The contact lens of claim 43, wherein a shape of at least a portion of the nanoparticles is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

45. The contact lens of claim 42, wherein a shape of at least a portion of the nanoparticles is tuned such that the composition exhibits an filtering spectrum having a full-width at half maximum of about 54nm – 58nm.

46. The contact lens of claim 45, wherein a shape of at least a portion of the nanoparticles is tuned by configuring one or more of: an aspect ratio defined by a quotient of major and minor axes length; and a volume.

47. The contact lens of claim 42, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length.

48. The contact lens of claim 42, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit a volume of about $1,250\text{nm}^3$ up to about $30,000\text{nm}^3$.

49. The contact lens of claim 42, wherein a shape of at least a portion of the nanoparticles is tuned to exhibit an aspect ratio of about 1.9 to about 2.9, as defined by a quotient of major and minor axes length and wherein the anisotropic shape is tuned to exhibit a volume of about $1,250\text{nm}^3$ up to about $30,000\text{nm}^3$.

50. The contact lens of claim 42, wherein the nanoparticles comprise plasmonic nanoparticles.

51. The contact lens of claim 42, wherein the nanoparticles comprise metal nanoparticles.

52. The contact lens of claim 42, wherein the nanoparticles comprise gold nanoparticles.

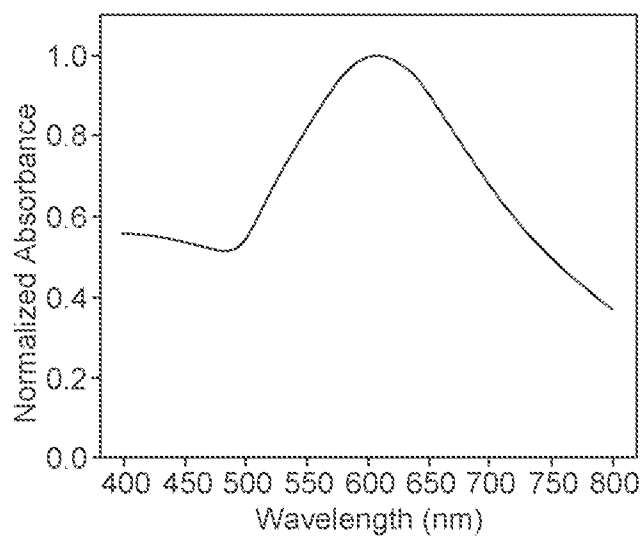


FIG. 1A

