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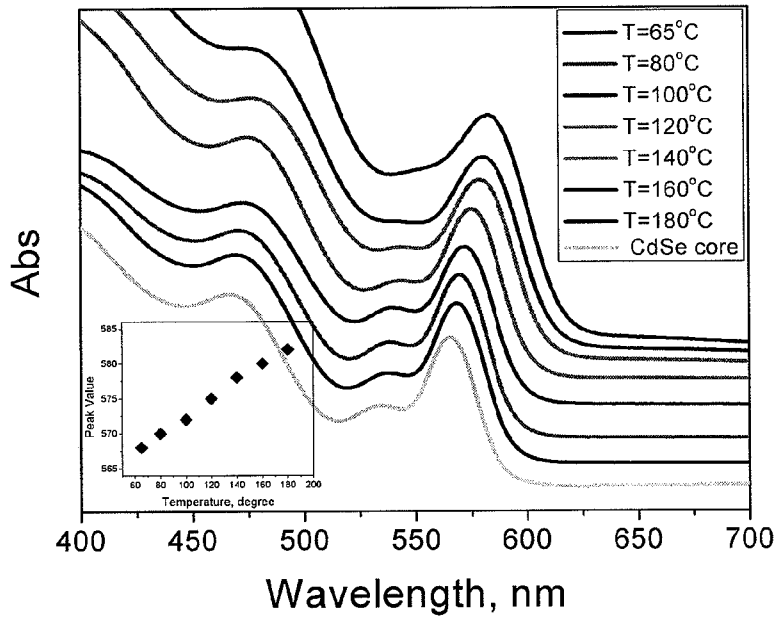
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(54) **Title**: SEMICONDUCTING NANOCRYSTALS COMPRISING A METAL SULFIDE SHELL AND METHODS FOR THEIR PREPARATION



(57) **Abstract**: Methods for synthesizing a semiconductor nanocrystal are provided comprising providing a semiconductive core; providing a metal precursor solution comprising a metal acetate, a non-polar solvent, trioctylphosphine, and trioctylphosphine oxide; providing a sulfur precursor solution; admixing the semiconductive core, the metal precursor solution, and the sulfur precursor solution to form a reaction dispersion; and heating the reaction dispersion to a temperature sufficient to induce formation of a metal sulfide shell on the semiconductive core. Nanocrystals synthesized by these methods are also provided.

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SEMICONDUCTING NANOCRYSTALS COMPRISING A METAL SULFIDE SHELL AND METHODS FOR THEIR PREPARATION

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application No. 61/168,491, filed April 10, 2009, which is incorporated herein by reference.

STATEMENT OF GOVERNMENT INTEREST

This disclosure was developed at least in part using funding from the U.S. Environmental Protection Agency (EPA 83253601) and the National Science Foundation through the Center for Biological and Environmental Nanotechnology (NSF EEC-0118007). The U.S. government has certain rights in the invention.

BACKGROUND

Semiconductor nanocrystals, also known as quantum dots, are commonly used in the healthcare, energy, and environmental industries. These nanocrystals show unique size dependent properties when their size is smaller than the excitation Bohr radius of the bulk materials. Due to their excellent optoelectronic properties, quantum dots are being widely investigated for their potential applications in many different types of applications, such as solar cells, light-emitting devices (LEDs), lasers, and biological labeling.

Among all the types of semiconductor nanocrystals, cadmium selenide (CdSe) remains the most thoroughly studied nanocrystal system, with well developed preparation methods in controlling the crystal shape, size, and size distribution. However, oftentimes these quantum dots are synthesized using highly toxic, air-sensitive, and expensive methods only to yield poor samples.

CdSe nanocrystals were originally synthesized by using salts as precursors and micellular methods for size control, which yielded poor samples lacking sharp absorption features. In 1993, Murray et al. developed the synthesis of CdSe nanocrystals by using high temperature pyrolysis of organometallic precursors. Greener methods were later developed by using cadmium oxide (CdO) and cadmium acetate ($Cd(OAc)_2$) to replace the highly toxic, pyroforic, and air-sensitive dimethylcadmium ($(CH_3)_2Cd$) that was used previously. As alternatives to CdSe nanocrystals prepared in organic phase, different methods were explored to synthesize CdSe semiconductor nanoparticles in aqueous solutions by using $CdCl_2$ and Na_2SeSO_3 solution with stabilizing agents. These water-soluble CdSe nanocrystals are useful for biomedical applications. However, they do not possess narrow size distributions or high fluorescence properties like those nanocrystals prepared in organic phase.

Some bare nanocrystals (i.e., nanocrystal cores) have low luminescence quantum yields, usually not higher than 15%. In general, the surface atoms of bare semiconductor nanocrystals usually have defects, such as fewer adjacent coordinate atoms and more dangling bonds, which are believed to induce additional electronic states in the band gap, mix with the intrinsic states significantly, influence the spacing of the energy levels, which therefore lead to diminished optical properties of the semiconductor nanocrystals. One improvement in the synthesis of semiconductor nanocrystals is to passivate their surface with an inorganic shell that has a wider band gap. In 1996, Hines and Guyot-Sionnest reported that the luminescence quantum yield of the CdSe nanocrystals can be substantially improved by growing an inorganic ZnS shell around the crystals. This work produced semiconductor nanocrystals with a quantum yield of 50%.

Subsequently, Dabbousi et al. presented their study on the synthesis and characterization of CdSe/ZnS nanocrystals with core size ranging from 23 to 55Å. The quantum yields of their nanocrystals ranged from 30% to 50%. Peng et al. also presented similar work by using CdS as capping material. However, all these studies used highly toxic, air-sensitive, and expensive organometallic reagents such as $(CH_3)_2Zn$ (or $(CH_3)_2Cd$) and bis(trimethylsilyl)sulfide ($(TMS)_2S$) as the sulfur and zinc (or cadmium) precursors. Currently, this technique is still being used widely to synthesize core/shell quantum dots.

"Greener" methods using less toxic and air-stable chemicals were later explored for the synthesis of core/shell semiconductor nanocrystals. Weller et al. developed a one-pot approach to grow CdSe/CdS nanocrystals by purging H_2S gas through crude CdSe nanocrystal solution. The excess cadmium acetate during CdSe core synthesis further formed a CdS shell with H_2S gas. The core/shell nanocrystals produced by this method have narrow size distribution and quantum yields as high as 50-85%. However, this one-pot method seems to be limited to CdS shell synthesis and is not applicable to grow ZnS shell on CdSe cores.

In 2003, Peng reported a "Successive Ionic Layer Adsorption and Reaction (SILAR)" method to grow CdSe/CdS nanocrystals with quantum yields ranged from 20-40%. The shell materials, cadmium oxide (with oleic acid) and sulfur, are generally air-stable, less toxic and cheaper than $(CH_3)_2Cd$ (or $(CH_3)_2Zn$) and $(TMS)_2S$ used by previous organometallic methods. However, even though the SILAR method has strides towards "greener" and cost-effective core/shell synthesis, the reaction has to be conducted at much higher temperatures (220-240°C) than organometallic methods (140-220°C), which could potentially lead to unintentional reactions such as thermal degradation and the nanoparticle surfaces may be subject to more stringent conditions. Similarly, another limitation of the SILAR method is that it may be less versatile since the shell has to grow "layer-by-layer" instead of gradually.

SUMMARY

The present disclosure relates generally to semiconductor nanocrystals. More particularly, at least in some embodiments, the present disclosure relates to methods for synthesizing semiconductor nanocrystals comprising a semiconductive core surrounded by a metal sulfide shell and nanocrystals prepared by such methods. In some embodiments, nanocrystals of the present disclosure have improved stability and quantum yield and may be used in a variety of applications, including but not limited to solar cells, light-emitting devices, lasers and biological labeling.

The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

These drawings illustrate certain aspects of some of the embodiments of the present disclosure, and should not be used to limit or define the disclosure.

Figures 1A-1C are images illustrating the different solubility of zinc in octadecene (ODE) at room temperature after heating. Figure 1A is $Zn(OAc)_2$ with the addition of TOP/TOPO. Figure 1B is $Zn(OAc)_2$ with the addition of TOPO. Figure 1C is ZnO with the addition of oleic acid (SILAR method). All the solutions appear homogenous at high temperature (>100°C) but only $Zn(OAc)_2$ with both TOP and TOPO (Figure 1A) appears homogenous at room temperature.

Figure 2 is the UV-Vis spectra of CdSe and CdSe/ZnS quantum dots produced at different temperatures from 65°C to 180°C. The inlet depicts the dominant peak value of each spectrum (except the CdSe core) vs. temperature.

Figures 3A-3H depict TEM images of CdSe and CdSe/ZnS quantum dots produced at different temperatures. Figure 3A is a TEM image of quantum dots with a CdSe core. Figures 3B-3H are TEM images of CdSe/ZnS quantum dots produced at 65°C, 80°C, 100°C, 120°C, 140°C, 160°C, 180°C, respectively.

Figures 4A-4F depict HR-TEM images of CdSe cores (Figures 4A and 4D) and CdSe/ZnS quantum dots synthesized at 120 °C (Figures 4B and 4E) and 160°C (Figures 4C and 4F).

Figure 5 is a graph of SAXS raw data and simulated data of CdSe core and CdSe/ZnS produced at 100 °C and 160 °C.

Figure 6A is a digital photo of CdSe and CdSe/ZnS quantum dots prepared at 65°C, 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C (from left to right) taken under regular light.

Figure 6B is a digital photo of CdSe and CdSe/ZnS quantum dots prepared at 65°C, 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C (from left to right) taken under UV light at 366 nm.

Figure 7 is the photoluminescence spectra of CdSe and CdSe/ZnS quantum dots produced at 100°C and 160°C.

Figure 8 is the UV-Vis spectra of CdSe/ZnS core/shell quantum dots produced at 120°C with multiple injections of thiourea solutions.

Figure 9 is the UV-Vis spectra of CdSe core and CdSe/ZnS core/shell nanocrystals. The CdSe cores were synthesized using a different approach.

Figure 10 is a comparison of the UV-Vis spectra of CdSe/ZnS and CdSe/CdZnS core/shell quantum dots produced at 140°C.

Figure 11 is the photoluminescence spectra of CdSe core, CdSe/ZnS and CdSe/CdZnS core/shell quantum dots synthesized at 140°C. The inset shows digital photos of nanocrystals under UV light. From left to right: CdSe core, CdSe/ZnS and CdSe/CdZnS core/shell quantum dots.

Figures 12A-12F depict TEM images from CdSe core (Figure 12A and 12D), CdSe/ZnS (Figure 12B and 12E), and CdSe/CdZnS (Figure 12C and 12F) core/shell quantum dots synthesized at 140°C. Figures 12A-12C have a scale bar of 50 nm and Figures 12D-12F have a scale bar of 2 nm.

Figure 13 represents XRD patterns of CdSe core, CdSe/ZnS and CdSe/CdZnS core/shell nanocrystals.

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

While the present disclosure is susceptible to various modifications and alternative forms, specific example embodiments have been shown in the figures and are described in more detail below. It should be understood, however, that the description of specific example embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, this disclosure is to cover all modifications and equivalents as illustrated, in part, by the appended claims.

DESCRIPTION

The present disclosure relates generally to semiconductor nanocrystals, and more particularly, at least in some embodiments, to methods for synthesizing semiconductor nanocrystals comprising a metal sulfide shell and nanocrystals prepared by such methods. In some embodiments, a semiconductor nanocrystal comprising a metal sulfide shell of the present disclosure may have improved stability and quantum yield. The present disclosure also provides

methods of using such nanocrystals in solar cells, light-emitting devices, lasers and biological labeling.

