

(12) United States Patent

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(54) OPTICAL STRUCTURES INCLUDING **NANOCRYSTALS**

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U.S. Cl.

Field of Classification Search

None

See application file for complete search history.

References Cited (56)

U.S. PATENT DOCUMENTS

5,187,765 A	2/1993	Muehlemann et al.
6,132,056 A	10/2000	Ruthenberg et al.
6,744,960 B2	6/2004	Pelka
6,819,845 B2	11/2004	Lee et al.
7,085,460 B2*	8/2006	Leu et al 385/120
2003/0044114 A1	3/2003	Pelka et al.
2004/0126072 A1	7/2004	Lee et al.
2005/0111805 A1	5/2005	Hertz et al.
2009/0238511 A1*	9/2009	Quitoriano et al
2010/0265734 A1*	10/2010	Bulovic et al 362/558

FOREIGN PATENT DOCUMENTS

JP	A-2003-217861	7/2003
JP	A-2004-296950	10/2004
JP	A-2004-303592	10/2004
JР	A-2005-38634	2/2005
WO	WO03/021694	3/2003
WO	WO 2004/099664	11/2004

^{*} cited by examiner

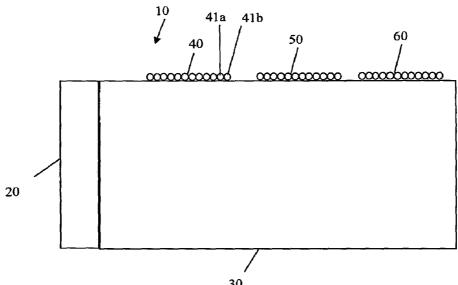
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ABSTRACT

An optical structure can include a nanocrystal on a surface of an optical waveguide in a manner to couple the nanocrystal to the optical field of light propagating through the optical waveguide to generate an emission from the nanocrystal.

42 Claims, 2 Drawing Sheets



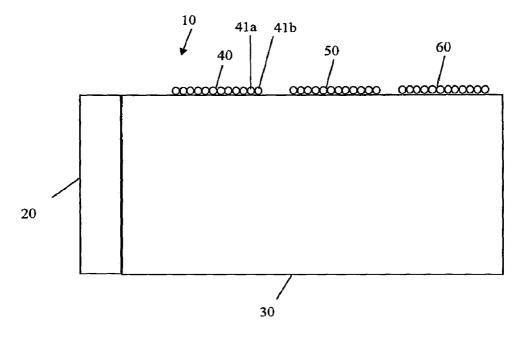


Figure 1

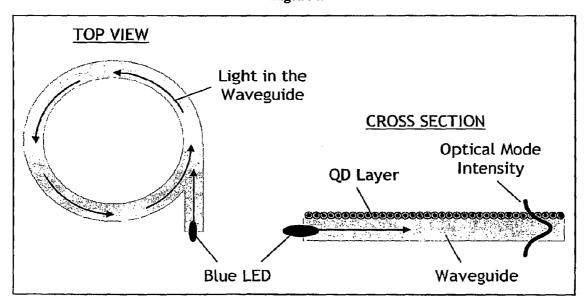


Figure 2

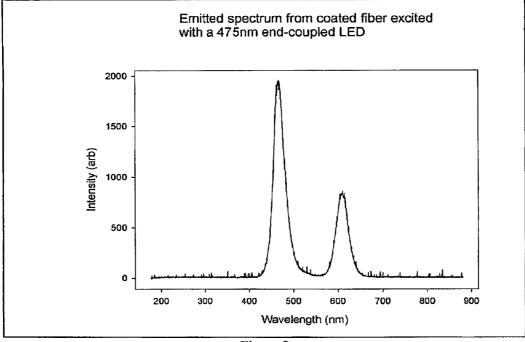


Figure 3

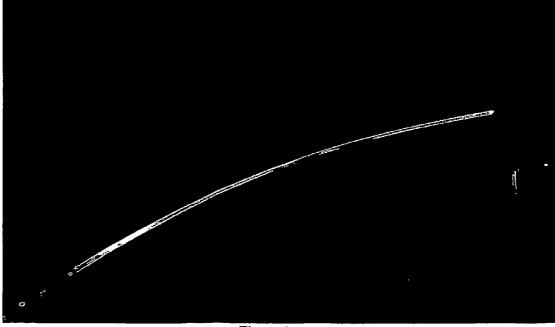


Figure 4

OPTICAL STRUCTURES INCLUDING NANOCRYSTALS

CLAIM OF PRIORITY

This application claims priority under 35 USC 371 to International Application No. PCT/US2007/012040, filed on May 21, 2007, which claims priority to U.S. Provisional Application Ser. No. 60/747,805, filed on May 21, 2006, each of which is incorporated by reference in its entirety.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support under ¹⁵ Grant Number FA9550-04-1-0462 awarded by the Air Force. The government has certain rights to the invention.

