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**Char et al.**(10) **Pub. No.: US 2010/0140586 A1**(43) **Pub. Date: Jun. 10, 2010**(54) **QUANTUM DOTS HAVING COMPOSITION  
GRADIENT SHELL STRUCTURE AND  
MANUFACTURING METHOD THEREOF**(75) Inventors: **Kookheon Char**, Seoul (KR);  
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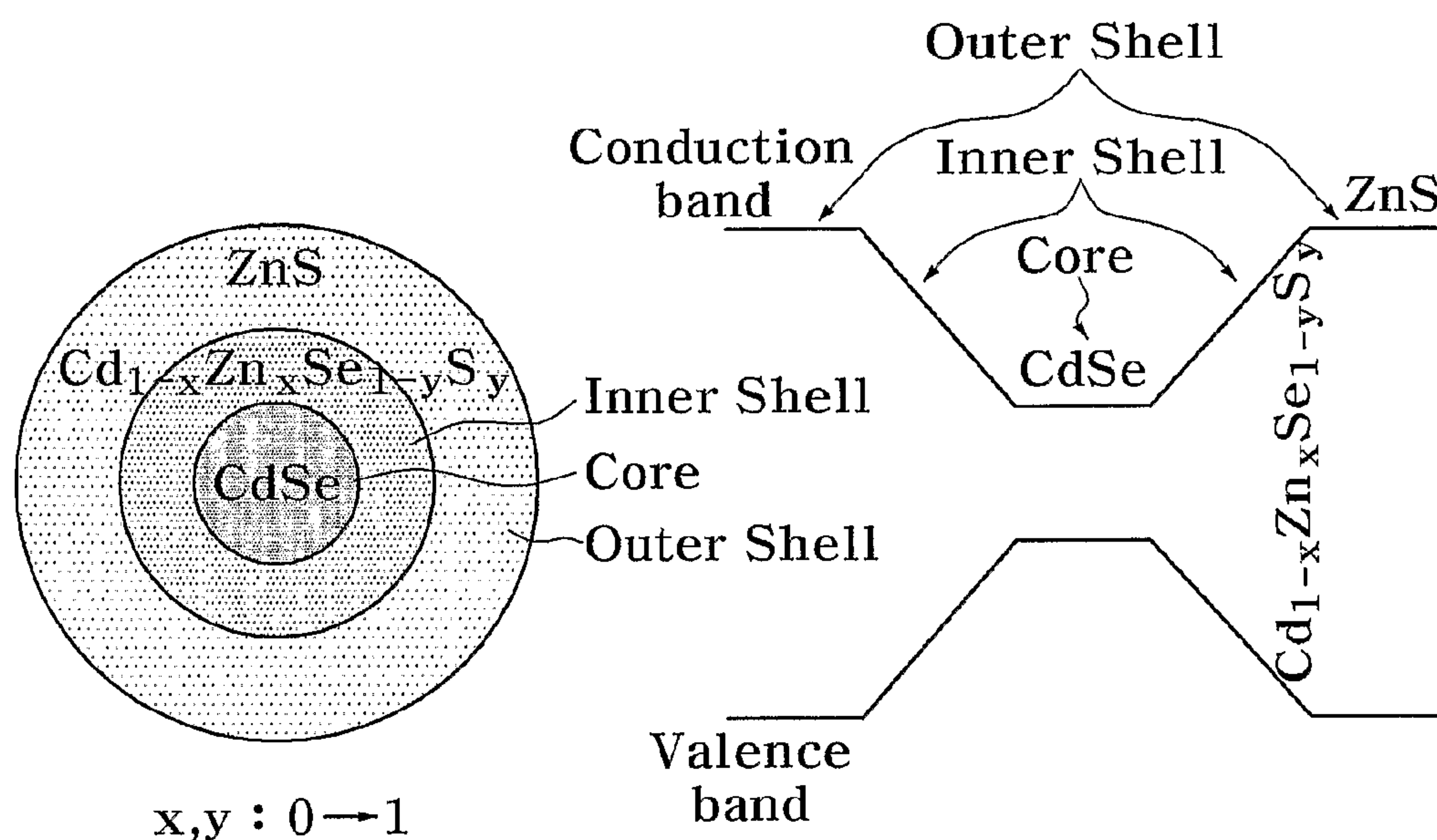
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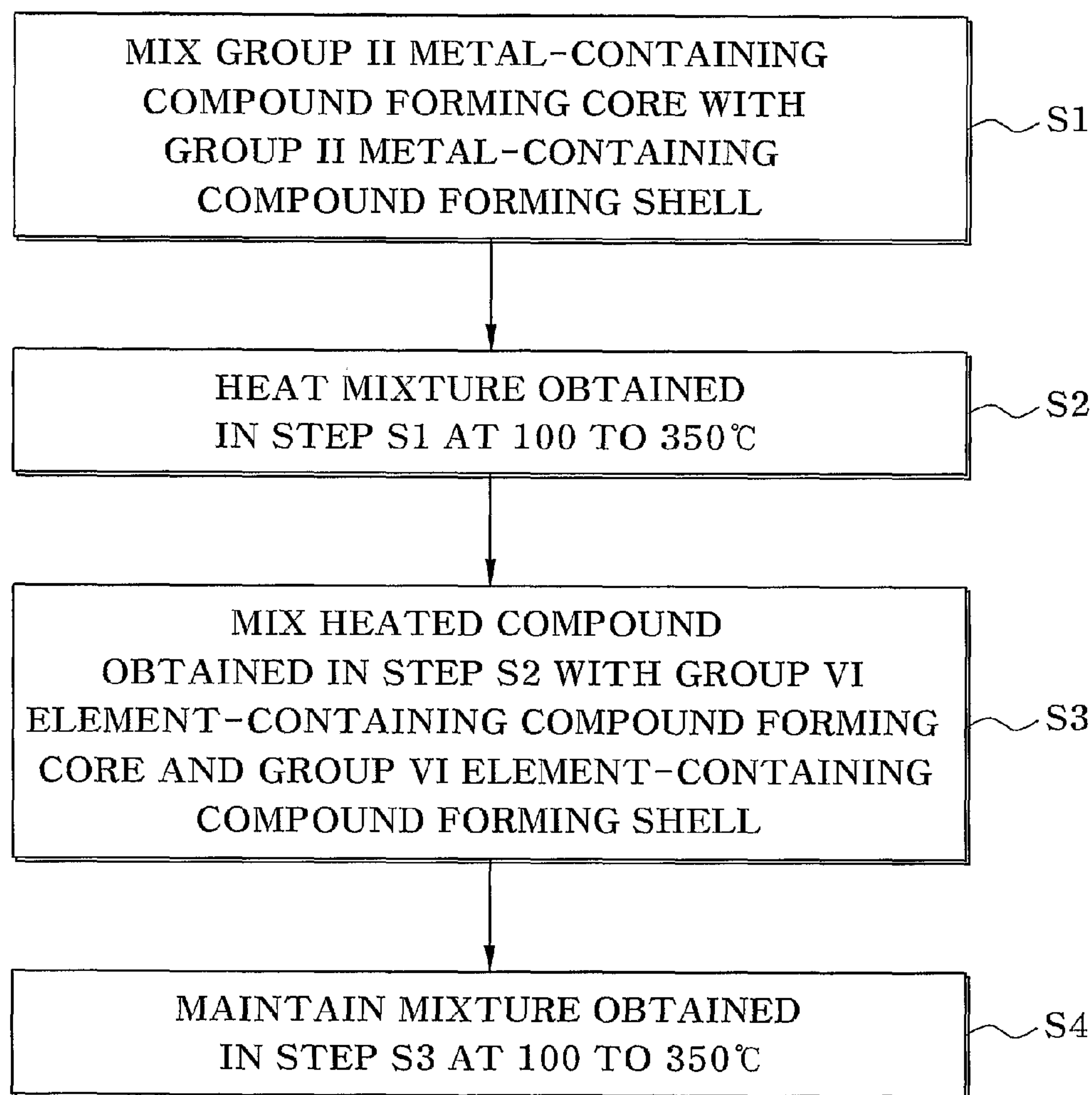
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**257/E21.461; 257/E21.068; 977/774**(57) **ABSTRACT**