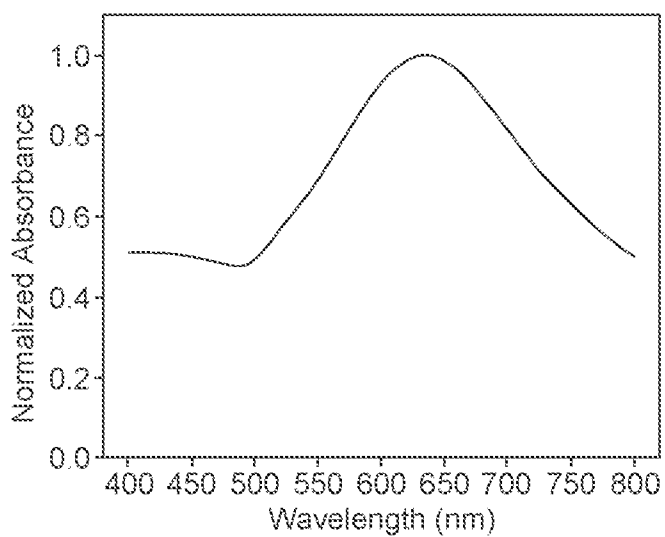


FIG. 1B

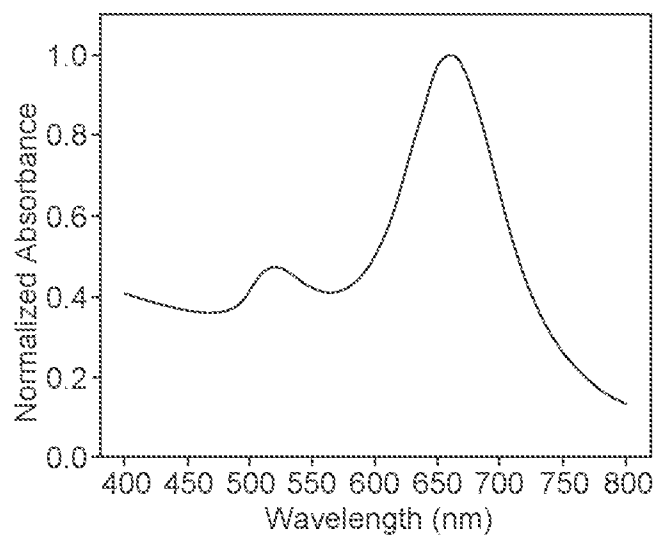


FIG. 1C

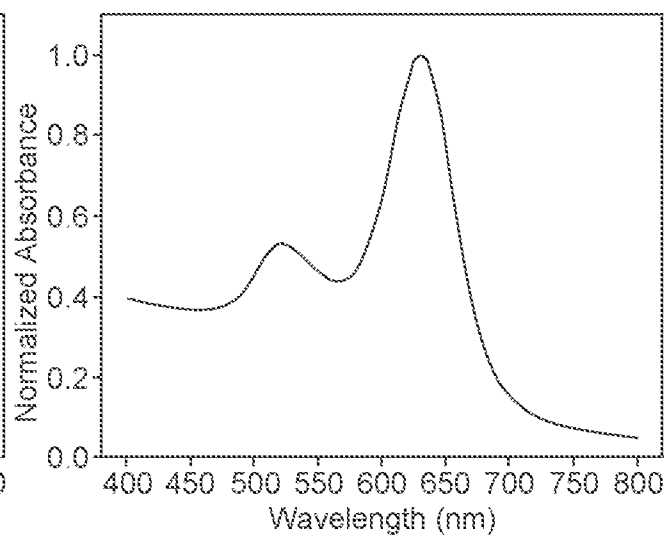


FIG. 1D

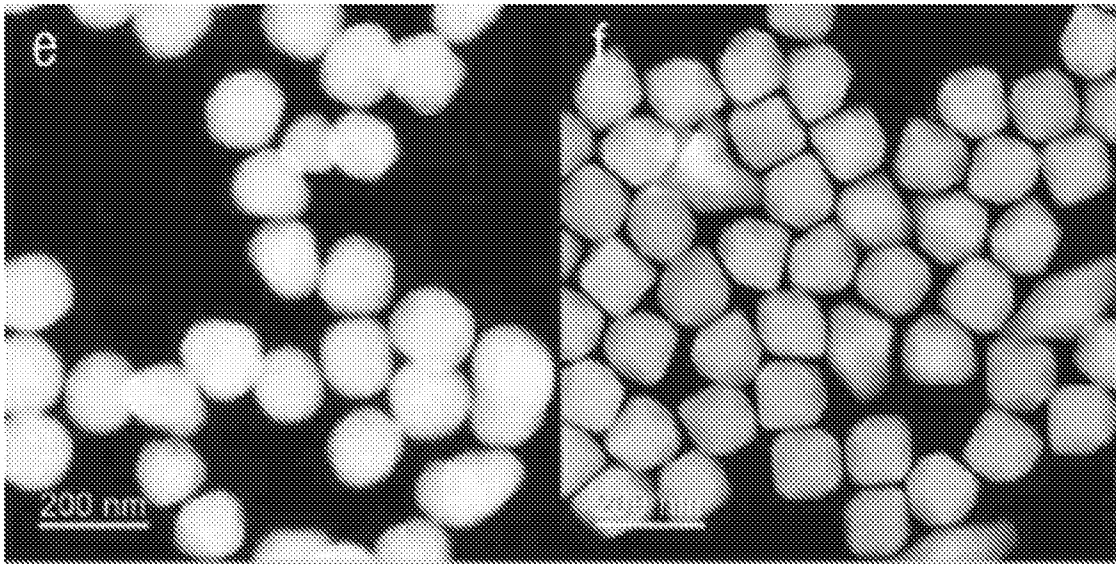


FIG. 1E

FIG. 1F

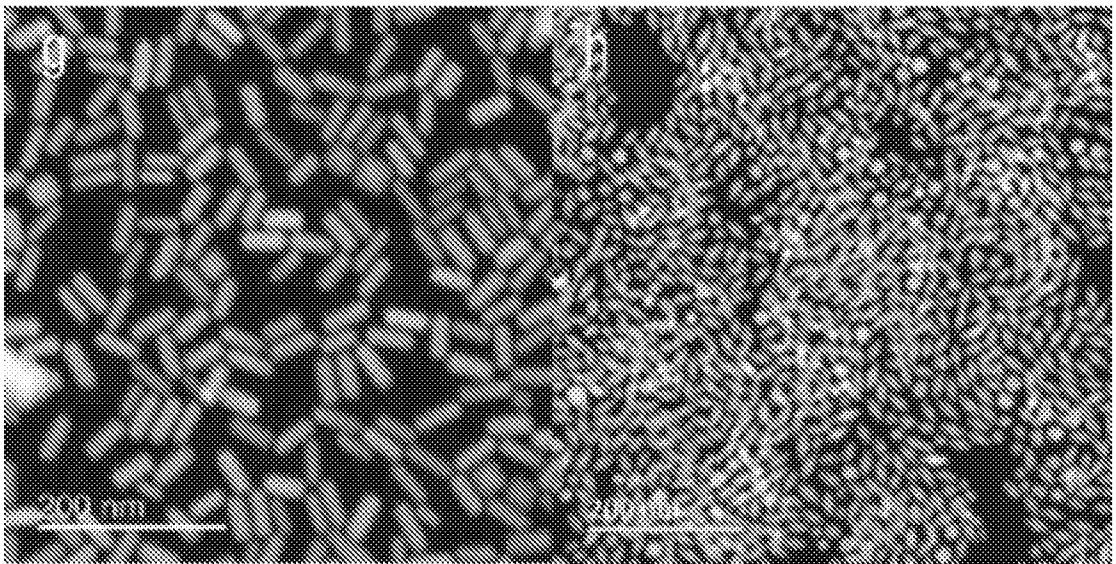


FIG. 1G

FIG. 1H

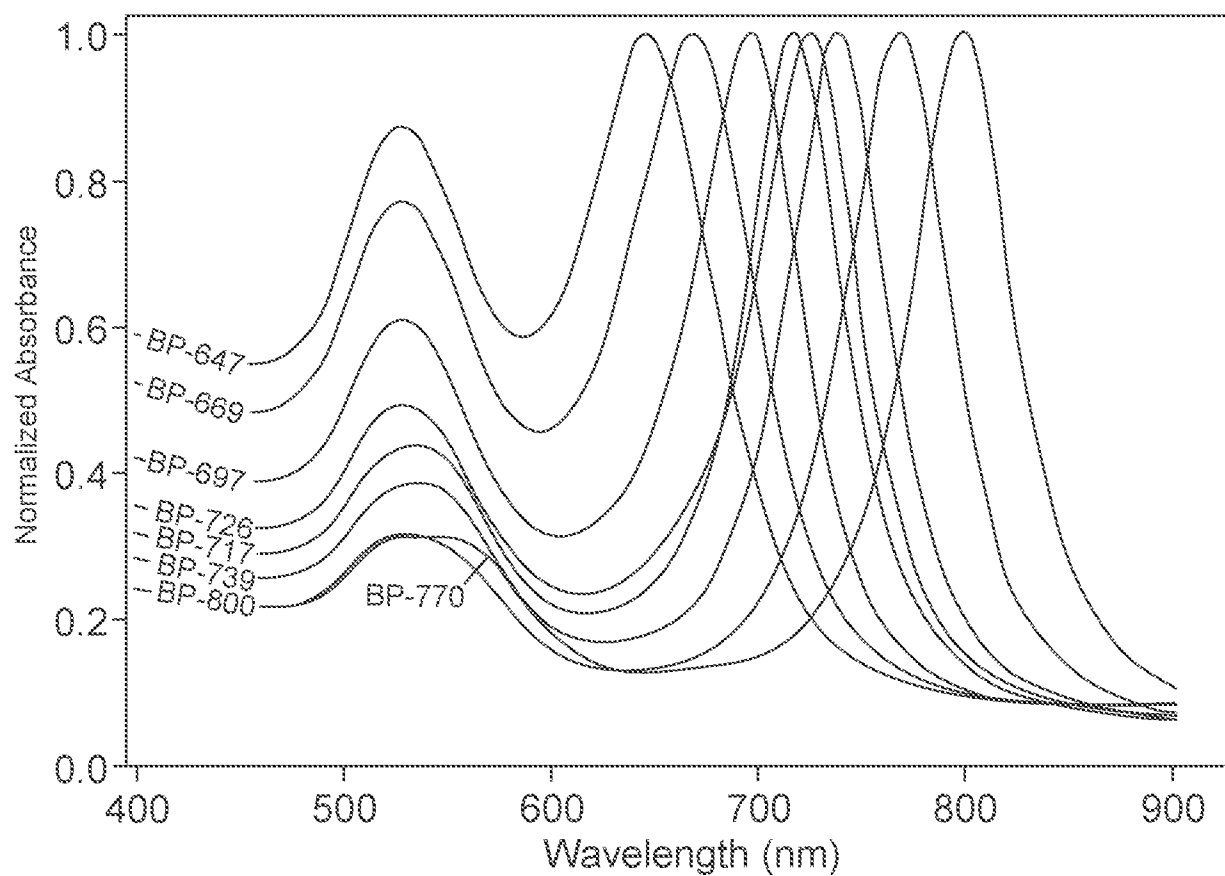


FIG. 2A

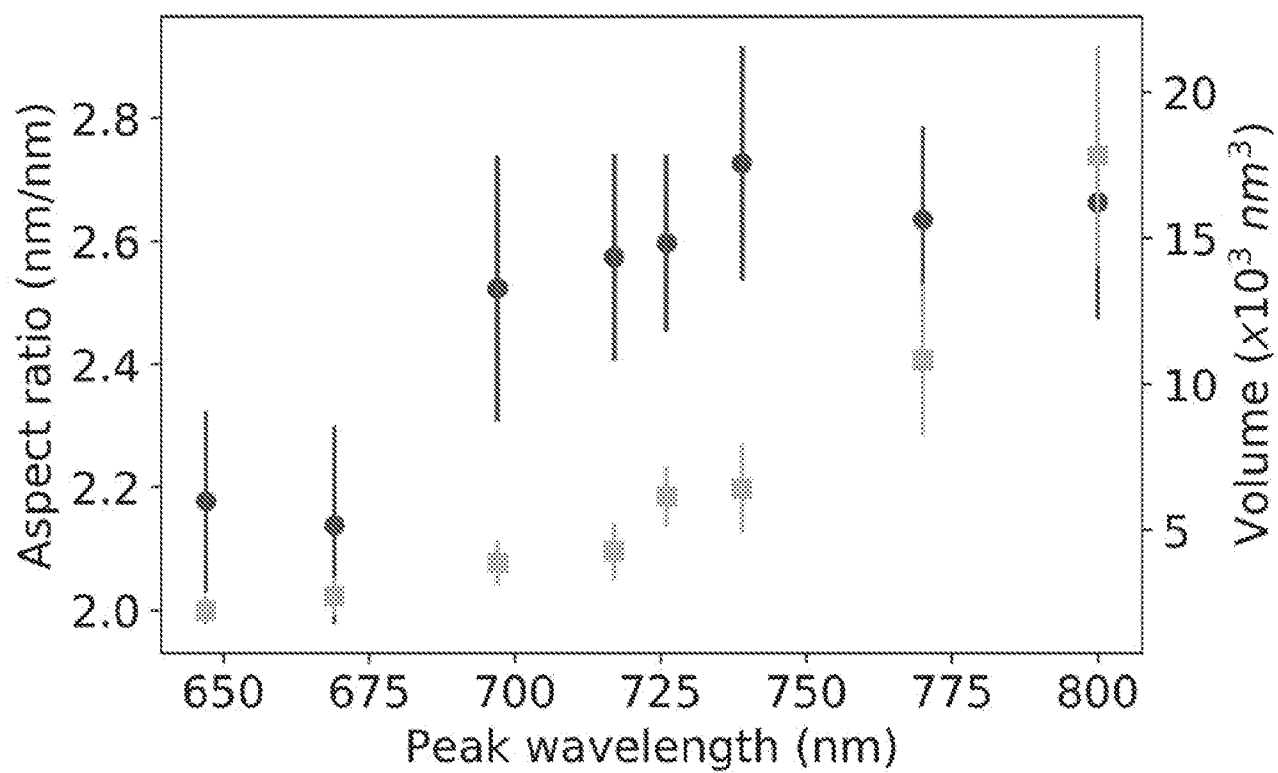


FIG. 2B

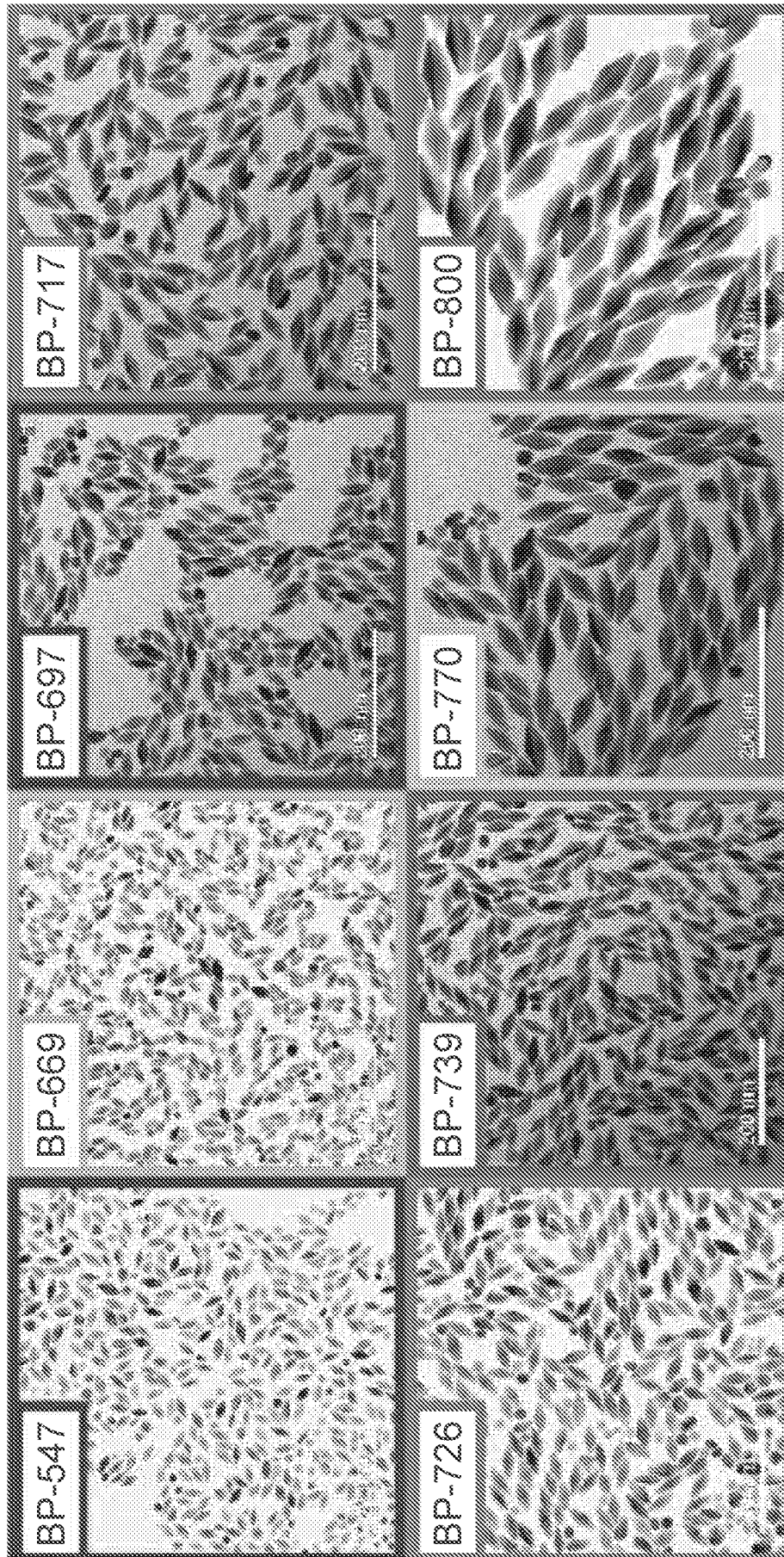


FIG. 2C

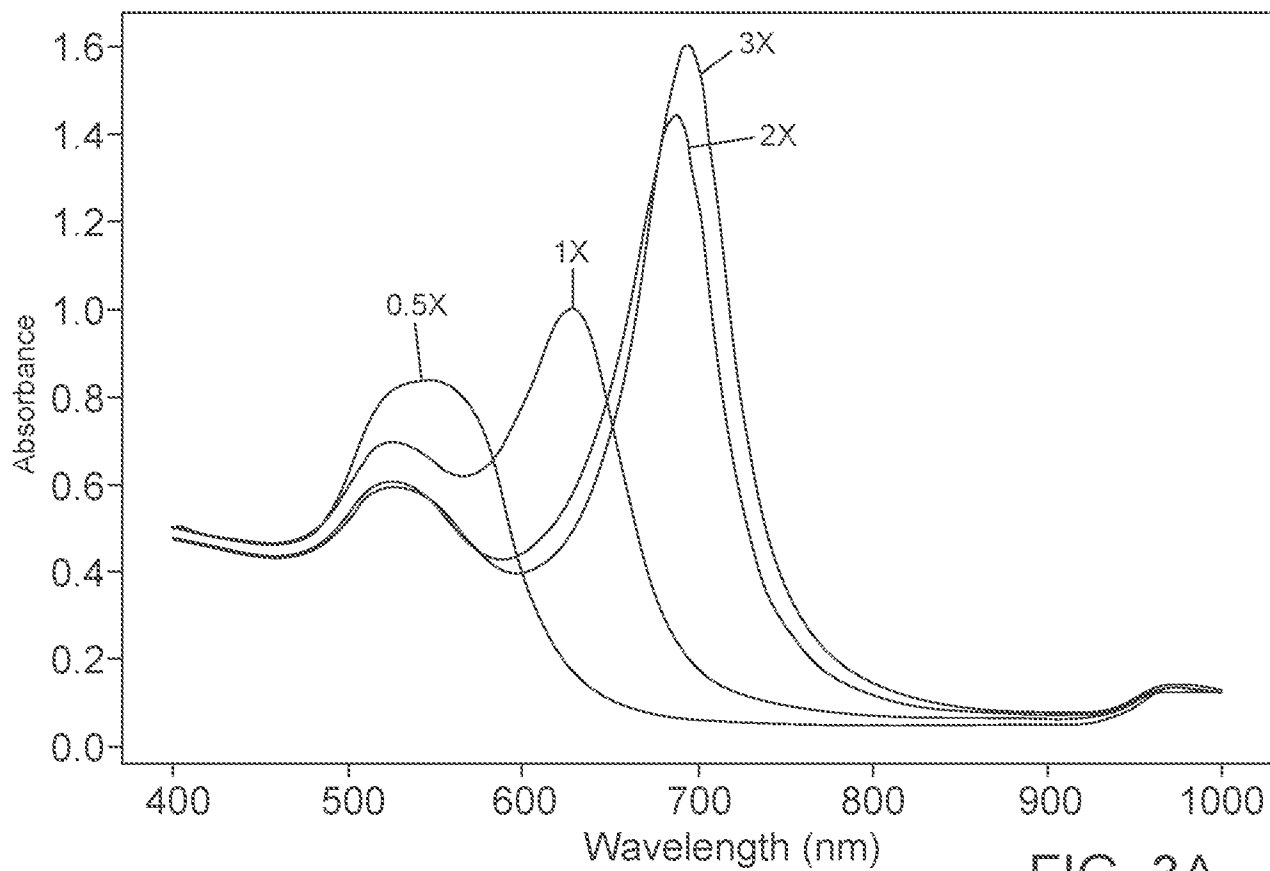


FIG. 3A

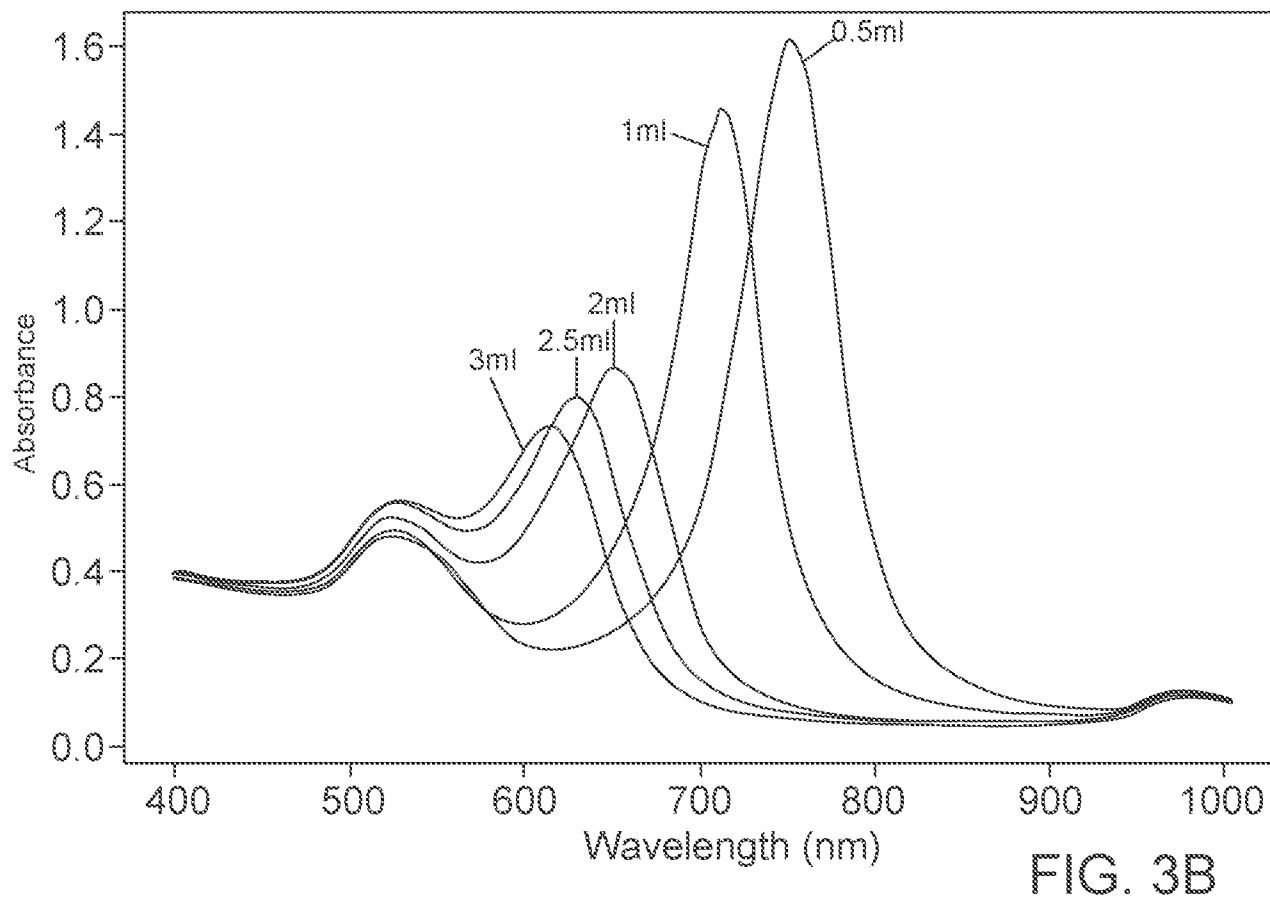


FIG. 3B

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2023/051955

A. CLASSIFICATION OF SUBJECT MATTER INV. G02B1/00 G02B1/04 G02C7/04 G02C7/10 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) G02C