TECHNICAL FIELD

The invention relates to optical structures including nanocrystals.

BACKGROUND

Optical waveguides, such as fibers and planar waveguides, which take advantage of total internal reflection have been used in a wide range of sensing, communication, and illumination applications. Light can be delivered through optical fibers with great efficiency over long distances because of the perfect mirroring that is provided by the core/cladding dielectric index step interface. Typically, the optical field in an optical fiber element is entirely confined because of this core/cladding interface.

SUMMARY

An optical structure can include a nanocrystal on a surface of an optical waveguide in a manner to couple the nanocrystal to the optical field of light propagating through the optical 40 waveguide to generate an emission from the nanocrystal. For example, one or more semiconductor nanocrystals, or quantum dots, can be placed in the vicinity of an optical structure such as a waveguide, for example, a fiber optic element. The optical field of light which is propagating through the 45 waveguide can couple with the nanocrystal and cause the nanocrystal to emit light.

Advantageously, the light emitting structure can allow for the straightforward and efficient distribution of an excitation light source and coupling to a highly efficient downconverting element which will be useful for a range of lighting applications, including optical displays, sensors, and other applications. The light emitting structure can have particular relevance to solid state lighting applications. An excitation source can be used to efficiently distribute excitation wavelength through the waveguide and downconverted at the point of use to an appropriate spectral composition by applying the right combination of downconverting elements, including nanocrystals. Nanocrystals are an especially appropriate material set because of their broad spectral tunability, long 60 lifetime in photoluminescence (far exceeding that of organic dyes), and easy solution processability.

The nanocrystal can be a semiconductor nanocrystal. The semiconductor nanocrystal includes a core including a first semiconductor material. The semiconductor nanocrystal can 65 include an overcoating on a surface of the core including a second semiconductor material. The semiconductor nanocrystal can 65 include an overcoating on a surface of the core including a second semiconductor material.

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rystal can include an outer layer including a compound linked to a surface of the nanocrystal.

In one aspect, an optical structure includes a nanocrystal on a surface of an optical waveguide, the nanocrystal being positioned to be optically coupled to an optical field propagating through the optical waveguide.

In another aspect, a light emitting structure includes a light source arranged to introduce light including an excitation wavelength into an optical waveguide, and a nanocrystal on a surface of the optical waveguide, the nanocrystal being positioned to be optically coupled to an optical field propagating through the optical waveguide and capable of absorbing the excitation wavelength of light and emitting an emission wavelength of light.

In another aspect, a method of producing light includes introducing light from a light source including an excitation wavelength into an optical waveguide, the excitation wavelength propagating through the optical waveguide and optically coupling to a nanocrystal on a surface of the optical waveguide, the nanocrystal absorbing the excitation wavelength and emitting an emission wavelength from the surface.

In another aspect, a method of making an optical structure includes placing a nanocrystal on a surface of an optical waveguide in a position to optically couple the nanocrystal to an optical field propagating through the optical waveguide.

The waveguide can be an optical fiber or a planar waveguide. The optical fiber can have a cladding layer that allows light to escape at a selected amount along the length of the fiber. The nanocrystal can be a semiconductor nanocrystal. The semiconductor nanocrystal can include a core including a first semiconductor material. The semiconductor nanocrystal can include an overcoating on a surface of the core including a second semiconductor material.

A plurality of nanocrystals can be distributed at a first portion of the surface. A plurality of nanocrystals can be distributed at a second portion of the surface. The plurality of nanocrystals distributed at the first portion of the surface can have a composition different from the plurality of nanocrystals distributed at the first portion of the surface. The plurality of nanocrystals distributed at the first portion of the surface has an emission wavelength different from the plurality of nanocrystals distributed at the first portion of the surface.

The surface of the optical waveguide can be modified to increase coupling between the optical field and the nanocrystal to allow light to escape at a selected amount at selected locations. The excitation wavelength can propagate through the optical waveguide and optically couple to a plurality of nanocrystals on a first portion of a surface of the optical waveguide. The excitation wavelength propagates through the optical waveguide and optically couple to a plurality of nanocrystals on a second portion of the surface.

The nanocrystal can be placed on the surface by dip coating, spin coating, painting or printing. The surface of the optical waveguide can be processed prior to placing the nanocrystal.

Other features, objects and advantages will be apparent from the description, the drawings and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of an optical structure including nanocrystals.