In one embodiment, the present disclosure provides a method for synthesizing a semiconductor nanocrystal comprising providing a semiconductive core; providing a metal precursor solution comprising a metal acetate, a non-polar solvent, trioctylphosphine, and trioctylphosphine oxide; providing a sulfur precursor solution; admixing the semiconductive core, the metal precursor solution, and the sulfur precursor solution to form a reaction dispersion; and heating the reaction dispersion to a temperature sufficient to induce formation of a metal sulfide shell on the semiconductive core.

One of the many potential advantages of the methods and compositions of the present disclosure is that the chemicals used to form a metal sulfide shell on a semiconductive core are air-stable, less toxic and cost-effective. In addition, the shell thickness can be easily controlled by temperature and/or the quantity of the precursor solutions added. In some embodiments, the temperature for shell growth can be conducted in a wide range from 65°C to 250°C. Additionally, the growth of the shell and the resulting quality of the nanocrystals are not generally affected by the manner in which the metal and sulfur precursor solutions are added to the semiconductive core. For example, a slow dripping or a SILAR ("layer-by-layer") procedure is not necessary to obtain highly monodisperse core/shell nanocrystals. Therefore, as a result, the methods of the present disclosure can easily be used for commercial production of nanocrystals.

Semiconductive cores suitable for use in the present disclosure may comprise one or more materials including, but not limited to, (1) a first element selected from Groups 2, 12, 13 or 14 of the Periodic Table of the Elements and a second element selected from Group 16 of the Periodic Table of the Elements, (2) a first element selected from Group 13 of the Periodic Table of the Elements and a second element selected from Group 15 of the Periodic Table of the Elements, or (3) a Group 14 clement. Examples of materials suitable for use in the semiconductive core include, but are not limited to, MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, Al_2S_3, Al_2Se_3, Al_2Te_3, Ga_2S_3, Ga_2Se_3, Ga_2Te_3, In_2S_3, In_2Se_3, In_2Te_3, SnS, SnSe, SnTe, PbS, PbSe, PbTe, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, BP, Si, and Ge, and ternary and quaternary mixtures, compounds, and solid solutions thereof.

Semiconductive cores suitable for use in the present disclosure may be prepared by any method known in the art. Examples of suitable methods are well known to those skilled in the art and may include those methods disclosed in U.S. Patent Nos. 6,815,064, 6,576,291, 6,306,736, 6,225,198, 6,207,229, 6,048,616, 5,990,479, 5,985,173, 5,690,807, 5,505,928,

5,262,357; U.S. Patent Publication Nos. 2002/0066401 and 2002/0083888; PCT Publication No. WO 99/26299; and Murray et al. (1993) J. Am. Chem. Soc. 115:8706-8715; Guzelian et al. (1996) J. Phys. Chem. 100:7212-7219; Peng et al. (2001) J. Am. Chem. Soc. 123:183-184; Hines et al. (1996) J. Phys. Chem. 100:468; Dabbousi et al. (1997) J. Phys. Chem. B 101:9463; Peng et al. (1997) J. Am. Chem. Soc. 119:7019; Peng et al. (1998) J. Am. Chem. Soc. 120:5343; and Qu et al. (2001) Nano Left. 1:333-337, the disclosures of which are incorporated herein by reference.

Particle size and particle size distribution during the growth stage of the core reaction may be approximated by monitoring the absorption or emission peak positions and line widths of the samples. Dynamic modification of reaction parameters such as temperature in response to changes in the spectra allows the tuning of these characteristics.

In some embodiments, methods of the present disclosure also comprise providing a metal precursor solution comprising a metal acetate, a non-polar solvent, trioctylphosphine (TOP), and trioctylphosphine oxide (TOPO). Examples of metal acetates suitable for use in the metal precursor solutions of the present disclosure may include, but are not limited to, $Zn(OAc)_2$, $Cd(OAc)_2$, $Pt(OAc)_2$, $Fe(OAc)_2$, $Mn(OAc)_2$, $Co(OAc)_2$, and combinations thereof. In one embodiment, metal precursor solutions suitable for use in the present disclosure may comprise a metal acetate in an amount of about 0.1% to 5%. Examples of suitable non-polar solvents include, but are not limited to, linear alpha olefins, such as 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and higher blends of C20-C24, C24-C30. In some embodiments, metal precursor solutions suitable for use in the present disclosure may comprise a non-polar solvent in an amount of about 50% to about 80%. In some embodiments, metal precursor solutions suitable for use in the present disclosure may comprise TOP and TOPO in an amount sufficient to facilitate the dissolution of the metal acetate in the non-polar solvent. In one embodiment, a metal precursor solution may comprise TOP in an amount of about 10% to about 40%, and TOPO in an amount of about 2% to about 10%.

In some embodiments, the methods of the present disclosure also comprise providing a sulfur precursor solution. Sulfur precursor solutions suitable for use in the present disclosure generally comprise any chemical compound capable of releasing H_2S upon heating. In one embodiment, a sulfur precursor solution comprises thiourea. In some embodiments, a sulfur precursor solution may comprise, in addition to the chemical compound capable of releasing H_2S upon heating, an alcohol, such as ethanol. In one embodiment, sulfur precursor solutions suitable for use in the present disclosure may comprise thiourea in an amount of about 0.5% to 10% and an alcohol, such as ethanol, in an amount of about 90% to about 99.5%.

As mentioned above, in one embodiment, the methods of the present disclosure comprise admixing a semiconductive core, a metal precursor solution, and a sulfur precursor solution to form a reaction dispersion. This reaction dispersion may then be heated to a temperature sufficient to induce formation of a metal sulfide shell on the semiconductive core. In general, according to certain embodiments of the present disclosure, a reaction dispersion may be heated to a temperature of between about 65°C to about 250°C. In general, as the temperature of the reaction dispersion is increased, the thickness of the resulting shell formed on a semiconductive core is increased. Similarly, during the first ten to sixty minutes of applying heat to the reaction dispersion the shell begins to grow on a semiconductive core rather quickly, with growth proceeding slowly after approximately sixty minutes.

In some embodiments, the concentrations of the metal precursor solution and/or the sulfur precursor solution, and the number of injections of these precursors to a semiconductive core may be varied to obtain a desired shell thickness. For example, multiple injections of a precursor solution may be added to a semiconductive core to increase the thickness of the resulting shell.

Semiconductor nanocrystals of the present disclosure generally may be any shape including but not limited to a sphere, rod, wire, fiber, etc. In some embodiments, a semiconductor nanocrystal of the present disclosure may have a diameter in the range of approximately 1 nm to approximately 1000 nm, preferably in the range of about 2 nm to about 50 nm, and more preferably in the range of about 2 nm to about 20 nm.

When irradiated, a semiconductor nanocrystal of the present disclosure may emit light in a bandwidth not exceeding about 60 nm, preferably not exceeding about 40 nm, and more preferably not exceeding about 30 nm when measured at full width at half maximum (FWHM). In some embodiments, a semiconductor nanocrystal of the present disclosure may have a quantum yield of about 25% and 75%, and the narrow bandgap edge luminescence exhibited by a nanocrystal of the present disclosure may be in the spectral range of about 440 nm to about 660 nm.

Additionally, in some embodiments, a semiconductor nanocrystal of the present disclosure may also be covered with an organic or other overcoating on the shell. The overcoating may be comprised of materials selected to provide compatibility with a suspension medium, such as a short-chain polymer terminating in a moiety having affinity for the suspending medium, and moieties that possess an affinity for the surface. Suitable overcoating materials include, but are not limited to, polystyrene, polyacrylate, or other polymers, such as polyimide, polyacrylamide, polyethylene, polyvinyl, poly-diacetylene, polyphenylene-vinylene, polypeptide, polysaccharide, polysulfone, polypyrrole, polyimidazole, polythiophene, and

polyether; epoxies; silica glass; silica gel; titania; siloxane; polyphosphate; hydrogel; agarose; cellulose; and the like. The coating can be in the range of about 2 to 100 nm thick, preferably 2 to 20 nm thick.

To facilitate a better understanding of the present disclosure, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the disclosure.

EXAMPLES

Experimental Procedures

Chemicals. CdO (99.99+%), selenium powder (100 mesh, 99.99%), trioctylphosphine oxide (TOPO) (99%), trioctylphosphine (TOP) (97%), stearic acid (SA) (≥97.0%), hexadecylamine (HDA) (98%), octadecylamine (ODA) (97%), zinc acetate ($Zn(OAc)_2$) (99.99%), cadmium acetate hydrate ($Cd(OAc)_2 \cdot xH_2O$, 99.99+%), thiourea (TU) (≥99.0%), and 1-octadecene (ODE) (tech. 90%) were purchased from Aldrich; Chloroform, acetone, ethanol, and methanol were also obtained from Aldrich. All chemicals were used without further purification.

Synthesis of CdSe Nanocrystals. The method for CdSe quantum dots synthesis is adopted from published works. For a typical synthesis, 0.096 grams of CdO and 0.854 grams of SA were added into a 25 mL three-neck flask and heated to 200°C with stirring until the solid became a transparent liquid. The flask was cooled to room temperature. 1.875 grams of TOPO, 1.875 grams of HDA, and 10.0 grams of ODE were transferred into the flask and then heated to 280°C. An injection solution was prepared by mixing 0.356 grams of Se, 3.204 grams of TOP, and 1.375 grams of ODE. The solution was swiftly injected into the flask by using a 10 mL syringe with a large bore needle. Different sizes of CdSe quantum dots can be obtained by varying the reaction times (from a few seconds to a few minutes) at high temperature then quenched in cold chloroform. The reaction was run under ultra-pure N_2 flow. The crude quantum dots were precipitated by acetone and methanol, and then centrifuged at 4500 rpm for 10 minutes at least 3 times. The nanocrystal pellet was re-dissolved in chloroform, filtered through 1μm PTFE syringe filter and then store under dark. The absorption spectra were recorded on UV-Vis in order to estimate the concentration of quantum dots.

Preparation of precursor solutions for shell growth. Zinc acetate and thiourea were used as a Zn and S source for ZnS shell growth on CdSe plain cores. A 0.04M $Zn(OAc)_2$ stock solution was prepared by mixing 73.4 mg of $Zn(OAc)_2$, 0.5 grams of TOPO, 2.0 mL of TOP, and 8.0 mL of ODE and then heated to 200°C until a clear solution was formed. $Cd(OAc)_2$ stock solution can be made in a similar fashion. The solution stayed clear after it was cooled to room

temperature. For CdZnS shell growth, $Zn(OAc)_2$ was mixed with $Cd(OAc)_2$ (Zn/Cd molar ratio=4:1) and then injected into the flask. A 0.2M thiourea (TU) stock solution was prepared by dissolving 60 mg of TU in 4 mL of ethanol.

Shell growth on CdSe quantum dots. 2.0 mL of purified CdSe quantum dots (~0.1μmol) chloroform solution was transferred into a 25 mL three-neck flask. The solvent was pumped off by vacuum. 1.5 grams of ODA and 5.0 grams of ODE were then added into the flask and heated to various temperatures ranging from 65°C to 180°C. A certain amount of $Zn(OAc)_2$ (with or without $Cd(OAc)_2$) solution was injected into the flask via syringe and the mixture was stirred for 15 minutes. The TU solution was then injected into the flask and the mixture was stirred for another 25 minutes. The reaction was cooled to ~60°C and precipitated in acetone. The quantum dots were further rinsed with ethanol before they were redispersed into a variety of solvents including hexane, chloroform, and toluene.

Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy. UV-Vis absorption spectra of purified CdSe, CdSe/ZnS and CdSe/CdZnS quantum dots were acquired on a Varian Cary 5000 UV-VIS-NIR spectrophotometer. Dilute solutions of quantum dots in chloroform were placed in 1 cm quartz cuvettes, and their absorption was measured.

Photoluminescence (PL) Spectroscopy and Quantum Yield (QY) Measurement. Photoluminescence (PL) spectra of CdSe, CdSe/ZnS, and CdSe/CdZnS quantum dots were recorded on a Jobin Yvon Spex Fluorolog 3 fluorescence spectrophotometer. The absolute QYs of the quantum dots at room temperature were determined by comparison of the PL integrate intensity of the semiconductor nanocrystals with that of the Rhodamine 6G (R6G) in absolute ethanol. The absorption spectra of both the dye and the nanocrystals were measured and the values at 400 nm of both spectra were recorded. The standard expression used to calculate the quantum efficiency is as follows:

$$\Phi_x = \Phi_r \cdot \left[\frac{A_r}{A_x}\right] \cdot \left[\frac{I_r}{I_x}\right] \cdot \left[\frac{n_x^2}{n_r^2}\right] \cdot \left[\frac{D_x}{D_r}\right]$$

where Φ_x and Φ_r are the absolute QYs of the nanocrystal sample and Rhodamine 6G. The room-temperature QY of R6G in ethanol is 95% from literature. A_r and A_x are, respectively, compared to the absorption value at this excitation wavelength, *e.g.* 400 nm in this study. I_r and I_x are the intensities of excitation, and those of the sample are equal to the values of the standard sample. n_r and n_x are refractive indices of solvents. Ethanol and chloroform were used. $n_{ethanol}$ is 1.359 and $n_{chloroform}$ is 1.446 at room temperature. D_x and D_r, are the PL integrated intensities of the nanocrystals and R6G excited at 400 nm.

Transmission Electron Microscopy (TEM). TEM specimens were made by evaporating one drop of nanocrystal solution on carbon-coated copper grids. The TEM micrographs were taken by JEOL 2010 Transmission Electron Microscope operating at 100kV. The size and size distribution data were obtained by counting >1000 individual nanocrystalline particles using Image-Pro Plus 5.0 (Media Cybernetics, Inc., Silver Spring, MD). High resolution images were taken by Field Emission Gun Transmission Electron Microscope (JEM 2100F TEM) operating at 200kV.

Small-Angle X-ray Scattering (SAXS). SAXS samples were prepared by dissolving quantum dots in toluene and then sealing them in quartz capillaries with epoxy resin. The transmittance SAXS scanning of the quantum dot samples was conducted on Rigaku SmartLab XRD (SmartLab XRD) with scanning angle from 0.06 to 8 degrees. A Nanosolve software was then used to simulate and analyze the particle size and distribution.

X-ray Diffraction (XRD). X-ray powder diffraction patterns were recorded using a Siemens Model D5000 X-ray diffraction with Cu KR radiation. The samples were prepared by applying a highly concentrated solution of nanocrystals and allowing it to evaporate on a zero-background holder for measurement.

Results

Preparation of the stock solution for shell growth on CdSe nanocrystals. Zinc acetate ($Zn(OAc)_2$) and thiourea were used as zinc and sulfur sources to grow a ZnS shell on CdSe plain cores. $Zn(OAc)_2$ has limited solubility in ODE at room temperature. It can be heated to form a homogeneous solution at high temperature, similar to ZnO/oleic acid in ODE solution used by SILAR method. However, the solution becomes cloudy after it cools to room temperature, which suggests the solubility of the zinc compound is significantly reduced at room temperature. The solubility of $Zn(OAc)_2$ was improved significantly by adding both TOP and TOPO in ODE solution. The "as-prepared" zinc precursor solution then stayed homogeneous after heating and being cooled to room temperature (Figure 1A). Without being bound to any particular theory, it is believed that the substantial improvement of the solubility of the zinc precursor is the key to conducting shell synthesis at much lower temperatures, even below 100°C. This is a significant improvement over the SILAR method as shell synthesis is conducted under mild environment, which potentially minimize unintentional reactions at high temperature and also improve the quality of nanocrystals with a more uniform shell coating. For example, the homogeneous nucleation of the shell materials tends to happen at a higher temperature. In a similar fashion, cadmium acetate can be dissolved in this TOP/TOPO/ODE system as well. It should be noted that addition of either TOP or TOPO did not result in a homogeneous $Zn(OAc)_2$/ODE solution at room temperature after heating in our study (Figure

1B). As a comparison, ZnO with oleic acid (OA) in ODE as described in the SILAR method was also prepared and shown in Figure 1C. With the addition of both TOP and TOPO, the ZnO/OA/ODE solution stayed homogeneous at room temperature after heating.

Thiourea was chosen because it can release H_2S gas upon heating through a slow decomposition process, which can form ZnS with a zinc compound. Although the ethanol used to dissolve thiourea is not miscible with ODE, we found the addition of a small amount of ethanol did not cause a problem in the shell growth on CdSe quantum dots in the ODE system. The ethanol is not necessary to be used since solid thiourea powder can still decompose at high temperature.

To compare the acetate/thiourea method of the present example with the other three major shell synthesis methods, *e.g.* organometallic, one-pot method using H_2S gas, and SILAR, a few factors were listed in Table 1 and discussed below:

TABLE 1

	Shell materials used			Synthesis temperature	Quantum Yield	Growth Control
	Air-sensitive	Toxic	Cost*			
Organometallic	Yes	Highly	High	140-220°C	30-50%	Oxygen and moisture-free required
H_2S one-pot	No	less	less	140°C	50-85%	H_2S gas injected above the solution
SILAR	No	Less	Low	220-240°C	20-40%	Shell grows layer-by-layer
$M(OAc)_2$/thiourea	No	Less	Low	65-180°C	26.1-45.8%	Versatile by Temperature & precursor quantity

* The cost estimation of the shell materials is based on the prices listed on Sigma-Aldrich website.

Both $M(OAc)_2$ (metal acetates) and thiourea are environmentally friendly, being air-stable and much less toxic than $(CH_3)_2Zn$ and $(TMS)_2S$. An estimation of the cost based on the prices listed on the website of Sigma-Aldrich is that $(CH_3CH_2)_2Zn$ and $(TMS)_2S$ cost twice and ten times more than $Zn(OAc)_2$ and thiourea, respectively. $Zn(OAc)_2$/TU and ZnO/S are comparable in terms of air-stability, toxicity and even prices, which makes them more cost-effective than $Et_2Zn/(TMS)_2S$.

In addition, the methods disclosed herein may be conducted at much lower temperatures than the SILAR method, therefore minimizing unintentional reactions during shell synthesis and improving the nanocrystal quality. The methods disclosed herein can even be conducted at temperatures lower than the temperatures required for organometallic methods.

Because $Et_2Zn/(TMS)_2S$ are both highly reactive, an oxygen and moisture-free environment is crucial to their storage and during the shell synthesis. A very slow dripping procedure, usually using a syringe pump is needed to prevent them from self-nucleation. The methods of the present disclosure are very versatile in controlling the shell thickness, without a SILAR or "layer-by-layer" procedure.

Lastly, the one-pot method using H_2S gas is only applicable for CdSe/CdS synthesis and can't be used to synthesize ZnS or CdZnS shell on CdSe cores. The other three methods can be easily adjusted to synthesize ZnS, CdS or CdZnS shells on CdSe nanocrystals.

The Effect of Temperature on ZnS shell growth on CdSe nanocrystals. CdSe plain cores with ultraviolet-visible (UV-Vis) absorbance at 565 nm were used to grow ZnS shell at various temperatures including 65°C, 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C. 65°C was the lowest temperature that all the chemicals could be dissolved in ODE and a homogeneous solution could be formed for further shell growth. 2 mL of CdSe (~0.1μmol) chloroform solution was added into 1.5 grams of ODA and 5.0 grams of ODE solution. Chloroform was pumped off and then the mixture was heated to various temperatures under nitrogen flow. 0.75 mL of $Zn(OAc)_2$ solution was injected and the mixture was stirred for 15 minutes. Then 0.25 mL of thiourea solution was injected and the mixture was stirred for another 25 minutes. After that, the mixture was precipitated in acetone, rinse with ethanol and then re-dispersed in chloroform for later analysis.

Figure 2 shows the UV-Vis spectra of the CdSe cores and CdSe/ZnS core/shell nanocrystals prepared at different temperatures. It was found that all the samples had notable red-shifts of wavelength compared with the CdSe plain cores. Higher temperature resulted in more red-shifting of CdSe/ZnS nanocrystals, indicating a thicker shell was formed. The ZnS shell growth occurred at a temperature as low as 65°C, which is believed to be due to the improved solubility of the Zn precursor. Figure 2 inlet shows a linear increase for the peak shifting vs. temperature. The reason for this may be due to more H_2S released from thiourea which can form ZnS with $Zn(OAc)_2$ or increased reactivity of Zn/S precursor at higher temperature. The peak value shifted from 565 nm (CdSe core) to 568 nm (65°C, CdSe/ZnS), 570 nm (80°C, CdSe/ZnS), 572 nm (100°C, CdSe/ZnS), 575 nm (120°C, CdSe/ZnS), 578 nm (140°C, CdSe/ZnS), 580 nm (160°C, CdSe/ZnS), and 582 nm (180°C, CdSe/ZnS). Further study showed that the half width half maximum (HWHM) (which is used to roughly determine the monodispersity of quantum dots) of all CdSe and CdSe/ZnS quantum dots was 14 nm (CdSe core), 14 nm (65°C, CdSe/ZnS), 14 nm (80°C, CdSe/ZnS), 15 nm (100°C, CdSe/ZnS), 15 nm (120°C, CdSe/ZnS), 18 nm (140°C, CdSe/ZnS), 19 nm (160°C, CdSe/ZnS), and 20 nm (180°C,

CdSe/ZnS), which indicates the all the CdSe nanocrystals remain good monodispersity after the ZnS shell was formed. A comparison of the UV-Vis absorption peak and HWHM of CdSe cores and CdSe/ZnS nanocrystals produced at different temperatures is listed in Table 2.

TABLE 2

	CdSe	CdSe/ZnS					
Temperature (°C)		65	80	100	120	140	160	180
UV-Vis Abs. (nm)	565	568	570	572	575	578	580	582
HWHM (nm)	14	14	14	15	15	18	19	20

TEM images (Figure 3) were taken to show and calculate the shape, size, and size distribution of the CdSe plain cores and corresponding CdSe/ZnS nanocrystals synthesized at various temperatures. It can be seen that all the nanocrystals including the plain cores and core/shell nanocrystals are dot-shaped, with size slightly increasing from core to core/shell structure, and from low temperature to higher temperature. It is noticeable that all the nanocrystals remained highly monodispersed for the entire temperature range from 65 to 180°C tested. The average sizes of these dried nanocrystals measured by the Image Pro software were 4.01±0.35 nm (core), 4.05±0.43 nm (65°C), 4.16±0.54 nm (80°C), 4.26±0.48 nm (100°C), 4.36±0.45 nm (120°C), 4.69±0.57 nm (140°C), 4.87±0.51 nm (160°C), and 5.05±0.54 nm (180°C), respectively.

A high resolution TEM (HR-TEM) was further used to image the CdSe core and core/shell nanocrystals (Figure 4). The core/shell nanocrystals were clearly larger than the plain cores. SAXS is a widely used tool to characterize nanoparticle size and size distribution. Transmittance SAXS scanning was performed on Rigaku SmartLab XRD to analyze the core and core/shell nanocrystals and compared to the results from TEM analysis. Figure 5 shows the raw data and simulated data of CdSe core and CdSe/ZnS synthesized at 100°C and 160°C. The CdSe core was measured as 4.40 nm (14.3% normalized dispersion). The core/shell nanocrystals were 4.70 nm (15.2% norm. disp.) and 5.64 nm (19.0% norm. disp.), respectively. The particle size calculated from SAXS measurement was slightly bigger than the result from TEM analysis (Table 3).

