12-8-2010

Synthesis of Colloidal Metal Chalcogenide Nanocrystals

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Recommended Citation

Peng, Xiaogang; Peng, Zuoyan; and Qu, Lianhua, "Synthesis of Colloidal Metal Chalcogenide Nanocrystals" (2010). *Patents Granted*. 293.
http://scholarworks.uark.edu/pat/293

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 337 695 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
08.12.2010 Bulletin 2010/49

(21) Application number: **01986328.1**

(22) Date of filing: **04.10.2001**

(51) Int Cl.:
H01L 33/00 $^{(2010.01)}$ ***C30B 7/14*** $^{(2006.01)}$
C30B 29/40 $^{(2006.01)}$ ***C30B 29/48*** $^{(2006.01)}$

(86) International application number:
PCT/US2001/031239

(87) International publication number:
WO 2002/029140 (11.04.2002 Gazette 2002/15)

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(54) SYNTHESIS OF COLLOIDAL METAL CHALCOGENIDE NANOCRYSTALS

SYNTHESE VON KOLLOIDALEN METALL CHALCOGENIDE NANOKRISTALLEN

SYNTHESE DE NANOCRISTAUX DE CHALCOGENURES METALLIQUES COLLOIDAUX

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **04.10.2000 US 237903 P**
12.03.2001 US 275008 P

(43) Date of publication of application:
27.08.2003 Bulletin 2003/35

(60) Divisional application:
10175671.6 / 2 256 834

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EP 1 337 695 B1

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates generally to the synthesis of high-quality, colloidal nanocrystals, and more particularly to the use of metal oxides and metal salts as precursors to produce high-quality nanocrystals.

[0002] High-quality colloidal semiconductor nanocrystals are defined as nanometer sized, single crystalline fragments of the corresponding bulk crystals, which have a controlled size, distribution, and are soluble or dispersible in desired solvents and media. Semiconductor nanocrystals, especially cadmium telluride (CdTe), cadmium selenide (CdSe) and cadmium sulfide (CdS), are of great interest for fundamental research and technical applications due to their size and shape dependent properties and flexible processing chemistry. High-quality CdSe and CdTe nanocrystals with nearly monodisperse dots or elongated rods are actively being developed by industry as biological labeling reagents and for other applications such as LEDs.

[0003] Synthesis of high-quality semiconductor nanocrystals has a critical role in this very active field. The synthesis of CdSe nanocrystals using dimethyl cadmium (Cd $(CH_3)_2$) as the cadmium precursor has been well developed since first reported by Murray et al. [Journal of the American Chemical Society (1993), 115, 8706-8715]. Barbera-Guillem, et al. [U.S. Patent No. 6,179,912] disclose a continuous flow process for the production of semiconductor nanocrystals using the method of Murray et al. One method for the synthesis of colloidal inorganic nanocrystals is the method developed for II-VI semiconductor nanocrystals as described in Peng et al. [Nature (2000), 404, 69-61] and Peng et al. [Journal of the American Chemical Society, (1998), 120, 5343-5344]. This synthetic method requires the use of metal precursors, such as dimethyl cadmium, which are extremely toxic, pyrophoric, expensive, and unstable at room temperature. At the typical injection temperatures (340-360°C) required for nanocrystal synthesis using Cd $(CH_3)_2$ as the precursor, $Cd(CH_3)_2$ is explosive by releasing large amounts of gas. For these reasons, the Cd $(CH_3)_2$ related synthesis methods require very restrictive equipment and conditions and, thus, are not suitable for large-scale synthesis.

[0004] Monodispersity is another critical factor to be considered in synthesizing nanocrystals. Currently, CdSe nanocrystals are the only nanocrystals having a relatively monodisperse size distribution that can be directly synthesized by using dimethyl cadmium as the precursor. In the Journal of the American Chemical Society [(1998), 120, 5343-5344] Peng et al. reported that nanocrystal size and size distribution could be quantitatively determined by analyzing the growth kinetics of CdSe nanocrystals in a very hot non-aqueous solution. When the monomer concentration is controlled in the initial reaction solution, the size distribution of CdSe nanocrystals can reach close to monodispersity with a relatively low standard deviation (about 5%). This phenomenon is referred to as "focusing" of the size distribution. The size of the CdSe nanocrystals can be controlled by the amount of time allowed for growth. Recently, Peng et al. reported [Nature (2000), 404, 59-61] that the shape of CdSe nanocrystals can also be varied between dots (close to spherical shapes) and rods (elongated shapes). By comparison, the size and size distribution of CdTe and CdS nanocrystals cannot be controlled as well as the CdSe nanocrystals synthesized by the $Cd(CH_3)_2$ related method. There, thus, remains a need to develop a method for synthesizing high-quality semiconductor nanocrystals, whereby the size, size distribution, and shape of the nanocrystals can be well controlled during the growth stage.

SUMMARY OF THE INVENTION

[0005] The present invention overcomes the disadvantages of $Cd(CH_3)_2$ related schemes by providing a novel method for sythesizing high-quality nanocrystals utilising inexpensive and non-pyrophoric materials. The method of the present invention utilizes metal oxides as precursors, which are common, safe, and low-cost compounds to produce the nanocrystals of interest. The metals include most transition metals (i.e., Cd, Zn, Hg, Cu, Ag, Ni, Co, Fe, Mn, Ti, Zr, etc.), group III metals (i.e., Al, Ga, In) and group VI metals (i.e. Sn, Pb), as described in F.A. Cotton et al. [Advanced Inorganic Chemistry, 6th Edition, (1999)].

[0006] The metal oxides are combined with a ligand and a coordinating solvent, resulting in the formation of a soluble metal complex. A ligand for a cationic species is defined as a ligand that can bind to the precursor to form a complex that is soluble in certain compounds. The solubility of the complex should be sufficient for the synthesis of the nanocrystals using the reaction conditions described herein. The ligands include long-chain fatty amines or acids, phosphonic acids, and phosphine oxides. Specific species within these groups include dodecylamine (DA), hexadecylamine (HA), octadecylamine (OA), stearic acid (SA), lauric acid (LA), hexylphosphonic acid (HPA), tetrad ecylphosphonic acid (TDPA), and trioctylphosphine oxide (TOPO). The coordinating solvent refers to any compound which binds to the starting precursors or the resulting nanocrystals. The starting precursors include the metal and non-metal precursors.

[0007] In one embodiment, a high-boiling-point coordinating solvent, such as TOPO, is used. A high-boiling point coordinating solvent includes a solvent whose boiling point is between 100°-400°C. For colloidal nanocrystal synthesis, a coordinating solvent is always required. The ligand and the coordinating solvent may be the same chemical. For example, long-chain fatty acids and amines and TOPO may serve both the solvent and the ligand functions if $Cd(Ac)_2$ is used as the precursor.

[0008] If the melting point of the ligand is too high, the ligand will not function as a useful coordinating solvent because it will remain solid at elevated temperatures. With this scenario, the ligand must be used in combination with a separate solvent. For example, phosphonic acids may serve only as ligands and must be combined with a coordinating solvent. If CdO or $CdCO_3$ is the precursor, amines and TOPO cannot be used as the ligands and can only be used as coordinating solvents. If the precursor and the resulting nanocrystals are all soluble in the chosen coordinating solvent, no additional ligands are needed. If either the metal precursor or the resulting nanocrystals are insoluble in the chosen coordinating solvent alone, a ligand must be added.

[0009] Upon heating, the metal oxides are converted to stable soluble metal complexes. Therefore metal complexes can be formed by precursor species combined with the ligands alone, or if a solvent is used, the soluble complexes can be formed by combining the precursor species with the ligand/solvent molecules.

[0010] For example, using the precursor of cadmium oxide (CdO) in which a ligand such as phosphonic acid or carboxylic acid is added, the resulting cadmium complexes are either cadmium phosphonate or cadmium carboxylate respectively. Finally, an elemental chalcogenic precursor (such as Se, Te, or S) is introduced into the dissolved cadmium complex to complete the formation of the nanocrystals at a controllable rate. For instance, using CdO as a precursor, one can synthesize CdSe, CdTe, CdS or other types of cadmium nanocrystals just by varying the precursors.

[0011] Experimental results revealed that the method of the present invention generated nanocrystals with high crystallinity, high monodispersity, and high reproducibility. The metal precursors are not pyrophoric and are much less toxic than those required for use with the current synthetic methods which use dimethyl cadmium. Thus, the present metal precursors can be manipulated under common laboratory conditions. More importantly, the present invention provides a method for producing colloidal nanocrystals for large scale synthesis.

[0012] It is therefore an object of the present invention to provide a method for synthesizing nanocrystals utilizing inexpensive and non-pyrophoric materials.

[0013] In one aspect of the present invention, a method of synthesizing colloidal nanocrystals is disclosed, comprising the steps of: (a) combining a metal oxide precursor, a ligand, and a coordinating solvent to form a metal complex; and (b) admixing an elemental chalcogenic precursor with the metal complex at a temperature sufficient to form nanocrystals. A biological labeling reagent and LED may be produced by this method.

[0014] In another aspect, the coordinating solvent is a high-boiling point coordinating solvent having a boiling point range between about 100° to about 400°C.

[0015] In another aspect of the present invention, a method of synthesizing CdSe rods is disclosed, comprising the steps of: (a) combining a cadmium precursor and a coordinating solvent to form a solution upon heating; wherein the cadmium precursor is selected from the group consisting of Cd-ODPA complex, Cd-TDPA complex, and any other Cd phosphonic acid complex; and (b) admixing an elemental chalcogenic precursor with the solution at a temperature sufficient to form CdSe rods, wherein the chalcogenic precursor is selected from the group consisting of Se-TBP, Se-TOP, and any other Se phosphine compound.

[0016] In another aspect of the present invention, a method of synthesizing rice-shaped CdSe nanocrystals is disclosed, comprising the steps of: (a) combining a cadmium precursor and a coordinating solvent to form a solution upon heating, wherein the cadmium precursor is selected from the group consisting of Cd-ODPA complex, Cd-TDPA complex, and any other Cd phosphonic acid complex; and (b) admixing an elemental chalcogenic precursor with the solution at a temperature sufficient to form rice-shaped CdSe nanocrystals, wherein the chalcogenic precursor is selected from the group consisting of Se-TBP, Se-TOP, and any other Se phosphine compound.

[0017] In yet another aspect of the present invention, a method of synthesizing branched CdSe nanocrystals is disclosed, comprising the steps of: (a) combining a cadmium precursor and a coordinating solvent to form a solution upon heating, wherein the cadmium precursor is selected from the group consisting of Cd-ODPA complex, Cd-TDPA complex, and any other Cd phosphonic acid complex; and (b) admixing an elemental chalcogenic precursor with the solution at a temperature sufficient to form branched CdSe nanocrystals, wherein the chalcogenic precursor is selected from the group consisting of Se-TBP, Se-TOP, and any other Se phosphine compound.

[0018] These and other features, objects and advantages of the present invention will become better understood from a consideration of the following detailed description of the preferred embodiments and appended claims in conjunction with the drawings described as follows:

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

FIG. 1 (a) is a graph illustrating the temporal evolution of size and size distribution of CdTe nanocrystals as quantified by UV-Vis absorption.

FIG. 1 (b) is a graph illustrating the temporal evolution of size and size distribution of CdSe nanocrystals as quantified by UV-Vis absorption.

FIG. 1 (c) is a graph illustrating the temporal evolution of size and size distribution of CdS nanocrystals as quantified by UV-Vis absorption.

FIG. 2 is a graph of the absorption spectra of different sized CdTe nanocrystals ranging from 2-10 nm as quantified by UV-Vis absorption. Inset: photoluminescence (PL) and absorption of a CdTe nanocrystal sample.

FIG. 3(a) is a transmission electron micrograph of CdTe quantum dots synthesized using the method of the present invention with CdO as the cationic precursor.

FIG. 3(b) is a transmission electron micrograph of CdTe quantum rods synthesized using the method of the present invention with CdO as the cationic precursor.

FIG. 4 is a graph illustrating the reproducibility of synthesizing CdTe nanocrystals using CdO as the precursor. Data points are within experimental error.

FIG. 5 is an UV-Vis and photoluminescence (PL) spectra of different sized wurtzite CdSe nanocrystals synthesized using different cadmium precursors, ligands, and solvents.

FIG. 6(a) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(b) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(c) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(d) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(e) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(f) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(g) is a transmission electron micrograph of wurtzite CdSe nanocrystals synthesized using Cd $(Ac)_2$ as the precursor, stearic acid as the solvent, and without additional size sorting.

FIG. 6(h) is a powder x-ray diffraction pattern of a 6 nm-sized wurtzite CdSe nanocrystal sample demonstrating the highly crystalline features.

FIG. 7(a) is a graph illustrating the growth kinetics of CdSe nanocrystals utilizing $Cd(Ac)_2$ as the precursor and TOPO as the solvent.

FIG. 7(b) is a graph illustrating the growth kinetics of CdSe nanocrystals utilizing $Cd(Ac)_2$ as the precursor, stearic acid (SA) as the ligand, and TOPO as the solvent.

FIG. 7(c) is a graph illustrating the growth kinetics of CdSe nanocrystals utilizing $Cd(Ac)_2$ as the precursor and stearic acid (SA) as the ligand.

FIG. 7(d) is a graph illustrating the growth kinetics of CdSe nanocrystals utilizing $Cd(Ac)_2$ as the precursor and technical grade (Tech) TOPO as the solvent.

FIG. 7(e) is a graph illustrating the growth kinetics of CdSe nanocrystals utilizing $Cd(Ac)_2$ as the precursor, hexylphosphonic acid (HPA) as the ligand, and TOPO as the solvent.

FIG. 7(f) is a graph illustrating the growth kinetics of CdSe nanocrystals utilizing $Cd(Ac)_2$ as the precursor, dodecylamine (DA) as the ligand, and TOPO as the solvent.

FIG. 8(a) is a graph illustrating the growth kinetics of CdSe nanocrystals using stearic acid as the ligand, TOPO as the solvent, and cadmium carbonate ($CdCO_3$) as the precursor.

FIG. 8(b) is a graph illustrating the growth kinetics of CdSe nanocrystals using stearic acid as the ligand, TOPO as the solvent, and cadmium oxide (CdO) as the precursor.

FIG. 8(c) is a graph illustrating the growth kinetics of CdSe nanocrystals using stearic acid as the ligand, TOPO as the solvent, and cadmium acetate (Cd $(Ac)_2$) as the precursor.

FIG. 9 is a transmission electron micrograph of the different shapes of CdSe nanocrystals using Cd-TDPA or Cd-ODPA.

DETAILED DESCRIPTION OF THE INVENTION

[0020] With reference to FIGS. 1-9, the preferred embodiments of the present invention are disclosed using nanocrystals derived from cadmium precursors as the following examples. Such examples are presented for illustration and discussion purposes only and should not be construed as limiting the scope of the present invention.

[0021] The present invention discloses the use of cadmium compounds, such as cadmium oxides, as a precursor replacement for dimethyl cadmium ($Cd(CH_3)_2$). Overall, the use of these compounds resulted in significant improvements in the quality of the nanocrystals. This novel synthetic method produces monodisperse cadmium chalcogenide quantum dots and quantum rods without the need for size selective precipitation [See Murray et al., Journal of the American Chemical Society, (1993), 115, 8706-8715]. Using the method of the present invention, cadmium nanocrystal production is simple and reproducible (see Fig. 4). By contrast, the $Cd(CH_3)_2$ related methods are very hard to control and almost impossible to reproduce [See Peng et al., Journal of the American Chemical Society, (2001), 123, 183-184]. As an additional benefit, all the precursors used in the present invention are less expensive, safer, and less toxic than $Cd(CH_3)_2$. Additionally, the present precursors are not pyrophoric and require less restrictive conditions for producing nanocrystals. These advantages provide the basis for the potential use of the present method in industrial scale production of high-quality nanocrystals.