FIG. 2 is a schematic illustration of an optical structure including nanocrystals viewed from the top and from the side.

FIG. 3 is a graph displaying a light emission from an optical structure including nanocrystals.

FIG. 4 is a photograph illustrating light emission from an optical structure including nanocrystals.

DETAILED DESCRIPTION

A light emitting structure can include a nanocrystal on a surface of an optical structure. The nanocrystal is coupled to the optical field of light propagating through the optical structure. For example, one or more semiconductor nanocrystals, or quantum dots, can be placed in the vicinity of an optical structure such as a waveguide, for example, a fiber optic element. In one example, a portion of the surface of the waveguide is coated with a thin layer of nanocrystals. The thin layer can be a monolayer or a multilayer. The optical field of light which is propagating through the waveguide can couple 15 with the nanocrystal and cause them to emit light at an emission wavelength.

The layer has a thickness sufficient to generate a desired amount of light at the emission wavelength, and is thin enough to avoid significant self absorption of the emission 20 wavelength. The composition and thickness of the nanocrystal layer, and the size, and distribution of sizes of the individual nanocrystals in the layer can be selected to generate a particular emission wavelength profile from each particular portion of the surface of the waveguide. In addition, the 25 confinement of the propagating excitation wavelength of light provided by the waveguide can be tuned, for example by modifying the structure of the surface of the waveguide or thickness of the waveguide, to select the amount of excitation wavelength the nanocrystal will encounter at different posi- 30 tions along the surface. For example, it is possible to thin or remove portions of the cladding layer of a core-cladding optical fiber to couple the light propagating inside the fiber to materials which have been placed on its surface. This occurs because the optical field penetrates beyond the core/cladding 35 or core/air interface a very small distance. The resulting evanescent optical field can be used to excite the nanocrystal on the surface of the waveguide with the light which is normally otherwise confined to the fiber.

The light emitted from the nanocrystals on different portions of the waveguide surface can generate a variety of colors and intensity levels, making the light emitting structure useful in a broad range of lighting applications, such as, for example, solid state lighting applications. An efficient excitation wavelength source can be distributed through the waveguide and downconverted at the point of use to an appropriate spectral composition by applying the right combination of downconverting elements at the surface of the waveguide, for example, a nanocrystal or combination of nanocrystals. Nanocrystals are an especially appropriate material to use for the downconversion because of their broad spectral tunability, long lifetime in photoluminescence (far exceeding that of organic dyes), and easy solution processability.

The nanocrystals can be placed on a surface of a waveguide by dip coating, drop coating, spin coating, painting or printing 55 the nanocrystal on the surface. Printing can include ink jet printing or microcontact printing. Microcontact printing and related techniques are described in, for example, U.S. Pat. Nos. 5,512,131; 6,180,239; and 6,518,168, each of which is incorporated by reference in its entirety. In some circumstances, the stamp can be a featureless stamp having a pattern of ink, where the pattern is formed when the ink is applied to the stamp. See U.S. patent application Ser. No. 11/253,612, filed Oct. 21, 2005, which is incorporated by reference in its entirety.

Referring to FIG. 1, light emitting structure 10 includes light source 20 arranged to couple light into optical

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waveguide 30. Light source 20 can be, for example, a laser or light emitting diode that emits light at a wavelength suitable to excite the nanocrystal and cause emission, for example, a blue light emitting diode. Nanocrystals on portions of the surface of optical waveguide 30 form nanocrystal regions, such as regions 40, 50 and 60. In each of these regions, one or more nanocrystals, for example, nanocrystals 41a and 41b form a layer. The layer can be a monolayer or a multilayer. The nanocrystals 41a and 41b can have a similar composition or size, i.e., can have a similar emission wavelength, or can have a different composition or size, i.e., can have a different emission wavelength. In each of the regions, the nanocrystals are selected to provide particular emission wavelengths of light, which in turn can provide different colors and intensities (or the same) at the various positions. The nanocrystal can be, for example, a semiconductor nanocrystal. The regions 40, 50 and 60 can contain other additives, including dyes, pigments, organic or inorganic matrix materials, or other components that can help protect the regions from degradation. Optionally, the regions can be coated by a protective material.

The waveguide can have a variety of different shapes or configurations. For example, another optical structure that can also contribute to efficient light downconversion is shown in FIG. 2. In this structure, the light is injected, for example by a blue light emitting diode (LED) in an optical waveguide coated with nanocrystals. The evanescent tail of the waveguide optical mode can be absorbed by the nanocrystal layer. The blue light that is not absorbed continues circling the waveguide until eventually absorbed by nanocrystals, which in turn convert the blue light into an emission wavelength of a different color. Again, the emission wavelength arises from the size and/or composition of the nanocrystal.