TABLE 3

	CdSe cores	CdSe/ZnS@100°C	CdSe/ZnS@160°C
TEM	4.01 nm	4.26 nm	4.87 nm
SAXS	4.40 nm	4.70 nm	5.64 nm

Figure 6 shows two digital photos of the CdSe core and CdSe/ZnS core/shell nanocrystals in chloroform taken under regular light and hand-held UV light at 366 nm. Under regular light,

all the samples were deeply red with no significant difference in appearance; however, the ZnS shell coated CdSe showed much stronger fluorescence as compared with the CdSe core nanocrystals. In addition, the fluorescence changed slowly from orange to red (from left to right) with increasing of the shell growth temperature.

Further results of the photoluminescence study of the core and core/shell nanocrystals is shown in Figure 7 (Figure 7 only shows representative spectra of CdSe core and CdSe/ZnS synthesized at 100 and 160°C). The spectra were collected by using 400 nm as the excitation wavelength. It was found that the emission peaks were 578 nm, 580 nm, 581 nm, 583 nm, 588 nm, 592 nm, 595 nm, and 598 nm for CdSe core, CdSe/ZnS synthesized at 65°C, 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C respectively. The quantum yield (QY) of the plain CdSe nanocrystals was calculated as 9.9% comparing with R6G. The QYs increased to 26.1%, 29.5%, 27.2%, 32.2%, 34.5%, 43.0%, and 45.8% for CdSe/ZnS core/shell nanocrystals synthesized at 65°C, 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C respectively (Table 4).

TABLE 4

	CdSe	CdSe/ZnS						
Temperature (°C)		65	80	100	120	140	160	180
Emission (nm)	578	580	581	583	588	592	595	598
QY (%)	9.9	26.1	29.5	27.2	32.2	34.5	43.0	45.8

Multiple Injections of $Zn(OAc)_2$/thiourea for ZnS shell growth on CdSe nanocrystals. Various ZnS shell thickness can be obtained simply by varying the reaction temperature. Furthermore, multiple injections of Zn(OAc)2/thiourea can be applied to control the ZnS shell growth on CdSe core nanocrystals as well. Figure 8 shows the spectra shifting on UV-Vis measurements with the injection of excess $Zn(OAc)_2$ followed by multiple injections of thiourea solutions. With a reaction temperature of 120°C, 3 mL of $Zn(OAc)_2$ was injected. Following injections of 0.05 mL, 0.05 mL, 0.1 mL, 0.2 mL, 0.3 mL, and 0.3 mL of thiourea solution every 10 minutes. UV-Vis spectra was recorded by taking out small aliquots from the reaction mixture before each injection. The UV-Vis spectrum blue-shifted about 3 nm after the addition of $Zn(OAc)_2$. This blue-shifting suggests that a Zn alloy with the CdSe cores may have formed instead of a Zn shell on the surface of CdSe nanocrystals. The following injection of thiourea solution caused a significant red-shift (10 nm) which indicated the formation of a ZnS shell on the CdSe nanocrystals. The shell thickness then grew gradually with further additions of thiourea solution. However, the shell growth slowed down significantly after several injections.

Figure 8 shows the UV-Vis results with the UV-Vis absorption peak value shifting from 565 nm for CdSe plain cores to 562 nm after addition of $Zn(OAc)_2$, then to 572 nm, 574 nm, 576

nm, 578 nm, and 580 nm with each injection of thiourea solution. Their corresponding HWHMs were 14 nm (CdSe plain core), 14 nm (addition of $Zn(OAc)_2$), 15 nm (1st injection of TU), 16 nm (2nd injection of TU), 15 nm (3rd injection of TU), 16 nm (4th injection of TU), 18 nm (5th injection of TU), which indicated that the core/shell nanocrystals remained highly monodispersed during the shell growing process. Growth of a ZnS shell with more than 30 nm red shifting usually requires a very long time. The maximum red-shifting is limited by the reaction temperature, however, as shown in this example, it is possible to grow a ZnS shell on CdSe nanocrystals gradually by using multiple injections of small amounts of $Zn(OAc)_2$ and thiourea solutions.

Further studies have also shown that these methods are also applicable to grow a ZnS shell on both smaller (green fluorescence, UV-Vis Abs. at ~540 nm) and bigger (red fluorescence, UV-Vis Abs. at ~610 nm) CdSe with HWHM less than 20 nm. It is also possible to grow a ZnS shell on CdSe nanocrystals synthesized by a different approach. For example, ZnS shells were grown on CdSe cores synthesized by using oleic acid, bis-(2,2,4-trimethylpentyl) phosphinic acid (TMPPA) and TOP as surfactants (Figure 9). The core/shell nanocrystals are clearly much brighter than the cores under UV light, with UV-Vis absorption peak shifted from 587 nm to 595 nm.

CdSe/CdZnS core/shell synthesis. Since CdZnS shells have been reported to possess better photoluminescence efficiency, stability and robustness than ZnS shell coated quantum dots, a small amount of $Cd(OAc)_2$ was further added into the $Zn(OAc)_2$ precursor solution to synthesize a CdZnS alloy shell on CdSe cores. Figure 10 shows the UV-Vis spectra of CdSe/ZnS and CdSe/CdZnS core/shell nanocrystals synthesized at 140°C. The CdSe cores used in this study had a UV-Vis absorption peak at 555 nm. The spectra were taken at 15, 15, 30, and 30 minutes after injecting 0.5/0.5, 0.5/0.5, 1.0/1.0, and 1.0/1.0 mL of $Zn(OAc)_2$/TU precursor solutions. It can be seen that both CdSe/ZnS and CdSe/CdZnS core/shell nanocrystals had significant red-shifting on the UV-Vis spectra. The CdSe/ZnS shifted from 555 nm to 565 nm, 567 nm, 569 nm and then 572 nm after the fourth injection, while the CdSe/CdZnS shifted from 555 nm to 571 nm, 579 nm, 582 nm and then 584 nm.

Further results of the photoluminescence study of the nanocrystals is shown in Figure 11. It was found that the emission peaks were 565 nm, 588 nm, and 598 nm for CdSe cores, CdSe/ZnS, and CdSe/CdZnS core/shell nanocrystals, respectively. The full width half maximum (FWHM) from the photoluminescence spectra are 29.6 nm, 36.7 nm and 36.9 nm, respectively, indicating these nanocrystals maintain narrow size distribution. The quantum yield (QY) of the plain CdSe nanocrystals was calculated as 10.5%. The QYs of CdSe/ZnS and CdSe/CdZnS

core/shell nanocrystals were 35.6 and 40.0%, respectively. The QY of CdSe/CdZnS was slightly higher than the CdSe/ZnS core/shell quantum dots.

TEM images were also taken to compare the CdSe plain cores, CdSe/ZnS and CdSe/CdZnS core/shell quantum dots synthesized at 140°C (Figure 12). As can be seen from these images, both core/shell nanocrystals remained dot shaped and were larger than the plain cores. The average sizes of these dried nanocrystals measured by the Image Pro software were 3.85±0.36 nm, 5.08±0.81 nm and 5.62±0.90 nm for CdSe core, CdSe/ZnS and CdSe/CdZnS quantum dots, respectively.

Figure 13 shows the diffraction patterns of CdSe plain cores, CdSe/ZnS and CdSe/CdZnS core/shell nanocrystals synthesized at 140°C. The XRD patterns scanned from 5° to 60° showed significant changes after CdSe cores were coated with ZnS and CdZnS shells: a broadening and shift to higher angles at around 25°, a decrease in the intensity between 40 and 52°, and the appearance of a new peak around 56°.

Large Scale Synthesis of core/shell nanocrystals. The above procedures can be readily extended to a multigram level or even larger scale. In a typical synthesis, 100 mL of CdSe quantum dots (UV-Vis Abs. peak at 565 nm) chloroform solution was transferred into a 500 mL three-neck flask. The chloroform was gradually pumped off by vacuum. 75 grams of ODA and 250 grams of ODE were added into the flask and then heated to 140°C. 37.5 mL of $Zn(OAc)_2$ and 12.5 mL of thiourea solutions were alternatively injected into the flask. The mixture was stirred for 40 minutes and then the reaction was stopped. The CdSe/ZnS core/shell quantum dots were precipitated in acetone then rinsed with ethanol. The quantum dots were then re-dispersed and stored in chloroform. The UV-Vis measurements showed a peak at 577 nm and the photoluminescence spectra showed an emission peak at 591 nm with FWHM 37.3 nm. These results prove that the shell synthesis can be easily scaled up at least 50 times and core/shell nanocrystals can be obtained in multigram levels or higher. It should be noted that the ethanol used to dissolve thiourea is not necessary for the shell synthesis, since solid thiourea powder can be added to the reaction system and still decompose to release H_2S at high temperature.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are

considered within the scope and spirit of the present invention. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Moreover, the indefinite articles "a" or "an", as used in the claims, are defined herein to mean one or more than one of the element that it introduces. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee.

References

[1] Andres, R.P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J.I.; Kubiak, C.P.; Mahoney, W.; Osifchin, R.G.; Reifenberger, R. "Coulomb Staircase" at Room Temperature in a Self-Assembled Molecular Nanostructure. Science 1996, 272, 1323-1325.

[2] Gittins, D.I.; Bethell, D.; Schiffrin, D.J.; Nichols, R.J. A nanometre-scale electronic switch consisting of a metal cluster and redox-addressable groups. Nature 2000, 408, 67-69.

[3] Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A.P. Semiconductor Nanocrystals as Fluorescent Biological Labels. Science 1998, 281, 2013-2016.

[4] Klein, D.L.; Roth, R.; Lim, A.K.L.; Alivisatos, A.P.; McEuen, P.L. A single-electron transistor made from a cadmium selenide nanocrystal. Nature 1997, 389, 699-701.

[5] Coe, S.; Woo, W.K.; Bawendi, M.G.; Bulovic, V. Electroluminescence from single monolayers of nanocrystals in molecular organic devices. Nature 2002, 420, 800-803.

[6] Murray C.B.; Norris D.J.; Bawendi M.G. Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. J Am. Chem. Soc. 1993, 115, 8706-8715.

[7] Rossetti R.; Nakahara S.; Brus L.E. Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution. J Chem. Phys., 1983, 79, 1086-1088.

[8] Huynh, W.U.; Peng, X.; Alivisatos, A.P. CdSe Nanocrystal Rods/Poly(3-hexylthiophene) Composite Photovoltaic Devices. Adv. Mater. 1999, 11, 923-928.

[9] Colvin V.L.; Schlamp M.C.; Alivisatos A.P. Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer. Nature 1994, 370, 354-357.

[10] Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. Efficient Near-Infrared Polymer Nanocrystal Light-Emitting Diodes. Science 2002, 295, 1506-1508.

[11] Klimov, V.I.; Mikhailovsky, A.A.; Xu, S.; Malko, A.; Hollingsworth, J.A.; Leatherdale, C.A.; Eisler, H.J.; Bawendi, M.G. Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots. Science 2000, 290, 314-317.

[12] Chan, W.C.W.; Nie, S. Quantum Dot Bioconjugates for Ultrasensitive Nonisotopic Detection. Science 1998, 281, 2016-2018.