G02B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/275596 A1 (PAYNE J D [US] ET AL) 7 December 2006 (2006-12-07) paragraph [0032]; figure 5 -----	1-52
X	LI QIAN ET AL: "Production of Monodisperse Gold Nanobipyramids with Number Percentages Approaching 100% and Evaluation of Their Plasmonic Properties", ADVANCED OPTICAL MATERIALS, vol. 3, no. 6, 9 February 2015 (2015-02-09), pages 801-812, XP093046957, DE ISSN: 2195-1071, DOI: 10.1002/adom.201400505	1-40
A	page 804; table 1 purification of Au NBP; page 802, paragraph 2.1 -----	41-52
-/--		
☒ Further documents are listed in the continuation of Box C. ☒ 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 15 August 2023		Date of mailing of the international search report 25/08/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Le Masson, Nicolas

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2023/051955

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2021/389731 A1 (GU FRANK [CA] ET AL) 16 December 2021 (2021-12-16) paragraphs [0305], [0306], [0316] -----	1-52
A	US 2021/003754 A1 (GU FRANK [CA] ET AL) 7 January 2021 (2021-01-07) claim 45 paragraph [0290] -----	1-52
A	SÁNCHEZ-IGLESIAS ANA ET AL: "High-Yield Seeded Growth of Monodisperse Pentatwinned Gold Nanoparticles through Thermally Induced Seed Twinning", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 139, no. 1, 29 December 2016 (2016-12-29), pages 107-110, XP093049687, ISSN: 0002-7863, DOI: 10.1021/jacs.6b12143 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/j acs.6b12143> the whole document -----	1-52