[0022] With the current method for synthesizing nanocrystals, dimethyl cadmium is decomposed in hot trioctylphosphine oxide (TOPO) to generate an insoluble metallic precipitate. When TOPO is combined with either hexylphosphonic acid (HPA) or tetradecylphosphonic acid (TDPA), the dimethyl cadmium is converted into a cadmium-HPA or cadmium-TDPA complex (Cd-HPA/Cd-TDPA). If the cadmium-to-phosphoric acid ratio is less than one, a colorless clear solution results. After the cadmium complex is formed, an injection of Se dissolved in tributylphosphine (TBP) will generate CdSe nanocrystals. In the method of the present invention, use of dimethyl cadmium as the precursor to nanocrystal formation is unnecessary, if a cadmium complex precursor is generated by other means.

[0023] The co-inventors of the present invention first synthesized and purified the cadmium HPA and cadmium TDPA complex (Cd-HPA and Cd-TDPA) from cadmium chloride ($CdCl_2$) as disclosed in Z. A. Peng and X. Peng [Journal of the American Chemical Society, (2001) 123, 183-184]. The resulting Cd-HPA/Cd-TDPA complex was subsequently combined with TOPO and heated to 300-360°C to produce a clear colorless solution. An injection of selenium-TBP solution into this complex generated CdSe nanocrystals with a qualitative growth pattern mimicking that generated with $Cd(CH_3)_2$ as the precursor.

[0024] When cadmium oxide (CdO), cadmium acetate ($Cd(Ac)_2$), cadmium carbonate, or other cadmium salts formed by cadmium and an anion of a weak acid, are used as the cadmium source, the synthesis is even simpler. Nanocrystals can be synthesized without purifying the cadmium complex, which means the entire synthesis can be done in a "one pot or vessel" manner. For example, when a cadmium precursor such as $Cd(Ac)_2$ is combined with a ligand such as phosphonic acid, carboxylic acid, or an amine, a cadmium complex is formed. Finally, an elemental chalcogenic precursor (such as Se, Te, or S) is introduced into the cadmium complex to complete the formation of the nanocrystals. For all three cadmium chalcogenides, using CdO as the precursor within a single vessel will generate CdTe and CdSe quantum rods as demonstrated in the experimental examples below and shown in Figs. 1(a-c), Fig. 2, and Fig. 3 (a-b).

[0025] The one pot or vessel approach to synthesizing cadmium chalcogenide nanocrystals does not work when cadmium chloride ($CdCl_2$), cadmium sulfide ($CdSO_4$) or other metal salts formed by the reaction of cadmium with a strong acid are used as cadmium precursors. This may be due to the relatively low stability of cadmium chalcogenides in acidic conditions compared to using cadmium precursors such as $CdCl_2$ and $CdSO_4$.

[0026] The growth reactions of semiconductor nanocrystals can be conveniently monitored by absorption and emission spectroscopy. Based on the theory of quantum confinement, the first absorption peak and the band edge emission of nanocrystals shift blue as the size decreases if the size of the nanocrystals is smaller than the Bohr radius of the exciton. The average size of semiconductor nanocrystals can be monitored by peak positions, while sharpness of the peaks indicates size distribution. Nanocrystals exhibiting quantum confinement effects are called quantum dots if dot-shaped, or quantum rods if rod-shaped.

[0027] Monodispersity is represented by a sharp absorption peak if the growth ceases in the "focusing of size distribution" regime [Peng et al., Journal of the American Chemical Society, (1998), 120, 5343-5344]. As shown in Figs. 1(a-c), 2, 5, 7(a-f), and 8(a-c), the size distribution of the cadmium chalcogenide nanocrystals is monodisperse at the focusing point of size distribution. The size and size distribution temporal evolution of the three cadmium chalcogenide nanocrystals possess a similar absorption and emission pattern to the CdSe nanocrystals formed by using $Cd(CH_3)_2$ as the precursor. Monodisperse CdSe, CdTe, and CdS nanocrystals can be synthetically produced without the need to use any size separating techniques.

[0028] The size range of close to monodisperse CdSe dots (Figs. 5 and 6(a-g)) covers a range from approximately 1.5 nm to over 25 nm. By comparison, with the current $Cd(CH_3)_2$ method, the dot-shaped CdSe dots larger than approximately 5 nm are very difficult to generate. For the $Cd(CH_3)_2$ method, even with the aid of size selective precipitation, the largest sized CdSe dots with good size distribution as disclosed in the scientific literature are about 12 nm [Murray et al., Journal of the American Chemical Society, (1093), 115, 8706-8715].

[0029] By using CdO as the precursor, different sized CdTe quantum dots can be synthesized. This is represented by the different absorption spectra that are shown in Fig. 2. Transmission electron microscopy (TEM) measurements indicate that these nanocrystals have a very narrow size distribution as shown in Figs. 3(a) and 3(b). The relative standard deviation for these nanocrystals is approximately 10%.

[0030] As shown in Figs. 1(a-c), 2, 5, 6(a-g), and 7(a-f), varying the growth conditions and the cadmium precursors can easily control the size of the nanocrystals. The initial size of the nanocrystals as well as their focusing size depend strongly on the initial monomer concentration, the ratio of cationic and anionic precursors, reaction temperatures, and the duration of the reaction.

[0031] X-ray powder diffraction indicates that in most cases, CdTe, CdSe, and CdS nanocrystals are highly crystalline wurtzite nanocrystals (see Fig. 6(h)). However, if amines are used as the ligands, CdSe nanocrystals seem to form zinc blend crystals.

[0032] When using phosphonic acids as the ligand, the initial nucleation can be tuned tenths of seconds later after the injection. This is shown in Fig. 4. It is believed that the slow initial nucleation is due to the stability of Cd-HPA/Cd-TDPA complex. When $Cd(CH_3)_2$ is used as the precursor, it is believed that the instant initial nucleation is due to the extremely high reactivity of $Cd(CH_3)_2$.

[0033] The slow initial nucleation rate bears three important advantages in practice. First, the injection temperature does not need to be 350-360°C, but can be around 250-300°C. Second, both nucleation and growth of nanocrystals are not dependent on the initial injection. As a result, the synthesis is very reproducible (see Fig. 4 as an example). Third, the time delay of initial nucleation implies that the initial injection process can take as long as tenths of seconds.

[0034] In order to take the advantage of the "focusing of size distribution" and the "1D-growth" when using Cd $(CH_3)_2$ as the precursor, the Se dissolved in TBP injection had to be performed within sub-seconds at a temperature range of 340-360°C. The concept of the "1D-growth" refers to a specific growth stage in which all nanocrystals are growing only along one dimension, which is the unique axis of the crystal structure [Z.A. Peng and X. Peng, Journal of the American Chemical Society, 2001, in press]. Therefore, if $Cd(CH_3)_2$ is used as the precursor and if the injection volume is more than approximately 5-6 ml, the operation requires special caution and is very dangerous.

[0035] With the present invention, a large quantity of an elemental chalcogenic precursor (such as Se, Te, or S) solution can be added into the reaction vessel, provided that non-pyrophoric and non-explosive reactants are used. When approximately 5-20 ml of an elemental chalcogenic precursor stock solution was added to a 100ml flask, the reaction yielded approximately 700 mg of high-quality CdTe nanocrystals. In addition, because the injection temperature of the elemental chalcogenic precursor in TBP, TOP, or an amine solvent can be as low as 150-300°C, the explosive nature is further reduced.

[0036] Currently, CdTe, CdSe, and CdS nanocrystals are of great industrial interest for developing photoluminescence-based bio-medical labeling reagents. The photoluminescence properties of the nanocrystals synthesized by this CdO approach are comparable to the nanocrystals synthesized with $Cd(CH_3)_2$ precursors. Fig. 2 (inset) illustrates the absorption and emission spectra of a CdTe sample. In general, the photoluminoscence of CdTe nanocrystals synthesized by the new method of the present invention is well above 20%. The photoluminescence properties of the nanocrystals synthesized by using carboxylic acids are significantly better than any existing methods. For instance, the photoluminescence quantum efficiency, as defined by the number of photons released by the number of photons absorbed, of CdSe nanocrystals synthesized in stearic acid is as high as 20-30%.

[0037] The CdO approach is well suitable for studying growth mechanisms of colloidal nanocrystals especially for nucleation for several reasons. First, in contrast to the $Cd(CH_3)_2$ related synthesis, the cadmium precursor in the entire nucleation and growth period is one species, Cd-HPA or Cd-TDPA. Second, the initial nucleation is reasonably slow, which makes it possible to access the nucleation process with better accuracy. Also, due to the slow nucleation and growth rate, time-resolved, *in-situ* study of crystallization is possible.

[0038] In conclusion, a reproducible method of synthesizing high-quality quantum rods and dots was developed using common metal oxides and metal salts as the cationic precursor. The cost of chemicals and equipment is considerably less than the existing $Cd(CH_3)_2$ approach. The resulting nanocrystals are nearly monodisperse without any size separation. The size range of close to monodisperse CdSe quantum dots achieved by the present invention is about four times larger than that achieved with the current synthetic methods, which utilize $Cd(CH_3)_2$ as the cadmium precursor. For CdTe nanocrystals, the size distribution is better than that reported for any CdTe nanocrystals. The shape of the nanocrystals synthesized by the present invention can be controllably varied between dots and rods. The crystal structure of CdSe nanocrystals can be between wurtzite and zinc blend types.

[0039] Overall, the reaction conditions of the present invention are very mild and simple as compared to the current $Cd(CH_3)_2$ approach. In principle, large-scale synthesis of high-quality colloidal nanocrystals can be achieved without using a glovebox. The present synthetic method is a major step towards a green chemistry approach for synthesizing high-quality semiconductor nanocrystals. This new approach may also be used for time-resolved, *in-situ* study of crystallization. Furthermore, the present method suggests that spontaneous formation of shape controlled high-quality colloidal nanocrystals under mild conditions is possible.

[0040] The following examples illustrate the method of the present invention with cadmium chalcogenides nanocrystals as well as other types of semiconductor nanocrystals. The reaction conditions of the following examples can be varied over a wide range. Using the synthesis of CdSe nanocrystals as an example, the conditions can be altered as follows. The cadmium precursor can be cadmium phosphonic acid complexes, cadmium fatty acids, CdO, CdCO3, Cd metal, or any other inexpensive and safe cadmium compound. The selenium precursor can be selected from different types of selenium-phosphine compounds. The temperature of the synthesis varies between 150 and 380°C. The concentration of the cadmium precursor is in the range of about 0.005 mol/kg to about 0.8 mol/kg. The cadmium precursor to selenium precursor ratio varies between approximately 1:5 and about 5:1.

EXAMPLE 1

CdTe Quantum Dots

[0041] CdTe quantum dots were synthesized by loading 0.0514g (0.4 mmol) CdO, 0.2232g (0.8 mmol) TDPA, and 3.78g TOPO into a 25-ml flask and then heated to 300-320°C under an Argon flow to dissolve the CdO. The mixture was maintained at 320°C for 10 to 15 minutes in order to obtain an optically clear, colorless solution. This solution was then heated to 360°C. In a glove box, 0.0664g Te powder was dissolved in TBP-toluene (1.8g/0.2g) to obtain a solution, which was then injected into the above reaction flask at 360°C. After injection, the nanocrystals grew at 250°C. Nanocrystal growth was monitored by removing aliquots for UV-Vis measurements. After the nanocrystals reached the desired size, the heating mantle was removed quickly and the reaction solvent was cooled down to stop the reaction. After the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The nanocrystal precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum (see the CdTe UV-Vis spectra in Figs. 1(a) and 2 and the TEM picture for CdTe quantum dots in Fig. 3(a)).

EXAMPLE 2

CdTe Quantum Rods

[0042] CdTe quantum rods were synthesized by dissolving 0.1542g (1.2 mmol) CdO in 0.6696g (2.4 mmol) TDPA mixed with 3.55g TOPO at 300°C. The optically clear solution was then heated to 360°C. Next, 0.2g Te powder was dissolved in 1.8g TBP, injected into the reaction flask at 360°C, and subsequently cooled to 250°C to allow the quantum rods to grow. The reaction was monitored by UV-Vis spectra and then characterized by photo-luminescence spectra and TEM. After reaching the desired size, the heating mantle was removed quickly and the reaction solvent was cooled down to stop the reaction. After the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The nanocrystal precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum (see the quantum rods TEM picture in Fig. 3(b) as one sample).

EXAMPLE 3

Synthesis of CdSe Nanocrystals in CdO/TDPA/TOPO System

[0043] Initially, 0.0899g (0.7 mmol) CdO, 0.4010g (1.4 mmol) TDPA, and 3.78g TOPO were loaded into a 25-mil flask and then heated to 300-320°C under an Argon flow to dissolve the CdO. The mixture was maintained at 320°C for 10 to 15 minutes in order to obtain an optically clear, colorless solution. This solution was then heated to 360°C. In a glove box, 0.0719g (0.91 mmol) Se powder was dissolved in 2g TBP to obtain a solution. This solution was then injected into the above reaction flask at 360°C. After injection, the temperature of the reaction solution was quickly cooled down to 250°C for nanocrystals growth. Aliquots were used to monitor the reaction by UV-Vis measurement. After reaching the desired size, the heating mantle was removed quickly and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding about 10 ml methanol. The nanocrystal precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum. Photo-luminescence spectra and TEM were used to characterize the samples (see the CdSe UV-Vis spectra in Fig. 1(b)).

EXAMPLE 4

Synthesis of CdSe Nanocrystals in CdO/SA (Stearic Acid) System

[0044] First, 0.0512g CdO (about 0.4 mmol) and 4.027g stearic acid were loaded into a 25-ml flask and heated up to 150°C for 5 to 10 minutes to dissolve all CdO into stearic acid. This optically clear solution was then heated to 360°C. Then, 0.05g Se (about 0.63 mmol) was dissolved in TBP-toluene (1.75g/0.2g) to obtain a solution, which was injected into the above reaction flask at 360°C. The reaction mixture was then cooled down to 250°C for nanocrystal growth. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding about 20 ml acetone. The nanocrystal precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum.

COMPARATIVE EXAMPLE 5

Synthesis of CdSe Nanocrystals in $Cd(Ac)_2$/SA System

[0045] First, 0.2 mmol $Cd(Ac)_2$ was dissolved in 4g stearic acid at approximately 100-150°C, with subsequent heating of the solution to 360°C. Then, 2g TOP, 1.0 mmol Se, and 0.2g toluene were combined to form a solution, which was subsequently injected at 360°C. After injection, the reaction solution was allowed to cool down to 250°C for nanocrystal growth. After the nanocrystals reached the desired size, the heating mantle was quickly removed, and the reaction solvent was cooled to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding about 10 ml acetone. The nanocrystal precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum (see the UV-Vis spectra in Fig. 7(b)).

EXAMPLE 6

Low Temperature Synthesis

[0046] First, 0.4 mmol CdO, 0.8 mmol HPA, and 3.83g TOPO were loaded into a reaction flask and heated to 320°C to obtain a clear solution, then cooled to 200°C. Next, 0.31 mmol Se powder was dissolved in 2g TBP to obtain a solution. The solution was then injected into the flask. Nanocrystals were grown at 170°C after injection. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding about 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum.

COMPARATIVE EXAMPLE 7

Synthesis of CdSe Nanocrystals using $CdCl_2$

[0047] The synthesis of CdSe nanocrystals using $CdCl_2$ and HPA is different from the above reactions in that the Cd-HPA complex must first be isolated and purified to remove all the chloride ions. The $CdCl_2$ precursor was dissolved in water and subsequently precipitated using NH_3H_20. This precipitate was centrifuged and separated from the liquid. The pellet was washed with distilled water and centrifuged again. This process was repeated three times to remove all the Cl^- ions absorbed in the solid. The final pellet is purified $Cd(OH)_2$x H_2O. The Cd $(OH)_2$ x H_2O was then dissolved in a mixture of HPA and TOPO with the Cd/HPA ratio of 1:2 at 120-150°C. This solution was cooled down to 50-80°C. Methanol was added into the flask to completely precipitate the Cd-HPA complex. The Cd-HPA complex was separated from the liquid and dried.