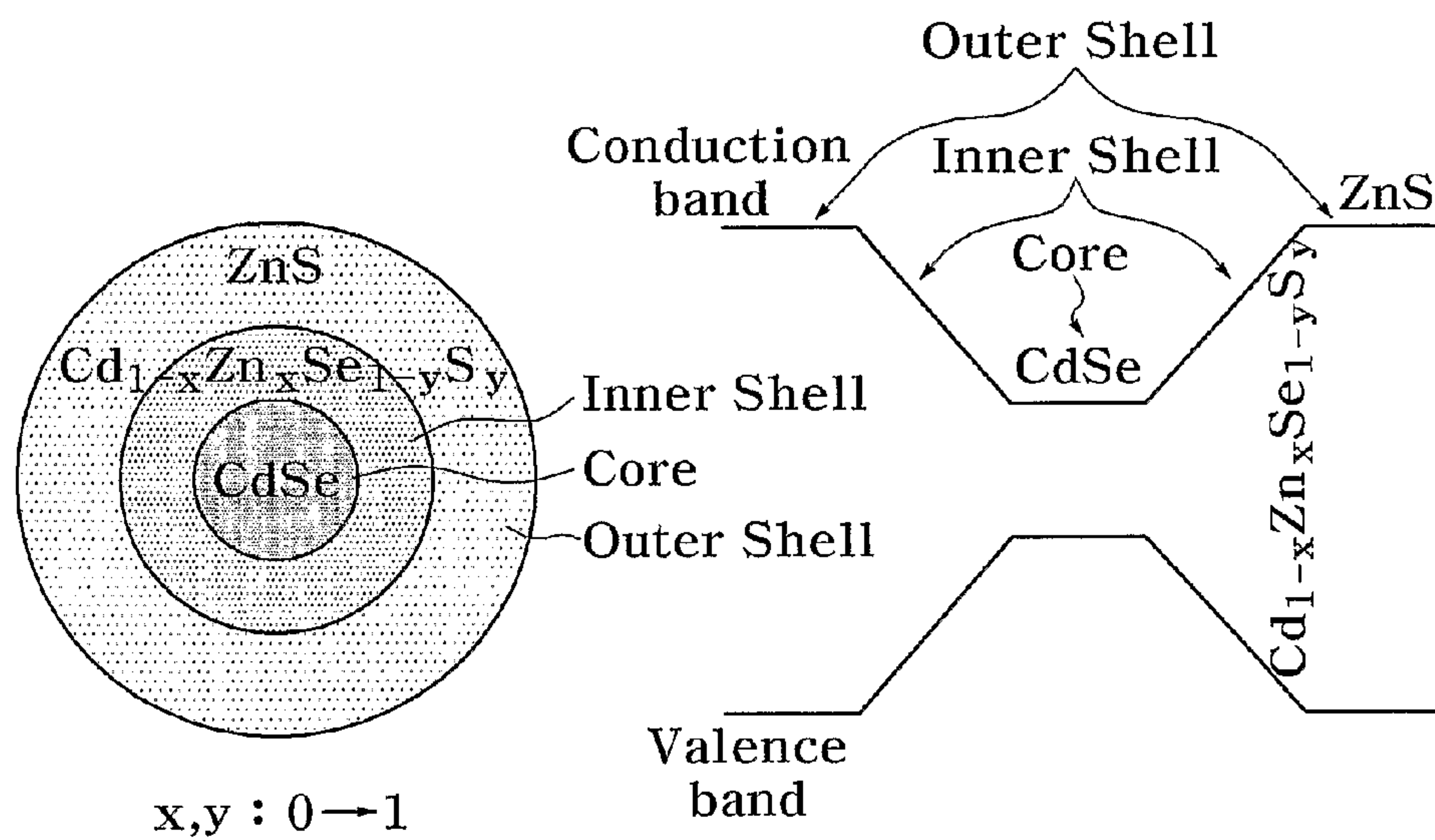
Provided are quantum dots having a gradual composition gradient shell structure which have an improved luminous efficiency and optical stability, and a method of manufacturing the quantum dots in a short amount of time at low cost. In the method, the quantum dots can be manufactured in a short amount of time at low cost using a reactivity difference between semiconductor precursors, unlike in uneconomical and inefficient conventional methods where shells are formed after forming cores and performing cleaning and redispersion processes. Also, formation of the cores is followed by formation of shells having a composition gradient. Thus, even if the shells are formed to a large thickness, the lattice mismatch between cores and shells is relieved. Furthermore, on the basis of the funneling concept, electrons and holes generated in the shells are transferred to the cores to emit light, thereby obtaining a high luminous efficiency of 80% or more. The quantum dot structure is not limited to Group II-IV semiconductor quantum dots but can be applied to other semiconductor quantum dots, such as Group III-V semiconductor quantum dots and Group IV-IV semiconductor quantum dots. Also, the manufacturing method can be utilized in the development of semiconductor quantum dots having different physical properties, and in various other fields.



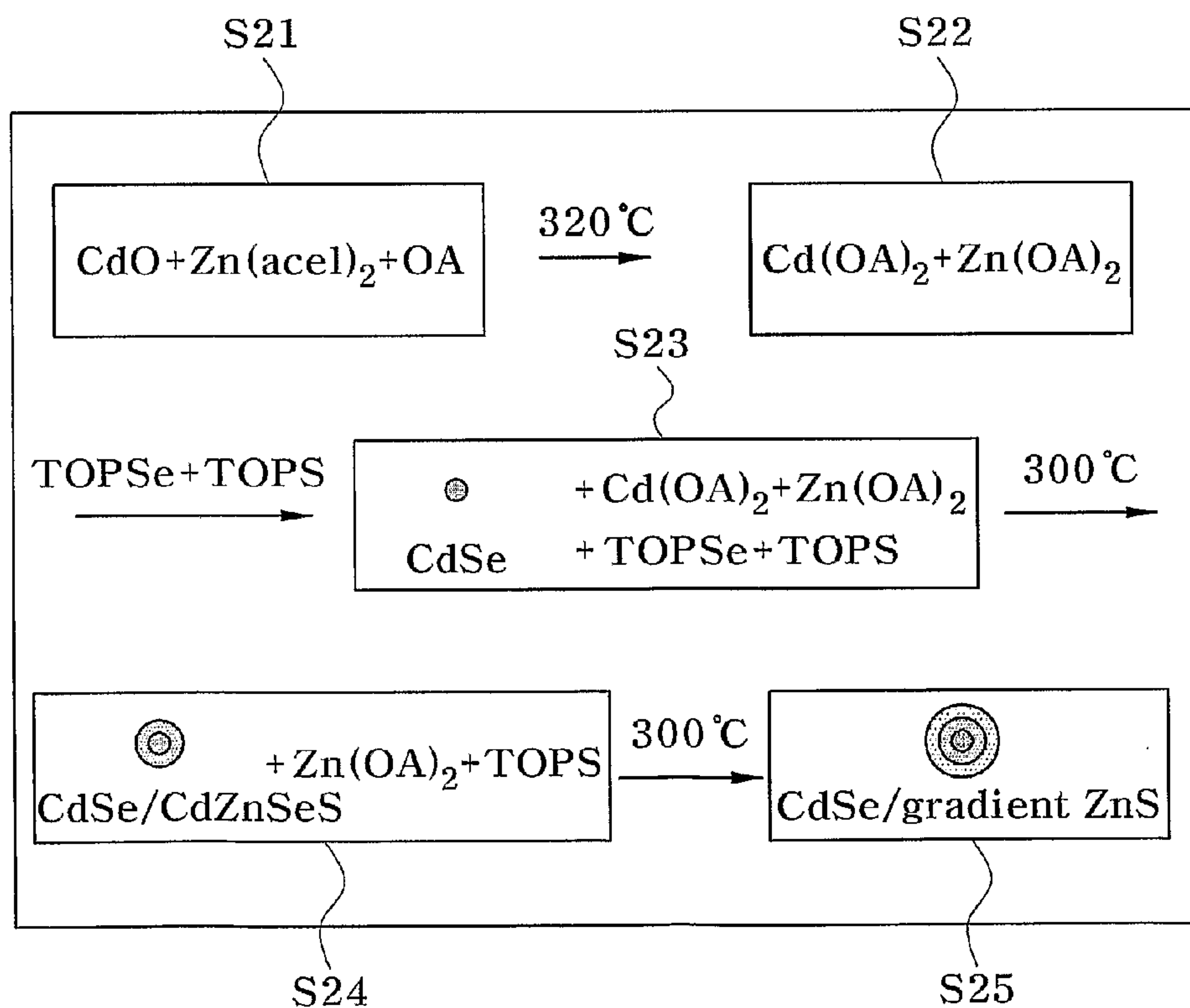
[Fig. 1]



