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(71) Applicant (for all designated States except US): **MASSACHUSETTS INSTITUTE OF TECHNOLOGY** [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02142-1324 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HALPERT, Jonathan, E.** [US/US]; 12 Beech Street, Apt. 2, Cambridge, MA 02140 (US). **BAWENDI, Mounqi, G.** [US/US]; 17 Lowell Street, Cambridge, MA 02138 (US). **PORTER, Venda, Jane** [US/US]; 42 Fulkerson Street, Cambridge, MA 02141 (US).

(74) Agents: **FOX, Harold, H.** et al.; Steptoe & Johnson LLP, 1330 Connecticut Avenue, NW, Washington, DC 20036 (US).

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(54) Title: SEMICONDUCTOR NANOCRYSTAL HETEROSTRUCTURES

(57) Abstract: A semiconductor nanocrystal can have a barbell shape. The nanocrystal can include two semiconductor materials selected so that upon excitation, one charge carrier is substantially confined to the one semiconductor material and the other charge carrier is substantially confined to the other semiconductor material.



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SEMICONDUCTOR NANOCRYSTAL HETEROSTRUCTURES

TECHNICAL FIELD

The invention relates to semiconductor nanocrystal heterostructures.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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BACKGROUND

Nanocrystals having small dimensions can have properties intermediate between molecular and bulk forms of matter. For example, nanocrystals of semiconductor materials having sufficiently small dimensions can exhibit quantum confinement of excitons (excited state electron-hole pair) in all three dimensions. Quantum confinement 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 (i.e., to higher energies) as the size of the nanocrystal decreases.

The quantum efficiency of emission from nanocrystals having a core of a first semiconductor material can be enhanced by applying an overcoating of a second semiconductor material such that the conduction band of the second semiconductor material is of higher energy than that of the first semiconductor material, and the valence band of the second semiconductor material is of lower energy than that of the first semiconductor material. As a result, both charge carriers of an exciton, i.e., electrons and holes, are confined in the core of the nanocrystal.

SUMMARY OF THE INVENTION

In general, a semiconductor nanocrystal heterostructure has a first semiconductor material adjacent to a second semiconductor material. The first semiconductor material and second semiconductor material are selected so that, upon excitation, one carrier is substantially confined to the first material and the other carrier is substantially confined to the second material. In one example, the conduction band of the first semiconductor

material is at higher energy than the conduction band of the second semiconductor material and the valence band of the first semiconductor material is at higher energy than the valence band of the second semiconductor material. In another example, the conduction band of the first semiconductor material is at lower energy than the conduction band of the second semiconductor material and the valence band of the first semiconductor material is at lower energy than the valence band of the second semiconductor material. These band alignments make spatial separation of carriers, i.e. the hole and the electron, energetically favorable upon excitation. These structures are type II heterostructures. In contrast, in a type I heterostructure the conduction band of the second semiconductor material is of higher energy than that of the first semiconductor material, and the valence band of the second semiconductor material is of lower energy than that of the first semiconductor material. Type I heterostructure nanocrystals favor confinement of both the hole and the electron in the first semiconductor material.

Nanocrystals having type II heterostructures have advantageous properties that result of the spatial separation of carriers. In some nanocrystals having type II heterostructures the effective band gap, as measured by the difference in the energy of emission and energy of the lowest absorption features, can be smaller than the band gap of either of the two semiconductors making up the structure. By selecting particular first semiconductor materials and second semiconductor materials, nanocrystal shapes and dimensions (such as core diameter and overcoating thickness for core/shell nanocrystals), nanocrystals having type II heterostructures can have emission wavelengths, such as infrared wavelengths, that are otherwise unavailable with a given semiconductor material in other structures. In addition, the spatial separation of charges in the lowest excited states of nanocrystals having type II heterostructures can make these materials more efficient in photovoltaic or photoconduction devices where the nanocrystals are chromophores and one of the carriers needs to be transported away from the excitation site prior to recombination.

Advantageously, a wide variety of nanocrystals having type II heterostructures can be prepared using colloidal synthesis. Colloidal synthesis allows nanocrystals to be prepared with controllable dispersibility imparted from coordinating agents. The nanocrystal can have a barbell shape which can pack densely in a film compared to other nanocrystal shapes, and does not enclose charge carriers inside a shell.

In one aspect, a semiconductor nanocrystal includes a central region and a first end, the central region including a first semiconductor material, and a distal region at the first end of the rod, the distal region including a second semiconductor material. The first semiconductor material and the second semiconductor material are selected so that, upon
5 excitation, one charge carrier is substantially confined to the central region and the other charge carrier is substantially confined to the distal region.

The nanocrystal can include a second distal region at a second end of the central region. The central region can be rod-shaped. The distal regions can each be approximately spherical, or rod-shaped. The nanocrystal can have a length ratio of, of
10 between 0.1 and 0.5, or of between 0.2 and 0.9. The nanocrystal can have a radius ratio of between 0.1 and 10, or of between 0.3 and 3.5. The nanocrystal can include an overcoating of a third semiconductor material.

The first semiconductor material can be a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI
15 compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound. The first semiconductor material can be 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, TiN, TiP, TiAs, TiSb, PbS, PbSe, PbTe, or a mixture thereof.

The second semiconductor material can be a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI
20 compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound. The second semiconductor material can be 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, TiN, TiP, TiAs, TiSb, PbS, PbSe, PbTe, or a mixture thereof.

In another aspect, a method of making a nanocrystal includes forming a semiconductor nanocrystal having a central region and a first end, the central region including a first semiconductor material, and contacting the semiconductor nanocrystal
30 with an M donor and an X donor at a temperature sufficient to cap the first end with a second semiconductor material, thereby forming a capped semiconductor nanocrystal having a central region including the first semiconductor material and a distal region including the second semiconductor material. The first semiconductor material and the

second semiconductor material are selected so that, upon excitation, one charge carrier is substantially confined to the central region and the other charge carrier is substantially confined to the distal region.

The method can include contacting the semiconductor nanocrystal with an etching agent before contacting the semiconductor nanocrystal with the M donor and the X donor. Contacting the semiconductor nanocrystal with an M donor and an X donor at a temperature sufficient to cap the first end with a second semiconductor material can also be sufficient to cap the second end with the second semiconductor material.

The method can include selecting a coordinating solvent and a temperature to influence a shape of a distal region. The coordinating solvent and the temperature can be selected to form an approximately spherical distal region. The method can include overcoating the nanocrystal with a third semiconductor material.

In another aspect, a photovoltaic device includes a first electrode, a second electrode, a voltage source configured to apply a voltage across the first electrode and the second electrode, and an active layer in electrical communication with the first electrode and the second electrode. The active layer includes a population of semiconductor nanocrystals. Each semiconductor nanocrystal of the population has a central region and a first end, the central region including a first semiconductor material, and a distal region at the first end of the rod, the distal region including a second semiconductor material. The first semiconductor material and the second semiconductor material are selected so that, upon excitation, one charge carrier is substantially confined to the central region and the other charge carrier is substantially confined to the distal region.

In the device, the population of semiconductor nanocrystals can substantially aligned. The first electrode and the second electrode can be parallel. The population of semiconductor nanocrystals can be substantially aligned with an alignment direction substantially perpendicular to the first electrode and the second electrode. The nanocrystal can include an overcoating of a third semiconductor material.

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

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A-1C are schematic depictions of nanocrystals.

FIGS. 2A-2D are transmission electron microscope images of semiconductor nanocrystals.