In general, the light source, such as the blue LED, can be any other LED or other light source. In addition, any nanocrystals can be coated on the surface of the optical structures, but only the nanocrystals that can absorb the excitation spectrum produced by the light source will be excited by the light. The nanocrystal film can consist of a mixture of different nanocrystals. For example, combinations of nanocrystals can be used to generate a white light spectrum. The thickness of the nanocrystal film can be adjusted in order to optimize the spectral emission. Also, it is usually desirable to minimize nanocrystal light self absorption which predicates use of the very thin nanocrystal films.

The semiconductor nanocrystals can have a broad absorption band with an intense, narrow band emission. The peak wavelength of emission can be tuned from throughout the visible and infrared regions, depending on the size, shape, composition, and structural configuration of the nanocrystals. The nanocrystals can be prepared with an outer surface having desired chemical characteristics (such as a desired solubility). Light emission by nanocrystals can be stable for long periods of time.

When a nanocrystal achieves an excited state (or in other words, an exciton is located on the nanocrystal), emission can occur at an emission wavelength. The emission has a frequency that corresponds to the band gap of the quantum confined semiconductor material. The band gap is a function of the size of the nanocrystal. Nanocrystals having small diameters can have properties intermediate between molecular and bulk forms of matter. For example, nanocrystals based on semiconductor materials having small diameters can exhibit quantum confinement of both the electron and hole in all three dimensions, which leads to an increase in the effective band gap of the material with decreasing crystallite size.

Consequently, both the optical absorption and emission of nanocrystals shift to the blue, or to higher energies, as the size of the crystallites decreases.

The emission from the nanocrystal can be a narrow Gaussian emission band that can be tuned through the complete 5 wavelength range of the ultraviolet, visible, or infrared regions of the spectrum by varying the size of the nanocrystal, the composition of the nanocrystal, or both. For example, CdSe can be tuned in the visible region and InAs can be tuned in the infrared region. The narrow size distribution of a population of nanocrystals can result in emission of light in a narrow spectral range. The population can be monodisperse and can exhibit less than a 15% rms deviation in diameter of the nanocrystals, preferably less than 10%, more preferably less than 5%. Spectral emissions in a narrow range of no 15 greater than about 75 nm, preferably 60 nm, more preferably 40 nm, and most preferably 30 nm full width at half max (FWHM) for nanocrystals that emit in the visible can be observed. IR-emitting nanocrystals can have a FWHM of no greater than 150 nm, or no greater than 100 nm. Expressed in 20 terms of the energy of the emission, the emission can have a FWHM of no greater than 0.05 eV, or no greater than 0.03 eV. The breadth of the emission decreases as the dispersity of nanocrystal diameters decreases. Semiconductor nanocrystals can have high emission quantum efficiencies such as 25 greater than 10%, 20%, 30%, 40%, 50%, 60%, 70%, or 80%.

The semiconductor forming the nanocrystals can include a Group II-VI compound, a Group III-V compound, a Group III-VI compound, a Group III-VI compound, a Group IV-VI compound, a Group II-III-VI compound, a Group II-IV-VI 30 compound, or a Group II-IV-V compound, for example, ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, CdTe, MgO, MgS, MgSe, MgTe, HgO, HgS, HgSe, HgTe, AIN, AIP, AIAs, AISb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, TIN, TIP, TIAs, TISb, TISb, PbS, PbSe, PbTe, or mixtures thereof.

Methods of preparing monodisperse semiconductor nanocrystals include pyrolysis of organometallic reagents, such as dimethyl cadmium, injected into a hot, coordinating solvent. This permits discrete nucleation and results in the controlled growth of macroscopic quantities of nanocrystals. 40 Preparation and manipulation of nanocrystals are described, for example, in U.S. Pat. Nos. 6,322,901 and 6,576,291, and U.S. patent application Ser. No. 60/550,314, each of which is incorporated by reference in its entirety. The method of manufacturing a nanocrystal is a colloidal growth process. 45 Colloidal growth occurs by rapidly injecting an M donor and an X donor into a hot coordinating solvent. The injection produces a nucleus that can be grown in a controlled manner to form a nanocrystal. The reaction mixture can be gently heated to grow and anneal the nanocrystal. Both the average 50 size and the size distribution of the nanocrystals in a sample are dependent on the growth temperature. The growth temperature necessary to maintain steady growth increases with increasing average crystal size. The nanocrystal is a member of a population of nanocrystals. As a result of the discrete 55 nucleation and controlled growth, the population of nanocrystals obtained has a narrow, monodisperse distribution of diameters. The monodisperse distribution of diameters can also be referred to as a size. The process of controlled growth and annealing of the nanocrystals in the coordinating solvent 60 that follows nucleation can also result in uniform surface derivatization and regular core structures. As the size distribution sharpens, the temperature can be raised to maintain steady growth. By adding more M donor or X donor, the growth period can be shortened.