[0048] Upon purification, the Cd-HPA complex (1 mmol) was mixed with 3.7 g TOPO and subsequently heated to 360°C. Two grams of Se (1.3 mmol Se dissolved in TBP) was then injected into the flask at 360°C. After injection, the reaction was cooled to 250°C in order to allow the nanocrystals to grow. After reaching the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution reached below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. After purification, the nanocrystals can be stored in a powder form or directly in the non-polar solvent.

COMPARATIVE EXAMPLE 8

Synthesis of CdSe Nanocrystals in $Cd(Ac)_2$/dodecylamine System

[0049] First, 0.2 mmol of $Cd(Ac)_2$ was dissolved in a mixture of 2g dodecylamine and 2g of TOPO at approximately 100°C. The mixture was heated to 250°C. Then, 1.0 mmol Se dissolved in 2g TOP and 0.2g toluene to form a solution, which was subsequently injected into the flask. The nanocrystals were allowed to grow at 230°C to the desired size. After reaching the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by I centrifugation and decantation. Nanocrystals were either stored as precipitate or were dried in a vacuum.

COMPARATIVE EXAMPLE 9

Synthesis of CdSe Nanocrystals in $Cd(Ac)_2$/Pure TOPO (99%)

[0050] First, 0.2 mmol of $Cd(Ac)_2$ was dissolved in 4g of TOPO. The mixture was heated to 360°C, and 1.0 mmol Se dissolved in 2 g TOP and 0.2g toluene was injected. The nanocrystals were allowed to grow at 250°C to the desired size. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum (see the UV-Vis spectra presented in Fig. 7(a)).

COMPARATIVE EXAMPLE 10

Synthesis of CdSe Nanocrystals in $CdCO_3$/SA/TOPO System

[0051] CdSe nanocrystals were synthesized by dissolving 0.2 mmol $CdCO_3$ in a mixture of 2g stearic acid and 2g TOPO at approximately 100-150°C. This solution was then hated to 360°C. 1.0 mmol Se was dissolved in 2 g TOP and 0.2 g toluene to form a solution. This solution was injected at 360°C into the flask. The reaction mixture was cooled to 250°C for nanocrystal growth. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum (see Fig. 8(a)).

EXAMPLE 11

CdS Nanocrystals

[0052] First, 0.4 mmol (0.0514g) CdO, 0.8 mmol (about 0.2232g) TDPA, 3.78g TOPO were mixed in a reaction flask and heated to 300°C for 5 to 10 minutes. After an optically clear solution was obtained, the solution was then cooled down to 270°C for injection under argon flow. In a glove box, 3.2mg (0.2 mmol) sulfur was dissolved in 2g benzylamine to obtain a sulfur solution. At 270°C, this solution was injected into the reaction flask and the nanocrystals were grown at 220°C. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution reached below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum (see the CdS UV-vis spectra in Fig. 1(c)).

COMPARATIVE EXAMPLE 12

InP Nanocrystals

[0053] Indium phosphate (InP) nanocrystals were synthesized by dissolving 0.1 mmol (0.02g) fresh $In(OH)_3$ in 3mmol (0.5g) HPA and 3.5g TOPO at approximately 200°C under argon flow. Then the solution was cooled to 120-130°C and the reaction system was flushed with argon, vacuum pumped for 20-30 minutes, followed by another argon flow for 10-15 minutes. The process of argon flow and vacuum pumping was repeated for three times in order to remove all the absorbed water and oxygen in the reaction system. The reaction mixture was heated to 300°C with a subsequent injection of a 2g stock solution which contained 0.0277g (0.1 mmol) $P(TMS)_3$, 1.8g TOP, and 0.2g toluene. The reaction mixture was cooled to 250°C in order to allow the nanocrystals to grow. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum. The size distribution of nanocrystals using this reaction is broad, producing a standard deviation of greater than 20%.

EXAMPLE 13

ZnSe Nanocrystals

[0054] ZnSe nanocrystals were synthesized by dissolving 0.4 mmol ZnO in a mixed solvent consisting of 2g stearic acid and 2g TOPO with subsequent heating to 340°C. After the ZnO was completely dissolved, the mixture was cooled to 280°C. Next, 0.3077mmol Se dissolved in 2g TBP was injected at 280°C. The reaction mixture was cooled to 250°C for nanocrystals growth. After nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum. The size distribution of nanocrystals using this reaction is broad, producing a standard deviation of greater than 20%.

COMPARATIVE EXAMPLE 14

ZnS Nanocrystals

[0055] ZnS nanocrystals were synthesized by dissolving 0.4 mmol Zn(Ac) in a mixture solvent of 2g stearic acid and 2g TOPO with subsequent heating to 340°C. After the Zn(Ac) is completely dissolved, the solution was cooled to 280°C. Then, 0.8 mmol S dissolved in 2g benzylamine was injected at 280°C. The reaction mixture was cooled to 250°C in order to allow nanocrystals to grow. After the nanocrystals reached the desired size, the heating mantle was quickly removed and the reaction solvent was cooled down to stop the reaction. When the temperature of the solution was below 80°C, the nanocrystals were precipitated from the reaction mixture by adding approximately 10 ml methanol. The precipitate was separated by centrifugation and decantation. Nanocrystals were either stored as precipitate or dried in a vacuum. The size distribution of nanocrystals using this reaction is broad, producing a standard deviation of greater than 20%.

EXAMPLE 15

Synthesis of CdSe Rods

[0056] This example provides a two-step process by which nearly monodisperse CdSe rods were prepared.

[0057] A. Step 1- Preparation of Cd-TDPA/TOPO Complex - 5 mmol CdO (0.6420g), 10 mmol of TDPA (2.79 g), and 2g TOPO (99%) were loaded into a reaction flask and heated up to 320 °C with stirring under argon flow. After an optically clear solution was obtained (i.e., essentially all the CdO was dissolved in the TDPA and TOPO mixture solvent), the heating was stopped, and the solution was allowed to cool to room temperature. A solid product, the Cd-TDPA/TOPO complex, was obtained. This solid product was taken out of the reaction flask and stored in a vial for the following CdSe rod synthesis.

[0058] B. Step 2 Synthesis of nearly Monodisperse CdSe rods - 1.6 mmol Cd-TDPA/TOPO complex prepared above (1.72 g) and 2.28g TOPO (99%) were loaded into a reaction flak and heated up to 320°C with stirring and argon flow. In a glove box, 0.256g Se:TBP solution (contains 0.064g Se, 0.8 mmol) was mixed with 1.444g TOP and 0.3g anhydrous toluene to obtain an injection solution. This Se solution was transferred out from the glove box and loaded into a syringe, and then injected into the reaction flask at 320°C. The nanocrystals were allowed to grow at 250°C and aliquots were taken out from flask to monitor the reaction by UV-vis, PL and TEM. After the nanocrystals grew to predetermined size, the reaction was stopped and the reaction mixture was allowed to cool to about 80°C, followed by addition of 20 ml methanol to precipitate the nanocrystals. TEM, UV-vis, PL results indicated that the obtained rods have a relatively uniform size distribution. A statistical analysis of a TEM image from rods taken in one aliquot at 45 minutes after injection showed that the average short axis was 6.18 nm with a standard deviation of 5.03% and the aspect ratio was 6.98 with a standard deviation of 11.51%.

EXAMPLE 16

Synthesis of CdSe Nanocrystals in Stearic Acid/ Hexadecylamine/TOPO

[0059] This example describes a procedure for preparing highly luminescent and essentially monodisperse CdSe nanocrystal dots in a three-component solvent system, steric acid/hexadecylamine/TOPO solvent system.

[0060] CdO (0.2 mmol) and stearic acid (0.8 mmol) were loaded into a reaction flask an heated to about 150°C with stirring and argon flow. The clear hot solution was cooled down to room temperature. Hexadecylamine and TOPO (1 : 1 in mass) were added into the flask and the final total mass was 4.0 grams. Consequently, the mixture was heated to 270°C under argon flow. Se (1 mmol) was dissolved in 1.2 mmol TBP and diluted with dioctylamine to 2 grams total. The Se solution was quickly injected into the reaction flask at 270°C. The system was then set at 250°C for growth of the CdSe nanocrystals to reach predetermined sizes. The nanocrystals were essentially monodisperse in the size range between 2 nm and 6 nm, typically with 5-10% standard derivation. The as-prepared nanocrystals also possess very high photoluminescence quantum efficiency.

EXAMPLE 17

Synthesis of CdSe Nanocrystals in Stearic Acid/ Octadecylamine/TOPO

[0061] This example describes a procedure for preparing highly luminescent and essentially monodisperse CdSe nanocrystal dots in a three-component solvent system, stearic acid/octadecylamine/TOPO solvent system.

[0062] CdO (0.4 mmol) and SA (1.6 mmol) were loaded into a reaction flask and heated to about 150°C with stirring and argon flow. The clear hot solution was cooled down to room temperature. Octadecylamine and TOPO (1 : 1 in mass) were added into the flask and the final total mass was 4.0 grams. The mixture was heated to 270°C under argon flow. Se (2 mmol) was dissolved in 2.4 mmol TBP and diluted by dioctylamine to 2 grams total. The Se solution was quickly injected into the reaction flask at 270°C. The system was then set at 250°C for growth to reach different sized CdSe nanocrystals. The nanocrystals were essentially monodisperse in the size range between 2 nm to 6 nm and highly luminescent.

EXAMPLE 18

Synthesis of Cadmium-TDPA Complex

[0063] 0.6420g CdO (5 mmol), 2.7900g TDPA (10 mmol), and 2g TOPO were loaded into the reaction flask, then heated up under Argon flow. The CdO was dissolved into the solvent around 300°C and an optical clear solution was obtained. After kept for 5 to 10 minutes, the solution was cooled down to room temperature under argon flow. A solid product was obtained and then removed from the reaction flask. This is the Cd-TDPA complex, which was used as the precursor for synthesis of CdSe nanocrystals.

EXAMPLE 19

Synthesis of Cadmium-ODPA (Octadecyl Phosphonic Acid) Complex

[0064] 0.6420g CdO (5 mmol), 3.3447g ODPA (10 mmol), and 2.2g TOPO were loaded into the reaction flask, then heated up under Argon flow. The CdO was dissolved into the solvent around 200°C and an optical clear solution was obtained. After kept for 5 to 10 minutes, the solution was cooled down to room temperature under argon flow. A solid product was obtained and then removed from the reaction flask. This is the Cd-ODPA complex, which was used as the precursor for synthesis of CdSe nanocrystals.

EXAMPLE 20

Synthesis of Rice-Shaped CdSe Nanocrystals

[0065] 1.3259g Cd-TDPA complex (1.31 mmol) and 1.8204 g TOPO were loaded into the reaction flask, and then heated up to 350°C under Argon flow. In the glove box, two kind of Se solutions were prepared separately. In one vial, 0.205g Se-TBP (25% Se) solution (contains 0.655 mmol Se), 1.097g TOP, and 0.228g toluene were loaded and mixed together. This was named as Se solution 1. In another vial, 0.259g Se (3.275 mmol) was mixed with 2.037g TOP and 0.15g toluene. This mixture was stirring until all the Se powder was dissolved in the solution and an optical solution was obtained. This solution was named as Se solution 2. Se solution 1 was loaded into a 5-ml syringe and then quickly injected into the reaction flask at 350°C. The temperature of reaction solution dropped quickly after the injection and then was kept at 300°C for nanocrystals growth. Needle-tip aliquots were taken out to monitor the reaction at certainly reaction time. 0.6 ml Se solution 2 (one third of whole solution) was loaded into a 1-ml syringe and then introduced into the reaction solution at 300°C with the dropwise rate of 1drop per second started around 4 minute after the first injection. After finished the slow injection, one needle tip aliquot was taken out and then another 0.6 ml Se solution 2 was added again with the same method. Another needle tip aliquot was taken out and then the left Se solution 2 was added into the reaction solution as descript above. After all the Se solution 2 was added into the reaction solution, the reaction was running until the nanocrystals were insoluble in hexanes. Finally, the heating mantle was removed and the temperature was cooled down. Around 80°C, 5 ml toluene and 10 ml methanol were added into the reaction flask to precipitate down the nanocrystals. The nanocrystal precipitate was separated by centrifugation and decantation and then nanocrystals were either stored as precipitate or dried in a vacuum.

EXAMPLE 21

Synthesis of CdSe Rods using Cd-ODPA Complex

[0066] 2g Cd-ODPA complex (about 1.6 mmol) and 2g TOPO were loaded in a 25-ml reaction flask and then heated up to 350°C under Argon flow. In the glove box, 0.256g Se-TBP solution (contains 25% Se, 0.8 mmol) was mixed with 1.444g TOP and 0.3g toluene as the Se solution. Then, this solution was injected into the reaction flask at 350°C, and the reaction was kept at 300°C for nanocrystals growth. Aliquots were taken out to monitor the reaction at certainly period of time scale. The reaction was stopped around 1 hour by removing the heating mantle and cooling down the reaction solvent. 5 ml toluene and 10 ml methanol were added in the reaction flask around 80°C to precipitate the nanocrystals.

[0067] The Cd-ODPA complex can be replaced by a Cd-TDPA complex or other Cd phosphonic acid complexes with the same number of moles of cadmium using the same reaction conditions and procedures to make the CdSe rods. The Cd-ODPA complex or the Cd-TDPA complex concentration ranges between 0.33 mol/kg and about 0.6 mol/kg.

[0068] The Cd precursor and the Se precursor are in the range between 5:1 and 1:5. The Se precursor, Se-TBP, can be replaced by Se-TOP or other Se phosphine compounds. The Cd precursor, Cd-ODPA, can be replaced by the Cd-TDPA complex or other Cd phosphonic acid complexes.

[0069] The reaction temperature can vary between approximately 250° and about 380°C for the synthesis of the rod shaped CdSe nanocrystals.

EXAMPLE 22

Synthesis of Brached CdSe Nanocrystals

[0070] 2g Cd-ODPA complex (about 1.6 mmol) and 2g TOPO were loaded in a 25-ml reaction flask and then heated up to 250°C under Argon flow. In the glove box, 0.256g Se-TBP solution (contains 25% Se, 0.8 mmol) was mixed with 1.444g TOP and 0.3g toluene as the Se solution. Then, this solution was injected into the reaction flask at 250°C and the reaction was kept at 180°C for nanocrystals growth. Aliquots were taken out to monitor the reaction at certainly period of time scale. The reaction was stopped around 24 hour by removing the heating mantle and cooling down the reaction solvent. 5 ml toluene and 10 ml methanol were added in the reaction flask around 80°C to precipitate the nanocrystals.

[0071] It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the - scope of the present invention and without diminishing its attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

Claims

1. A method of synthesizing colloidal nanocrystals, comprising the steps of :

   (a) combining a metal oxide precursor, a ligand, and a coordinating solvent to form a metal complex; and
   (b) admixing an elemental chalcogenic precursor with the metal complex at a temperature sufficient to form nanocrystals.

2. The method according to claim 1, wherein the metal oxide precursor comprises a transition metal.

3. The method according to claim 1, wherein the metal oxide precursor comprises Sn or Pb.

4. The method according to any of claims 1-3, wherein the ligand is selected from long-chain fatty amines,

long-chain fatty acids, phosphonic acids, and phosphine oxides.

5. The method according to claim 4, wherein the ligand includes dodecylamine (DA), hexadecylamine (HA), octadecylamine (OA), stearic acid (SA), lauric acid (LA), hexylphosphonic acid (HPA), tetradecylphosphonic acid (TDPA), octadecyl phosphonic acid (ODPA), and trioctylphosphine oxide (TOPO).

6. The method according to claim 1 or claim 2, wherein the metal oxide precursor is cadmium oxide.

7. The method according to any preceding claim, wherein the elemental chalcogenic precursor is selected from Se, Te, and S.

8. The method according to any preceding claim, wherein the coordinating solvent is a high boiling point coordinating solvent having a boiling point range between 100° to 400°C.