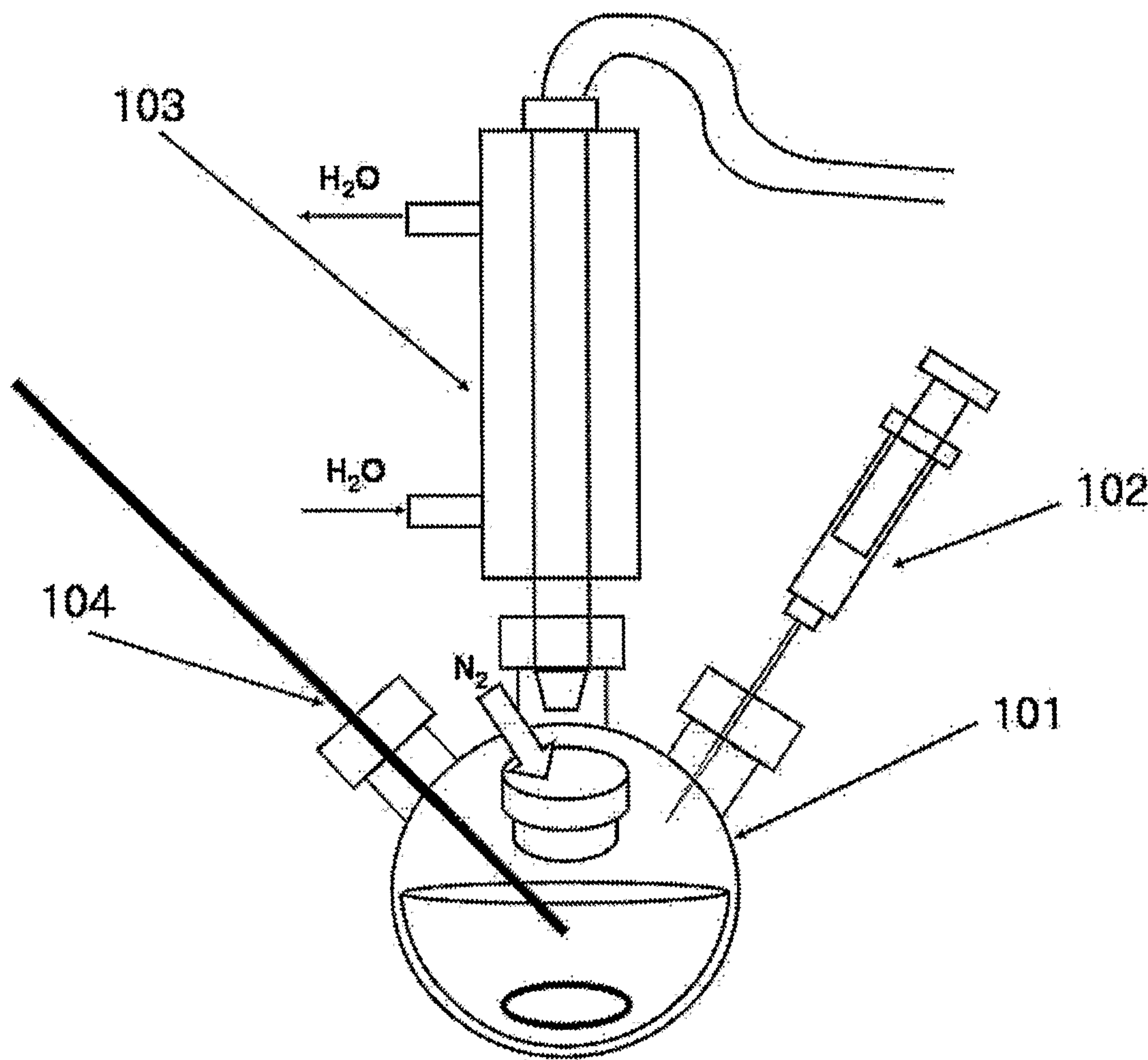
[Fig. 2]



[Fig. 3]