The M donor can be an inorganic compound, an organometallic compound, or elemental metal. M is cadmium, zinc, 6

magnesium, mercury, aluminum, gallium, indium or thallium. The X donor is a compound capable of reacting with the M donor to form a material with the general formula MX. Typically, the X donor is a chalcogenide donor or a prictide donor, such as a phosphine chalcogenide, a bis(silyl) chalcogenide, dioxygen, an ammonium salt, or a tris(silyl) pnictide. Suitable X donors include dioxygen, bis(trimethylsilyl) selenide ((TMS)₂Se), trialkyl phosphine selenides such as (tri-n-octylphosphine) selenide (TOPSe) or (tri-n-butylphosphine) selenide (TBPSe), trialkyl phosphine tellurides such as (tri-n-octylphosphine) telluride (TOPTe) or hexapropylphosphorustriamide telluride (HPPTTe), bis(trimethylsilyl)telluride ((TMS), Te), bis(trimethylsilyl)sulfide ((TMS), S), a trialkyl phosphine sulfide such as (tri-n-octylphosphine) sulfide (TOPS), an ammonium salt such as an ammonium halide (e.g., NH₄Cl), tris(trimethylsilyl) phosphide ((TMS)₃P), tris (trimethylsilyl) arsenide ((TMS)₃As), or tris(trimethylsilyl) antimonide ((TMS)₃Sb). In certain embodiments, the M donor and the X donor can be moieties within the same molecule.

A coordinating solvent can help control the growth of the nanocrystal. The coordinating solvent is a compound having a donor lone pair that, for example, has a lone electron pair available to coordinate to a surface of the growing nanocrystal. Solvent coordination can stabilize the growing nanocrystal. Typical coordinating solvents include alkyl phosphines, alkyl phosphine oxides, alkyl phosphonic acids, or alkyl phosphinic acids, however, other coordinating solvents, such as pyridines, furans, and amines may also be suitable for the nanocrystal production. Examples of suitable coordinating solvents include pyridine, tri-n-octyl phosphine (TOP), tri-n-octyl phosphine oxide (TOPO) and tris-hydroxylpropylphosphine (tHPP). Technical grade TOPO can be used.

Size distribution during the growth stage of the reaction can be estimated by monitoring the absorption line widths of the particles. Modification of the reaction temperature in response to changes in the absorption spectrum of the particles allows the maintenance of a sharp particle size distribution during growth. Reactants can be added to the nucleation solution during crystal growth to grow larger crystals. By stopping growth at a particular nanocrystal average diameter and choosing the proper composition of the semiconducting material, the emission spectra of the nanocrystals can be tuned continuously over the wavelength range of 300 nm to 5 microns, or from 400 nm to 800 nm for CdSe and CdTe. The nanocrystal has a diameter of less than 150 Å. A population of nanocrystals has average diameters in the range of 15 Å to 125 Å

The nanocrystal can be a member of a population of nanocrystals having a narrow size distribution. The nanocrystal can be a sphere, rod, disk, or other shape. The nanocrystal can include a core of a semiconductor material. The nanocrystal can include a core having the formula MX, where M is cadmium, zinc, magnesium, mercury, aluminum, gallium, indium, thallium, or mixtures thereof, and X is oxygen, sulfur, selenium, tellurium, nitrogen, phosphorus, arsenic, antimony, or mixtures thereof.

The core can have an overcoating on a surface of the core. The overcoating can be a semiconductor material having a composition different from the composition of the core: The overcoat of a semiconductor material on a surface of the nanocrystal can include a Group III-VI compound, a Group III-V compound, a Group III-VI compound, a Group IV-VI compound, a Group III-VI compound, a Group III-VI compound, a Group III-VI compound, a Group III-VV compound, for example, ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, CdTe, MgO, MgS, MgSe, MgTe, HgO, HgS, HgSe,

HgTe, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, TlN, TlP, TlAs, TlSb, TlSb, PbS, PbSe, PbTe, or mixtures thereof For example, ZnS, ZnSe or CdS overcoatings can be grown on CdSe or CdTe nanocrystals. An overcoating process is described, for example, in U.S. Pat. No. 56,322,901. By adjusting the temperature of the reaction mixture during overcoating and monitoring the absorption spectrum of the core, over coated materials having high emission quantum efficiencies and narrow size distributions can be obtained. The overcoating can be between 1 and 10 monolayers thick.