[13] Michalet, X.; Pinaud, F.F.; Bentolila, L.A.; Tsay, J.M.; Doose, S.; Li, J.J.; Sundaresan, G.; Wu, A.M.; Gambhir, S.S.; Weiss, S. Quantum Dots for Live Cells, in Vivo Imaging, and Diagnostics. Science 2005, 307, 538-544.

[14] Esteves, A.C.C.; Trindade, T. Synthetic studies on II/VI semiconductor quantum dots. Curr. Opin. Solid State Mater. Sci. 2002, 6(4):347–53.

[15] Peng, X. Green chemical approaches toward high-quality semiconductor nanocrystals. Chem. Eur. J. 2002. 8(2): 335–39.

[16] Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. Photochemistry of colloidal semiconductors. Surface modification and stability of strong luminescing CdS particles. J. Am. Chem. Soc. 1987. 109: 5649–55.

[17] Wang, W.; Geng, Y.; Yan, P.; Liu, F.; Xie, Y.; Qian, Y. A novel mild route to nanocrystalline selenides at room temperature. J. Am. Chem Soc. 1999, 121: 4062–63.

[18] Heath, J.R.; Shiang, J.J. Covalency in semiconductor quantum dots. Chem. Soc. Rev. 1998, 27(1):65–71.

[19] Green, M. Solution routes to III–V semiconductor quantum dots. Curr. Opin. Solid State Mater. Sci. 2002, 6:355–63.

[20] Battaglia, D.; Peng, X. Formation of high quality InP and InAs nanocrystals in a non-coordinating solvent. Nano Lett. 2002, 2(9):1027–1030.

[21] Green, M.; O'Brien, P. Recent advances in the preparation of semiconductors as isolated nanometric particles: new routes to quantum dots. Chem. Commun. 1999, 22:2235–41.

[22] Trindade, T.; O'Brien, P.; Pickett, N.L. Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives. Chem. Mater. 2001, 13, 3843-3858.

[23] Michalet, X.; Pinaud, F.F; Lacoste, T.D.; Dahan, M.; Bruchez, M.P.; Alivisatos A.P.; Weiss. S. Properties of Fluorescent Semiconductor Nanocrystals and their Application to Biological Labeling. Single Mol. 2001, 2, 261-276.

[24] Murray, C.B.; Kagan, C.R.; Bawendi, M.G. Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. Annu. Rev. Mater. Sci. 2000, 30, 545–610.

[25] Peng, X., Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A.P. Shape control of CdSe nanocrystals. Nature 2000, 404, 59-61.

[26] Peng, Z.A.; Peng, X. Nearly Monodisperse and Shape-Controlled CdSe Nanocrystals via Alternative Routes: Nucleation and Growth. J. Am. Chem. Soc. 2002, 124, 3343-3353.

[27] Talapin, D.V.; Rogach, A.L.; Kornowski, A.; Haase, M.; Weller, H. Highly Luminescent Monodisperse CdSe and CdSe/ZnS Nanocrystals Synthesized in a Hexadecylamine-Trioctylphosphine Oxide-Trioctylphospine Mixture. Nano Lett. 2001, 1, 207-211.

[28] Qu, L.; Peng, X. Control of Photoluminescence Properties of CdSe Nanocrystals in Growth. J. Am. Chem. Soc.2002, 124, 2049-2055.

[29] de Mello Donegá, C.; Hickey, S.G.; Wuister, S.F.; Vanmaekelbergh,D.; Meijerink, A. Single-Step Synthesis to Control the Photoluminescence Quantum Yield and Size Dispersion of CdSe Nanocrystals. J. Phys. Chem. B 2003, 107, 489-496.

[30] Henglein, A. Photochemistry of colloidal cadmium sulfide. 2. Effects of adsorbed methyl viologen and of colloidal platinum. J. Phys. Chem. 1982, 86, 2291–2293.

[31] Dung, D.; Ramsden, J.; Graetzel, M. Dynamics of interfacial electron-transfer processes in colloidal semiconductor systems. J. Am. Chem. Soc. 1981, 104, 2977–2985.

[32] Peng, Z.A.; Peng, X. Formation of High-Quality CdTe, CdSe, and CdS Nanocrystals Using CdO as Precursor. J. Am. Chem. Soc. 2001, 123, 183–184.

[33] Qu, L.; Peng, Z.A.; Peng, X. Alternative Routes toward High Quality CdSe Nanocrystals. Nano Lett. 2001, 1, 333–337.

[34] Mekis, I.; Talapin, D.V.; Kornowski, A.; Haase, M.; Weller, H. One-Pot Synthesis of Highly Luminescent CdSe/CdS Core-Shell Nanocrystals via Organometallic and "Greener" Chemical Approaches. J. Phys. Chem. B 2003, 107, 7454–7462.

[35] Zhao, W.B.; Zhu J.J.; Chen, H.Y. Photochemical preparation of rectangular PbSe and CdSe nanoparticles. J. Crystal Growth 2003, 252, 587.

[36] Ma, X.D.; Qian, X. F.; Yin, J.; Xi, H.A.; Zhu, Z. K. Preparation and Characterization of Polyvinyl Alcohol-Capped CdSe Nanoparticles at Room Temperature. J. Colloid Interface Sci. 2002, 252, 77.

[37] Han, H.-Y.; Sheng, Z.-H.; Liang, J.-G. A novel method for the preparation of water-soluble and small-size CdSe quantum dots. Materials Letters 2006, 60, 3782-3785.

[38] Hines, M.A., Guyot-Sionnest, P. Synthesis and Characterization of Strongly Luminescing ZnS-Capped CdSe Nanocrystals. J. Phys. Chem. 1996, 100, 468–471.

[39] Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. (CdSe)ZnS Core-Shell Quantum Dots: Synthesis and

Characterization of a Size Series of Highly Luminescent Nanocrystallites. J. Phys. Chem. B 1997, 101, 9463–9475.

[40] Peng, X.; Schlamp, M.C.; Kadavanich, A.V.; Alivisatos, A.P. Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility. J. Am. Chem. Soc. 1997, 119, 7019–7029.

[41] Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M.B.; Peng, X. Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/Shell Nanocrystals Using Air-Stable Reagents via Successive Ion Layer Adsorption and Reaction. J. Am. Chem. Soc. 2003, 125, 12567-12575.

[42] Talapin, D.V.; Mekis, I.; Go1tzinger, S.; Kornowski, A.; Benson, O.; Horst, W. CdSe/CdS/ZnS and CdSe/ZnSe/ZnS Core-Shell-Shell Nanocrystals. J. Phys. Chem. B 2004, 108, 18826-18831.

[43] Rosenthala, S.J.; McBridea, J.; Pennycookc, S.J.; Feldmanb, L.C. Synthesis, surface studies, composition and structural characterization of CdSe, core/shell and biologically active nanocrystals. Surface Science Reports 2007, 62, 111–157.

[44] Liu, W.; Howarth, M.; Greytak, A.B.; Zheng, Y.; Nocera, D.G.; Ting, A.Y.; Bawendi, M.G. Compact Biocompatible Quantum Dots Functionalized for Cellular Imaging. J. Am. Chem. Soc. 2008, 130, 1274-1284.

[45] Reiss, P.; Carayon, S.; Bleuse, J.; Pron, A. Low polydispersity core/shell nanocrystals of CdSe/ZnSe and CdSe/ZnSe/ZnS type: preparation and optical studies. Synthetic Metals 2003, 139, 649–652.

[46] Manna, L.; Scher, E.C.; Li, L.-S.; Alivisatos, A.P. Epitaxial Growth and Photochemical Annealing of Graded CdS/ZnS Shells on Colloidal CdSe Nanorods. J. Am. Chem. Soc. 2002, 124, 7136-7145.

[47] Asokan, S.; Krueger, K.M.; Alkhawaldeh, A.; Carreon, A.R.; Mu, Z.Z.; Colvin, V.L.; Mantzaris, N.V.; Wong, M.S. The use of heat transfer fluids in the synthesis of high-quality CdSe quantum dots, core/shell quantum dots, and quantum rods. Nanotechnology 2005, 16, 2000-2011.

[48] Sapra, S.; Rogach, A.L.; Feldmann, J. Phosphine-free synthesis of monodisperse CdSe nanocrystals in olive oil. J. Mater. Chem. 2006, 16, 3391-3395.

[49] Yu, W.W.; Peng, X. Formation of High-Quality CdS and Other II±VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. Angew. Chem., Int. Ed. 2002, 41, 2368-2371.

[50] Yu, W.W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction. Coefficient of CdTe, CdSe, and CdS Nanocrystals. Chem. Mater. 2003, 15, 2854-2860.

[51] Crosby, G.A.; Demas, J.N. Measurement of photoluminescence quantum yields. J Phys Chem. 1971, 75, 991-1024.

[52] Yu, W.W.; Falkner, J.C.; Shih, B.S.; Colvin, V.L. Preparation and Characterization of Monodisperse PbSe Semiconductor Nanocrystals in a Noncoordinating Solvent. Chem. Mater. 2004, 16, 3318-3322.

[53] Yu, W.W.; Falkner, J.C.; Yavuz, C.T.; Colvin, V.L. Synthesis of monodisperse iron oxide nanocrystals by thermal decomposition of iron carboxylate salts. Chem. Commun. 2004, 20, 2306-2307.

[54] Pan, D.C.; Jiang, S.C.; An, L.J.; Jiang, B.Z. Controllable Synthesis of Highly Luminescent and Monodisperse CdS Nanocrystals by a Two-Phase Approach under Mild Conditions. Adv. Mater. 2004, 16, 982.

[55] Sheu, H.-S.; Jeng, U.-S.; Shih, W.-J.; Lai, Y.-H.; Su, C.-H.; Lai, C.-W.; Yang, M.-J.; Chen, Y.-C.; Chou. P.-T. Phase Separation Inside the CdTe-CdSe Type II Quantum Dots Revealed by Synchrotron X-ray Diffraction and Scattering. J. Phys. Chem. C 2008, 112, 9617–9622.

[56] Murray, C.B.; Sun, S.; Gaschler, W.; Doyle, H.; Betley, T.A.; Kagan, C.R. Colloidal synthesis of nanocrystals and nanocrystal superlattices. IBM J. RES. & DEV. 2001, 45, 47-56.

[57] Kagan, C.R.; Murray, C.B. Nirmal, M.; Bawendi, M. G. Electronic Energy Transfer in CdSe Quantum Dot Solids. PHYS I CAL RE V I EW LETTERS. 76, 1517-1520.

[58] van Embden, J.; Mulvaney, P. Nucleation and Growth of CdSe Nanocrystals in a Binary Ligand System. Langmuir 2005, 21, 10226-10233.

CLAIMS

What is claimed is:

1. A method of preparing a semiconductor nanocrystal comprising:

providing a semiconductive core;

providing a metal precursor solution comprising a metal acetate, a non-polar solvent, trioctylphosphine, and trioctylphosphine oxide;

providing a sulfur precursor solution;

admixing the semiconductive core, the metal precursor solution, and the sulfur precursor solution to form a reaction dispersion; and

heating the reaction dispersion to a temperature sufficient to induce formation of a metal sulfide shell on the semiconductive core thereby forming a semiconductor nanocrystal.

2. The method of claim 1 wherein the metal acetate is $Zn(OAc)_2$, $Cd(OAc)_2$, $Pt(OAc)_2$, $Fe(OAc)_2$, $Mn(OAc)_2$, $Co(OAc)_2$, or a combination thereof.

3. The method of claim 1 wherein the non-polar solvent is octadecene.

4. The method of claim 1 wherein the semiconductive core comprises a material selected from the group consisting of MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, Al_2S_3, Al_2Se_3, Al_2Te_3, Ga_2S_3, Ga_2Se_3, Ga_2Te_3, In_2S_3, In_2Se_3, In_2Te_3, SnS, SnSe, SnTe, PbS, PbSe, PbTe, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, BP, Si, and Ge, and ternary and quaternary mixtures, compounds, and solid solutions thereof.