FIG. 3 is a schematic graph depicting band gap structure of a semiconductor nanocrystal.

FIGS. 4A-4B are graphs depicting optical properties of semiconductor nanocrystals.

FIG. 5A is a STEM image of a semiconductor nanocrystal. FIGS. 5B-5C are graphs depicting electron energy loss data measurements on the semiconductor nanocrystal.

FIG. 6 is a graph depicting electrical measurements on semiconductor nanocrystals.

DETAILED DESCRIPTION

Colloidal synthesis of nanocrystals can be used to manufacture nanocrystals that have type II heterostructures. Colloidal synthesis is described, for example, in Murray, C.B., et al., J. Am. Chem. Soc. 1993, 115, 8706, Peng, X., et al., J. Am. Chem. Soc. 1997, 119, 7019, Dabbousi, B.O., et al., J. Phys. Chem. B 1997, 101, 9463, and Cao, Y.W. and Banin, U., Angew. Chem. Int. Edit. 1999, 38, 3692, each of which is incorporated by reference in its entirety. The colloidal synthetic route can be applied to any II-VI and III-V semiconductor materials. Colloidal synthesis as applied to type II heterostructure semiconductor nanocrystals is described in U.S. Patent Application Publication No. 2004/0110002, which is incorporated by reference in its entirety.

Upon excitation of a nanocrystal having a type II heterostructure, the carriers are not confined in one semiconductor material. A nanocrystal having a type II heterostructure includes a first semiconductor material adjacent to a second semiconductor material. One carrier can become confined to the first semiconductor material, while the other is mostly confined to the second semiconductor material. The relative location of the carriers can depend on the materials in the core and the shell. The band offsets of the two semiconductor materials can make spatial separation of the hole and the electron energetically favorable. See, e.g., U.S. Patent Application Publication No. 2004/0110002, which is incorporated by reference in its entirety. Nanocrystals having type II heterostructures can have advantageous properties because of the spatial separation of carriers, which does not occur in nanocrystals having type I

heterostructures. For example, nanocrystals having type II structures can access emission wavelengths (i.e. wavelengths of maximum emission intensity) that would not otherwise be available with the semiconductors making up the nanocrystal.

A semiconductor nanocrystal can have an approximately spherical shape, as illustrated (in cross-section) in FIG. 1A. Semiconductor nanocrystal 100 includes core 110 of a first semiconductor material. Core 110 is optionally overcoated by a second semiconductor material 120. Ligand layer 130 includes organic compounds with affinity for a semiconductor nanocrystal surface. The organic compounds can be selected for desired properties, such as solubility in a desired solvent or a desired reactivity. FIG. 1B depicts a side view of a rod-shaped semiconductor nanocrystal 150. Semiconductor nanocrystal 150 includes first semiconductor material 160. For simplicity, the ligand layer on semiconductor nanocrystal 150 has been omitted from FIG. 1B. FIG. 1C depicts barbell-shaped semiconductor nanocrystal 200. Barbell-shaped semiconductor nanocrystals can also be described as dumbbell-shaped, or as nanobarbells or nanodumbbells. Nanocrystal 200 includes a central region 160 including first semiconductor material, and distal regions 170 including a second semiconductor material. Nanocrystal 200 can be prepared by adding a second semiconductor material to the ends of rod-shaped nanocrystal 150. FIG. 1C is a schematic depiction of nanocrystals with two substantially similar distal regions at each end of a rod-shaped central region. Alternatively, nanocrystals can be prepared where only one end of a rod-shaped nanocrystal is modified with a second semiconductor material. Distal regions 170 can be approximately spherical ("dots") or approximately rod-shaped as shown in FIG. 1C. Nanocrystal 200 can be referred as barbell shaped whether the distal regions are approximately spherical or rod-shaped. If distal regions 170 are rod-shaped, distal regions 170 can have approximately the same diameter as the central region. In either case, a nanocrystal having a central region and a distal region (or regions) can be described by a length ratio. The length ratio can be defined as the length of the central region divided by the total length of the nanocrystal. When referring to a population of nanocrystals, a length ratio can be an aggregate length ratio for the population (e.g., a mean length ratio, median length ratio, or rms length ratio for the population). The central region can have length in the range of 3 nm to 100 nm (such as between 5 nm and 40 nm), and the distal region can have a radius in the range of 1 nm to 10 nm (such as

between 1.5 nm and 5 nm). Accordingly, the nanocrystal can have a length ratio in the range of 0.1 to 0.95 (such as between 0.2 and 0.9).

A nanocrystal having a central region and a distal region (or regions) can be described by a radius ratio. The radius ratio can be defined as the ratio of the radius of the distal region to the radius of the central region. The central region can have a radius in the range of 1 nm to 7 nm (such as between 1.5 nm and 5 nm), and the distal regions can have a radius in the range of 1 nm to 10 nm (such as between 1.5 nm and 5 nm). Accordingly, a barbell-shaped nanocrystal can have a radius ratio in the range of 0.1 to 10 (such as between 0.3 and 3.5). In some embodiments the radius ratio can be about 1. In other embodiments it can be substantially different than about 1, such as, for example, between 0.1 and 0.95 or between 1.05 and 10.

Spatial separation of the carriers in type II nanocrystals suggests poor overlap between the electron and hole wavefunctions. As a result, the quantum efficiency of photoluminescence can be lower for type II nanocrystals than for type I nanocrystals. See, e.g., U.S. Patent Application Publication No. 2004/0110002, which is incorporated by reference in its entirety. The emission from nanocrystals having type II structures originates from the radiative recombination of the carriers across the interface of the different semiconductor materials. Therefore, the energy of the emission depends on the band offsets, which are controlled by the semiconductor materials and sizes (e.g., for core/shell nanocrystals, the core diameter and shell thickness). Type II nanocrystals can have a smaller effective bandgap, and therefore emit at longer wavelengths, than nanocrystals composed of either the core or shell material in the type II nanocrystal. The nanocrystals having type II structures can be considered to have quasi-indirect, or virtual, bandgaps whose energies are determined by the band offsets. The effective bandgap can be engineered in such structures, since many possible combinations of semiconductor materials can be used to tailor the virtual bandgaps.

Quantum efficiency in nanocrystals having type II structures can be increased by adding additional semiconductor materials to the nanocrystals. For example, a second coating of ZnTe can be added to a CdTe/CdSe (core/shell) nanocrystal to increase the quantum efficiency to as high as 20%. The overcoating procedure can be similar to the CdSe/ZnTe (core/shell) nanocrystal shell preparation. The enhanced quantum efficiency is thought to originate from the increased carrier wavefunction overlap induced by the mismatched bandgaps. For increased quantum efficiency, it can be important for the first

coating and second coating to have a mismatched band offset. For example, when a second coating of ZnS was deposited on CdTe/CdSe (core/shell) nanocrystals, the emission was red-shifted, but the quantum efficiency decreased. Although ZnS layers can help passivate the CdSe shell layer surface, the effect was overwhelmed by the decreased wavefunction overlaps due to the electron wavefunction leakage into the ZnS layers.

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 first semiconductor material. The nanocrystal can include a first semiconductor material 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 first semiconductor material can include a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, a Group II-IV-V compound, or mixtures thereof. For example, the first semiconductor material can include 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, TiN, TiP, TiAs, TiSb, PbS, PbSe, PbTe, or mixtures thereof.