The particle size distribution can be further refined by size selective precipitation with a poor solvent for the nanocrystals, such as methanol/butanol as described in U.S. Pat. No. 6,322,901. For example, nanocrystals can be dispersed in a 15 solution of 10% butanol in hexane. Methanol can be added dropwise to this stirring solution until opalescence persists. Separation of supernatant and flocculate by centrifugation produces a precipitate enriched with the largest crystallites in the sample. This procedure can be repeated until no further 20 sharpening of the optical absorption spectrum is noted. Sizeselective precipitation can be carried out in a variety of solvent/nonsolvent pairs, including pyridine/hexane and chloroform/methanol. The size-selected nanocrystal population can have no more than a 15% rms deviation from mean diameter, 25 absorption spectrum. preferably 10% rms deviation or less, and more preferably 5% rms deviation or less.

The outer surface of the nanocrystal can include compounds derived from the coordinating solvent used during the growth process. The surface can be modified by repeated 30 is described below. exposure to an excess of a competing coordinating group. For example, a dispersion of the capped nanocrystal can be treated with a coordinating organic compound, such as pyridine, to produce crystallites which disperse readily in pyridine, methanol, and aromatics but no longer disperse in ali- 35 phatic solvents. Such a surface exchange process can be carried out with any compound capable of coordinating to or bonding with the outer surface of the nanocrystal, including, for example, phosphines, thiols, amines and phosphates. The nanocrystal can be exposed to short chain polymers which 40 exhibit an affinity for the surface and which terminate in a moiety having an affinity for a suspension or dispersion medium. Such affinity improves the stability of the suspension and discourages flocculation of the nanocrystal. Nanocrystal coordinating compounds are described, for example, in 45 U.S. Pat. No. 6,251,303, which is incorporated by reference in its entirety.

More specifically, the coordinating ligand can have the formula:

$$(Y \xrightarrow{)_{k-n}} X \xrightarrow{-(-L)_n}$$

wherein k is 2, 3 or 5, and n is 1, 2, 3, 4 or 5 such that k-n is not less than zero; X is O, S, S=O, SO₂, Se, Se=O, N, N=O, P, P=O, As, or As=O; each of Y and L, independently, is aryl, heteroaryl, or a straight or branched C_{2-12} hydrocarbon chain optionally containing at least one double bond, at least one triple bond, or at least one double bond and one triple bond. The hydrocarbon chain can be optionally substituted with one or more C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{1-4} alkoxy, hydroxyl, halo, amino, nitro, cyano, C_{3-5} cycloalkyl, 3-5 membered heterocycloalkyl, aryl, heteroaryl, C_{1-4} alkylcarbonyloxy, C_{1-4} alkyloxycarbonyl, C_{1-4} alkylcarbonyl, or 65 formyl. The hydrocarbon chain can also be optionally interrupted by -O—, -S—, $-N(R^a)$ —, $-N(R^a)$ —C(O)—

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O—, —O—C(O)— $N(R^a)$ —, — $N(R^a)$ —C(O)— $N(R^b)$ —, —O—C(O)—O—, — $P(R^a)$ —, or — $P(O)(R^a)$ —. Each of R^a and R^b , independently, is hydrogen, alkyl, alkenyl, alkynyl, alkoxy, hydroxylalkyl, hydroxyl, or haloalkyl.

An aryl group is a substituted or unsubstituted cyclic aromatic group. Examples include phenyl, benzyl, naphthyl, tolyl, anthracyl, nitrophenyl, or halophenyl. A heteroaryl group is an aryl group with one or more heteroatoms in the ring, for instance furyl, pyiridyl, pyrrolyl, phenanthryl.

A suitable coordinating ligand can be purchased commercially or prepared by ordinary synthetic organic techniques, for example, as described in J. March, *Advanced Organic Chemistry*, which is incorporated by reference in its entirety.

Transmission electron microscopy (TEM) can provide information about the size, shape, and distribution of the nanocrystal population. Powder X-ray diffraction (XRD) patterns can provide the most complete information regarding the type and quality of the crystal structure of the nanocrystals. Estimates of size are also possible since particle diameter is inversely related, via the X-ray coherence length, to the peak width. For example, the diameter of the nanocrystal can be measured directly by transmission electron microscopy or estimated from X-ray diffraction data using, for example, the Scherrer equation. It also can be estimated from the UV/V is absorption spectrum.