5. The method of claim 1 wherein the semiconductive core comprises a material selected from the group consisting of CdSe, CdTe, CdS, ZnSe, InP, InAs, and PbSe.

6. The method of claim 1 wherein the sulfur precursor solution comprises thiourea.

7. The method of claim 1 wherein the sulfur precursor solution comprises an alcohol.

8. The method of claim 1 further comprising heating the reaction dispersion to a temperature of about 65°C to about 250 °C.

9. The method of claim 1 wherein admixing the semiconductive core, the metal precursor solution, and the sulfur precursor solution comprises first adding the metal precursor solution to the semiconductive core and second adding the sulfur precursor solution.

10. The method of claim 1 further comprising redispersing a semiconductor nanocrystal in hexane, chloroform, toluene and any combination thereof.

11. A semiconducting nanocrystal formed by any of the methods of claims 1-10.

12. A method of preparing a semiconductor nanocrystal comprising:

providing a semiconductive core;

providing a metal precursor solution comprising a metal acetate, octadecene, trioctylphosphine, and trioctylphosphine oxide;

providing a sulfur precursor solution comprising thiourea;

admixing the semiconductive core, the metal precursor solution, and the sulfur precursor solution to form a reaction dispersion; and

heating the reaction dispersion to a temperature sufficient to induce formation of a metal sulfide shell on the semiconductive core thereby forming a semiconductor nanocrystal.

13. The method of claim 12 wherein the metal acetate is $Zn(OAc)_2$, $Cd(OAc)_2$, $Pt(OAc)_2$, $Fe(OAc)_2$, $Mn(OAc)_2$, $Co(OAc)_2$, or a combination thereof.

14. The method of claim 12 wherein the semiconductive core comprises a material selected from the group consisting of MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, Al_2S_3, Al_2Se_3, Al_2Te_3, Ga_2S_3, Ga_2Se_3, Ga_2Te_3, In_2S_3, In_2Se_3, In_2Te_3, SnS, SnSe, SnTe, PbS, PbSe, PbTe, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, BP, Si, and Ge, and ternary and quaternary mixtures, compounds, and solid solutions thereof.

15. The method of claim 12 wherein the semiconductive core comprises a material selected from the group consisting of CdSe, CdTe, CdS, ZnSe, InP, InAs, and PbSe.

16. The method of claim 12 wherein the sulfur precursor solution comprises an alcohol.

17. The method of claim 12 further comprising heating the reaction dispersion to a temperature of about 65°C to about 250 °C.

18. The method of claim 12 wherein admixing the semiconductive core, the metal precursor solution, and the sulfur precursor solution comprises first adding the metal precursor solution to the semiconductive core and second adding the sulfur precursor solution.

19. The method of claim 12 further comprising redispersing a semiconductor nanocrystal in hexane, chloroform, toluene and any combination thereof.

20. A semiconducting nanocrystal formed by any of the methods of claims 12-19.

FIGS. 1A-1C

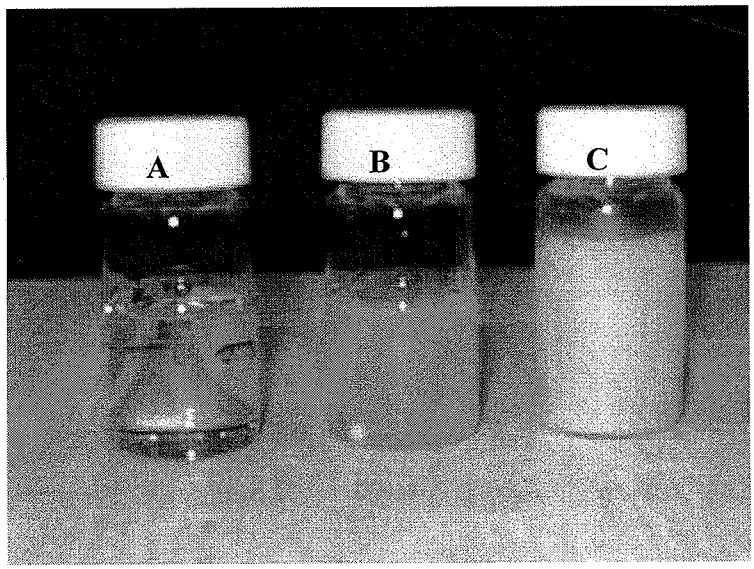
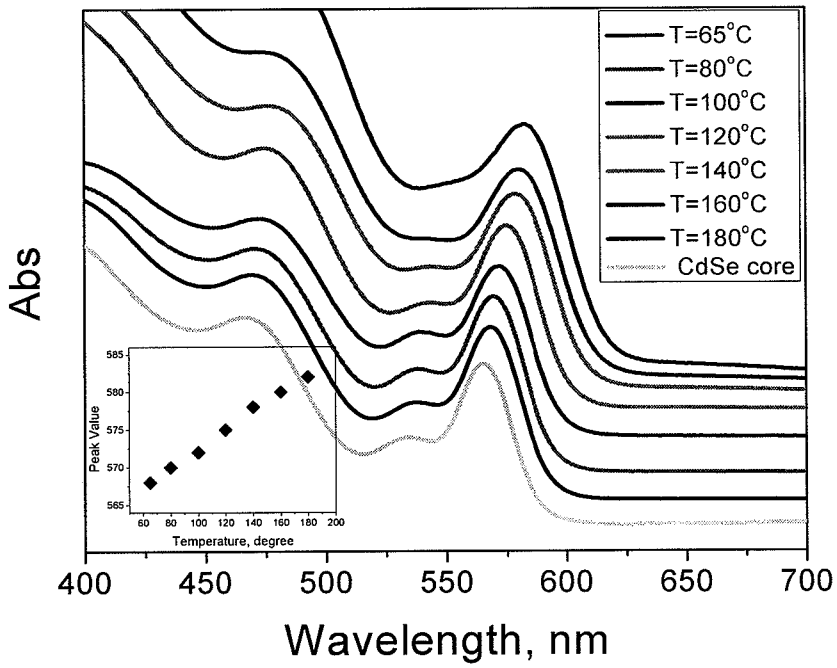
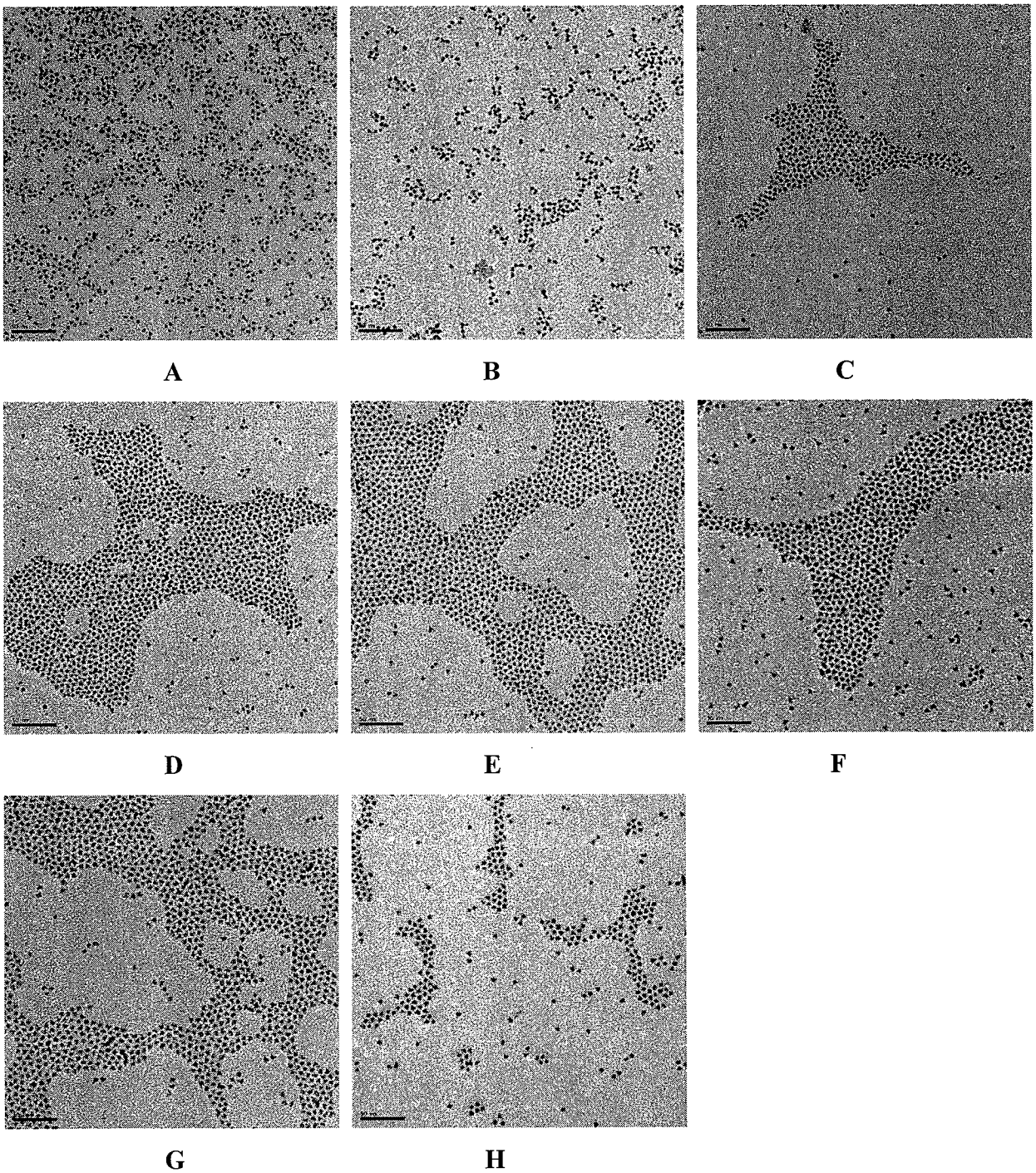