The nanocrystal can include a second semiconductor material. The second semiconductor material can have a composition different from the composition of the first semiconductor material. The first and second semiconductor materials can be selected to provide a desired band structure, such as a type I or a type II heterostructure. The second semiconductor material can be adjacent to the first semiconductor material, such that a junction is formed. The junction can be abrupt or graded. In a graded junction, the first material blends with the second material in the junction, providing a graded change in material. In contrast, in an abrupt junction there is little or substantially no blending of the materials.

The junction between two semiconductor materials can have different configurations depending on the shape of the nanocrystal. For example, a spherical nanocrystal can have a spherical core of a first semiconductor material coated with a shell of a second semiconductor material. A rod shaped nanocrystal can have a rod of a first semiconductor material and a second semiconductor material. The second semiconductor material can coat the length and ends of the rods substantially evenly. Alternatively, the

length and ends of the rod can be coated to different degrees. In particular the ends of the rod can be coated to a greater degree than the length of the rod. The ends of the rod each can be coated by an approximately spherical region of a second semiconductor material. In this case, the nanocrystal can have a barbell shape.

5 The second semiconductor material of the nanocrystal can include a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, a Group II-IV-V compound, or mixtures thereof. For example, the second semiconductor material can include ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, CdTe, MgO, MgS, MgSe,
10 MgTe, HgO, HgS, HgSe, HgTe, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, TiN, TiP, TiAs, TiSb, PbS, PbSe, PbTe, or mixtures thereof. For example, ZnS, ZnSe or CdS overcoatings can be grown on CdSe or CdTe nanocrystals.

 The emission from the nanocrystal can be a narrow Gaussian emission band that can be tuned through the complete wavelength range of the ultraviolet, visible, or infrared
15 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 population of nanocrystals can have a narrow size distribution. The population can be monodisperse and can exhibit less than a 15% rms deviation in size of
20 the nanocrystals, preferably less than 10%, more preferably less than 5%. Spectral emissions in a narrow range of between 10 and 150 nm full width at half max (FWHM) can be observed (in other words, FWHM of less than 0.05 eV, or of less than 0.03 eV). Semiconductor nanocrystals having type II structures can have emission quantum efficiencies of greater than 2%, 5%, 10%, 20%, 40%, 60%, 70%, or 80%.

25 The absorption spectra of nanocrystals having type II heterostructures can feature smoothly increasing absorptions to the shorter wavelength region and long tails to the longer wavelength regions. The precise shape of the spectra can depend on the semiconductor materials in the nanocrystal, their geometry (e.g., spherical core/shell or barbell) and the amounts of each material. Nanocrystals having type II structures can
30 have indirect band characteristics with spatially indirect excitons. Nanocrystals having type II structures can have relatively weak oscillator strength since the oscillator strengths are strongly governed by the carrier wavefunction overlaps. See, for example, Laheld,

U.E.H., et al., *Phys. Rev. B* **1995**, 52:2697, and Morrison, J.M., *Phys. Rev. B* **1993**, 48:4643, each of which is incorporated by reference in its entirety.

Nanocrystals that promote spatial separation of excited state charge carriers can be advantageous in photovoltaic devices. The spatial separation can allow a lower applied
5 voltage to separate charge carriers in the device. Previous studies have produced type II structures such as spherical CdTe/CdSe core/shell nanocrystals and CdSe tetrapods having CdTe branches. See, e.g., Kim, S. et al., *J. Am. Chem. Soc.* **2003**, 125, 11466-11467, U.S. Patent Application No. 2004/0110002, and Milliron, D. et al., *Nature* **2004**, 430,190-195, each of which is incorporated by reference in its entirety. However,
10 spherical core/shell and tetrapodal type II heterostructures have disadvantages with regards to use in a photovoltaic device, even though these structures spatially separate the exciton within the nanocrystal. In each case, the charge carriers cannot easily move towards the electrodes in order to generate sizeable currents: tetrapods cannot pack tightly, and therefore leave empty space when deposited into a film, and core/shell
15 particles trap one of the carriers in the core.

Unlike other type II heterostructure nanocrystals, type II nanobarbells spatially separate exciton charge carriers, and the rod-like nanocrystals can pack tightly into a film. Tightly packed nanocrystals increase the number of photons which can be absorbed by a film and reduce the tunnel barrier for charge tunneling from one nanocrystal to the next,
20 facilitating charge movement from the site of exciton generation to the electrodes of a photovoltaic device.

Charge transport in nanocrystal films is generally limited by a carrier tunneling mechanism (see, for example, Drndic, M., et al., *Journal of Applied Physics*, **2002**, 92, 7498-7503; Jarosz, M.V., et al., *Physical Review B*, **2004**, 70, 195327; and Leatherdale, C.A., et al., *Physical Review B* **2000**, 62, 2669-2680, each of which is incorporated by
25 reference in its entirety). Consequently, obtaining good conductivity and high photocurrent requires minimizing the distance between adjacent particles, such as by forming close-packed films. The desirability of close-packed films illustrates the need for well formed, monodisperse rodlike nanocrystals.

30 The method of manufacturing a nanocrystal is a colloidal growth process and can produce a monodisperse particle population. Colloidal growth occurs by rapidly injecting an M donor and an X donor into a hot coordinating agent. 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 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. Preparation and manipulation of nanocrystals are described, for example, in U.S. Patent No. 6,322,901, which is incorporated by reference in its entirety.

The nanocrystal is a member of a population of nanocrystals. As a result of the discrete nucleation and controlled growth, the population of nanocrystals obtained has a narrow, monodisperse distribution of sizes. The process of controlled growth and annealing of the nanocrystals in the coordinating agent 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. The inorganic compound can be a salt. The salt can be combined with a coordinating agent, such as an amine. See, for example, U.S. Patent No. 6,576,291, which is incorporated by reference in its entirety. M is cadmium, zinc, 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 pnictide 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)₂Te), bis(trimethylsilyl)sulfide ((TMS)₂S), 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 agent can help control the growth of the nanocrystal. The coordinating agent 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. The coordinating agent can be a solvent. Solvent coordination can stabilize the growing nanocrystal. Typical coordinating agents include alkyl phosphines, alkyl phosphine oxides, alkyl phosphonic acids, or alkyl phosphinic acids, however, other coordinating agents, such as pyridines, furans, and amines may also be suitable for the nanocrystal production. Examples of suitable coordinating agents include pyridine, tri-n-octyl phosphine (TOP) and tri-n-octyl phosphine oxide (TOPO). Technical grade TOPO can be used.

Nanocrystal shape can be determined by synthesis conditions, notably by the coordinating solvent(s) present during nanocrystal synthesis. The nanocrystal can be a sphere, rod, disk, or other shape. See, e.g., U.S. Patent Nos. 6,225,198; 6,306,736; and 6,855,202, each of which is incorporated by reference in its entirety. Nanocrystal shape can be further controlled by the conditions under which a second semiconductor material is added to the nanocrystal.

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 size, a population having a desired average nanocrystal size can be obtained. For example, a population of rod-shaped nanocrystals can have an average length of between 3 nm and 100 nm, such as between 5 nm and 40 nm. The population can have an average radius of between 1 nm and 10 nm, such as between 1.5 nm and 5 nm.

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. Patent No. 6,322,901, incorporated herein by reference in its entirety. For example, nanocrystals can be dispersed in a 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 sharpening of the optical absorption spectrum is noted. Size-selective 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 size, preferably 10% rms deviation or less, and more preferably 5% rms deviation or less.