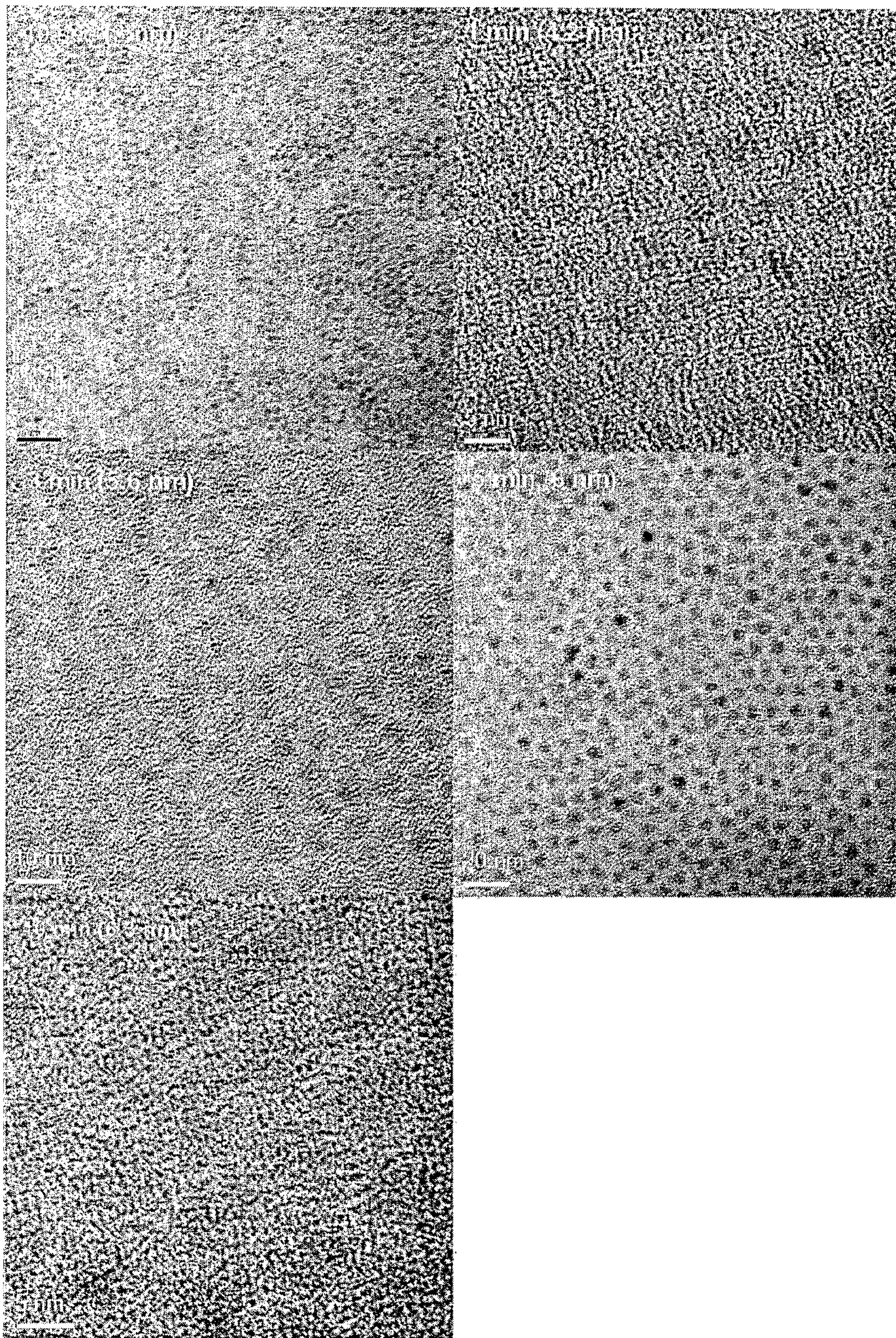


[Fig. 4]



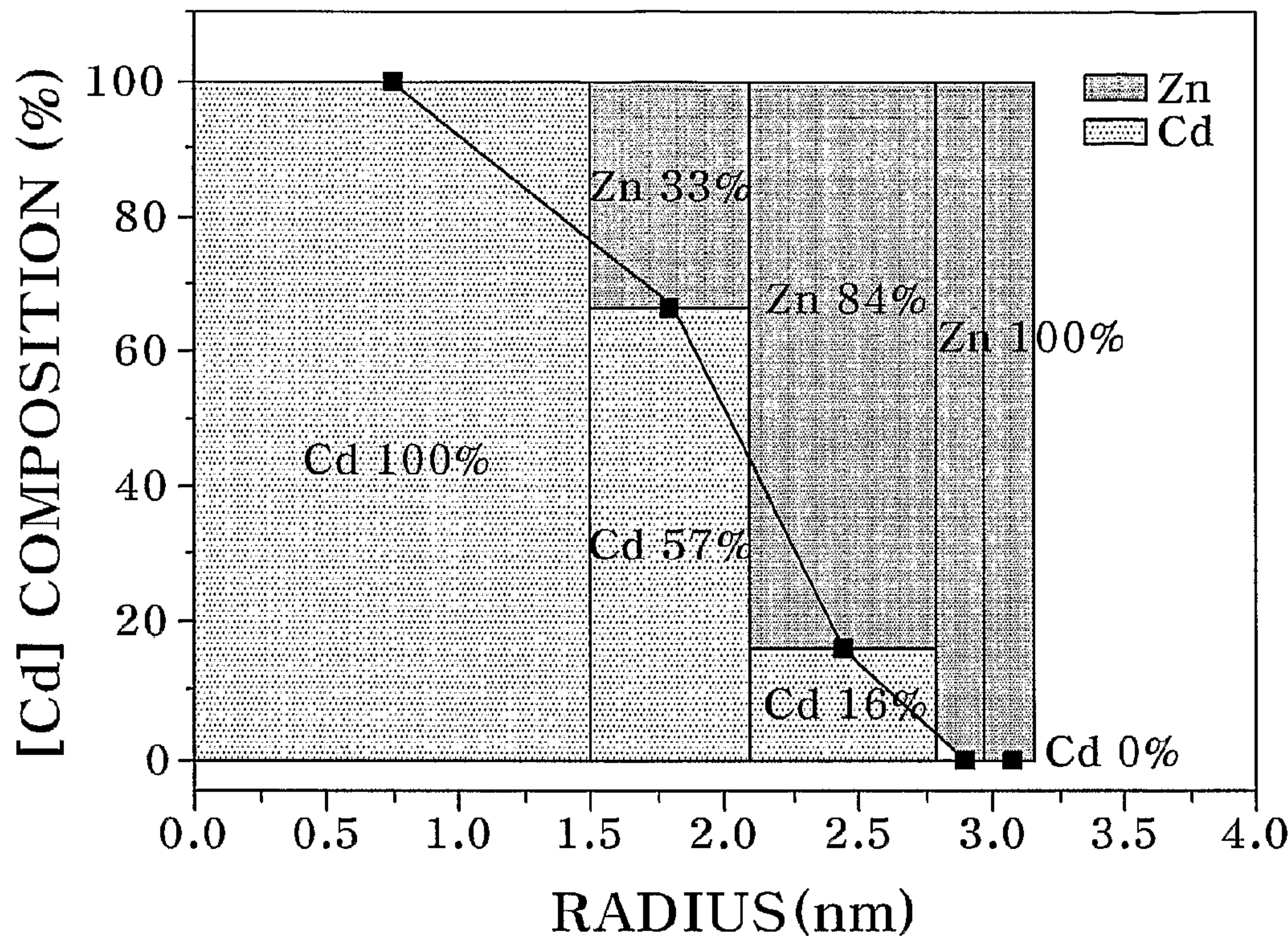


[Fig. 5]