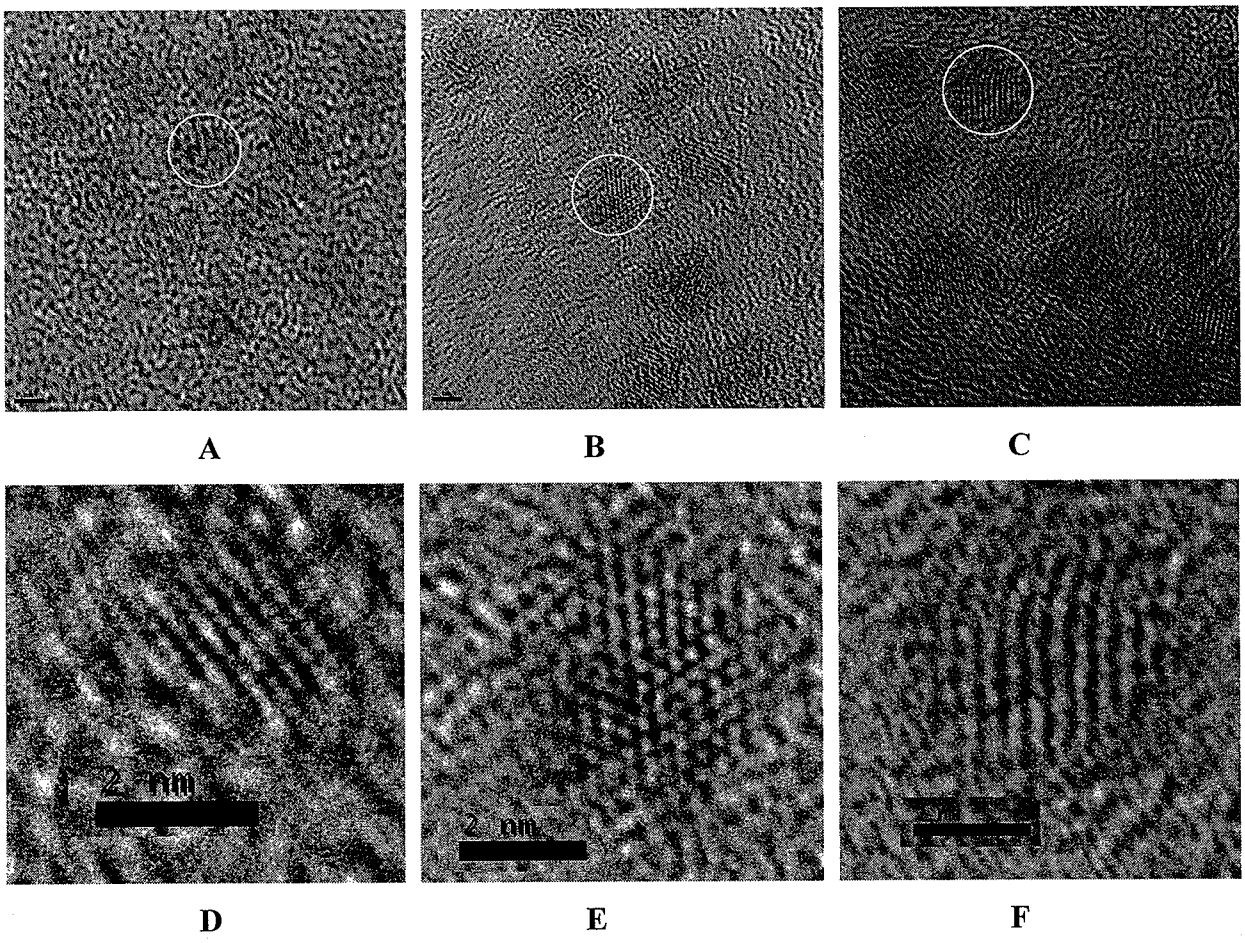
FIG. 2



FIGS. 3A-3H



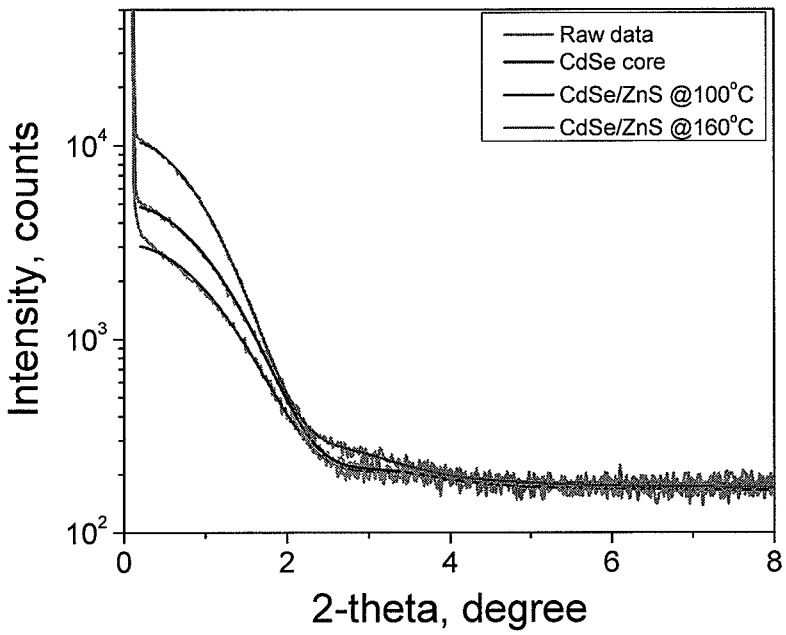
FIGS. 4A-4F



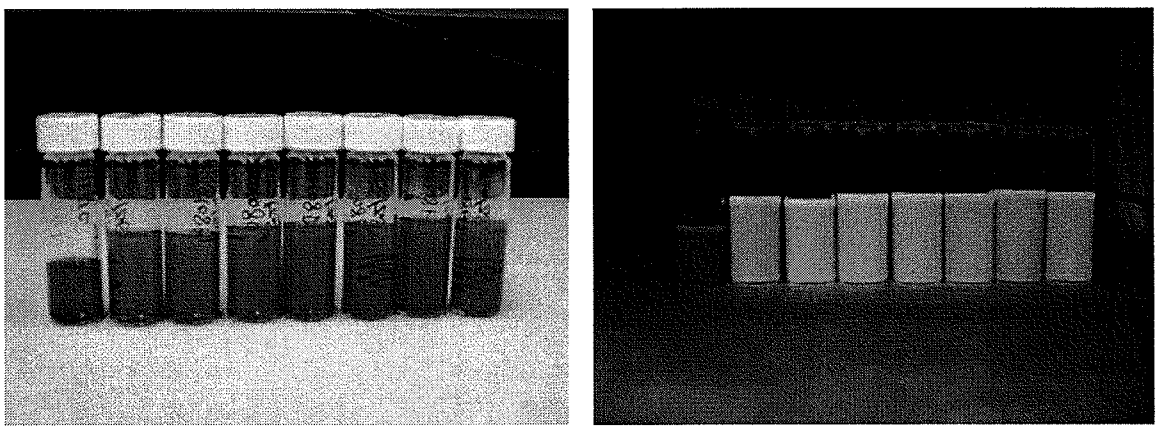
A B C

D E F

FIG. 5



FIGS. 6A-6B



A B

FIG. 7

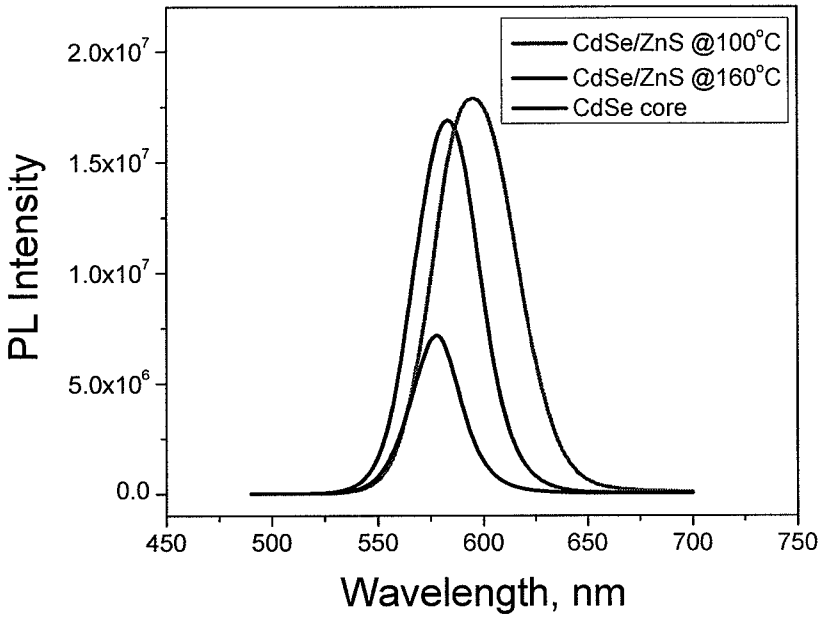

CdSe/ZnS @100°C
CdSe/ZnS @160°C
CdSe core
PL Intensity
2.0x10^7
1.5x10^7
1.0x10^7
5.0x10^6
0.0
450
500
550
600
650
700
750
Wavelength, nm

FIG. 8

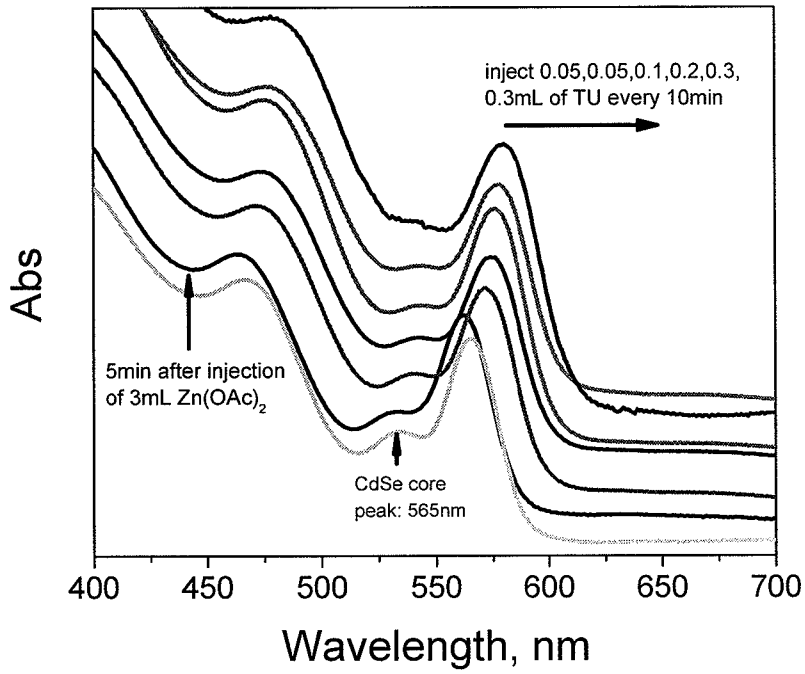

inject 0.05,0.05,0.1,0.2,0.3,
0.3mL of TU every 10min
5min after injection
of 3mL Zn(OAc)2
CdSe core
peak: 565nm
Abs
400
450
500
550
600
650
700
Wavelength, nm