5 The outer surface of the nanocrystal can include a layer of compounds derived from the coordinating agent used during the growth process. The surface can be modified by repeated exposure to an excess of a competing coordinating group to form an overlayer. For example, a dispersion of the 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 aliphatic solvents. Such a
10 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 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
15 stability of the suspension and discourages flocculation of the nanocrystal.

A cap including a second semiconductor material can be added to the nanocrystal. An capping process is described, for example, in U.S. Patent No. 6,322,901, which is incorporated by reference in its entirety. By adjusting the temperature of the reaction mixture during capping and monitoring the absorption spectrum of the core, capped
20 materials having high emission quantum efficiencies and narrow size distributions can be obtained. The shape of the cap can depend on the shape of the initial nanocrystal and the capping conditions used. For example, a cap grown on an approximately spherical nanocrystal can also be approximately spherical. In this case, the cap can substantially coat the spherical nanocrystal. If the initial nanocrystal is rod-shaped, the cap can be
25 grown primarily on the ends of the rod and very little of the second semiconductor material added along the axis of the rod. A rod-shaped nanocrystal can be capped with a rod-shaped cap, or with an approximately spherical cap. Capping conditions, such as solvent composition and temperature, can determine the shape of the cap. For example, when caps are added under conditions that favor rod-shaped growth, rod-shaped caps can
30 be formed; in contrast, approximately spherical caps are formed when the capping conditions favor approximately spherical growth.

It can be advantageous to purify semiconductor nanocrystals before a second semiconductor material is added to the nanocrystal. As discussed above, the nanocrystals

can be purified by size-selective precipitation. After purification the nanocrystals can be treated with an etching agent. The etching agent can reduce the number of defect sites on the nanocrystals. Defect sites can act as undesired nucleation sites during addition of a second semiconductor nanocrystal. In making barbell-shaped nanocrystals, nucleation is desired at the ends of rods, but defect sites can cause nucleation along the length of a rod. Because the etching agent reduces the number of defect sites, the resulting barbells will have fewer defects along the length of the rods than barbells prepared without a prior etching treatment. The etching agent can be an amine, such as a primary amine, e.g., octylamine. An etching agent can be included during addition of a second semiconductor material to a nanocrystal.

Two-pot synthesis of barbell-shaped nanocrystals can improve (compared to one-pot synthesis) the quality of the heterojunction by minimizing contamination of the dot material with rod material. Adding the dots at temperatures normally used for core growth (rather than nucleation) can reduce overcoating of the rod (e.g., along the length of the rod) by the second semiconductor material.

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/Vis absorption spectrum.

Examples

CdSe rods were synthesized by heating cadmium oxide (CdO), octadecylphosphonic acid (ODPA) and trioctylphosphine oxide (TOPO) to 300 °C until solution is clear, heating to 320 °C and injecting a solution of toluene, trioctylphosphine (TOP) and trioctylphosphine selenide (TOP-Se), and growing the rods at 260 °C for fifteen minutes, as adapted from previously reported methods. See, for example, Peng, Z. et al., *J. Am. Chem. Soc.*, **2002**, *124*, 3343-3353; and Peng, Z., et al., *J. Am. Chem. Soc.*, **2001**, *123*, 1389-1395, each of which is incorporated by reference in its entirety. The rods were then precipitated from solution twice by adding methanol/butanol, centrifuging

the solution at 3900 RPM and redispersing in hexane. After the second precipitation rods were redispersed in hexane with a few drops of octylamine and allowed to sit for several days until a significant increase in quantum yield occurred. Rods were then precipitated as above, redispersed in hexane and filtered.

5 To create CdSe/CdTe nanobarbells, a pot of TOPO, hexadecylamine (HDA) and hexylphosphonic acid (HPA) were degassed at 140 °C then cooled to 80 °C, at which time rods dispersed in hexane are added to the pot, and the hexane pulled off under vacuum. Meanwhile a solution of cadmium 2,4-pentadionate, 1,2-hexadecanediol, and TOP was degassed at 110 °C in a separate flask. After degassing the solution was cooled and
10 trioctylphosphine telluride (TOP-Te) was added to the flask, the contents of which were transferred to the addition funnel and added to the pot at 260 °C dropwise. Except for the presence of the CdSe rods, these conditions were identical to those used for preparation of CdTe dots. See, for example, Snee, P.T. et al., *Advanced Materials*, **2005**, *17*, 1131-1136, which is incorporated by reference in its entirety. The total reaction time after the start of
15 the addition of the precursor solution did not exceed 15 minutes after which the resulting solution was cooled to room temperature and transferred under argon to a nitrogen glovebox to avoid oxidization of the CdTe tips. The CdSe/CdTe nanobarbells were then precipitated by the addition of toluene, and sonicated (although insoluble) in hexane from which they were once again precipitated. These steps extracted any CdTe dots formed
20 during the synthesis from the solid CdSe/CdTe nanobarbells. After this CdSe/CdTe nanobarbells can be redispersed in chloroform and precipitated several times using methanol in order to remove any excess organic material from the solution. The CdSe/CdTe nanobarbells appeared to be light sensitive and remained dispersed in solution for several days only if stored under nitrogen in the dark.

25 As expected for such a heterostructure, the nanobarbells exhibited absorption spectra typical to a type II structure, with large apparent molar absorptivity across the visible spectrum. See, for example, Kim, S. et al., *J. Am. Chem. Soc.* **2003**, *125*, 11466-11467, which is incorporated by reference in its entirety. The hole should be trapped in the valence band of the CdTe tips, and the electron in the conduction band of the CdSe.
30 There was no emission, unlike in core/shell type II heterostructures. This was not unreasonable since the carriers are spatially well separated and the barbell was not capped with a higher band gap material (such as ZnS). Recombination was thus likely to occur

primarily through non-radiative pathways involving trap states along the surface and so the heterostructure appeared non-emissive.

FIG. 2 show TEM images of multiple nanobarbells, showing both monodisperse formation of the rod and growth of the CdTe dots on either end. Unlike previous preparations, CdTe dots grow symmetrically on either end without branching or other deviations that may increase excluded "empty" volume in a film. Nanobarbells synthesized in this manner are presumed to show packing properties similar to CdSe rods. See, e.g., Liang-shi Li, et al. *Advanced Materials* **2003**, *15*, 408-411, which is incorporated by reference in its entirety. In other words, the nanocrystals can become substantially aligned in a film. The direction of alignment can be perpendicular to the length of the rod. When the film is arranged on a substrate, the nanorods can be aligned so that the lengths of the rods are substantially perpendicular to the substrate. Preferably, when arranged on a substrate, aligned substantially perpendicular to the substrate and are close-packed in the lateral dimensions along the substrate.

Transmission electron microscope images were taken on a JEOL 200 TEM and expanded (FIGS. 2A-2B) and JEOL 2010 HR-TEM (FIGS. 2C-2D) showing CdSe/CdTe nanobarbells. High resolution images show that the c-axis of the wurtzite CdTe dots are not always oriented along the c-axis of the rod onto which they have grown, and that zinc blende defect planes often demarcate the heterojunction between the dot and rod.