9. The method according to any of claims 1-7, wherein the coordinating solvent is selected from long-chain fatty amines, long-chain fatty acids, phosphonic acids, and phosphine oxides.

10. The method according to claim 9, wherein the coordinating solvent includes dodecylamine (DA), hexadecylamine (HA), octadecylamine (OA), stearic acid (SA), lauric acid (LA), hexylphosphonic acid (HPA), tetradecylphosphonic acid (TDPA), octadecyl phosphonic acid (ODPA) and trioctylphosphine oxide (TOPO).

11. The method according to any preceding claim, wherein the formation of the nanocrystals may be pre-selected by varying the elemental chalcogenic precursor that is introduced into the metal complex at step (b).

12. The method according to any preceding claim, wherein CdSe nanocrystals are formed.

13. The method according to any of claims 1-11, wherein CdTe nanocrystals are formed.

14. The method according to any of claims 1-11, wherein CdS nanocrystals are formed.

15. The method according to any preceding claim, wherein the ligand and the coordinating solvent are the same chemical.

16. The method according to any preceding claim, wherein the nanocrystals that are formed are quantum dots or quantum rods.

17. The method according to any preceding claim, wherein steps (a) and (b) are carried out in a single reaction vessel.

18. A method of synthesizing high-quality cadmium nanocrystals, comprising the steps of:

(a) combining a metal oxide precursor, a ligand, and a coordinating solvent to form a metal complex; wherein the metal oxide precursor is CdO; and
(b) admixing an elemental chalcogenic precursor with the metal complex at a temperature sufficient to form cadmium nanocrystals.

19. The method of claim 18, wherein the ligand is selected from long-chain fatty amines, long-chain fatty acids, phosphonic acids, and phosphine oxides.

20. The method according to claim 19, wherein the ligand includes dodecylamine (DA), hexadecylamine (HA), octadecylamine (OA), stearic acid (SA), lauric acid (LA), hexylphosphonic acid (HPA), tetradecylphosphonic acid (TDPA), octadecylphosphonic acid (ODPA) and trioctylphosphine oxide (TOPO).

21. The method according to any of claims 18-20, wherein the elemental chalcogenic precursor is selected from Se, Te, and S.

22. The method according to any of claims 18-21, wherein the coordinating solvent is a high boiling-point coordinating solvent having a boiling point range between 100° to 400°C.

23. The method according to any of claims 18-22, wherein the coordinating solvent is selected from long-chain fatty amines, long-chain fatty acids, phosphonic acids, and phosphine oxides.

24. The method according to claim 23, wherein the coordinating solvent includes dodecylamine (DA), hexadecylamine (HA), octadecylamine (OA), stearic acid (SA), lauric acid (LA), hexylphosphonic acid (HPA), tetradecylphosphonic acid (TDPA), octadecylphosphonic acid (ODPA) and trioctylphosphine oxide (TOPO).

25. The method according to claim any of claims 18-24, wherein CdTe nanocrystals are formed.

26. The method according to any of claims 18-24, wherein CdSe nanocrystals are formed.

27. The method according to any of claims 18-24, wherein CdS nanocrystals are formed.

28. The method according to any of claims 18-27, wherein the cadmium nanocrystals are quantum dots or quantum rods.

29. The method according to claim 28, wherein the size range of close to monodisperse CdSe dots ranges from 1.5 nm to over 25 nm.

30. The method according to any of claims 18-29, wherein steps (a) and (b) are carried out in a single reaction vessel.

31. A method of synthesizing CdSe rods, comprising the steps of:

(a) combining a cadmium precursor and a coordinating solvent to form a solution upon heating; wherein the cadmium precursor is selected from Cd-ODPA complex, Cd-TDPA complex, and any other Cd phosphonic acid complex; and
(b) admixing an elemental chalcogenic precursor with the solution at a temperature sufficient to form CdSe rods, wherein the chalcogenic precursor is selected from Se-TBP, Se-TOP, and any other Se phosphine compound.

32. The method according to claim 31, wherein the coordinating solvent is a phosphine oxide.

33. The method according to claim 32, wherein the phosphine oxide is selected from trioctylphosphine oxide (TOPO) and tributylphosphine oxide (TBPO).

34. The method according to any of claims 31-33, wherein the coordinating solvent is a high boiling point coordinating solvent having a boiling point range between 100° to 400°C.

35. The method according to any of claims 31-34, wherein the heating steps are carried out between 250-380°C.

36. A method of synthesizing rice-shaped CdSe nanocrystals, comprising the steps of:

(a) combining a cadmium precursor and a coordinating solvent to form a solution upon heating, wherein the cadmium precursor is selected from the group consisting of Cd-ODPA complex, Cd-TDPA complex, and any other Cd phosphonic acid complex; and
(b) admixing an elemental chalcogenic precursor with the solution at a temperature sufficient to form rice-shaped CdSe nanocrystals, wherein the chalcogenic precursor is selected from the group consisting of Se-TBP, Se-TOP, and any other Se phosphine compound.

37. The method according to claim 36, wherein the coordinating solvent is a phosphine oxide.

38. The method according to claim 37, wherein the phosphine oxide is selected from trioctylphosphine oxide (TOPO) and tributylphosphine oxide (TBPO).

39. The method according to any of claims 36-38, wherein the coordinating solvent is a high boiling point coordinating solvent having a boiling point range between 100° to 400°C.

40. The method according to any of claims 36-39, wherein the heating steps are carried out between 250°-380°C.

41. A method of synthesizing branched CdSe nanocrystals, comprising the steps of:

(a) combining a cadmium precursor and a coordinating solvent to form a solution upon heating, wherein the cadmium precursor is selected from Cd-ODPA complex, Cd-TDPA complex, and any other Cd phosphonic acid complex; and
(b) admixing an elemental chalcogenic precursor with the solution at a temperature sufficient to form branched CdSe nanocrystals, wherein the chalcogenic precursor is selected from Se-TBP, Se-TOP, and any other Se phosphine compound.

42. The method according to claim 41, wherein the coordinating solvent is a phosphine oxide.

43. The method according to claim 42, wherein the phosphine oxide is selected from trioctylphosphine oxide (TOPO) and tributylphosphine oxide (TBPO).

44. The method according to any of claims 41-43, wherein the coordinating solvent is a high boiling point coordinating solvent having a boiling point range between 100° to 400°C.

45. The method according to any of claims 41-44, wherein the heating steps are carried out between 250-380°C.

Patentansprüche

1. Verfahren zur Synthese kolloidaler Nanokristalle, umfassend die Schritte:

(a) Kombinieren eines Metalloxidpräkursors, eines Liganden und eines koordinativen Lösungsmittels zur Bildung eines Metallkomplexes, und
(b) Mischen eines elementaren Chalkogen-Präkursors mit dem Metallkomplex bei einer Temperatur, die für eine Bildung von Nanokristallen

ausreichend ist.

2. Verfahren nach Anspruch 1, wobei der Metalloxidpräkursor ein Übergangsmetall umfasst.

3. Verfahren nach Anspruch 1, wobei der Metalloxidpräkursor Sn oder Pb umfasst.

4. Verfahren nach einem der Ansprüche 1-3, wobei der Ligand aus langkettigen Fettsäureaminen, langkettigen Fettsäuren, Phosphonsäuren und Phosphinoxiden ausgewählt ist.

5. Verfahren nach Anspruch 4, wobei der Ligand Dodecylamin (DA), Hexadecylamin (HA), Octadecylamin (OA), Stearinsäure (SA), Laurinsäure (LA), Hexylphosphonsäure (HPA), Tetradecylphosphonsäure (TDPA), Octadecylphosponsäure (ODPA) und Trioctylphosphinoxid (TOPO) einschließt.

6. Verfahren nach Anspruch 1 oder Anspruch 2, wobei der Metalloxidpräkursor Cadmiumoxid ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei der elementare Chalkogen-Präkursor aus Se, Te und S ausgewählt ist.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das koordinative Lösungsmittel ein hochsiedendes koordinatives Lösungsmittel mit einem Siedepunktsbereich zwischen 100 °C bis 400 °C ist.

9. Verfahren nach einem der Ansprüche 1-7, wobei das koordinative Lösungsmittel aus langkettigen Fettsäureaminen, langkettigen Fettsäuren, Phosphonsäuren und Phosphinoxiden ausgewählt ist.

10. Verfahren nach Anspruch 9, wobei das koordinative Lösungsmittel Dodecylamin (DA), Hexadecylamin (HA), Octadecylamin (OA), Stearinsäure (SA), Laurinsäure (LA), Hexylphosphonsäure (HPA), Tetradecylphosphonsäure (TDPA), Octadecylphosponsäure (ODPA) und Trioctylphosphinoxid (TOPO) einschließt.

11. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Bildung der Nanokristalle vorausgewählt werden kann durch Variieren des elementaren Chalkogen-Präkursors, der im Schritt (b) in den Metallkomplex eingebracht wird.

12. Verfahren nach einem der vorhergehenden Ansprüche, wobei CdSe-Nanokristalle gebildet werden.

13. Verfahren nach einem der Ansprüche 1-11, wobei CdTe-Nanokristalle gebildet werden.

14. Verfahren nach einem der Ansprüche 1-11, wobei CdS-Nanokristalle gebildet werden.

15. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Ligand und das koordinative Lösungsmittel dieselbe Chemikalie sind.

16. Verfahren nach einem der vorhergehenden Ansprüche, wobei die gebildeten Nanokristalle Quantenpunkte oder Quantenstäbe sind.

17. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Schritte (a) und (b) in einem einzelnen Reaktionsgefäß durchgeführt werden.

18. Verfahren zur Synthese hochwertiger Cadmium-Nanokristalle, umfassend die Schritte:

(a) Kombinieren eines Metalloxidpräkursors, eines Liganden und eines koordinativen Lösungsmittels zur Bildung eines Metallkomplexes, wobei der Metalloxidpräkursor CdO ist, und
(b) Mischen eines elementaren Chalkogen-Präkursors mit dem Metallkomplex bei einer Temperatur, die für eine Bildung von Cadmium-Nanokristallen ausreichend ist.

19. Verfahren nach Anspruch 18, wobei der Ligand aus langkettigen Fettsäureaminen, langkettigen Fettsäuren, Phosphonsäuren und Phosphinoxiden ausgewählt ist.

20. Verfahren nach Anspruch 19, wobei der Ligand Dodecylamin (DA), Hexadecylamin (HA), Octadecylamin (OA), Stearinsäure (SA), Laurinsäure (LA), Hexylphosphonsäure (HPA), Tetradecylphosphonsäure (TDPA), Octadecylphosponsäure (ODPA) und Trioctylphosphinoxid (TOPO) einschließt.

21. Verfahren nach einem der Ansprüche 18-20, wobei der elementare Chalkogen-Präkursor aus Se, Te und S ausgewählt ist.

22. Verfahren nach einem der Ansprüche 18-21, wobei das koordinative Lösungsmittel ein hochsiedendes koordinatives Lösungsmittel mit einem Siedepunktsbereich zwischen 100 °C bis 400 °C ist.

23. Verfahren nach einem der Ansprüche 18-22, wobei das koordinative Lösungsmittel aus langkettigen Fettsäureaminen, langkettigen Fettsäuren, Phosphonsäuren und Phosphinoxiden ausgewählt ist.

24. Verfahren nach Anspruch 23, wobei das koordinative Lösungsmittel Dodecylamin (DA), Hexadecylamin (HA), Octadecylamin (OA), Stearinsäure (SA), Laurinsäure (LA), Hexylphosphonsäure (HPA), Tetradecylphosphonsäure (TDPA), Octadecylphosponsäure (ODPA) und Trioctylphosphinoxid (TOPO) einschließt.

25. Verfahren nach einem der Ansprüche 18-24, wobei CdTe-Nanokristalle gebildet werden.

26. Verfahren nach einem der Ansprüche 18-24, wobei CdSe-Nanokristalle gebildet werden.

27. Verfahren nach einem der Ansprüche 18-24, wobei CdS-Nanokristalle gebildet werden.

28. Verfahren nach einem der Ansprüche 18-27, wobei die Cadmium-Nanokristalle Quantenpunkte oder Quantenstäbe sind.

29. Verfahren nach Anspruch 28, wobei der Größenbereich von nahezu monodispersen CdSe-Punkten von 1,5 nm bis über 25 nm reicht.

30. Verfahren nach einem der Ansprüche 18-29, wobei die Schritte (a) und (b) in einem einzelnen Reaktionsgefäß durchgeführt werden.

31. Verfahren zur Synthese von CdSe-Stäben, umfassend die Schritte:

(a) Kombinieren eines Cadmiumpräkursors und eines koordinativen Lösungsmittels zur Bildung eine Lösung unter Erwärmung, wobei der Cadmiumpräkursor aus Cd-ODPA-Komplex, Cd-TDPA-Komplex und irgendeinem anderen Cd-Phosphonsäurekomplex ausgewählt ist, und
(b) Mischen eines elementaren Chalkogen-Präkursors mit der Lösung bei einer Temperatur, die für eine Bildung von CdSe-Stäben ausreichend ist, wobei der Chalkogen-Präkursor aus Se-TBP, Se-TOP und irgendeiner anderen Se-Phosphinverbindung ausgewählt ist.

32. Verfahren nach Anspruch 31, wobei das koordinative Lösungsmittel ein Phosphinoxid ist.

33. Verfahren nach Anspruch 32, wobei das Phosphinoxid aus Trioctylphosphinoxid (TOPO) und Tributylphosphinoxid (TBPO) ausgewählt ist.

34. Verfahren nach einem der Ansprüche 31-33, wobei das koordinative Lösungsmittel ein hochsiedendes koordinatives Lösungsmittel mit einem Siedepunktsbereich zwischen 100 °C bis 400 °C ist.

35. Verfahren nach einem der Ansprüche 31-34, wobei die Erwärmungsschritte zwischen 250-380 °C ausgeführt werden.

36. Verfahren zur Synthese reiskornförmiger CdSe-Nanokristalle, umfassend die Schritte:

(a) Kombinieren eines Cadmiumpräkursors und eines koordinativen Lösungsmittels zur Bildung eine Lösung unter Erwärmung, wobei der Cadmiumpräkursor aus der aus Cd-ODPA-Komplex, Cd-TDPA-Komplex und irgendeinem anderen Cd-Phosphonsäurekomplex bestehenden Gruppe ausgewählt ist, und
(b) Mischen eines elementaren Chalkogen-Präkursors mit der Lösung bei einer Temperatur, die für eine Bildung von reiskornförmigen CdSe-Nanokristallen ausreichend ist, wobei der Chalkogen-Präkursor aus der aus Se-TBP, Se-TOP und irgendeiner anderen Se-Phosphinverbindung bestehenden Gruppe ausgewählt ist.

37. Verfahren nach Anspruch 36, wobei das koordinative Lösungsmittel ein Phosphinoxid ist.

38. Verfahren nach Anspruch 37, wobei das Phosphinoxid aus Trioctylphosphinoxid (TOPO) und Tributylphosphinoxid (TBPO) ausgewählt ist.

39. Verfahren nach einem der Ansprüche 36-38, wobei das koordinative Lösungsmittel ein hochsiedendes koordinatives Lösungsmittel mit einem Siedepunktsbereich zwischen 100 °C bis 400 °C ist.

40. Verfahren nach einem der Ansprüche 36-39, wobei die Erwärmungsschritte zwischen 250 °C - 380 °C ausgeführt werden.

41. Verfahren zur Synthese verzweigter CdSe-Nanokristalle, umfassend die Schritte:

(a) Kombinieren eines Cadmiumpräkursors und eines koordinativen Lösungsmittels zur Bildung eine Lösung unter Erwärmung, wobei der Cadmiumpräkursor aus Cd-ODPA-Komplex, Cd-TDPA-Komplex und irgendeinem anderen Cd-Phosphonsäurekomplex ausgewählt ist, und
(b) Mischen eines elementaren Chalkogen-Präkursors mit der Lösung bei einer Temperatur, die für eine Bildung von verzweigten CdSe-Nanokristallen ausreichend ist, wobei der Chalkogen-Präkursor aus Se-TBP, Se-TOP und irgendeiner anderen Se-Phosphinverbindung ausgewählt ist.