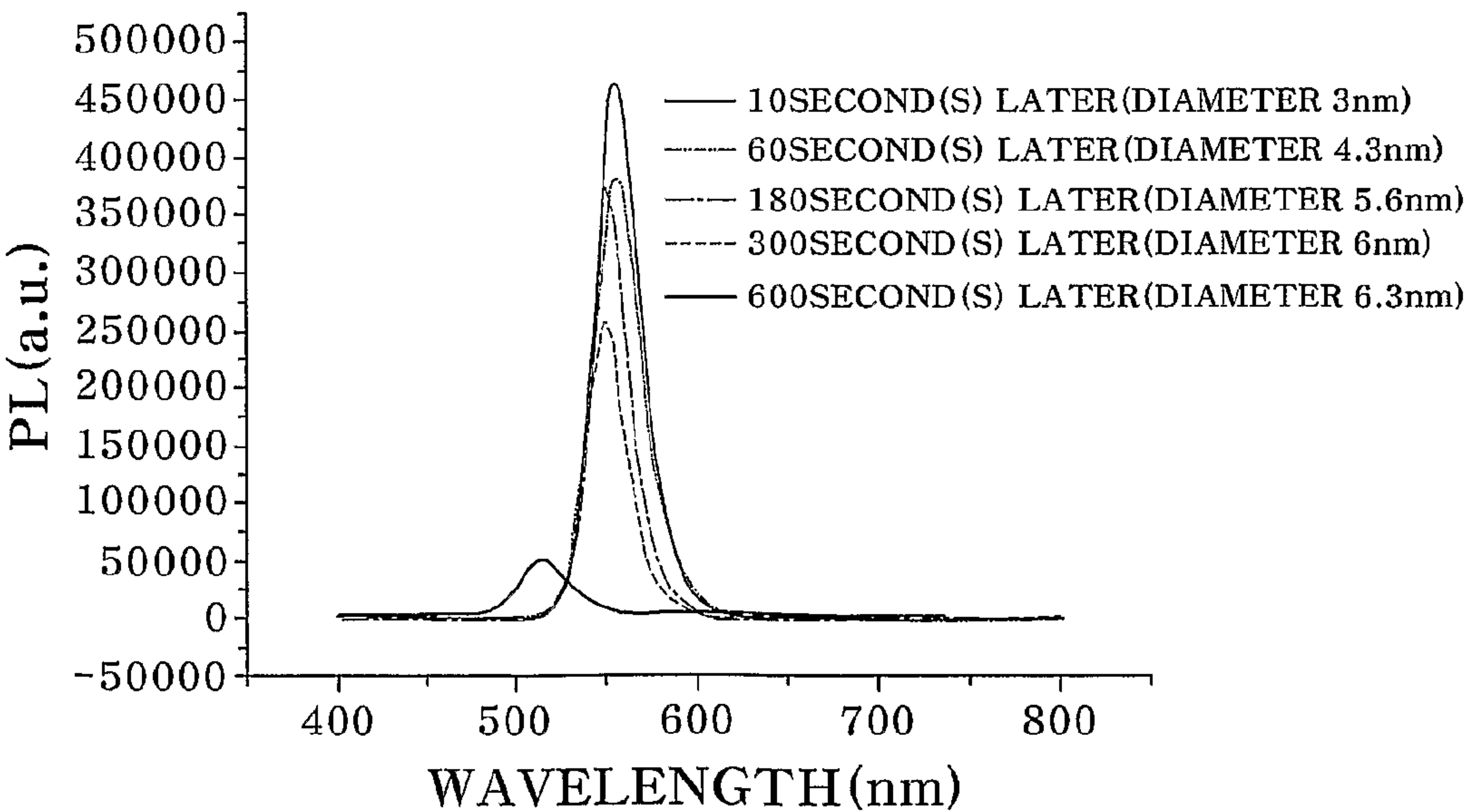




[Fig. 6]



[Fig. 7]





# QUANTUM DOTS HAVING COMPOSITION GRADIENT SHELL STRUCTURE AND MANUFACTURING METHOD THEREOF

## TECHNICAL FIELD

**[0001]** The present invention relates to quantum dots having a gradual composition gradient shell structure and a method of manufacturing the same, and more particularly, quantum dots which have improved luminous efficiency and optical stability owing to a gradual composition gradient shell structure, and a method of manufacturing the same.

## BACKGROUND ART

**[0002]** Conventionally, quantum dots have been manufactured using a dry chemical process, specifically, by inducing lattice mismatch between a substrate prepared in a vacuum and a layer deposited using a metal organic chemical vapor deposition (MOCVD) process. In this case, although nanoparticles may be formed and arranged on the substrate, expensive equipments are required. And it is also difficult to produce large quantities of quantum dots with a uniform size through conventional semiconductor fabrication methods. In order to solve these problems, a wet chemical process for synthesizing quantum dots with a uniform size using a surface active agent (surfactant) has been developed.

**[0003]** A method of manufacturing quantum dots through a wet chemical process includes preventing nanoparticles from aggregating together using a surfactant and controlling the reactivity of crystal surfaces by moderate choices of surfactants to synthesize quantum dots with various shapes with an uniform size. In 1993, the Bawendi group succeeded in synthesizing cadmium selenide (CdSe) quantum dots with a uniform size by means of a wet chemical process using trioctylphosphineoxide (TOPO) and trioctylphosphine (TOP) as surfactants, dimethylcadmium (Me)<sub>2</sub>Cd and selenium as precursors of Group II and Group VI. Also, the Alivisatos group developed a method of synthesizing CdSe quantum dots in a safer manner using hexadecylamine (HDA), trioctylphosphineoxide, and trioctylphosphine as surfactants, cadmium oxide (CdO), and TOPSe as precursors of Group II and Group VI.

**[0004]** Subsequently, a substantial amount of research has been conducted to passivate the surfaces of CdSe quantum dots with compound semiconductor having a larger bandgap in order to improve luminous characteristics and optical and environmental stability of the CdSe quantum dots. For example, CdSe/ZnS (refer to J. Phys. Chem. B, 1997, 101, 9465-9475), CdSe/ZnSe (refer to Nano Letters, 2002, 2, 781-874), CdSe/

**[0005]** WO CdS (refer to J. Am. Chem. Soc., 1997, 119, 7019-7029), and ZnSe/ZnS (Korean Patent Registration No. 10-0376403) have been proposed.

**[0006]** However, in conventional core-shell quantum dots, when a thick shell is formed, an interface between the core and shell of the quantum dot becomes unstable due to the lattice mismatch between a core semiconductor material and a shell semiconductor material, thereby causes formation of defects which lower quantum efficiency of quantum dots. Thus, the conventional core-shell quantum dots have thin shell structures. As a result, the shell semiconductor material functions only to stabilize the surface state of the core of the quantum dot and cannot funnel electrons and holes to the core. Therefore the conventional core-shell quantum dots have limitations in luminous efficiency, optical stability, and environmental stability.

**[0007]** Therefore, research into the manufacture of a multishell including an intermediate shell has been progressed in order to minimize lattice mismatch between core structure and shell structure of quantum dots. For example, CdSe/CdS/ZnS (Korean Patent Registration No. 10-2005-0074779) and CdSe/CdS/Zn<sub>0.5</sub>Cd<sub>0.5</sub>S/ZnS (refer to J. Am. Chem. Soc. 2005, 127, 7480-7488) were proposed. Since the core-multishell quantum dots described above have high luminous efficiencies and sufficient optical and environmental stability, they can be applied to practical applications such as various emission materials, laser materials, and biological marker materials. However, the manufacture of conventional core-multishell quantum dots involves complicated synthetic processes. Specifically, after each synthetic steps (i.e., synthesis of cores or each intermediate shells of quantum-dot), the synthetic process should be ended, all surfactants and precursors should be cleaned away, and a precursor required for intermediate shells should be injected into a new surfactant at an appropriate temperature to react over a long period. Also, during the sequential purification steps, some quantum dots and nonreacted precursors are removed too, which is counterproductive. Furthermore, in quantum dots having a stacked shell structure obtained according to the synthesis process described above, only excitons generated in quantum-dot cores are used, while excitons generated in quantum-dot shells do not contribute to light emission, which limits luminous efficiency of quantum dots.

**[0008]** Accordingly, there is still room to develop highly crystalline quantum dots having high luminous efficiency and optical and environmental stability, and a straightforward technique for synthesizing the quantum dots in large quantities at low cost.

## DISCLOSURE OF INVENTION

### Technical Problem

**[0009]** The present invention is as to quantum dots of highly luminous efficiency and optical stability which is due to a gradual composition gradient shell structure, and this is a method of manufacturing the quantum dots in a short time at low cost.

### Technical Solution

**[0010]** In their efforts to overcome the disadvantages of conventional quantum dots and methods of manufacturing them, the present inventors have developed a new method of economically manufacturing quantum dots having a gradual composition gradient shell structure through a single-step process using the reactivity difference between Group II metal-containing compounds and that between Group VI element-containing compounds. Also, the present inventors confirm that optically stable quantum dots of highly luminous efficiency can be manufactured by this method.

**[0011]** One aspect of the present invention provides a quantum dot including a Group II-VI compound core and a Group II-VI compound shell. A Group II-VI compound forming the shell has a larger bandgap than a Group II-VI compound forming the core and the Group II-VI compound shell has a gradual composition gradient.

**[0012]** Another aspect of the present invention provides a method of manufacturing quantum dots. The method includes the steps of: (1) mixing a Group II metal-containing compound forming a core with a Group II metal-containing compound forming a shell; (2) heating the mixture at a temperature of 100 to 350° C. (3) mixing the heated mixture with a Group VI element-containing compound forming the core and a Group VI element-containing compound forming the



shell; and (4) forming the shell to have a composition gradient by maintaining the mixture of step (3) at a temperature of 100 to 350° C.