STEM measurements presented in FIG. 4 revealed an abrupt junction between the CdSe rod and the CdTe dots. FIG. 4A shows a STEM image of a single nanobarbell. The line labeled 'start-end' indicates where electron energy loss data illustrated in FIGS. 4B and 4C were recorded. Cd, Se and Te counts were collected at intervals of 1.7 Å and continuously averaged over ~5 nm to approach the expected diameter of the electron probe. In FIG. 4B, intensity (which was related to concentration) is plotted for all three elements. The relative intensities of Se and Te is displayed in FIG. 4C. Although accuracy of the instrument limited the ability to distinguish closely between the rod and dot sections of the nanobarbell, spots measured in the center of the rod indicate a concentration of less than 30% CdTe. This concentration corresponded to a CdTe thickness of about two monolayers around a rod with radius ~3 nm. However, the thickness of CdTe on the rod was likely thinner, because the closeness of the Cd and Te peaks in the X-ray spectrum can lead to overcounting of tellurium. Moreover, no discernable shell can be seen in the HR-TEM images (see FIG. 2D).

In a previous study of photoconductivity in CdSe nanocrystal films, one hundred percent exciton separation was observed after soaking the film in a dilute solution of butylamine. See, for example, Jarosz, M.V., et al., *Physical Review B* **2004**, *70*, 195327, which is incorporated by reference in its entirety. The butylamine partially exchanged
5 with the TOP surface ligands on the CdSe nanocrystal, decreasing the distance between nanocrystals in the film. With decreased distance between nanocrystals, a smaller applied voltage was required to generate electrical current. The applied voltage serves to separate the exciton charge carriers by providing enough energy to overcome the coulomb attraction between the electron and hole. The applied voltage also assists in the tunneling
10 of carriers to a neighboring nanocrystal. The photocurrent for the CdSe nanocrystal films was exponential with voltage while there was a competition between exciton ionization and recombination but once every exciton created in the film was separated into charge carriers the photocurrent displayed a linear dependence on voltage. A transition between the exponential and linear voltage dependence typically occurred at 1.4×10^5 V/cm in the
15 CdSe nanocrystal films (see Jarosz, M.V., et al., *Physical Review B* **2004**, *70*, 195327).

The photocurrent of a CdSe/CdTe nanobarbell film treated with butylamine exhibited a linear voltage dependence down to 0 V (lowest field applied is 6×10^3 V/cm). This indicated that exciton separation was nearly independent of applied voltage and therefore the nanostructure was internally assisting in separating the exciton into carriers.
20 In this way, CdSe/CdTe barbell thin films show good potential as possible active layer in photodetectors and solar cells or photovoltaics.

Nanobarbell cores have also been used in photovoltaic devices. These devices consist of ITO coated with a layer of poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) which was then coated with several layers of
25 nanobarbells (up to 100 nm). Layers were prepared by spin coating concentrated nanobarbells and baking them at 120 °C for five minutes in nitrogen before spin coating another layer directly on top of the first. In this way, multiple layers were produced. A silver, gold, or other high work function metal electrode was then be evaporated, in a pattern by shadow masking, directly onto the thick CdSe/CdTe nanobarbell layer.
30 Devices were tested in a fixture designed to provide connectivity between electrodes and the test leads as well as fit into the vacuum cryostat, so as to conduct experiments in vacuum or under inert conditions. Devices were tested using a 514 nm laser to ascertain the efficiency of the device which was found to be low ($\text{EQE} < 10^{-3}\%$) even at that

wavelength. Fill factor for the device was 0.33, and on/off ratio was found to be about 10. Dark currents reached up to 100s of nanoamps and the device was found to be poorly rectifying. High dark currents, which can be mediated by traps on the surface of the CdTe tips can be reduced by overcoating the nanobarbells to passivate the CdTe surface.

5 For example, a ZnS overcoating was formed on the CdSe/CdTe nanobarbells. This was done by immersing nanobarbells, after precipitation and redispersion in chloroform in a degassed solution of trioctylphosphine oxide and hexylphosphonic acid, then pulling off the chloroform. This solution was then heated to 190 °C and a mixture of diethyl zinc and hexamethyldisilathiane in trioctylphosphine was added dropwise for
10 about 5 minutes before cooling the solution. The overcoated (CdSe/CdTe)/ZnS nanobarbells can be precipitated by addition of polar solvents, such as acetone or methanol, in the same way as bare cores. They were soluble in hexane and toluene as well as chloroform, unlike bare nanobarbell cores, and samples generally exhibit two emission peaks upon excitation with a 365 nm mercury lamp. The first peak was sharp
15 with FWHM ~40nm peaked at around 750-810 nm most likely corresponds to emission from CdTe dots which may have formed from materials donated by the tips of the CdSe/CdTe nanobarbells at high temperature. The second peak, a broad peak with FWHM ~70 nm occurs at 950 nm and is presumed to be the true emission peak of the nanobarbells. Upon selective crashing samples can be obtained which contain the second
20 peak but not the first. TEM revealed them to be mostly nanobarbells in shape.

Other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A semiconductor nanocrystal comprising:
a central region and a first end, the central region including a first semiconductor
5 material; and
a distal region at the first end of the rod, the distal region including a second
semiconductor material, wherein the first semiconductor material and the second
semiconductor material are selected so that, upon excitation, one charge carrier is
substantially confined to the central region and the other charge carrier is substantially
10 confined to the distal region.
2. The nanocrystal of claim 1, further comprising a second distal region at a
second end of the central region.
- 15 3. The nanocrystal of claim 2, wherein the central region is rod-shaped.
4. The nanocrystal of claim 3, wherein the distal regions are each
approximately spherical.
- 20 5. The nanocrystal of claim 3, wherein the distal regions are each rod-shaped.
6. The nanocrystal of claim 3, wherein the nanocrystal has a length ratio of
between 0.1 and 0.95.
- 25 7. The nanocrystal of claim 3, wherein the nanocrystal has a length ratio of
between 0.2 and 0.9.
8. The nanocrystal of claim 3, wherein the nanocrystal has a radius ratio of
between 0.1 and 10.
- 30 9. The nanocrystal of claim 3, wherein the nanocrystal has a radius ratio of
between 0.3 and 3.5.

10. The nanocrystal of claim 1, wherein the first semiconductor material is a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound.

11. The nanocrystal of claim 10, wherein the first semiconductor material is 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, TiN, TiP, TiAs, TiSb, TlSb, PbS, PbSe, PbTe, or a mixture thereof.

12. The nanocrystal of claim 1, wherein the second semiconductor material is a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound.

13. The nanocrystal of claim 12, wherein the second semiconductor material is 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, TiN, TiP, TiAs, TiSb, TlSb, PbS, PbSe, PbTe, or a mixture thereof.

14. The nanocrystal of claim 1, wherein the nanocrystal includes an overcoating of a third semiconductor material.

15. A method of making a nanocrystal, comprising:
forming a semiconductor nanocrystal having a central region and a first end, the central region including a first semiconductor material; and
heating a mixture including a coordinating solvent, the semiconductor nanocrystal, an M donor, and an X donor at a temperature sufficient to cap the first end with a second semiconductor material, thereby forming a capped semiconductor nanocrystal having a central region including the first semiconductor material and a distal region including the second semiconductor material, wherein the first semiconductor material and the second semiconductor material are selected so that, upon excitation, one

charge carrier is substantially confined to the central region and the other charge carrier is substantially confined to the distal region.

16. The method of claim 15, further comprising contacting the semiconductor
5 nanocrystal with an etching agent before heating the mixture.

17. The method of claim 15, wherein the semiconductor nanocrystal further includes a second end.

10 18. The method of claim 17, wherein heating the mixture further caps the second end with the second semiconductor material.