42. Verfahren nach Anspruch 41, wobei das koordinative Lösungsmittel ein Phosphinoxid ist.

43. Verfahren nach Anspruch 42, wobei das Phosphinoxid aus Trioctylphosphinoxid (TOPO) und Tributylphosphinoxid (TBPO) ausgewählt ist.

44. Verfahren nach einem der Ansprüche 41-43, wobei das koordinative Lösungsmittel ein hochsiedendes koordinatives Lösungsmittel mit einem Siedepunktsbereich zwischen 100 °C bis 400 °C ist.

45. Verfahren nach einem der Ansprüche 41-44, wobei die Erwärmungsschritte zwischen 250-380 °C ausgeführt werden.

Revendications

1. Méthode de synthèse de nanocristaux colloïdaux, comprenant les étapes consistant à :

(a) combiner un précurseur d'oxyde métallique, un ligand et un solvant de coordination pour former un complexe métallique ; et
(b) admixer un précurseur chalcogénique élémentaire avec le complexe métallique à une température suffisante pour former des nanocristaux.

2. Méthode selon la revendication 1, dans laquelle le précurseur d'oxyde métallique comprend un métal de transition.

3. Méthode selon la revendication 1 dans lequel le précurseur d'oxyde métallique comprend le Sn ou le Pb.

4. Méthode selon l'une des revendications 1-3, dans laquelle le ligand est sélectionné parmi les amines gras à chaîne longue, d'acides gras à chaîne longue, d'acides phosphoniques et d'oxydes de phosphine.

5. Méthode selon la revendication 4, dans laquelle le ligand inclut la dodécylamine (DA), l'hexadécylamine (HA), l'octadécylamine (OA), l'acide stéarique (SA), l'acide laurique (LA), l'acide hexylphosphonique (HPA), l'acide tétradécylphosphonique (TDPA), l'acide octadécyle phosphonique (ODPA) et l'oxyde de trioctylphosphine (TOPO).

6. Méthode selon la revendication 1 ou revendication 2, dans laquelle le précurseur d'oxyde métallique est l'oxyde de cadmium.

7. Méthode selon l'une des revendications précédentes dans laquelle le précurseur chalcogénique élémentaire est sélectionné parmi Se, Te et S.

8. Méthode selon l'une des revendications précédentes, dans laquelle le solvant de coordination est un solvant de coordination à point d'ébullition élevé ayant une plage de point d'ébullition entre 100°C et 400°C.

9. Méthode selon l'une quelconque des revendications 1 à 7, dans laquelle le solvant de coordination est sélectionné à partir d'amines gras à chaîne longue, d'acides gras à chaîne longue, d'acides phosphoniques et d'oxyde de phosphine.

10. Méthode selon la revendication 9, dans laquelle le solvant de coordination inclut la dodécylamine (DA), l'hexadécylamine (HA), l'octadécylamine (OA), l'acide stéarique (SA), l'acide laurique (LA), l'acide hexylphosphonique (HPA), l'acide tétradécylphosphonique (TDPA), l'acide octadécyle phosphonique (ODPA) et l'oxyde trioctylphosphine (TOPO).

11. Méthode selon l'une des revendications précédentes dans laquelle la formation des nanocristaux peut être présélectionnée en faisant varier le précurseur chalcogénique élémentaire qui est introduit dans le complexe métallique à l'étape (b).

12. Méthode selon l'une quelconque des revendications précédentes, dans laquelle des nanocristaux de CdSe sont formés.

13. Méthode selon l'une quelconque des revendications 1-11, dans laquelle des nanocristaux CdTe sont formés.

14. Méthode selon l'une quelconque des revendications 1-11, dans laquelle des nanocristaux CdS sont formés.

15. Méthode selon l'une quelconque des revendications précédentes, dans laquelle le ligand et le solvant de coordination sont le même composé chimique.

16. Méthode selon l'une quelconque des revendications précédentes, dans laquelle les nanocristaux qui sont formés sont des billes quantiques ou des tiges quantiques.

17. Méthode selon l'une quelconque des revendications précédentes, dans laquelle les étapes (a) et (b) sont conduites dans une seule et même cuve de réaction.

18. Méthode de synthèse de nanocristaux de cadmium de haute qualité, comprenant les étapes consistant à :

(a) combiner un précurseur d'oxyde métallique, un ligand et un solvant de coordination pour former un complexe métallique ; dans laquelle le précurseur d'oxyde métallique est CdO ; et
(b) admixer un précurseur chalcogénique élémentaire avec le complexe métallique à une température suffisante pour former des nanocristaux de cadmium.

19. Méthode selon la revendication 18, dans laquelle le ligand est sélectionné à partir d'amines gras à chaîne longue, d'acides gras à chaîne longue, d'acides phosphoniques et d'oxydes de phosphine.

20. Méthode selon la revendication 19, dans laquelle le ligand inclut la dodécylamine (DA), l'hexadécylamine (HA), l'octadécylamine (OA), l'acide stéarique (SA), l'acide laurique (LA), l'acide hexylphosphonique (HPA), l'acide tétradécylphosphonique (TDPA), l'acide octadécyle phosphonique (ODPA) et l'oxyde trioctylphosphine (TOPO).

21. Méthode selon l'une des revendications 18 à 20 dans laquelle le précurseur chalcogénique élémentaire est sélectionné parmi Se, Te et S.

22. Méthode selon l'une des revendications 18-21, dans laquelle le solvant de coordination est un solvant de coordination à point d'ébullition élevé ayant une plage de point d'ébullition entre 100°C et 400°C.

23. Méthode selon l'une des revendications 18-22, dans laquelle le solvant de coordination est sélectionné parmi les amines gras à chaîne longue, les acides gras à chaîne longue, les acides phosphoniques et les oxydes phosphines.

24. Méthode selon la revendication 23, dans laquelle le solvant de coordination inclut la dodécylamine (DA), l'hexadécylamine (HA), l'octadécylamine (OA), l'acide stéarique (SA), l'acide laurique (LA), l'acide hexylphosphonique (HPA), l'acide tétradécylphosphonique (TDPA), l'acide octadécyle phosphonique (ODPA) et l'oxyde trioctylphosphine (TOPO).

25. Méthode selon l'une quelconque des revendications 18-24, dans laquelle des nanocristaux CdTe sont formés.

26. Méthode selon l'une quelconque des revendications 18-24, dans laquelle des nanocristaux CdSe sont formés.

27. Méthode selon l'une quelconque des revendications 18-24, dans laquelle des nanocristaux CdS sont formés.

28. Méthode selon l'une quelconque des revendications 18-27, dans laquelle les nanocristaux qui sont formés sont des billes quantiques ou des tiges quantiques.

29. Méthode selon la revendication 28, dans laquelle la plage de taille des billes CdSe quasi-monodispersés va de 1,5 nm à plus de 25 nm.

30. Méthode selon l'une des revendications 18-29, dans laquelle les étapes (a) et (b) sont conduites dans une seule et même cuve de réaction.

31. Méthode de synthèse de tiges de CdSe, comprenant les étapes consistant à :

(a) combiner le précurseur de cadmium et un solvant de coordination pour former une solution par chauffage ; dans laquelle le précurseur de cadmium est sélectionné parmi le complexe Cd-ODPA, le complexe Cd-TDPA, et tout autre complexe d'acide phosphonique de Cd ; et
(b) admixer un précurseur chalcogénique élémentaire avec la solution à une température suffisante pour former des tiges de CdSe, dans laquelle le précurseur chalcogénique est sélectionné à partir de Se-TBP, Se-TOP et tout autre composé de phosphine de Se.

32. Méthode selon la revendication 31, dans laquelle le solvant de coordination est un oxyde de phosphine.

33. Méthode selon la revendication 32, dans laquelle l'oxyde de phosphine est sélectionné parmi l'oxyde trioctylphosphine (TOPO) et l'oxyde tributylphosphine (TBPO).

34. Méthode selon l'une quelconque des revendications 31-33, dans laquelle le solvant de coordination est un solvant de coordination à point d'ébullition élevé ayant une plage de point d'ébullition entre 100° et 400°C.

35. Méthode selon l'une quelconque des revendications 31-34, dans laquelle les étapes de chauffage sont conduites entre 250 et 380°C.

36. Méthode de synthèse de nanocristaux de CdSe en formes de tubes, comprenant les étapes consistant à :

(a) combiner un précurseur de cadmium et un solvant de coordination pour former une solution par chauffage dans laquelle le précurseur de cadmium est sélectionné parmi le groupe consistant en le complexe Cd-ODPA, le complexe Cd-TDPA et tout autre complexe acide phosphonique de Cd ; et
(b) admixer un précurseur chalcogénique élémentaire avec la solution à une température suffisante pour former des nanocristaux de CdSe en forme de grain de riz, dans laquelle le précurseur chalcogénique est sélectionné parmi le groupe composé du Se-TBP, du Se-TOP et de tout autre composé de phosphine Se.

37. Méthode selon la revendication 36, dans laquelle le solvant de coordination st un oxyde de phosphine.

38. Méthode selon la revendication 37, dans laquelle l'oxyde de phosphine est sélectionné parmi l'oxyde trioctylphosphine (TOPO) et l'oxyde tributylphosphine (TBPO).

39. Méthode selon l'une des revendications 36-38, dans laquelle le solvant de coordination est un solvant de coordination à point d'ébullition élevé ayant une plage de point d'ébullition entre 100°C et 400°C.

40. Méthode selon l'une des revendications 36-39, dans laquelle les étapes de chauffage sont effectuées entre 250°C et 380°C.

41. Méthode de synthèse de nanocristaux de CdSe ramifiés, comprenant les étapes consistant à :

(a) combiner le précurseur de cadmium et un solvant de coordination pour former une solution par chauffage, dans laquelle le précurseur de cadmium est sélectionné parmi le complexe Cd-ODPA, le complexe Cd-TDPA, et tout autre complexe d'acide phosphonique de Cd ; et

(b) admixer un précurseur chalcogénique élémentaire avec la solution à une température suffisante pour former des nanocristaux de CdSe ramifiés, dans laquelle le précurseur chalcogénique est sélectionné à partir de Se-TBP, Se-TOP et tout autre composé de phosphine de Se.

42. Méthode selon la revendication 41, dans laquelle le solvant de coordination est un oxyde de phosphine.

43. Méthode selon la revendication 42, dans laquelle l'oxyde de phosphine est sélectionné parmi l'oxyde trioctylphosphine (TOPO) et l'oxyde tributylphosphine (TBPO).

44. Méthode selon l'une quelconque des revendications 41-43, dans laquelle le solvant de coordination est un solvant de coordination à point d'ébullition élevé ayant une plage de point d'ébullition entre 100° et 400°C.

45. Méthode selon l'une quelconque des revendications 41-44, dans laquelle les étapes de chauffage sont conduites entre 250 et 380°C.

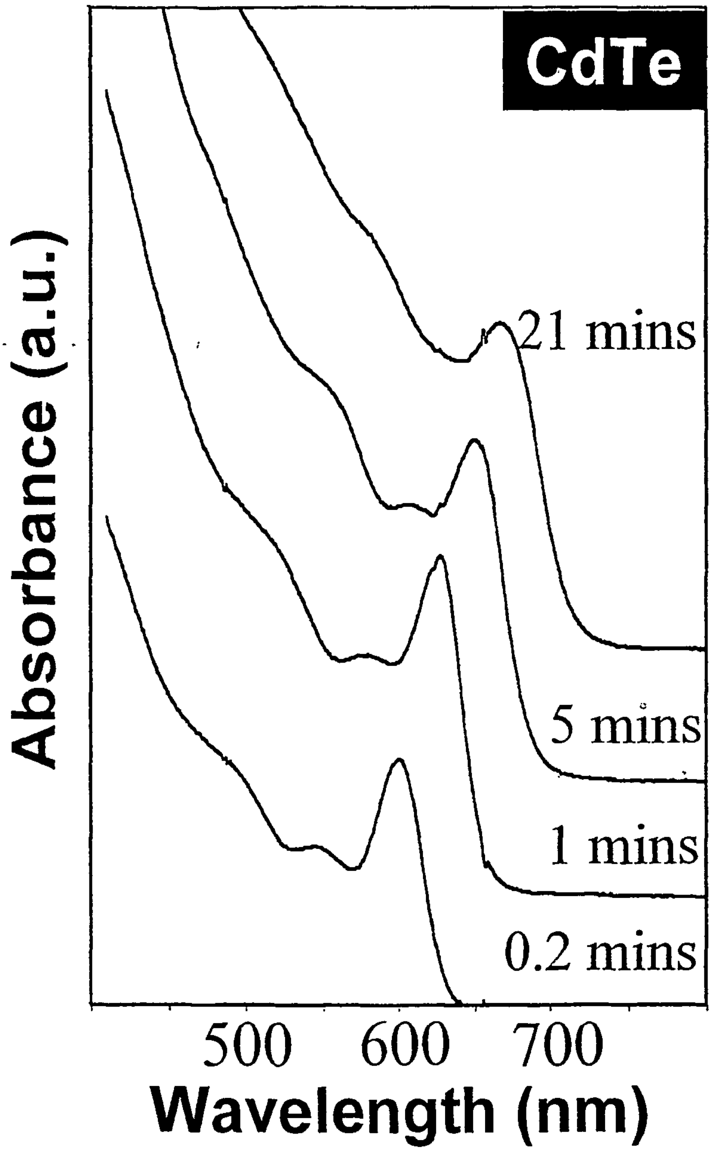
CdTe
21 mins
5 mins
1 mins
0.2 mins
Absorbance (a.u.)
500
600
700
Wavelength (nm)

Fig. 1(a)

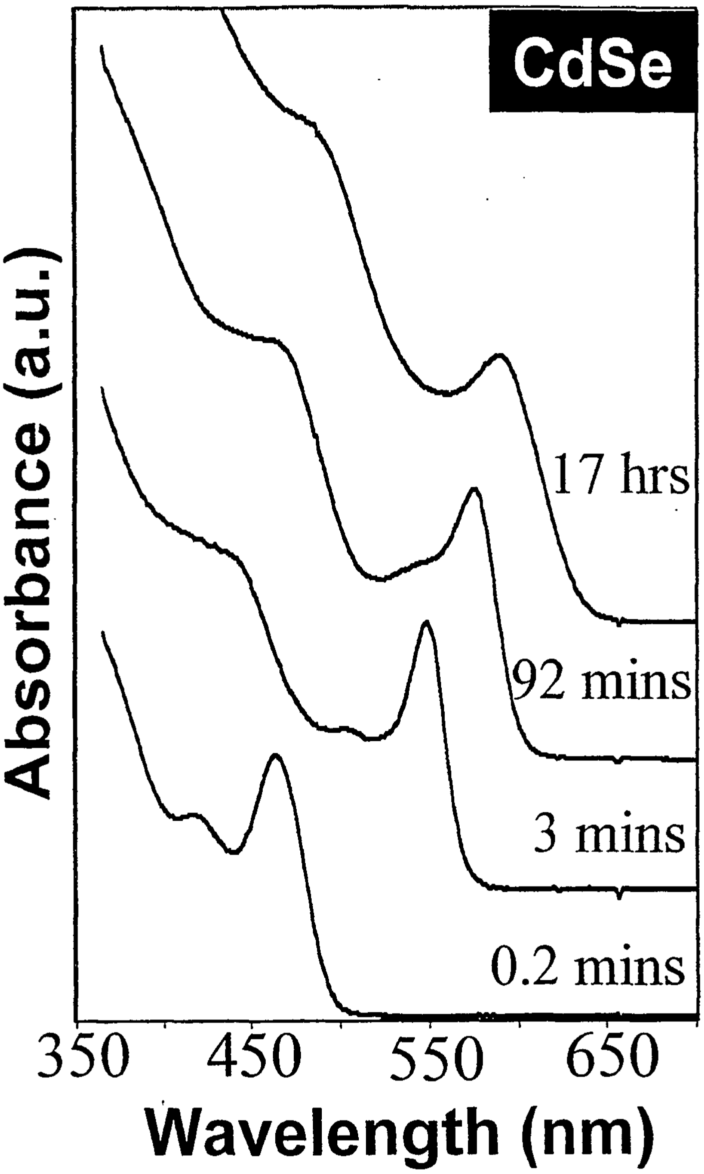
CdSe
Absorbance (a.u.)
17 hrs
92 mins
3 mins
0.2 mins
350
450
550
650
Wavelength (nm)