**[0013]** Still another aspect of the present invention provides a quantum dot including: a core; an outer shell having a predetermined bandgap energy higher than that of the core; and an inner shell surrounding the core and surrounded by the outer shell, the inner shell having a bandgap energy that gradually decreases from the outer shell toward the core.

**[0014]** Yet another aspect of the present invention provides a method of manufacturing quantum dots including the steps of: (a) reacting compounds to form cores; and (b) reacting remaining compounds to form shells having a gradual composition gradient, wherein step (a) and step (b) are sequentially performed due to a difference in reactivity between the compounds.

**[0015]** Still yet another aspect of the present invention provides a method of manufacturing quantum dots including the steps of: (a) forming cores; and (b) reacting compounds to form shells, wherein, in step (b), the shells are formed to have a gradual composition gradient due to a difference in reactivity between the compounds.

#### Advantageous Effects

**[0016]** According to the present invention, quantum dots can be manufactured in a short amount of time at low cost using a difference in reactivity between semiconductor precursors, unlike in uneconomical and inefficient conventional methods where shells are formed after forming cores through performing consecutive cleaning and redispersion processes. Also, according to the present invention, formation of cores is spontaneously followed by formation of shells having a composition gradient. Thus, even if shells are formed to a large thickness, the lattice mismatch between core and shell does not occur, unlike in conventional core-shell quantum dots. Furthermore, the funnel concept is applied to the present invention, so that electrons and holes absorbed in the shells are transferred to the cores to emit light, thereby a high luminous efficiency of 80% or higher is obtained. Moreover, the use of a surfactant can be minimized to facilitate a subsequent cleaning process, and the surfaces of synthesized quantum dots can be easily substituted, so that the quantum dots can be applied in different environments. As described above, the present invention provides new quantum dots having cores and shells with a gradual composition gradient, which can be applied to not only Group II-IV semiconductor quantum dots but also other semi-conductor quantum dots, such as Group III-V semiconductor quantum dots and Group IV-IV semiconductor quantum dots, and can be utilized in the development of semi-conductor quantum dots having different physical properties and in various other fields.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0017]** FIG. 1 is a flowchart illustrating a process of manufacturing quantum dots according to an exemplary embodiment of the present invention.

**[0018]** FIG. 2 is a diagram of a composition gradient and energy band of a quantum dot having a gradual composition gradient shell structure according to an exemplary embodiment of the present invention.

**[0019]** FIG. 3 is a diagram illustrating a process of manufacturing quantum dots according to an exemplary embodiment of the present invention.

**[0020]** FIG. 4 is a diagram of experimental equipment used for manufacturing quantum dots according to the present invention.

**[0021]** FIG. 5 is a transmission electron microscope (TEM) photograph showing changes in quantum dots manufactured according to the present invention as a function of reaction time.

**[0022]** FIG. 6 is a graph showing radial composition distribution of a quantum dot having a core and shell manufactured according to the exemplary embodiment of the present invention.

**[0023]** FIG. 7 is a graph showing the luminous efficiency of a quantum dot manufactured according to the present invention as a function of reaction time.

#### MODE FOR THE INVENTION

**[0024]** Hereinafter, exemplary embodiments of the present invention will be described in detail.

**[0025]** The present invention provides quantum dots having a gradual composition gradient and high luminous efficiency and a method of manufacturing the quantum dots in a short amount of time at low cost. FIG. 1 is a flowchart illustrating a process of manufacturing quantum dots according to an exemplary embodiment of the present invention.

**[0026]** A method of manufacturing quantum dots according to the present invention includes mixing a Group II metal-containing compound forming the core of a quantum dot and a Group II metal-containing compound forming the shell of the quantum dot, and heating the mixture in step S1.

**[0027]** In the present invention, the Group II metal used in step S1 may be one selected from the group consisting of cadmium (Cd), zinc (Zn), and mercury (Hg), and the Group II metal-containing compound may be one selected from the group consisting of cadmium oxide, zinc acetate, cadmium acetate, cadmium chloride, zinc chloride, zinc oxide, mercury chloride, mercury oxide, and mercury acetate. However, the present invention is not limited thereto and any compound containing a Group II metal such as cadmium, zinc, or mercury can be used.

**[0028]** The two compounds are mixed using an organic solvent. The organic solvent may be one selected from the group consisting of 1-oxadecene, hexadecylamine (HDA), trioctylamine (TOA), trioctylphosphine oxide, oleic acid, and oleyl amine, but the present invention is not limited thereto.

**[0029]** In addition to the organic solvent fatty acid may be added when mixing the two compounds. The fatty acid may be one selected from the group consisting of oleic acid, stearic acid, myristic acid, lauric acid, palmitic acid, elaidic acid, eicosanoic acid, heneicosanoic acid, tricosanoic acid, docosanoic acid, tetracosanoic acid, hexacosanoic acid, heptacosanoic acid, octacosanoic acid, and cis-13-docosenoic acid. However, the present invention is not limited thereto and any fatty acid may be used.

**[0030]** In the present invention, in step S1, the mixture of the Group II metal-containing compound forming the core and the Group II metal-containing compound forming the shell is heated in an atmosphere of N<sub>2</sub> or Ar, at no more than atmospheric pressure, at a temperature of about 100 to 350° C., for 10 to 600 minutes. When the mixture of the two compounds is heated under these conditions, a metal-fatty acid complex is formed. The metal-fatty acid complex is uniformly distributed in the solvent. Since the mixture of the Group II metal-containing compounds may react with oxygen, the heating process may be performed in the nonreactive N<sub>2</sub> or Ar atmosphere at atmospheric pressure to suppress reactivity. Also, when the heating process is performed at a temperature lower than 100° C., a complex is not formed, and when the heating process is performed at a temperature higher than 350° C., an organic compound may boil and



evaporate or be broken. Therefore, the heating process may be performed at a temperature of about 100 to 350° C.

[0031] After the metal-fatty acid complex is formed, the remaining oxygen and water, and impurities with a low boiling point are removed in a vacuum using a liquid nitrogen trap, and the metal-unsaturated fatty acid complex is heated in an N<sub>2</sub> or Ar atmosphere at atmospheric pressure and a temperature of about 100 to 350° C. in step S2. When the heating process is performed at a temperature lower than 100° C., forming quantum dots is difficult, and when the heating process is performed at a temperature higher than 350° C., an organic compound may boil and evaporate or be broken. Therefore, the heating process may be performed at a temperature of about 100 to 350° C.

[0032] In step S1, the Group II metal-containing compound forming the core may be mixed with the Group II metal-containing compound forming the shell in a 1:1 to 1:50 molar ratio. When the molar ratio is less than 1:1, quantum dots that emit long-wavelength light are formed. When the molar ratio is more than 1:50, quantum dots that emit short-wavelength light are formed and a slowly reacting material may form the core. By adjusting the molar ratio, the wavelength range of formed quantum dots may be controlled.

[0033] Thereafter, in step S3, the heated compound obtained in step S2 is mixed with a Group VI element-containing compound forming the core and a Group VI element-containing compound forming the shell.

[0034] The Group VI element may be one selected from the group consisting of sulfur (S), selenium (Se), tellurium (Te), and polonium (Po), and the Group VI element-containing compound may be one selected from the group consisting of tri-octylphosphine selenide, trioctylphosphine sulfide, trioctylphosphine telluride, trioctylphosphine polonide, tributylphosphine selenide, tributylphosphine sulfide, tributylphosphine telluride, and tributylphosphine polonide. However, the present invention is not limited thereto and any material containing a Group VI element such as sulfur, selenium, tellurium, and polonium may be used. In step S3, the Group VI element-containing compound forming the core may be mixed with the Group VI element-containing compound forming the shell in a 1:1 to 1:50 molar ratio. When a molar ratio is less than 1:1, quantum dots that emit long-wavelength light are formed. When the molar ratio is more than 1:50, quantum dots that emit short-wavelength light are formed and a slowly reacting material may form the core. Specifically, although the compound forming the core reacts rapidly and is formed earlier, when there is too much compound forming the shell, part of the compound does not form the shell and may form an additional core structure.