19. The method of claim 18, wherein the central region is rod-shaped.

15 20. The method of claim 18, further comprising selecting a coordinating solvent and a temperature to influence a shape of a distal region.

21. The method of claim 20, wherein the coordinating solvent and the temperature are selected to form an approximately spherical distal region.

20 22. The method of claim 19, wherein the distal regions are each approximately spherical.

23. The method of claim 19, wherein the distal regions are each rod-shaped.

25 24. The method of claim 18, wherein the capped nanocrystal has a length ratio of between 0.1 and 0.95.

25 25. The method of claim 18, wherein the capped nanocrystal has a length ratio
30 of between 0.2 and 0.9.

26. The method of claim 18, wherein the capped nanocrystal has a radius ratio of between 0.1 and 10.

27. The method of claim 18, wherein the nanocrystal has a radius ratio of between 0.3 and 3.5.

5 28. The method of claim 15, wherein the first semiconductor material is a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound.

10 29. The method of claim 28, wherein the first semiconductor material is 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, TiN, TiP, TiAs, TiSb, PbS, PbSe, PbTe, or a mixture thereof.

15 30. The method of claim 15, wherein the second semiconductor material is a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound.

20 31. The method of claim 30, wherein the second semiconductor material is 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, TiN, TiP, TiAs, TiSb, PbS, PbSe, PbTe, or a mixture thereof.

25 32. The method of claim 15, further comprising overcoating the nanocrystal with a third semiconductor material.

33. A photovoltaic device comprising:
a first electrode;
30 a second electrode;
a voltage source configured to apply a voltage across the first electrode and the second electrode; and

an active layer in electrical communication with the first electrode and the second electrode, wherein the active layer includes a population of semiconductor nanocrystals each having a central region and a first end, the central region including a first semiconductor material, and a distal region at the first end of the rod, the distal region including a second semiconductor material, wherein the first semiconductor material and the second semiconductor material are selected so that, upon excitation, one charge carrier is substantially confined to the central region and the other charge carrier is substantially confined to the distal region.

34. The device of claim 33, wherein the population of semiconductor nanocrystals are substantially aligned.

35. The device of claim 34, wherein the first electrode and the second electrode are parallel.

36. The device of claim 35, wherein the population of semiconductor nanocrystals are substantially aligned with an alignment direction substantially perpendicular to the first electrode and the second electrode.

37. The device of claim 33, wherein the nanocrystal further includes a second distal region at a second end of the central region.

38. The device of claim 37, wherein the central region is rod-shaped.

39. The device of claim 38, wherein the distal regions are each approximately spherical.

40. The device of claim 38, wherein the distal regions are each rod-shaped.

41. The device of claim 38, wherein the nanocrystal has a length ratio of between 0.1 and 0.95.

42. The device of claim 38, wherein the nanocrystal has a length ratio of between 0.2 and 0.9.

43. The device of claim 38, wherein the nanocrystal has a radius ratio of
5 between 0.1 and 10.

44. The device of claim 38, wherein the nanocrystal has a radius ratio of between 0.3 and 3.5.

10 45. The device of claim 33, wherein the first semiconductor material is a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound.

15 46. The device of claim 45, wherein the first semiconductor material is 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, TiN, TiP, TiAs, TiSb, TlSb, PbS, PbSe, PbTe, or a mixture thereof.

20 47. The device of claim 33, wherein the second semiconductor material is a Group II-VI compound, a Group II-V compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group I-III-VI compound, a Group II-IV-VI compound, or a Group II-IV-V compound.

25 48. The device of claim 47, wherein the second semiconductor material is 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, TiN, TiP, TiAs, TiSb, TlSb, PbS, PbSe, PbTe, or a mixture thereof.

30 49. The device of claim 33, wherein the nanocrystal includes an overcoating of a third semiconductor material.

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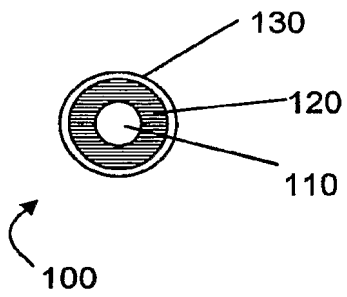


FIG. 1A

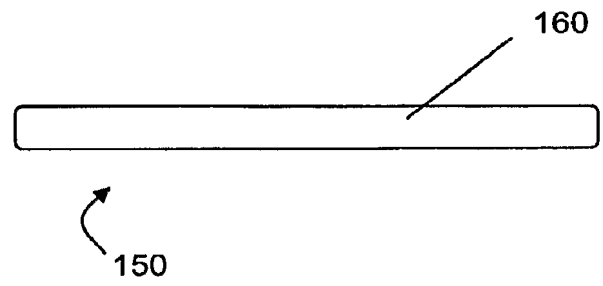


FIG. 1B

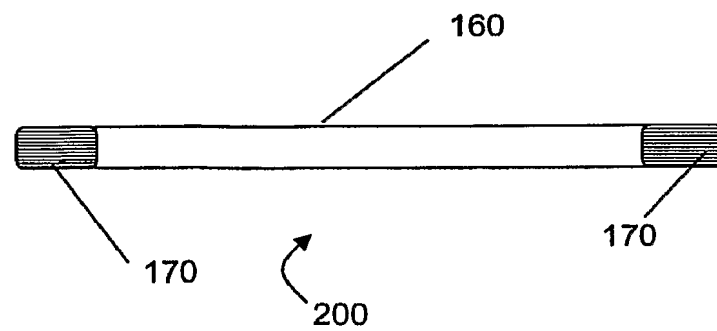
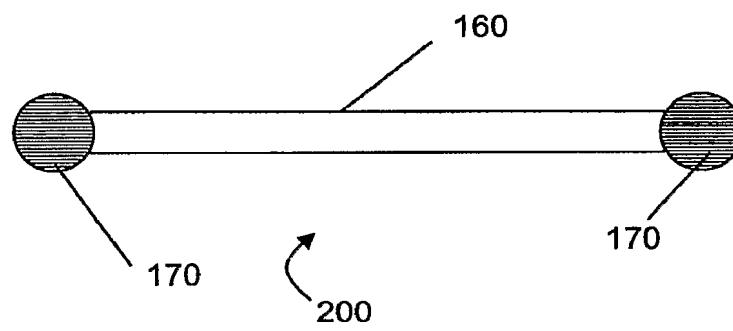