A	US 2013/235335 A1 (FORREST JAMES ARTHUR [CA] ET AL) 12 September 2013 (2013-09-12) paragraph [0070] -----	1-52
X,P	CLASKY AARON J. ET AL: "Polymer Co-Coating of Gold Nanoparticles Enables Their Integration Into Contact Lenses for Stable, Selective Ocular Light Filters", ADVANCED MATERIALS INTERFACES, vol. 9, no. 33, 10 November 2022 (2022-11-10), page 2201549, XP093043185, DE ISSN: 2196-7350, DOI: 10.1002/admi.202201549 Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/fu 11-xml/10.1002/admi.202201549> the whole document -----	1-52

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2023/051955

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-40

A composition for light filtering, the composition comprising: a plurality of metal nanoparticles, at least a portion of the plurality of metal nanoparticles having an anisotropic shape; anda stabilizing mechanism disposed to selectively couple with at least a portion of the plurality of metal nanoparticles, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm.

2. claims: 41-52

A contact lens comprising a composition for light filtering, wherein the composition exhibits a peak light filtering value in the range of about 600nm to about 850nm, and wherein the composition exhibits a filtering spectrum having a full-width at half maximum of about 54nm - 58nm, wherein the contact lens is a free radical reaction product of a reactive mixture comprising: one or more silicone-containing components and one or more hydrophilic components; the contact lens having a water content of at least about 20 weight percent and an oxygen permeability of at least about 80 barrers.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2023/051955

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006275596 A1	07-12-2006	NONE	
US 2021389731 A1	16-12-2021	EP 4165465 A1 JP 2023529030 A TW 202219661 A US 2021389731 A1 WO 2021255536 A1	19-04-2023 07-07-2023 16-05-2022 16-12-2021 23-12-2021
US 2021003754 A1	07-01-2021	EP 3994508 A1 JP 2022537899 A US 2021003754 A1 WO 2021001706 A1	11-05-2022 31-08-2022 07-01-2021 07-01-2021
US 2013235335 A1	12-09-2013	CA 2816768 A1 US 2013235335 A1 WO 2012058775 A1	10-05-2012 12-09-2013 10-05-2012