Example

One example of an optical structure including nanocrystals is described below

A conventional 0.5 mm plastic fiber optic element was stripped of its sheath and cladding. The cladding was removed by soaking the fiber in acetone and wiping the fiber to remove the dissolved cladding material. Red luminescent semiconductor nanocrystals (quantum dots) in an ethanol solution were then applied to the exterior of the stripped fiber. The nanocrystal layer was allowed to dry. A conventional fiber optic end-coupled 475 nm light emitting diode was then attached to the fiber and turned on. FIG. 3 shows the spectrum of light emitted from the fiber. It is clear from the spectrum that the evanescent wave couples to the nanocrystals, which then emitted red light. Some of the excitation light was also emitted from the fiber, likely because of the surface roughness of the fiber that scatters the fiber-guided blue light. FIG. 4 shows a photograph of the light emitting structure. Red light from the evanescent wave coupled nanocrystals is easily visible.

Other embodiments are within the scope of the following claims.

The invention claimed is:

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- 1. An optical structure comprising a nanocrystal on a surface of an optical waveguide, the nanocrystal being positioned to be optically coupled to an optical field propagating through the optical waveguide and emit light from the surface of the waveguide, wherein the optical waveguide is tuned to select the amount of excitation wavelength the nanocrystal encounters, wherein the intensity of the excitation wavelength propagating through the optical waveguide that each nanocrystal in the plurality of nanocrystals encounters is determined by the position of each nanocrystal on the surface of the optical waveguide.
- 2. The optical structure of claim 1, wherein the waveguide is an optical fiber.
- 3. The optical structure of claim 1, wherein the waveguide is a planar waveguide.
- **4**. The optical structure of claim **1**, wherein the nanocrystal is a semiconductor nanocrystal.

- 5. The optical structure of claim 2, wherein the optical fiber has a cladding layer that allows light to escape at a selected amount along the length of the fiber.
- 6. The optical structure of claim 4, wherein the semiconductor nanocrystal includes a core including a first semiconductor material.
- 7. The optical structure of claim 6, wherein the semiconductor nanocrystal includes an overcoating on a surface of the core including a second semiconductor material.
- 8. The optical structure of claim 1, further comprising a 10 plurality of nanocrystals distributed at a first portion of the surface.
- 9. The optical structure of claim 8, further comprising a plurality of nanocrystals distributed at a second portion of the surface.
- 10. The optical structure of claim 9, wherein the plurality of nanocrystals distributed at the first portion of the surface has a composition different from the plurality of nanocrystals distributed at the second portion of the surface.
 - 11. A light emitting structure comprising:
 - a light source arranged to introduce light including an excitation wavelength into an optical waveguide; and
 - a nanocrystal on a surface of the optical waveguide, the nanocrystal being positioned to be optically coupled to an optical field propagating through the optical 25 waveguide and capable of absorbing the excitation wavelength of light and emitting an emission wavelength of light and emit light from the surface of the waveguide, wherein the optical waveguide is tuned to select the amount of excitation wavelength the nanoc- 30 rystal encounters, wherein the intensity of the excitation wavelength propagating through the optical waveguide that each nanocrystal in the plurality of nanocrystals encounters is determined by the position of each nanocrystal on the surface of the optical waveguide.
- **12**. The light emitting structure of claim **11**, wherein the waveguide is an optical fiber.
- 13. The light emitting structure of claim 11, wherein the waveguide is a planar waveguide.
- 14. The light emitting structure of claim 11, wherein the 40 nanocrystal is a semiconductor nanocrystal.
- 15. The light emitting structure of claim 12, wherein the optical fiber has a cladding layer that allows light to escape at a selected amount along the length of the fiber.
- **16**. The light emitting structure of claim **14**, wherein the 45 semiconductor nanocrystal includes a core including a first semiconductor material.
- 17. The light emitting structure of claim 16, wherein the semiconductor nanocrystal includes an overcoating on a surface of the core including a second semiconductor material. 50
- 18. The light emitting structure of claim 11, further comprising a plurality of nanocrystals distributed at a first portion of the surface.
- 19. The light emitting structure of claim 18, further comprising a plurality of nanocrystals distributed at a second 55 the surface of the optical waveguide prior to placing the portion of the surface.
- 20. The light emitting structure of claim 19, wherein the plurality of nanocrystals distributed at the first portion of the surface has a composition different from the plurality of nanocrystals distributed at the second portion of the surface. 60
 - 21. A method of producing light comprising:
 - introducing light from a light source including an excitation wavelength into an optical waveguide, the excitation wavelength propagating through the optical waveguide and optically coupling to a nanocrystal on a 65 surface of the optical waveguide and emit light from the surface of the waveguide, the nanocrystal absorbing the

excitation wavelength and emitting an emission wavelength from the surface, and tuning the optical waveguide to select the amount of excitation wavelength the nanocrystal encounters, wherein the intensity of the excitation wavelength propagating through the optical waveguide that each nanocrystal in the plurality of nanocrystals encounters is determined by the position of each nanocrystal on the surface of the optical waveguide.

