Title: DUAL SITE SURFACE CAPPING FOR HIGHLY IMPROVING QUANTUM EFFICIENCY AND LIFE TIME OF LUMINESCENT NANO PARTICLES

Abstract: The invention provides a luminescent material 30 comprising semiconductor based luminescent nano particles 10, wherein the nano particles have an outer surface 11 coated with capping molecules 200, especially a first type of capping molecules 1 and a second type of capping molecules 2, wherein the first type of capping molecule comprises M°+R, wherein M is a metal, wherein R is at least 2, and wherein R is a hydrocarbon, and wherein the second type of capping molecule comprise an organic Lewis base. The coated nano particles 100 have a higher stability and quantum efficiency than state of the art quantum dots or nano particles.
Dual site surface capping for highly improving quantum efficiency and life time of luminescent nano particles

FIELD OF THE INVENTION

The invention relates to a luminescent material comprising semiconductor based luminescent nano particles (or quantum dots), a method for production of such luminescent nano particles, as well as to a lighting unit comprising a light converter comprising such luminescent material.

BACKGROUND OF THE INVENTION

The use of luminescent nano particles, such as quantum dots (QD), for lighting applications is known in the art. US20110240960, for instance, describes a light emitting device comprising a light emitting source, a first quantum dot wavelength converter disposed above the light emitting source, the first quantum dot wavelength converter comprising a plurality of first quantum dots for generating wavelength-converted light by converting wavelength of light from the light emitting source, a first dispersive medium embedding the first quantum dots dispersively therein, and a first sealer for sealing the entire outside surface of dispersive medium embedding the first quantum dots in a pack.

A first encapsulant is applied for encapsulating the entire outside surface of the first quantum dot wavelength converter. Further, a second quantum dot wavelength converter is disposed above the first quantum dot wavelength converter, the second quantum dot wavelength converter comprising a plurality of second quantum dots for generating wavelength-converted light by converting wavelength of light from the light emitting source, a second dispersive medium embedding the second quantum dots dispersively therein, and a second sealer for sealing the entire outside surface of the second dispersive medium embedding the second quantum dots in a pack, wherein the first quantum dot wavelength converter, the second quantum dot wavelength converter and the light emitting source are spaced apart from each other. The second encapsulant is disposed on the entire outside surface of the second quantum dot wavelength converter and for encapsulating the entire outside surface of the second quantum dot wavelength converter. Further, the light emitting source is a light emitting diode or a laser diode.
SUMMARY OF THE INVENTION

Nano particles, such as quantum dots (QDs), are interesting in lighting applications. They could serve as inorganic phosphor in converting blue light to other colors, such as green, yellow, orange and red, and have the advantage of narrow emission band and a size-dependent tunable color; thereby allowing to obtain high quality pure white light. For this purpose it is necessary to have QDs with quantum yield close to unity. Furthermore it is important to have QDs with a high photo-chemical stability. Nevertheless, quantum dots show time dependent quantum yield decrease under illumination at high temperatures. This behavior is known to be due to surface oxidization, which may dramatically decrease the stability and quantum efficiency of QDs including those quantum dots which are surface stabilized by ZnS and/or organic molecules.

Surface modification can increase the quantum efficiency of quantum dots with low quantum efficiency to higher levels. However, increasing the quantum yield of QDs with already high quantum yield (>50%) could be rather difficult, probably due to dangling bonds on the crystal surface especial for (non-spherical) QDs.

Quantum dots have theoretical high quantum efficiency (QE) and stability in light conversion and energy transfer. The desired properties provide them with high potential in light application such as inorganic phosphor in LEDs. However, the naked QDs may suffer from their high sensitivity to surface environments and usually exhibit low quantum yields and extremely low stability in air due to the unprotected surface. The exposed QDs surfaces contain dangling bonds that create many surface state energy bands and sufficiently trap the excitons in QDs.

Therefore, additional surface passivation processes are adopted to minimize the surface defects and to protect QDs against oxygen and water. The reported surface passivation are accomplished by modifying the surface of the QDs with organic molecules or overgrowth of an additional inorganic shell, such as ZnS. Usually, the inorganic shells are preferred because they have relative high chemical and physical stability and also wide band energy to confine the excitons within. Inorganic shelling has been successful achieved for spherical QDs such as CdSe/CdS/ZnS and InP/ZnS. Nevertheless, in many cases inorganic shelling still fails to achieve high air stability of the QDs due to two reasons. Firstly most inorganic shell materials, such as ZnS, are also oxygen and water sensitive. Secondly, for non-spherical shape nano particles, such as rods, tripods, and wires, the inorganic coating is rather difficult and unstable due to the lattice mismatch. Therefore, it is necessary to have homogenous surface modification with ligands for either unshelled or shelled quantum dots.
in order to improve both QEs and stability of the QDs. Nevertheless, with the current well known surface modification methods with organic molecules, which have effectively improved the QEs of the QDs from very low to as high as 50%, it may rather be difficult to further improve quantum yield and/or to further improve photo chemical stability with only organic capping. Typical organic molecules modified quantum dots fail to achieve a close to unity quantum yields compatible to inorganic, such as ZnS coated ones, are mainly due to the unstable and insufficient surface coating, where the surfaces always contain numerous dangling bonds.