[0035] As described above, when the Group VI element-containing compounds are added to the heated mixture, rapidly reacting Group II metal and Group VI element are separated earlier in a supersaturated state in a reactor containing the mixture to generate a nucleation reaction for forming the core. In this case, similar nucleation reactions are facilitated at the same time, thereby generating quantum-dot cores with a uniform size.

[0036] After adding and reacting the Group VI element-containing compounds, the mixture obtained in step S3 is maintained at a temperature of 100 to 350° C. in step S4. When a continuous reaction is induced by maintaining the temperature, the Group II metal and Group VI element, which form the cores on the surface of the quantum-dot cores, react and grow along with the Group II metal and Group VI element, which form the shells. After 10 minutes, reaction between rapidly reacting Group II metal and Group VI ele-

ment ends, while slowly reacting Group II metal and Group VI element continue to react to form the shells.

[0037] The quantum dots manufactured according to the above-described method of the present invention have Group II-VI compound cores and Group II-VI compound shells. The Group II-VI compound forming the shells has a larger bandgap than the Group II-VI compound forming the cores, and the Group II-VI compound shells have a gradual composition gradient.

[0038] Specifically, as shown in FIG. 2, the quantum dots manufactured according to the present invention have shell structures with a gradual composition gradient, so that they have the lowest conductance-band edge and the highest covalence-band edge in the cores. The conductance-band edge becomes gradually higher and the covalence-band edge becomes gradually lower from an inner portion of the shell toward an outer portion of the shell, so that the outermost portion of the shell has the highest conductance-band edge and the lowest covalence-band edge.

[0039] More specifically, the quantum dot manufactured according to the present invention is divided into the core and the shell, and the shell is divided into an inner shell and an outer shell. As illustrated in FIG. 2, the core may be formed of CdSe, the outer shell may be formed of ZnS, and the inner shell may be formed of Cd<sub>1-X</sub>Zn<sub>X</sub>Se<sub>1-Y</sub>S<sub>Y</sub> (0<X<1, 0<Y<1, X and Y become smaller from the outer shell toward the core). The inner shell surrounds the core and is surrounded by the outer shell. Each of the core and the outer shell is formed of a compound semiconductor with a predetermined composition ratio, while the inner shell is formed of a compound semiconductor whose composition ratio varies with position. The core has a small bandgap energy, and the outer shell has a larger bandgap energy than the core. Also, the inner shell has a bandgap energy that becomes smaller from the outer shell toward the core.

[0040] In the quantum dot described above, formation of the core is followed by formation of the shell having a composition gradient. Therefore, even if the shell is formed to a large thickness, the lattice mismatch between core and shell does not occur unlike in conventional core-shell quantum dots. Furthermore, since the quantum dots according to the present invention are based on the funnel concept, electrons and holes generated in the shell are transferred to the core to emit light, so that the quantum dots have a high luminous efficiency of about 80% or higher.

[0041] The present invention will now be described more explicitly hereinafter with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. This invention may, however, be embodied in different forms and should not be construed as limited to the exemplary embodiments set forth herein.

#### EXEMPLARY EMBODIMENT 1

[0042] Synthesis of Quantum Dots with CdSe Cores And ZnS Shells

[0043] FIG. 3 is a diagram illustrating a process of manufacturing quantum dots according to an exemplary embodiment of the present invention, and FIG. 4 is a diagram of experimental equipment used for manufacturing quantum dots according to the present invention. Hereinafter, a process of synthesizing quantum dots with CdSe cores and ZnS shells will be described with reference to FIGS. 3 and 4.

[0044] In step S21, 0.0512 g (0.4 mmol) of solid cadmium oxide (purity: 99.998%), 0.732 g (4 mmol) of zinc acetate, 4.4 ml (17.6 mmol) of oleic acid, and 13.6 ml of 1-octadecene (CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>) were put in a 100 ml round-bottom flask 101 including a syringe 101, a thermometer 104, and a



cooler **103**. In step **S22**, the mixture was heated at a pressure of 1 ton and a temperature of about 320° C. for 20 minutes to synthesize a cadmium-oleic acid complex and a zinc-oleic acid complex and remove remaining oxygen from the complexes.

**[0045]** Thereafter, the complexes were heated in an N<sub>2</sub> atmosphere at a pressure of 1 atmosphere and a temperature of about 320° C., and a 2 ml mixture of 0.2 ml of 2M trioctylphosphine selenide solution obtained by dissolving selenium in trioctylphosphine and 1.8 ml of 2M trioctylphosphine sulfide solution obtained by dissolving sulfur in trioctylphosphine was rapidly injected into a reactor **101** heated to a temperature of about 320° C. In this case, rapidly reacting cadmium and selenium are supersaturated and separated in the reactor **101**. As a result, a similar nucleation reaction is facilitated, thus generating uniform CdSe nuclei in step **S23**.

**[0046]** Subsequently, when a continuous reaction was induced by maintaining the reactor **101** at a temperature of about 300° C., cadmium, selenium, zinc, and sulfur reacted and grew on the surface of the CdSe nuclei in step **S24**. After a predetermined amount of time elapsed, cadmium and selenium stopped reacting, and only zinc and sulfur reacted to form ZnS shells in step **S25**. As a result, quantum dots having CdSe cores and ZnS shells with a composition gradient were generated.

**[0047]** After finishing the generation of the quantum dots having the cores and the shells with the composition gradient, the temperature of the reactor **101** was lowered to room temperature, and acetone was added to precipitate the quantum dots. After that, the quantum dots were separated using a centrifugal separator, cleaned three times using about 20 ml of acetone, and dried in a vacuum, thereby completing manufacture of quantum dots with CdSe cores and ZnS shells.

#### EXEMPLARY EMBODIMENT 2

**[0048]** Synthesis of Quantum Dots with CdSe Cores and ZnSe Shells

**[0049]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that 2 ml of 2M trioctylphosphine selenide solution was used instead of the mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXEMPLARY EMBODIMENT 3

**[0050]** Synthesis of Quantum Dots with CdTe Cores and ZnS Shells

**[0051]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that a 2 ml mixture of 0.2 ml of 2M trioctylphosphine telluride solution and 1.8 ml of 2M trioctylphosphine sulfide solution was used instead of the mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXEMPLARY EMBODIMENT 4

**[0052]** Synthesis of Quantum Dots with CdTe Cores and ZnSe Shells

**[0053]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that a 2 ml mixture of 0.2 ml of 2M trioctylphosphine telluride solution and 1.8 ml of 2M trioctylphosphine selenide solution was used instead of the

mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXEMPLARY EMBODIMENT 5

**[0054]** Synthesis of Quantum Dots with CdTe Cores and ZnTe Shells

**[0055]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that 2 ml of 2M trioctylphosphine telluride solution was used instead of the mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXEMPLARY EMBODIMENT 6

**[0056]** Synthesis of Quantum Dots with CdTe Cores and CdS Shells

**[0057]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that 0.0512 g (4 mmol) of cadmium oxide, 4 ml (16 mmol) of oleic acid, 14 ml of 1-octadecene were used instead of 0.0512 g (0.4 mmol) of cadmium oxide, 0.732 g (4 mmol) of zinc acetate, 4.4 ml (17.6 mmol) of oleic acid, 13.6 ml of 1-octadecene used in the first exemplary embodiment. And, a 2 ml mixture of 0.2 ml of 2M trioctylphosphine telluride solution and 1.8 ml of 2M trioctylphosphine sulfide solution was used instead of the mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXEMPLARY EMBODIMENT 7