Fig. 1(b)

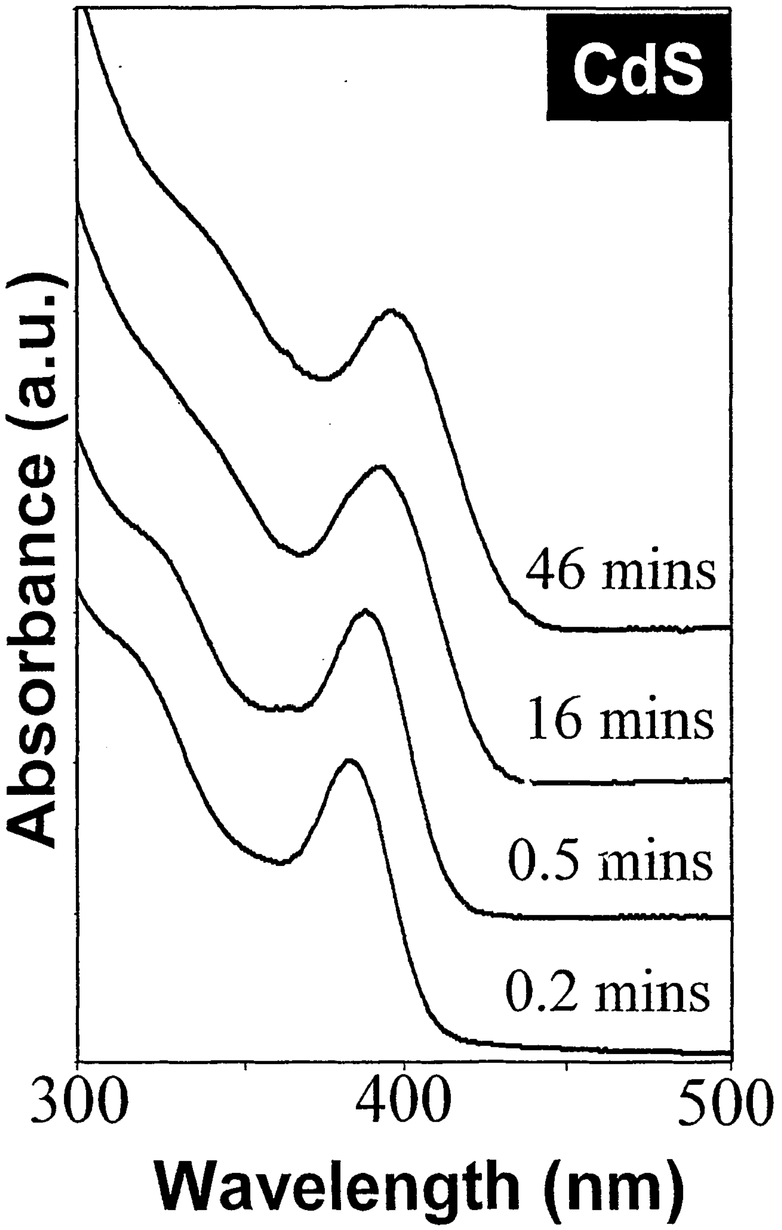
CdS
46 mins
16 mins
0.5 mins
0.2 mins
Absorbance (a.u.)
300
400
500
Wavelength (nm)

Fig. 1(c)

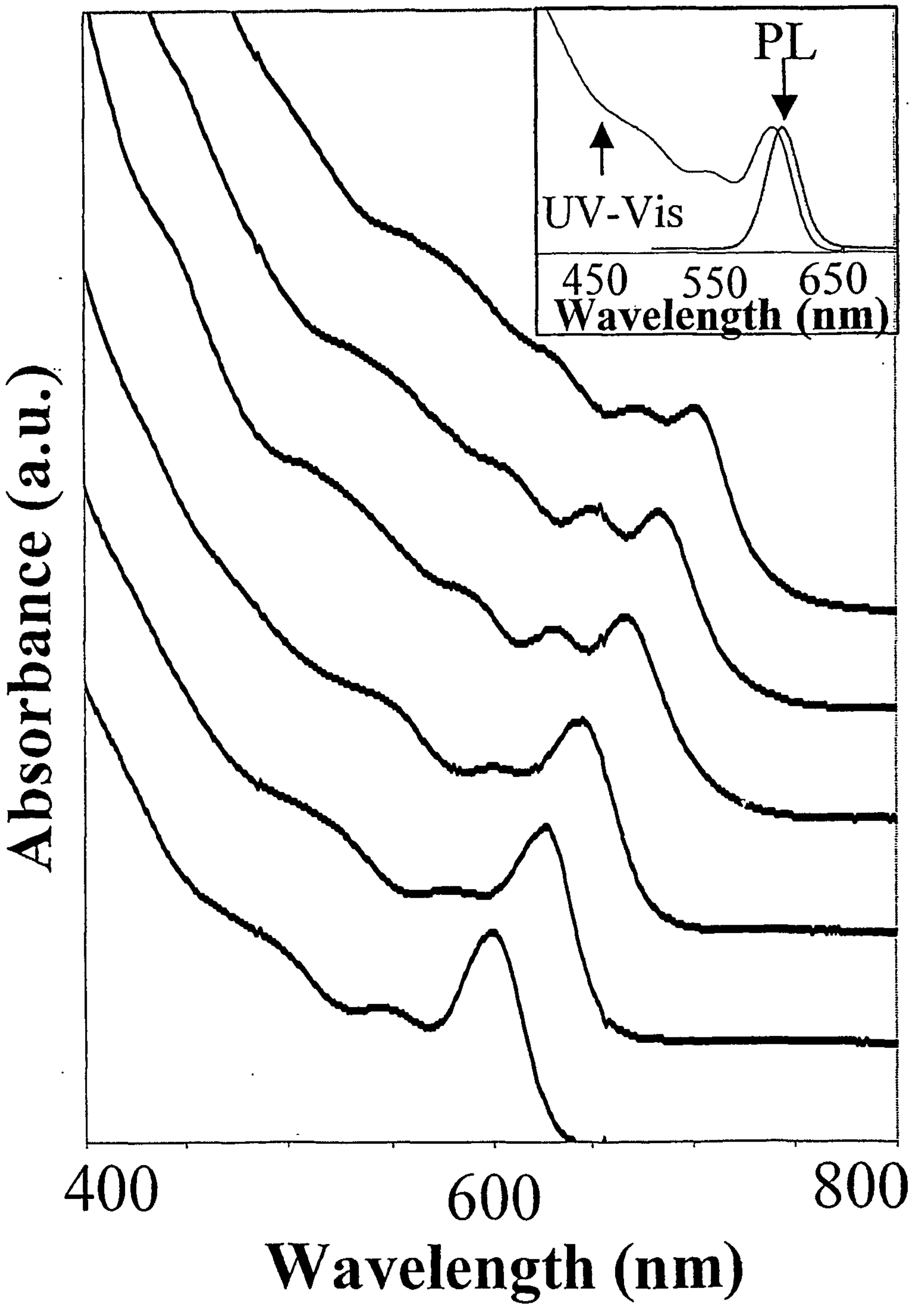
PL
UV-Vis
450
550
650
Wavelength (nm)
Absorbance (a.u.)
400
600
800
Wavelength (nm)

Fig. 2

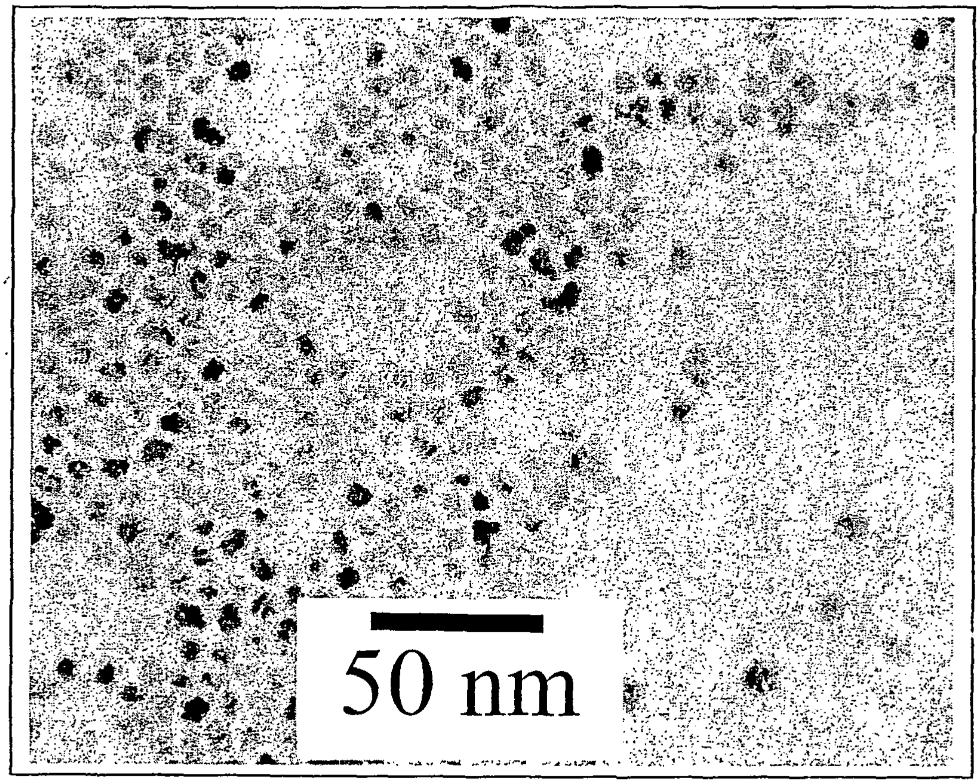

Fig. 3(a)

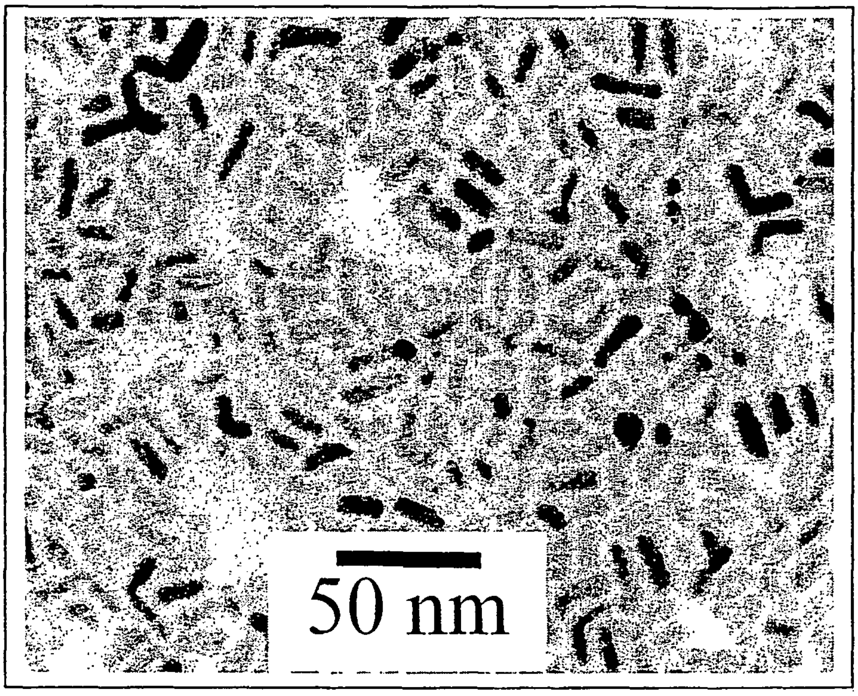

Fig. 3(b)

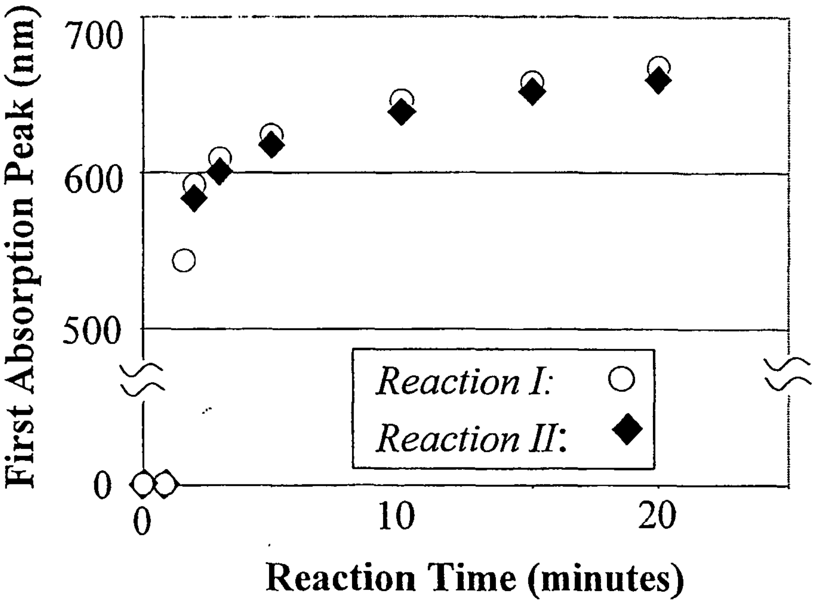
First Absorption Peak (nm)
700
600
500
0
0
10
20
Reaction Time (minutes)
Reaction I: ○
Reaction II: ◆

Fig. 4

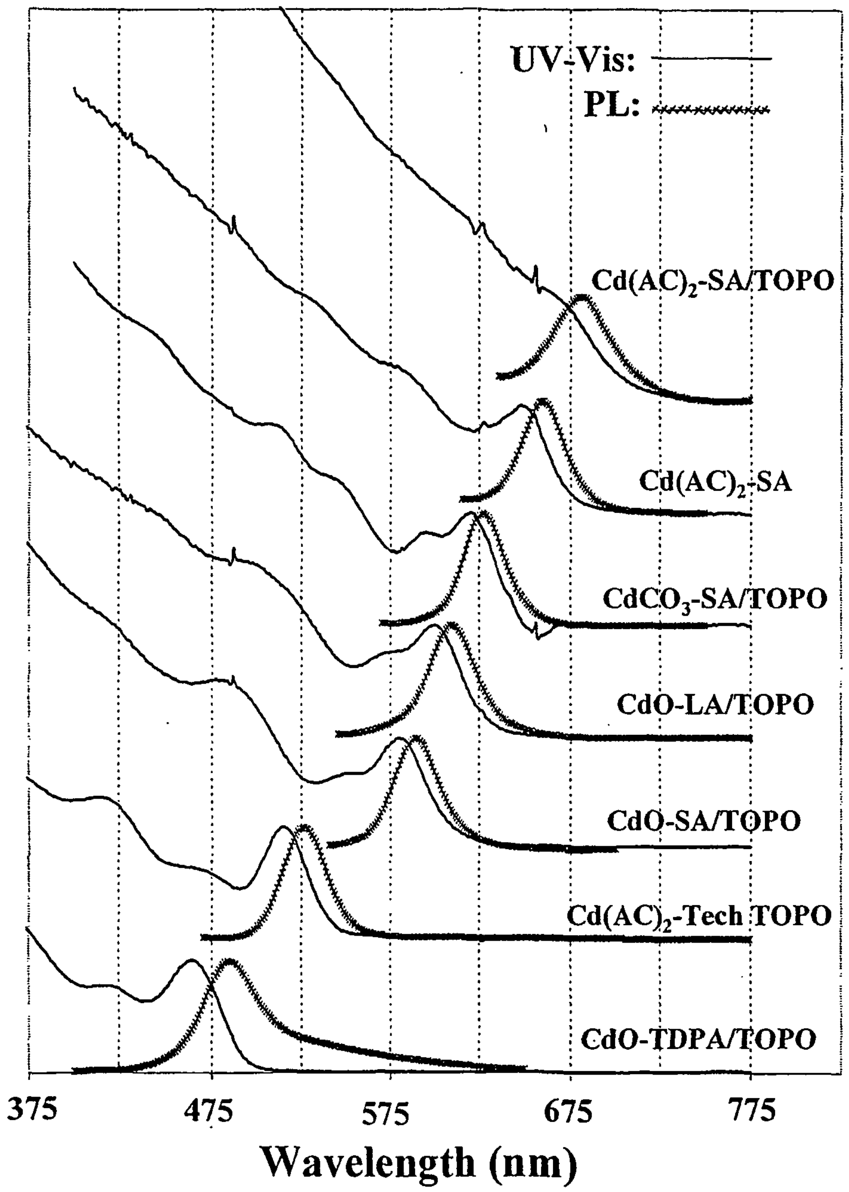
UV-Vis:
PL:
Cd(AC)$_2$-SA/TOPO
Cd(AC)$_2$-SA
CdCO$_3$-SA/TOPO
CdO-LA/TOPO
CdO-SA/TOPO
Cd(AC)$_2$-Tech TOPO
CdO-TDPA/TOPO
375
475
575
675
775
Wavelength (nm)