FIG. 1C

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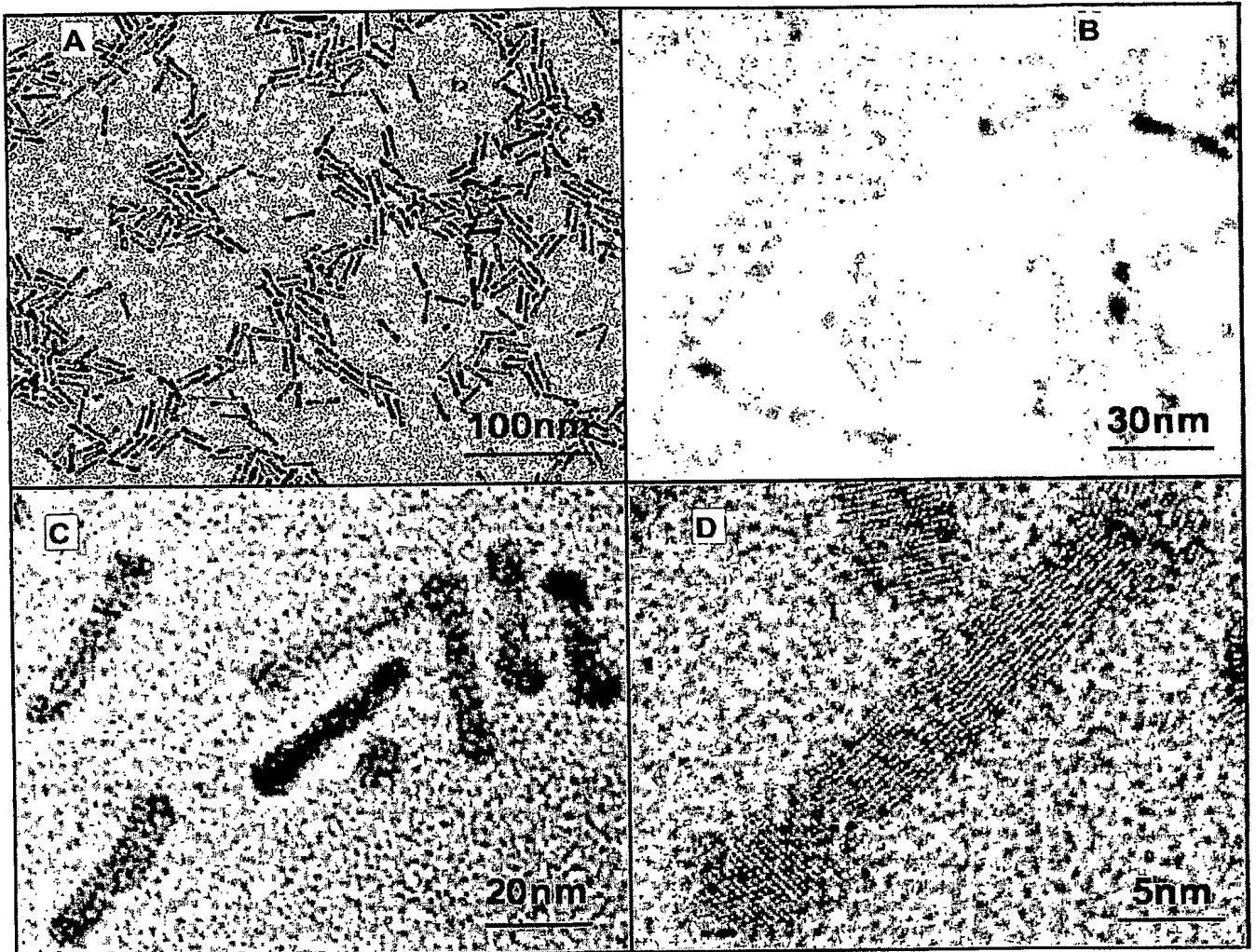


FIG. 2

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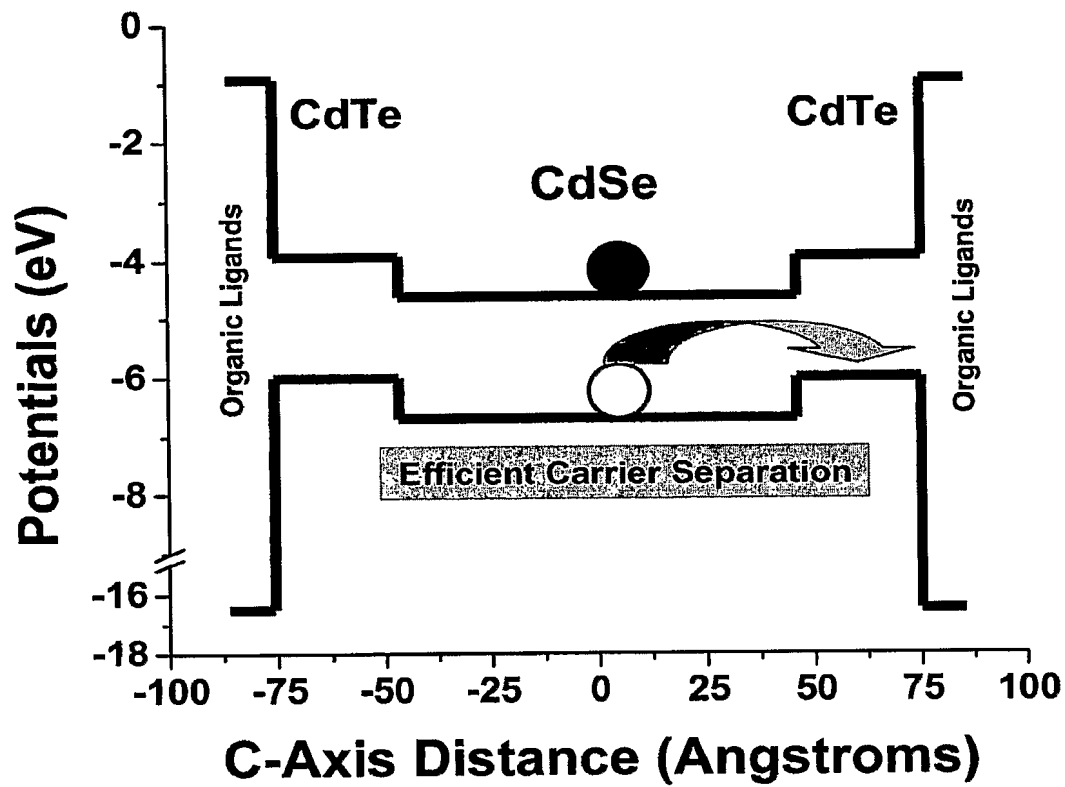