**[0058]** Synthesis of Quantum Dots with CdS Cores and ZnS Shells

**[0059]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that 2 ml of 2M trioctylphosphine sulfide solution was used instead of the mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXEMPLARY EMBODIMENT 8

**[0060]** Synthesis of Quantum Dots with ZnSe Cores and ZnS Shells

**[0061]** In the present exemplary embodiment, quantum dots were manufactured in the same manner as in the first exemplary embodiment except that 7.32 g (4 mmol) of zinc acetate, 4 ml (16 mmol) of oleic acid, and 14 ml of 1-octadecene were used instead of 0.0512 g (0.4 mmol) of cadmium oxide, 0.732 g (4 mmol) of zinc acetate, 4.4 ml (17.6 mmol) of oleic acid, and 13.6 ml of 1-octadecene used in the first exemplary embodiment. And, a 2 ml mixture of 0.2 ml of 2M trioctylphosphine selenide solution and 1.8 ml of 2M trioctylphosphine sulfide solution was used instead of the mixture of trioctylphosphine selenide and trioctylphosphine sulfide used in the first exemplary embodiment.

#### EXPERIMENTAL EXAMPLE

**[0062]** Analysis of Radial Composition Distribution and Quantum and Luminous Efficiencies of Quantum Dots with CdSe Cores and ZnS Shells

**[0063]** In the manufacture of the CdSe cores and ZnS shells with a composition gradient according to the method described in the first exemplary embodiment, at times of 10 seconds, 1 minute, 3 minutes, 5 minutes, and 10 minutes after injecting trioctylphosphine selenide and trioctylphosphine



sulfide into the reactor, 0.5 ml of a reactant was extracted using a glass syringe, refined three times, and dispersed in nucleic acid.

**[0064]** Each time a sample of quantum dots was extracted on a transmission electron microscope (TEM) grid from Jeol, a TEM analysis was carried out using JEM-3010 from Jeol. FIG. 5 shows the results of the TEM analysis. Also, in order to analyze the composition of each quantum dot, quantum dots were dispersed in 1 ml of nitric acid and 19 ml of water was added to dissolve and ionize the quantum dots. Thus, the compositions of the quantum dots were analyzed using an ICP-Atomic Emission Spectrometer from Shimadzu. FIG. 6 is a graph showing the distribution of Cd and Zn relative to the TEM results and the radius of the quantum dots. In addition, the luminous efficiency of the quantum dots was measured over time using an Agilent 8454 UV spectrometer from Agilent and an Acton photomultiplier spectrometer from Acton. The light absorptivity and fluorescence intensity of each quantum dot solution was measured using rhodamine 6 G pigment as shown in FIG. 7.

**[0065]** Referring to FIG. 5, the quantum dots grew with time and came to have very uniform globular shapes and a uniform distribution.

**[0066]** Referring to FIG. 6, as the quantum dots grew, cadmium (Cd) mainly reacted to generate the cores. Thereafter, zinc (Zn) started to grow to generate the shells with a gradient, and then Zn mainly grew.

**[0067]** Referring to FIG. 7, it can be confirmed that when the quantum-dot shells with a composition gradient began to form, the luminous efficiency of the quantum dots began to gradually increase. The luminous efficiency reached 80% in 5 minutes after the cores and the shells with a composition gradient began to form.

**[0068]** While the invention has been shown and described with reference to certain exemplary embodiments thereof, it will be understood by one skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

1-16. (canceled)

**17.** A quantum dot comprising a core and a shell, wherein: the core comprises a first Group II-VI compound; the shell comprises a second Group II-VI compound; the second Group II-VI compound has a larger bandgap than the first Group II-VI compound; and the shell has a gradual composition gradient.

**18.** A method of manufacturing quantum dots, comprising: mixing a compound comprising a core-forming Group II metal with a compound comprising a shell-forming Group II metal to form a mixture;

heating the mixture comprising the core-forming Group II metal and the shell-forming Group II metal at a temperature between approximately 100° C. and 350° C.;

forming a core by mixing the mixture with a compound comprising a core-forming Group VI element and a compound comprising a shell-forming Group VI element; and

forming a shell having a composition gradient by maintaining the mixture at a temperature between approximately 100° C. and 350° C.

**19.** The method according to claim 18, wherein at least one of the core-forming Group II metal and the shell-forming Group II metal comprises at least one of zinc, cadmium, and mercury.

**20.** The method according to claim 18, wherein heating the mixture occurs:

in at least one of one of a N<sub>2</sub> atmosphere and a Ar atmosphere;

at or below atmospheric pressure;

at a temperature between approximately 100° C. and 350° C.; and

for a duration between approximately 10 minutes and 600 minutes.

**21.** The method according to claim 18, wherein the compound comprising the core-forming Group II metal is mixed with the compound comprising the shell-forming Group II metal in a 1:1 molar ratio to 1:50 molar ratio.

**22.** The method according to claim 18, wherein at least one of the core-forming Group VI element and the shell-forming Group VI element comprises at least one of sulfur, selenium, tellurium, and polonium.

**23.** The method according to claim 18, wherein the compound comprising the core-forming Group VI element is mixed with the compound comprising the shell-forming Group VI element in a 1:1 molar ratio to 1:50 molar ratio.

**24.** A quantum dot comprising:

a core;

an outer shell having a predetermined bandgap energy that is higher than that of the core; and

an inner shell that surrounds the core and that is surrounded by the outer shell, wherein the inner shell has a bandgap energy that gradually decreases in a direction from the outer shell towards the core.

**25.** The quantum dot according to claim 24, wherein each of the core, the outer shell, and the inner shell is formed by a Group II-VI compound semiconductor comprising a Group II element and a Group VI element.

**26.** The quantum dot according to claim 25, wherein:

the Group II element comprises at least one of cadmium, zinc, and mercury; and

the Group VI element comprises at least one of sulfur, selenium, tellurium, and polonium.

**27.** The quantum dot according to claim 26, wherein the core and the outer shell comprise at least one of:

a cadmium selenide core and a zinc sulfide outer shell;

a cadmium selenide core and a zinc selenide outer shell;

a cadmium telluride core and a zinc sulfide outer shell;

a cadmium telluride core and zinc selenide outer shell;

a cadmium telluride core and a zinc telluride outer shell;

a cadmium telluride core and a cadmium sulfide outer shell;

a cadmium sulfide core and a zinc sulfide outer shell; and

a zinc selenide core and a zinc sulfide outer shell.

**28.** A method of manufacturing quantum dots, comprising: reacting compounds to form cores; and

reacting remaining compounds to form shells having a gradual composition gradient,

wherein said reacting compounds and said reacting remaining compounds are sequentially performed due to a difference in reactivity between the compounds.

**29.** The method according to claim 28, wherein the gradual composition gradient of the shells is achieved due to a reactivity difference between the remaining compounds.

**30.** The method according to claim 28, wherein the cores and the shells are formed by Group II-VI compound semiconductors comprising a core-forming Group II metal, a core-forming Group VI element, a shell-forming Group II metal, and a shell-forming Group VI element.

**31.** A method of manufacturing quantum dots, comprising: forming cores; and



reacting compounds to form shells, wherein the shells are formed having a gradual composition gradient due to a difference in reactivity between the compounds.

**32.** The method according to claim **31**, wherein the cores and the shells are formed by Group II-VI compound semi-

conductors comprising a core-forming Group II metal, a core-forming Group VI element, a shell-forming Group II metal, and a shell-forming Group VI element.

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