Fig. 5

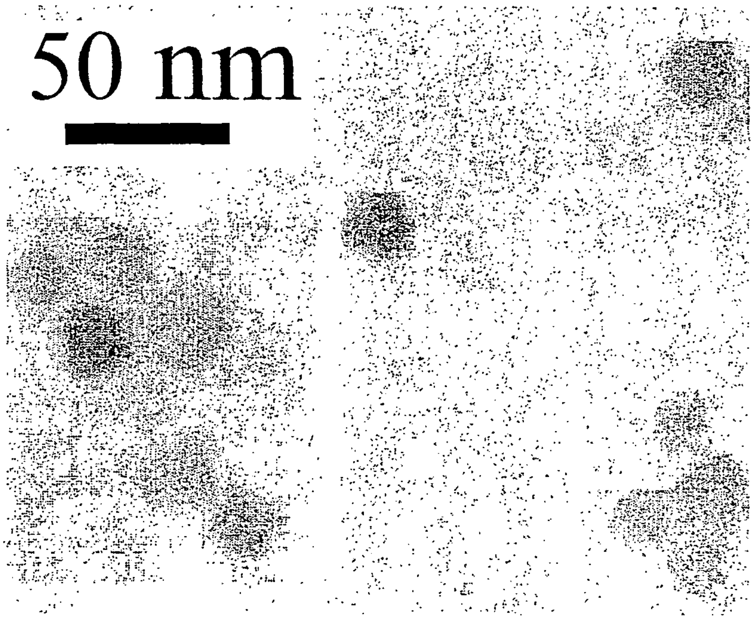

Fig. 6(a)

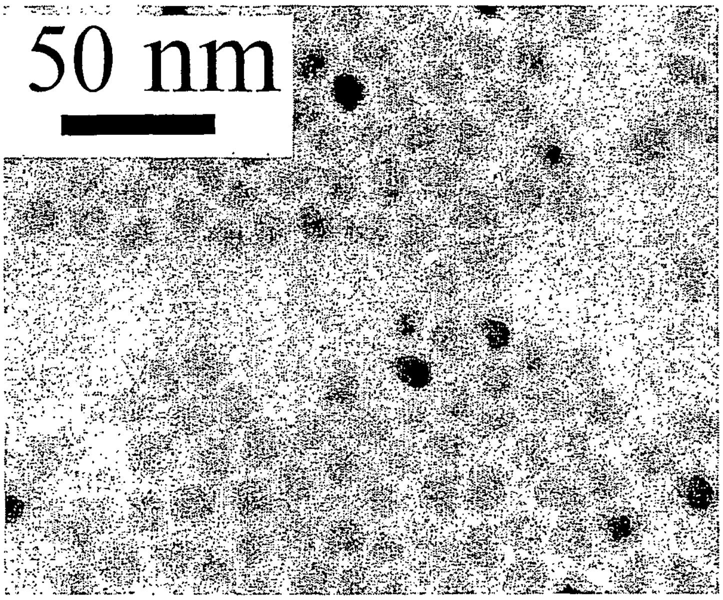

Fig. 6(b)

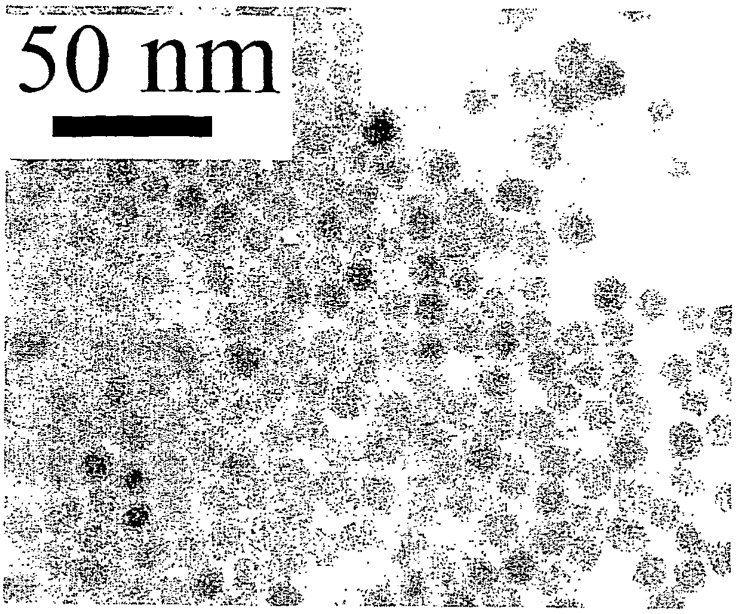

Fig. 6(c)

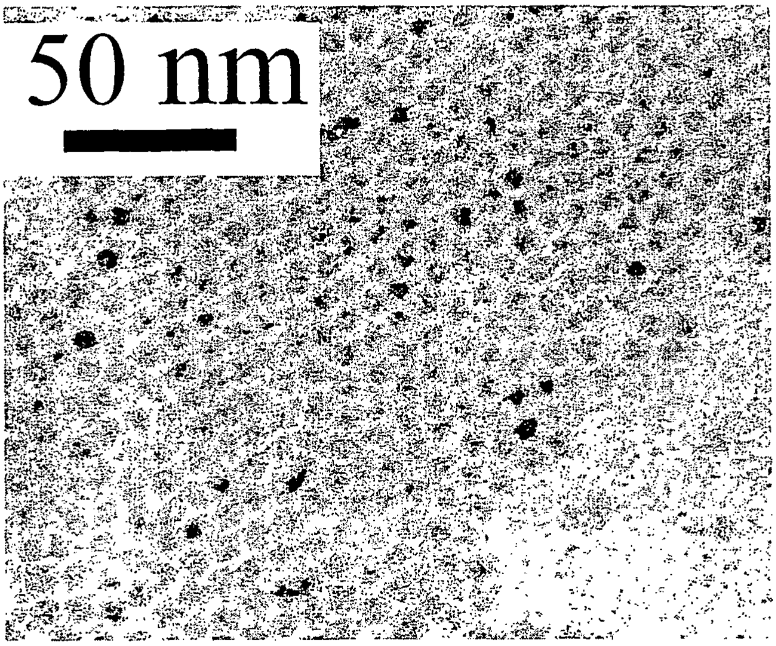

Fig. 6(d)

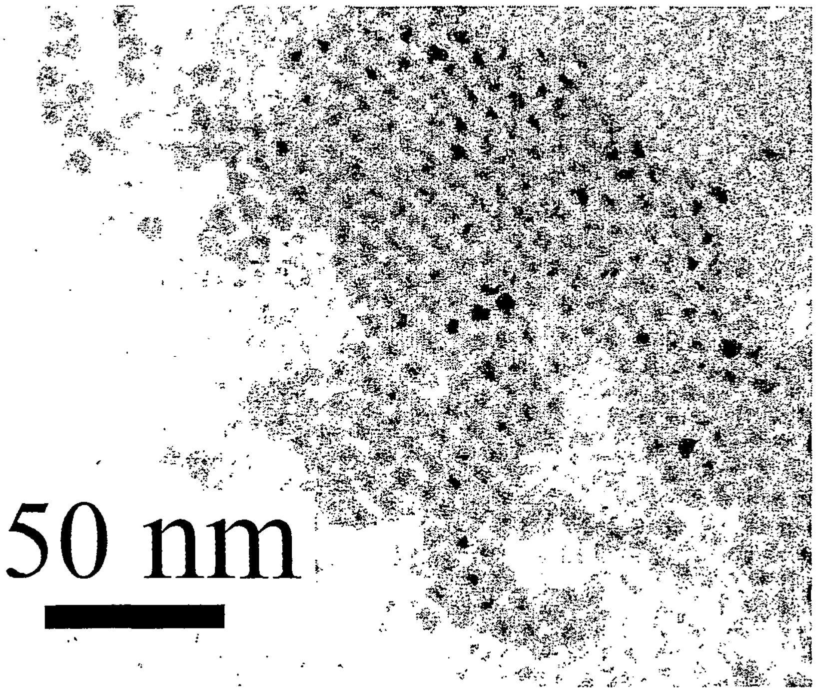

Fig. 6(e)

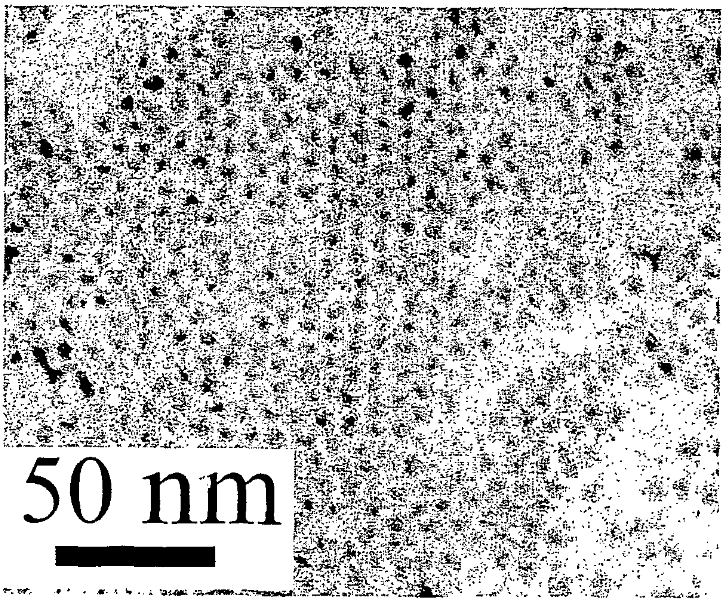

Fig. 6(f)

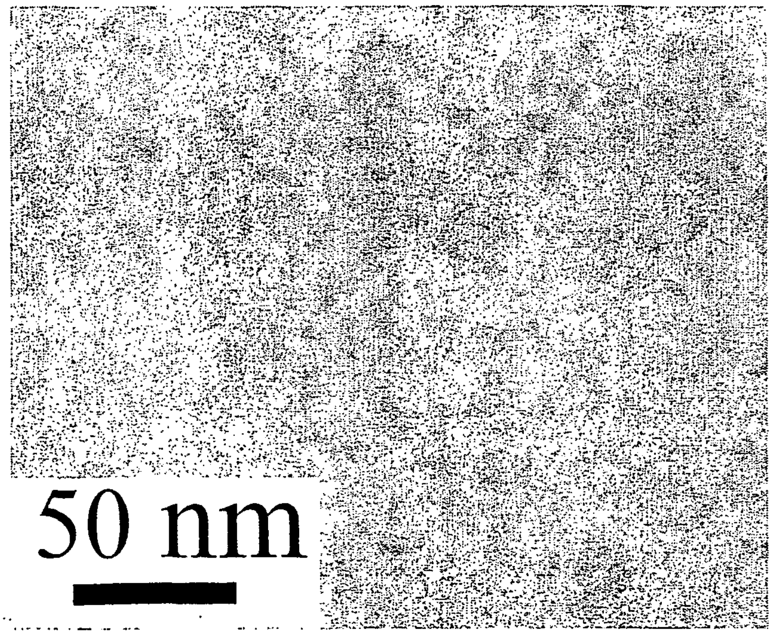

Fig. 6(g)

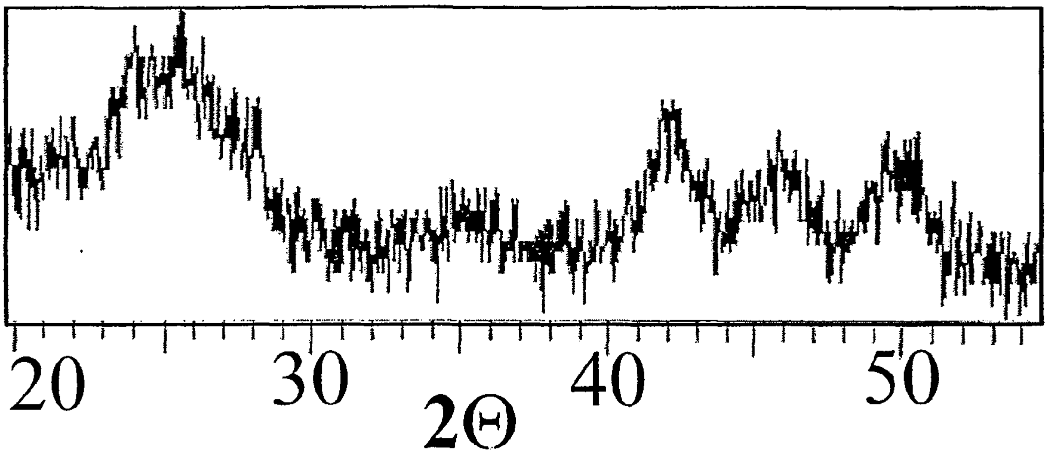

Fig. 6(h)

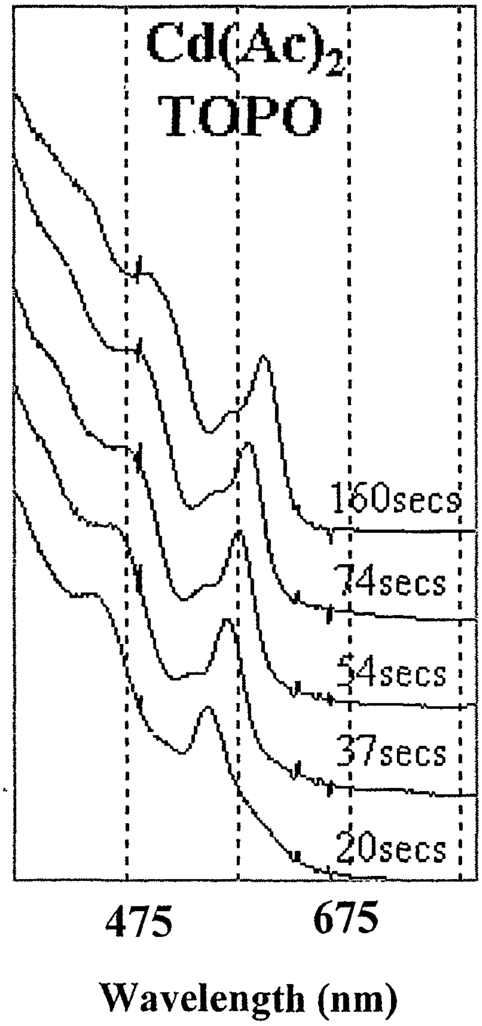
Cd(Ac)$_2$
TOPO
160secs
74secs
54secs
37secs
20secs
475
675
Wavelength (nm)