- 22. The method of claim 21, wherein the waveguide is an optical fiber.
- 23. The method of claim 21, wherein the nanocrystal is a semiconductor nanocrystal.
- 24. The method of claim 21, further comprising modifying the surface of the optical waveguide to increase coupling between the optical field and the nanocrystal to allow light to escape at a selected amount at selected locations.
- 25. The method of claim 21, wherein the semiconductor 20 nanocrystal includes a core including a first semiconductor material.
 - 26. The method of claim 21, wherein the excitation wavelength propagates through the optical waveguide and optically couples to a plurality of nanocrystals on a first portion of a surface of the optical waveguide.
 - 27. The method of claim 26, wherein the excitation wavelength propagates through the optical waveguide and optically couples to a plurality of nanocrystals on a second portion of the surface.
 - 28. The light emitting structure of claim 27, wherein the plurality of nanocrystals distributed at the first portion of the surface has a composition different from the plurality of nanocrystals distributed at the second portion of the surface.
- 29. The light emitting structure of claim 27, wherein the 35 plurality of nanocrystals distributed at the first portion of the surface has an emission wavelength different from the plurality of nanocrystals distributed at the second portion of the
 - 30. A method of making an optical structure comprising: placing a nanocrystal on a surface of an optical waveguide in a position to optically couple the nanocrystal to an optical field propagating through the optical waveguide and emit light from the surface of the waveguide, and tuning the optical waveguide to select the amount of excitation wavelength the nanocrystal encounters, wherein the intensity of the excitation wavelength propagating through the optical waveguide that each nanocrystal in the plurality of nanocrystals encounters is determined by the position of each nanocrystal on the surface of the optical waveguide.
 - 31. The method of claim 30, wherein placing includes dip coating, drop coating, spin coating, painting or printing the nanocrystal on the surface.
 - 32. The method of claim 30, further comprising processing nanocrystal.
 - 33. An optical structure comprising a nanocrystal on a surface of an optical waveguide, the nanocrystal being positioned to be optically coupled to an optical field propagating through the optical waveguide and emit light from the surface of the waveguide, a plurality of nanocrystals distributed at a first portion of the surface, and a plurality of nanocrystals distributed at a second portion of the surface, wherein the optical waveguide is tuned to select the amount of excitation wavelength the nanocrystal encounters, wherein the intensity of the excitation wavelength propagating through the optical waveguide that each nanocrystal in the plurality of nanocrys-

tals encounters is determined by the position of each nanocrystal on the surface of the optical waveguide.

- **34**. The optical structure of claim **33**, wherein the plurality of nanocrystals distributed at the first portion of the surface has a composition different from the plurality of nanocrystals distributed at the second portion of the surface.
 - **35**. A light emitting structure comprising:
 - a light source arranged to introduce light including an excitation wavelength into an optical waveguide; and
 - a nanocrystal on a surface of the optical waveguide, the nanocrystal being positioned to be optically coupled to an optical field propagating through the optical waveguide and capable of absorbing the excitation wavelength of light and emitting an emission wavelength of light and emit light from the surface of the waveguide, a plurality of nanocrystals distributed at a first portion of the surface, and a plurality of nanocrystals distributed at a second portion of the surface, wherein the optical waveguide is tuned to select the amount of excitation wavelength the nanocrystal encounters, wherein the intensity of the excitation wavelength propagating through the optical waveguide that each nanocrystal in the plurality of nanocrystals encounters is determined by the position of each nanocrystal on the surface of the optical waveguide.

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- **36**. The optical structure of claim **34**, wherein the plurality of nanocrystals distributed at the first portion of the surface has a composition different from the plurality of nanocrystals distributed at the second portion of the surface.
- **37**. The optical structure of claim **1**, wherein light not absorbed by the nanocrystal continues circling the waveguide.
- **38**. The light emitting structure of claim **11**, wherein light not absorbed by the nanocrystal continues circling the waveguide.
- **39**. The method of producing light in claim **21**, wherein light not absorbed by the nanocrystal continues circling the waveguide.
- **40**. The method of making an optical structure of claim **30**, wherein light not absorbed by the nanocrystal continues circling the waveguide.
- **41**. The optical structure of claim **33**, wherein light not absorbed by the nanocrystal continues circling the waveguide.
- **42**. The light emitting structure of claim **35**, wherein light not absorbed by the nanocrystal continues circling the waveguide.

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