FIG. 3

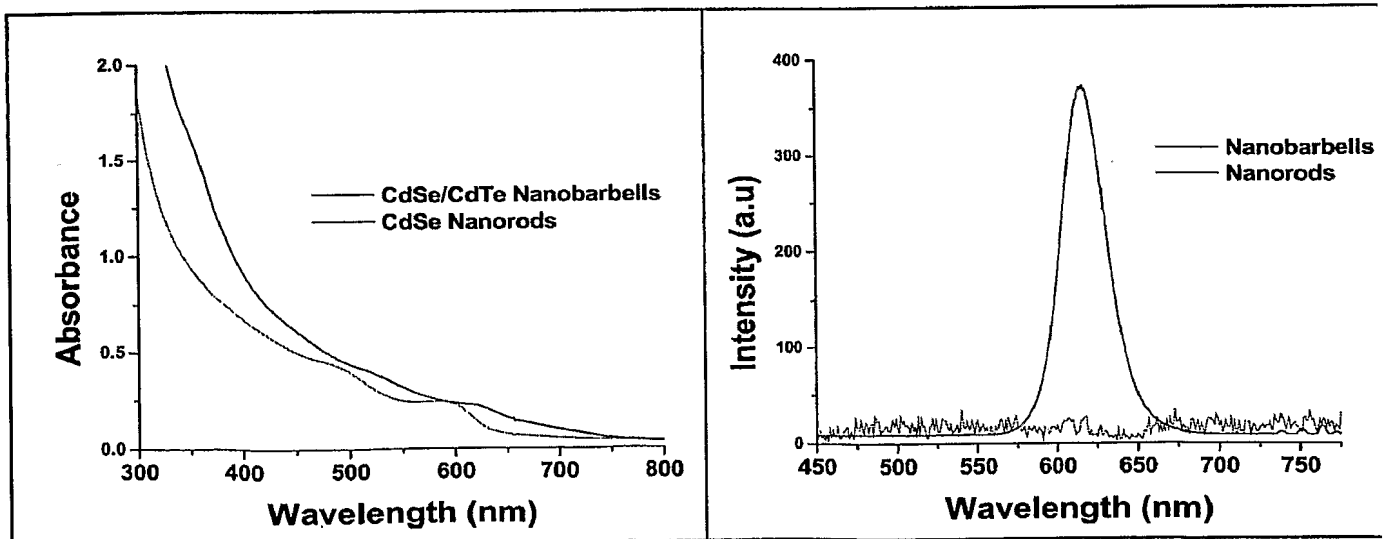


FIG. 4A

FIG. 4B

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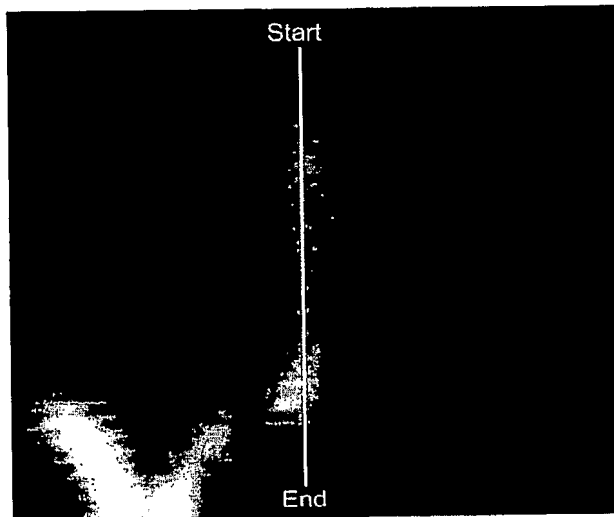


FIG. 5A

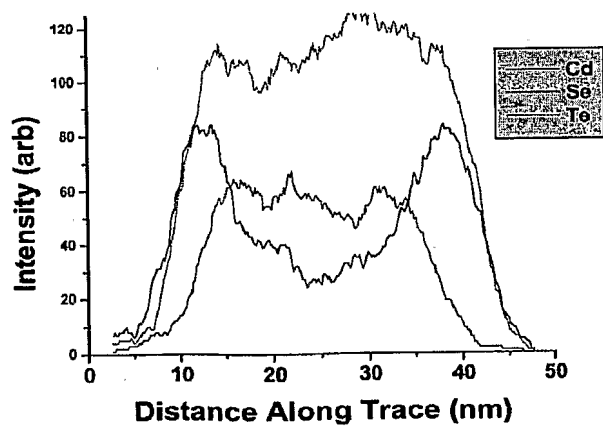


FIG. 5B

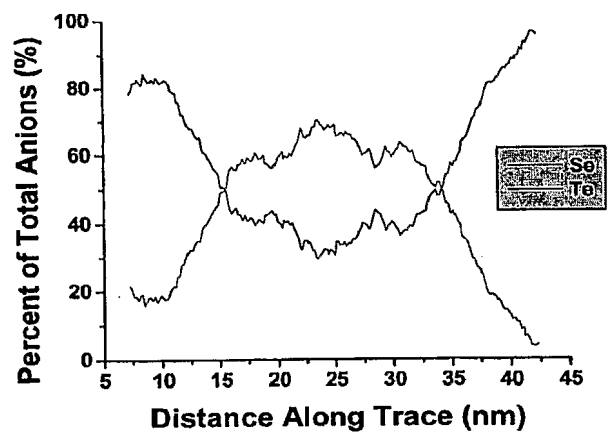


FIG. 5C

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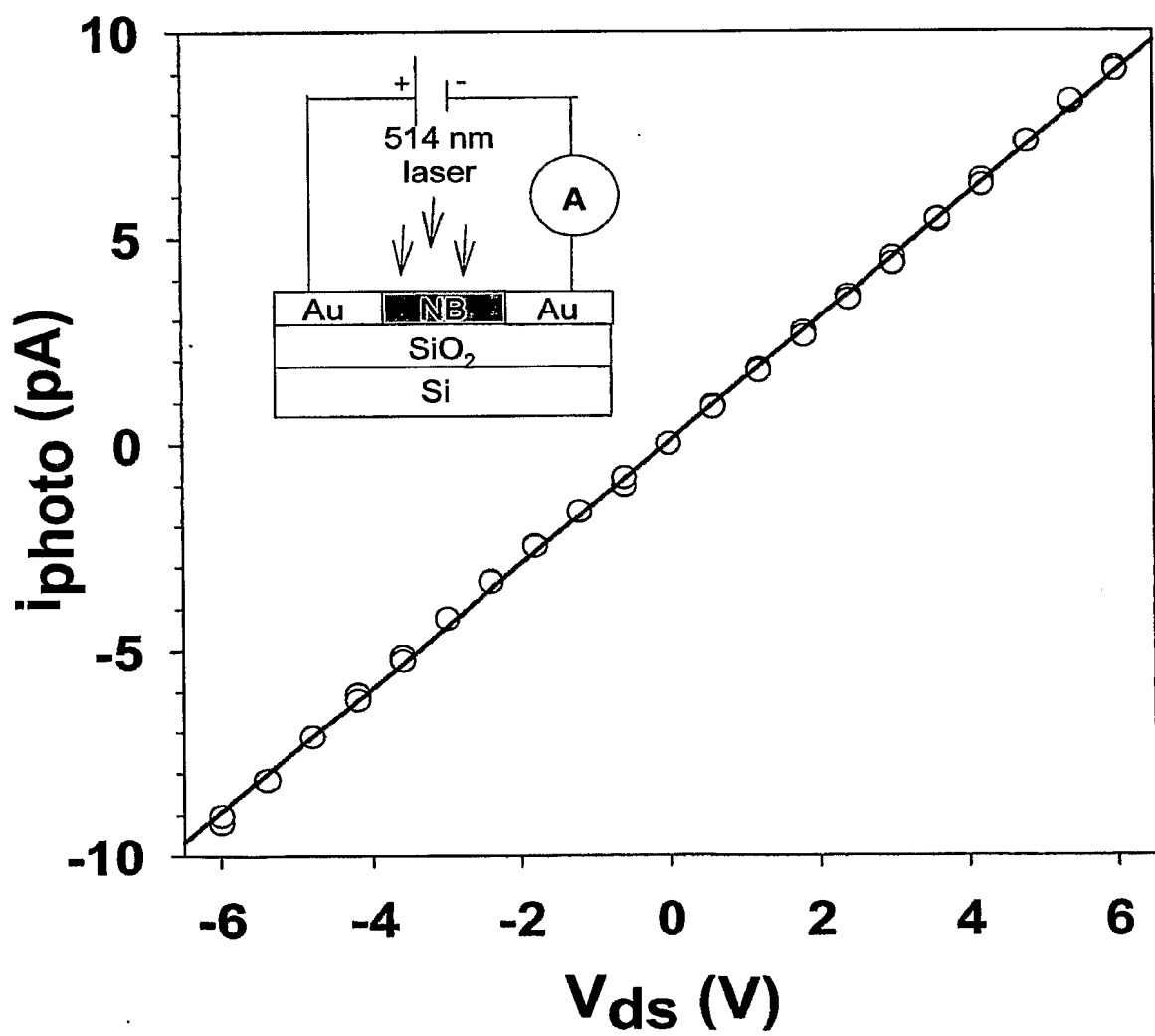


FIG. 6