Fig. 7(a)

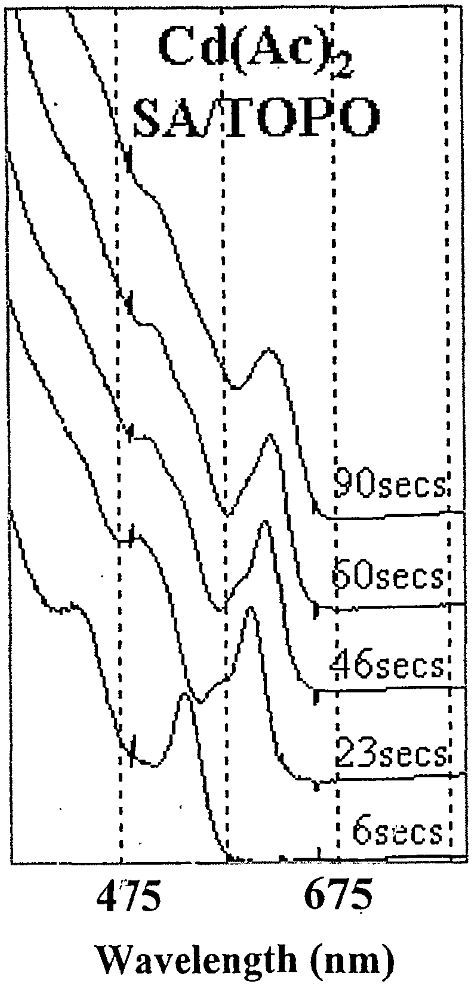
$Cd(Ac)_2$
SA/TOPO
90secs
60secs
46secs
23secs
6secs
475
675
Wavelength (nm)

Fig. 7(b)

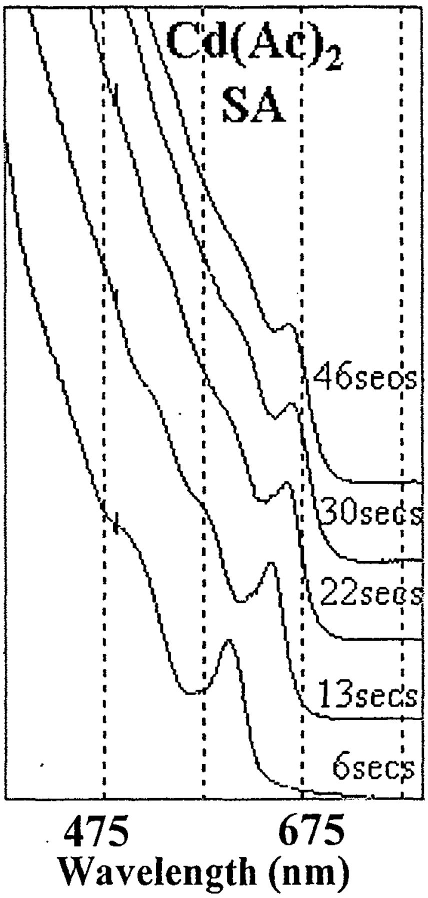
Cd(Ac)$_2$
SA
46secs
30secs
22secs
13secs
6secs
475
675
Wavelength (nm)

Fig. 7(c)

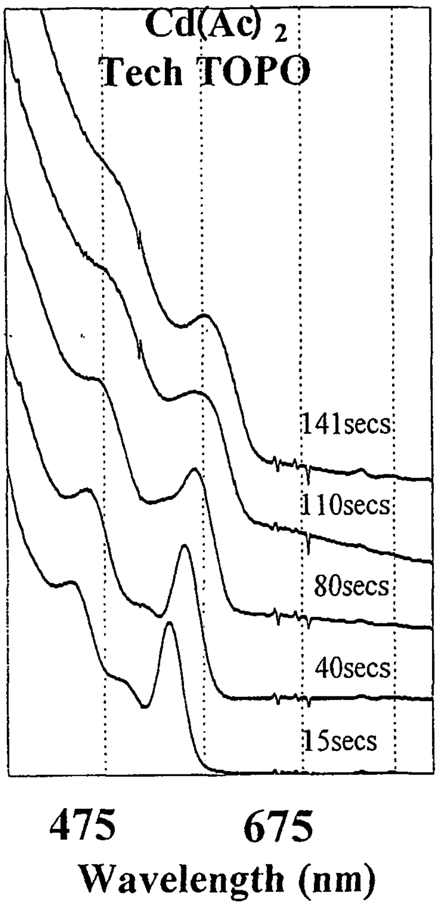
Cd(Ac)$_2$
Tech TOPO
141secs
110secs
80secs
40secs
15secs
475
675
Wavelength (nm)

Fig. 7(d)

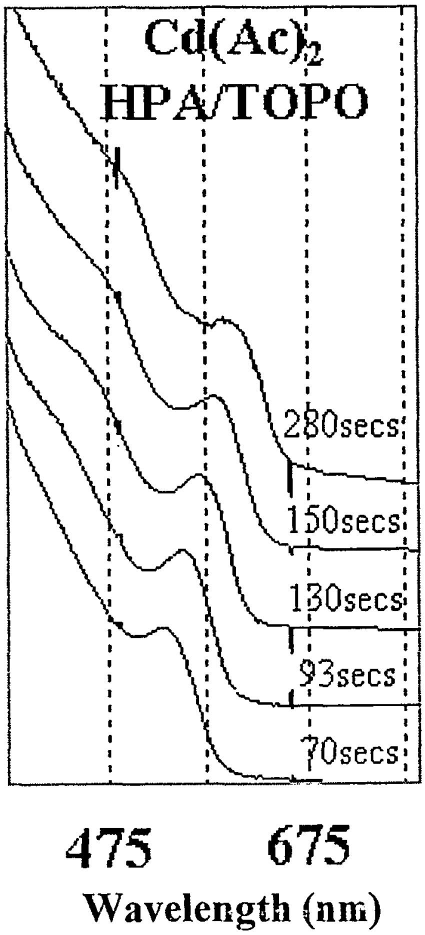
Cd(Ac)2
HPA/TOPO
280secs
150secs
130secs
93secs
70secs
475
675
Wavelength (nm)

Fig. 7(e)

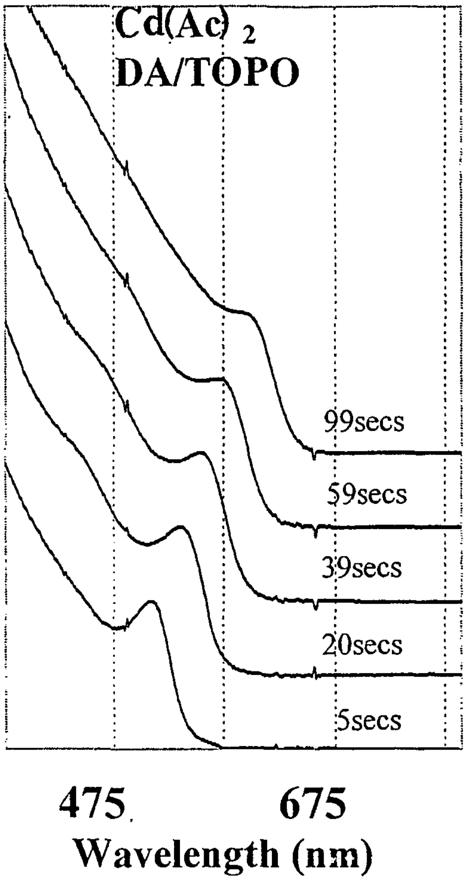
Cd(Ac) 2
DA/TOPO
99secs
59secs
39secs
20secs
5secs
475
675
Wavelength (nm)

Fig. 7(f)

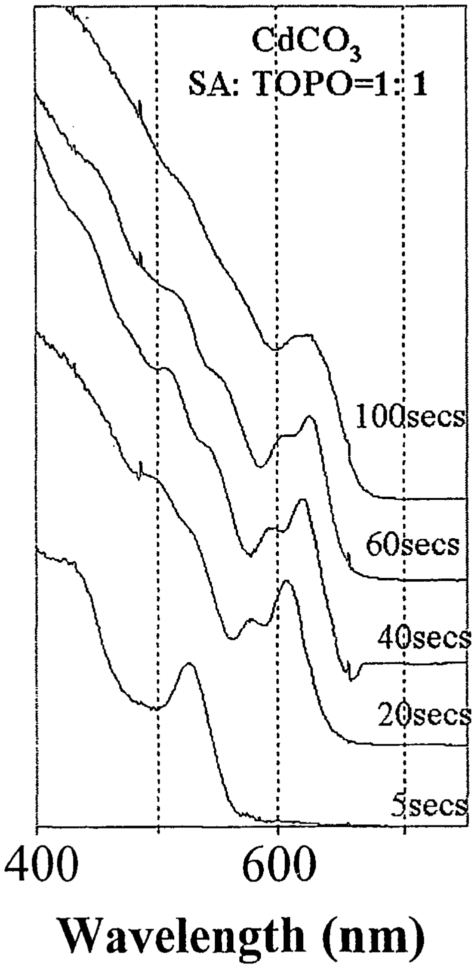
$CdCO_3$
SA: TOPO=1: 1
100secs
60secs
40secs
20secs
5secs
400
600
Wavelength (nm)

Fig. 8(a)

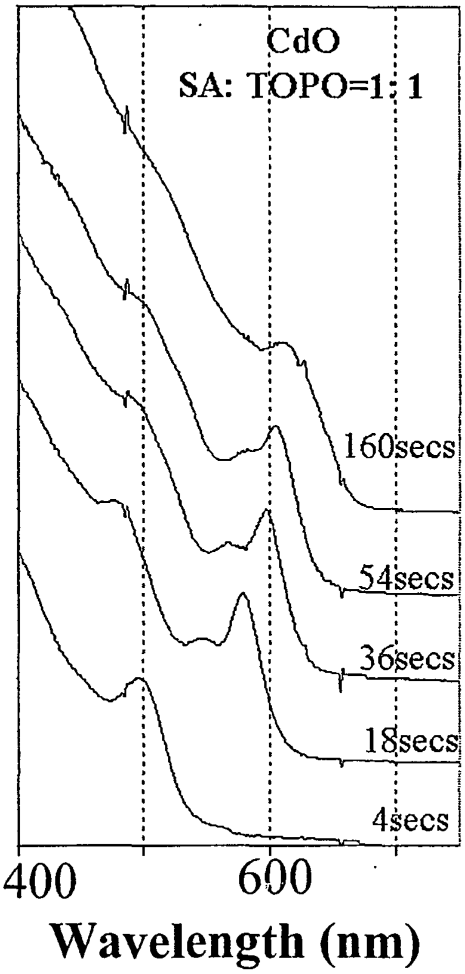
CdO
SA: TOPO=1: 1
160secs
54secs
36secs
18secs
4secs
400
600
Wavelength (nm)

Fig. 8(b)

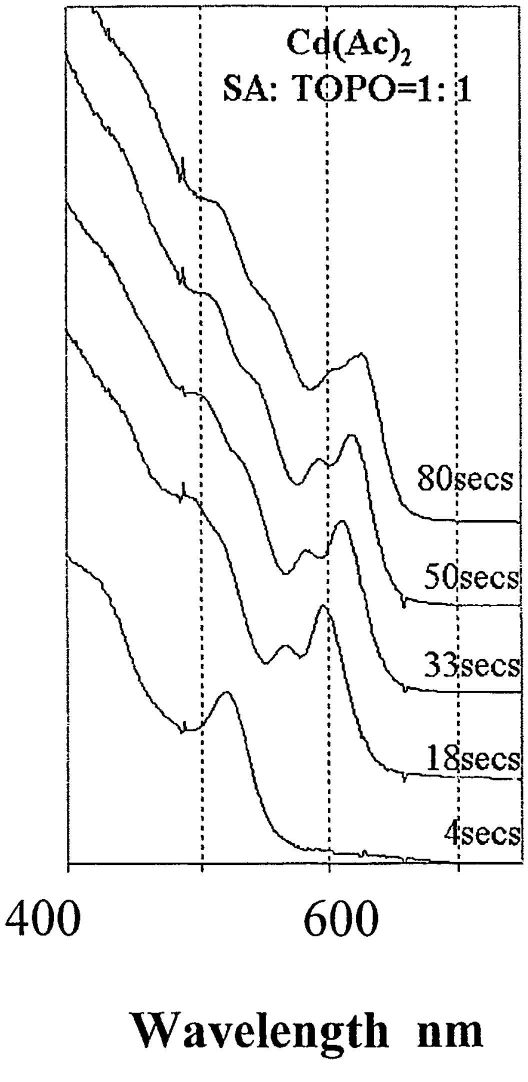
Cd(Ac)$_2$
SA: TOPO=1: 1
80secs
50secs
33secs
18secs
4secs
400
600
Wavelength nm

Fig. 8(c)

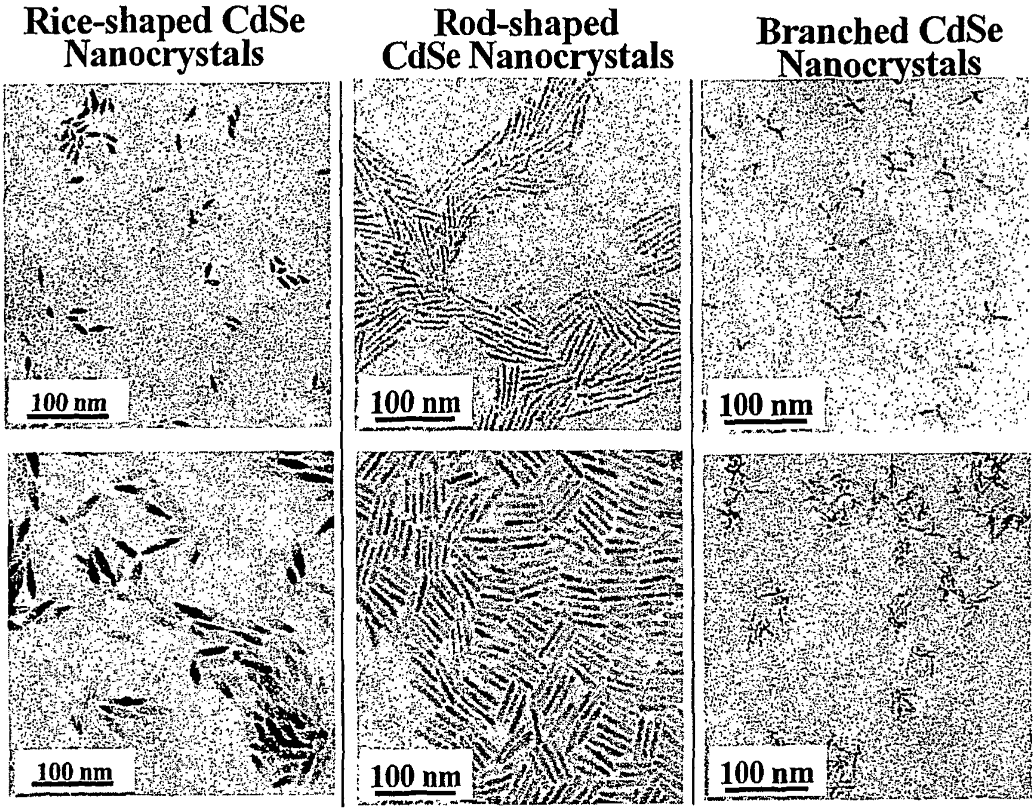
Rice-shaped CdSe Nanocrystals
Rod-shaped CdSe Nanocrystals
Branched CdSe Nanocrystals
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm

Fig. 9

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 6179912 B, Guillem **[0003]**

Non-patent literature cited in the description

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- **Peng et al.** *Nature,* 2000, vol. 404, 69-61 **[0003]**
- **Peng et al.** *Journal of the American Chemical Society,* vol. 120, 5343-5344 **[0003]**
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- **Z.A. Peng ; X. Peng.** *Journal of the American Chemical Society,* 2001 **[0034]**