FIG. 9

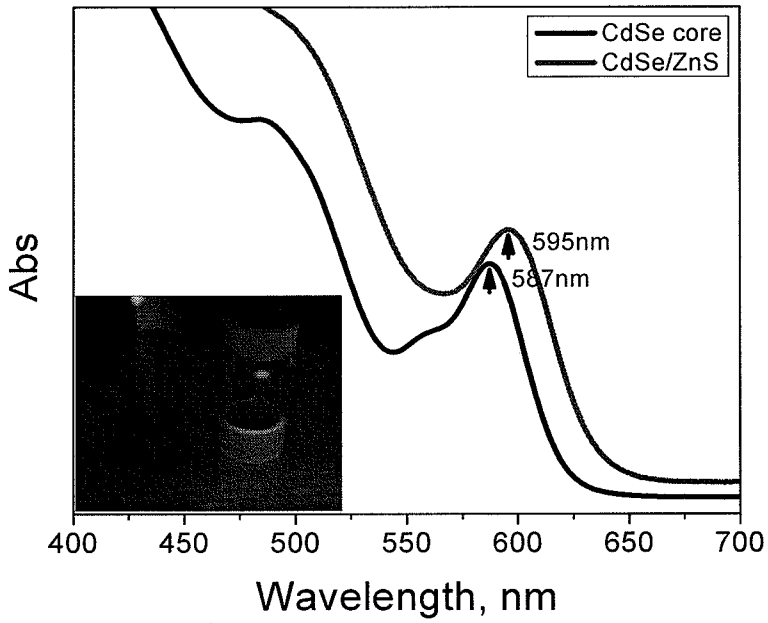

CdSe core
CdSe/ZnS
595nm
587nm
Abs
400
450
500
550
600
650
700
Wavelength, nm

FIG. 10

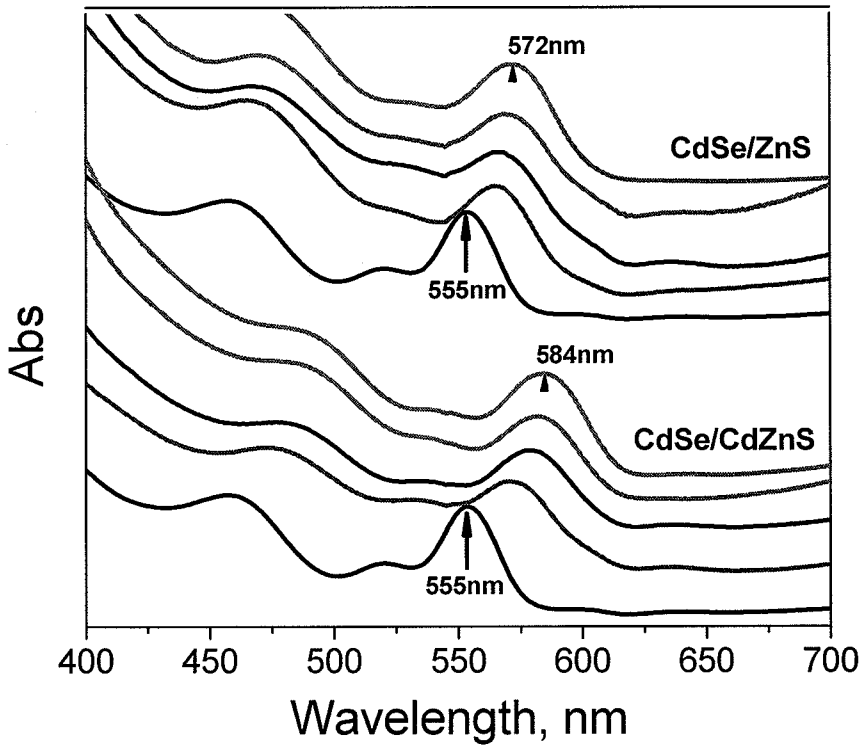
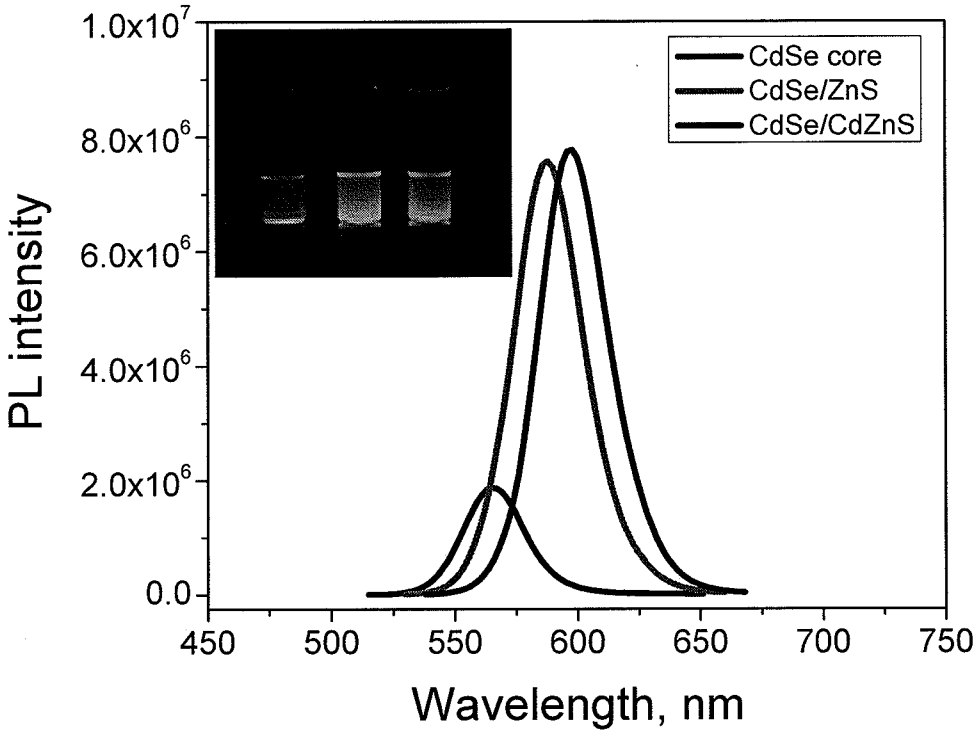
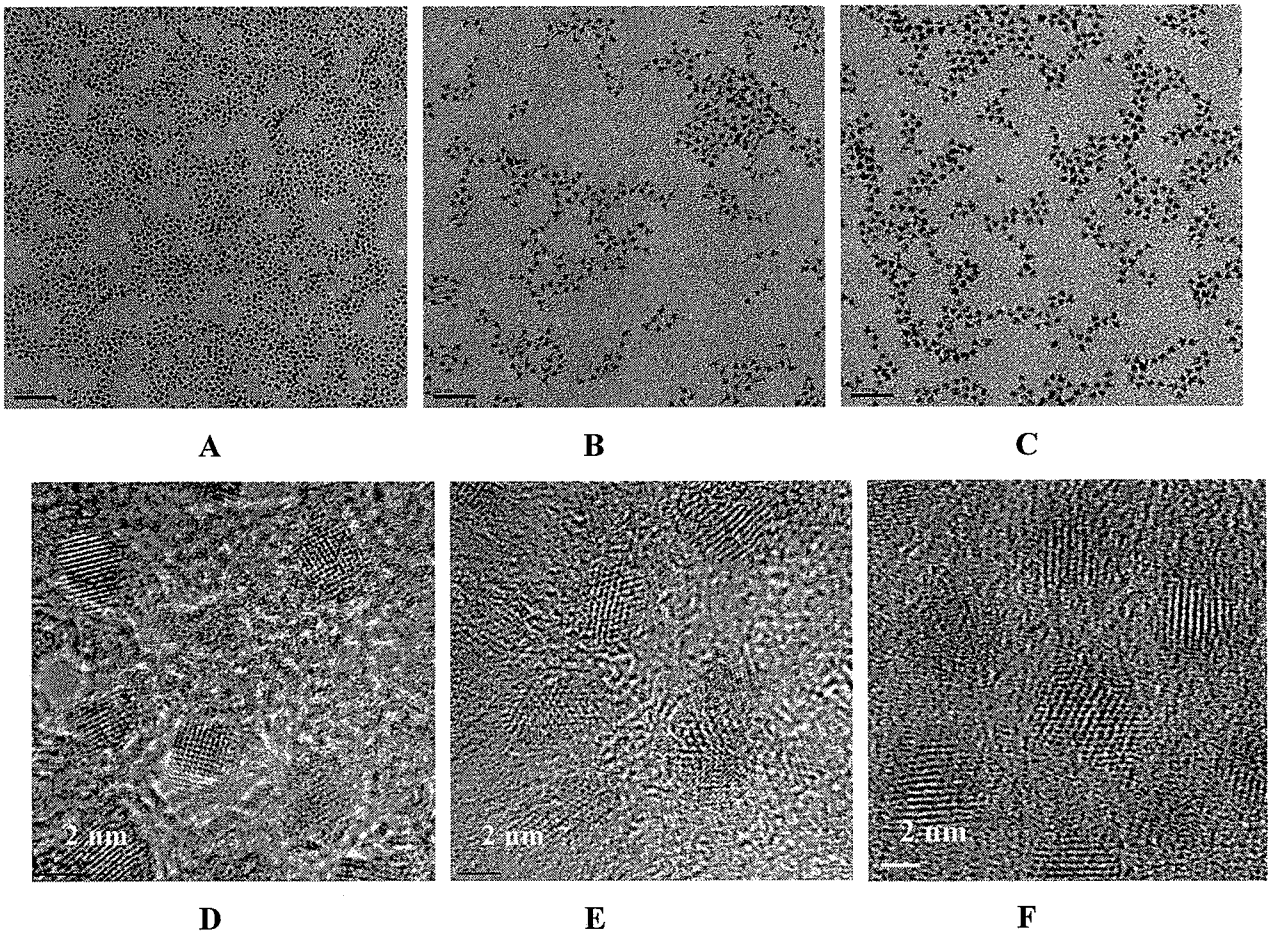

572nm
CdSe/ZnS
555nm
584nm
CdSe/CdZnS
555nm
Abs
400
450
500
550
600
650
700
Wavelength, nm

FIG. 11


1.0x10^7
8.0x10^6
6.0x10^6
4.0x10^6
2.0x10^6
0.0
PL intensity
450
500
550
600
650
700
750
Wavelength, nm
CdSe core
CdSe/ZnS
CdSe/CdZnS

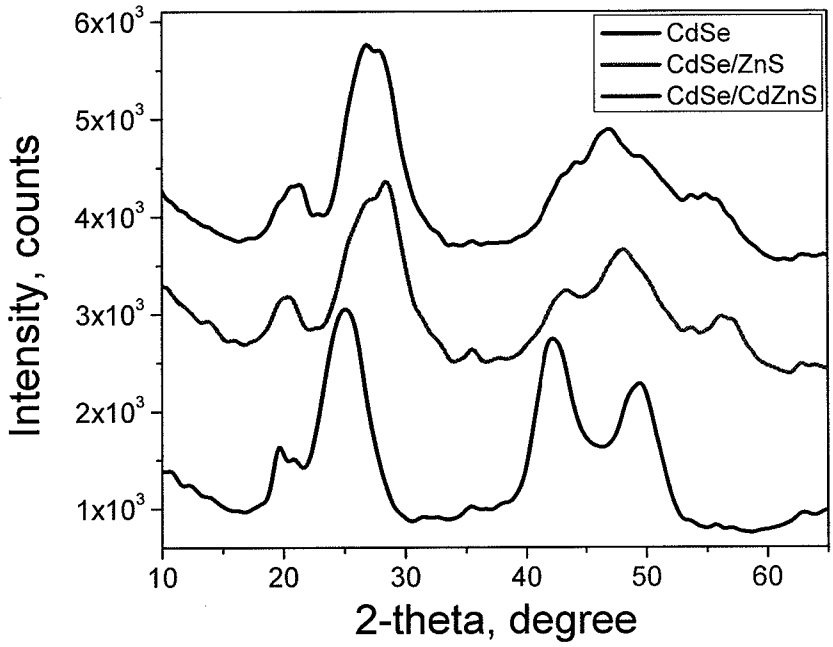
FIGS. 12A-12F



A B C

D E F

FIG. 13


CdSe
CdSe/ZnS
CdSe/CdZnS
Intensity, counts
6x10^3
5x10^3
4x10^3
3x10^3
2x10^3
1x10^3
10
20
30
40
50
60
2-theta, degree

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/30465

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B05D 5/12; C01B 19/04
USPC - 205/205; 204/157.4
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 205/205; 204/157.4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 423/509, 427/212

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest, Google Search Terms: semiconductor nanocrystal, quantum dots, semi conductive core, metal precursor solution, metal acetate, trioctylphosphine, trioctylphosphine oxide, a sulfur precursor solution, metal sulfide shell, thiourea, octadecene, (hexane or chloroform or toluene)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/0202383 A1 (Shi) 28 August 2008 (28.08.2008), especially abstract, Fig. 1, para [0024]-[0025], [0030]-[0031], [0038]-[0041, [0049], [0053]	1, 3-4, 7-11
–		----------
Y		2, 5-6, 12-20
Y	US 7,476,599 B2 (Wang et al.) 13 January 2009 (13.01.2009), especially col 3, ln 34-40	2, 6, 12-20
Y	US 2006/0202167 A1 (Landry et al.) 14 September 2006 (14.09.2006), especially para [0022]	5 and 15

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 May 2010 (10.05.2010)	28 MAY 2010

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)