The typical organic molecules modification for QDs has several disadvantages as: 1. Insufficient surface modification due to the cation or anion rich surface which creates dangling bonds, for example for Cd-rich CdSe containing Cd- dangling bonds, the ligands only cover surface Cd- and results in insufficient passivation. 2. Unstable surface ligands, for example TOP (triocetylphosphine) as ligands for surface Se- of CdSe, are very oxygen sensitive and not able to create stable surface bonding as well as energy band in air for effective exciton confinement. 3. Fast quench of quantum efficiency due to the weak coordinating bonds and flexibility of capping molecules on the QDs surfaces, especially at high temperature high mobility of unstable capping molecules may cause the surface reconstruction of QDs.

Therefore the current developed capping molecules modified QDs all suffer from the relative low quantum yields (QY or QE) and very low photo chemical stability in air and at high temperature, especial for those non-spherical QDs.

Hence, it is an aspect of the invention to provide an alternative luminescent material comprising semiconductor based luminescent nano particles (or quantum dots) and/or a method for the production thereof and/or a lighting unit including such semiconductor based luminescent nano particles (as (part of) a light converter material), which preferably further at least partly obviate one or more of above-described drawbacks.

Here a new surface modification method is described that may give QDs a highly improved quantum efficiency (80-95%) and a highly improved photo-chemical stability. In this method two types of molecules are applied on (a pre-treated dangling bonds free) outer surface of the QDs. For instance, in the case of CdSe/CdS nanorods one of the components forms a complex with Cd in the crystal lattice surface while the other component forms a complex with S in the crystal lattice surface to stabilize the surface and protects the surface from oxygen and water.
The surface modification is accomplished by precise surface modification with dual-surfactants combination. Since the surface of multi-components semiconductor QDs usually comprises negative charged atoms such as S- and positive charged atoms such as Cd-, such atoms may create dangling bonds at the surface of the particle (herein also indicated as outer surface). A ligands exchange approach is thus developed for this purpose and the key process in this approach is to pro-adjust the QDs surface to a (substantially) “neutral” state, which means neither positive charged nor negative charged atoms is rich on the surface. The neutral state is achieved by using two kinds of molecules to selectively cap on the surface positive and negative charged atoms.

The stable organic molecule caps preferentially on the surface the positive charged atoms including the metal atoms such as Cd- that creates a relative lower energy band. The organic molecules may have selected coordinating group such as amine, acid, thiol, etc. which bonds to metal to obtain tight bonds and adjusted energy band. This relates to one type of organic molecules or ligands (also indicated as capping molecules).

The organo metallic molecule preferentially caps on the negative charged atoms on the QDs surface which creates a relative higher energy band than inside QDs crystal. This relates to another type of inorganic/organic molecules (also indicated as capping molecules).

In summary, the surface modifications with the capping molecule(s) or ligand(s) give rise to a balance of the surface capping molecules where the total molecules capped on the surface positive charged atoms are equal or close to the ones capped on the surface negative charged atoms. For this consequence the surface pre-treatment with reactive reagents is necessary. The surface modification is accomplished regardless size and shape of QDs.

Hence, in a first aspect, the invention provides a luminescent material comprising semiconductor based luminescent nano particles, wherein the nano particles (or quantum dot (particles)) (further also indicated as “nano particles”) have an outer surface coated with a first type of capping molecules (herein also indicated as “first type of ligands” or “first ligands”) and a second type of capping molecules (herein also indicated as “second type of ligands” or “second ligands”), wherein the first type of capping molecule comprises $M^{m}R_{n}$, wherein M is a metal, wherein n is at least 2, and wherein R is a hydrocarbon, and wherein the second type of capping molecule comprise an organic Lewis base. Such quantum dots may have a high quantum efficiency and may be stable. Further, the current used air-
sensitive TOP (triocylphosphine) coating may be replaced with the dual ligand coating of the invention.

The quantum dots or luminescent nano particles may for instance comprise group II-VI compound semiconductor quantum dots selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, CdSeS, CdSeTe, CdSTe, ZnSeS, ZnSeTe, ZnSTe, HgSeS, HgSeTe, HgSTe, CdZnS, CdZnSe, CdZnTe, CdHgS, CdHgSe, CdHgTe, HgZnS, HgZnSe, HgZnTe, CdZnSeS, CdZnSeTe, CdZnSTe, CdHgSeS, CdHgSeTe, CdHgSTe, HgZnSeS, HgZnSeTe and HgZnSTe. In another embodiment, the luminescent nano particles may for instance be group III-V compound semiconductor quantum dots selected from the group consisting of GaN, GaP, GaAs, AlN, AlP, AlAs, InN, InP, InAs, GaNP, GaNAs, GaPAs, AlNP, AlNAs, ALPAs, InNP, InNAs, InPAs, GaALNP, GaALNAs, GaALPAs, GaINNP, GaINNAs, GaINPAs, GaAINP, GaAINAs, and GaALPAs. In yet a further embodiment, the luminescent nano particles may for instance be I-III-VI2 chalcopyrite-type semiconductor quantum dots selected from the group consisting of CuInS2, CuInSe2, CuGaS2, CuGaSe2, AgInS2, AgInSe2, AgGaS2, and AgGaSe2. In yet a further embodiment, the luminescent nano particles may for instance be I-V-VI2 semiconductor quantum dots, such as selected from the group consisting of LiAsSe2, NaAsSe2 and KAsSe2. In yet a further embodiment, the luminescent nano particles may for instance be group IV-VI compound semiconductor nano crystals such as SbTe. In a specific embodiment, the luminescent nano particles are selected from the group consisting of InP, CuInS2, CuInSe2, CdTe, CdSe, CdSeTe, AgInS2 and AgInSe2. In yet a further embodiment, the luminescent nano particles may for instance be one of the group II-VI, III-V, I-III-V and IV-VI compound semiconductor nano crystals selected from the materials described above with inside dopants such as ZnSe:Mn, ZnS:Mn. The dopant elements could be selected from Mn, Ag, Zn, Eu, S, P, Cu, Ce, Tb, Au, Pb, Tl, Sn and Tl. Herein, the luminescent nano particles based luminescent material may also comprise different types of QDs, such as CdSe and ZnSe:Mn.

It appears to be especially advantageous to use II-VI quantum dots. Hence, in an embodiment the semiconductor based luminescent quantum dots comprise II-VI quantum dots, especially selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, CdSeS, CdSeTe, CdSTe, ZnSeS, ZnSeTe, ZnSTe, HgSeS, HgSeTe, HgSTe, CdZnS, CdZnSe, CdZnTe, CdHgS, CdHgSe, CdHgTe, HgZnS, HgZnSe, HgZnTe, CdZnSeS, CdZnSeTe, CdZnSTe, CdHgSeS, CdHgSeTe, CdHgSTe, HgZnSeS, HgZnSeTe and HgZnSTe, even more especially selected from the group consisting of CdS, CdSe, CdSe/CdS and CdSe/CdS/ZnS.
The luminescent nano particles (without coating) may have dimensions in the range of about 2-50 nm, such as 2-20 nm, especially 2-10 nm, even more especially 2-5 nm; especially at least 90 % of the nano particles have dimension in the indicated ranges, respectively, (i.e. e.g. at least 90% of the nano particles have dimensions in the range of 2-50 nm, or especially at least 90% of the nano particles have dimensions in the range of 2-5 nm). Typical dots are made of binary alloys such as cadmium selenide, cadmium sulfide, indium arsenide, and indium phosphide. However, dots may also be made from ternary alloys such as cadmium selenide sulfide. These quantum dots can contain as few as 100 to 100,000 atoms within the quantum dot volume, with a diameter of 10 to 50 atoms. This corresponds to about 2 to 10 nanometers. For instance, spherical particles such as CdSe, InP, CuInSe2 with a diameter of about 3 nm may be provided. The luminescent nano particles (without coating) may have the shape of spherical, cube, rods, wires, disk, multi-pods, etc., with the size in one dimension of less than 10 nm. For instance, nanorods of CdSe with the length of 20 nm and a diameter of 4 nm may be provided. Hence, in an embodiment the semiconductor based luminescent quantum dots comprise core-shell quantum dots. In yet another embodiment, the semiconductor based luminescent quantum dots comprise dots-in-rods nano particles. A combination of different types of particles may also be applied. Here, the term “different types” may relate to different geometries as well as to different types of semiconductor luminescent material. Hence, a combination of two or more of (the above indicated) quantum dots or luminescent nano-particles may also be applied.

Hence, the above-mentioned outer surface may be the surface of a bare quantum dot or may be the surface of a coated quantum dot, such as a core-shell quantum dot, i.e. the (outer) surface of the shell.

As indicated above, two types of capping molecules or ligands are preferably used: the first type of capping molecules and the second type of capping molecules. These capping molecules or ligands occupy the surface of the quantum dot and may thereby remove or reduce the dangling bonds. In this way, quantum efficiency may be increased. The capping molecules may thus provide a kind of (organic) coating.

The first type of capping molecule comprises M\textsuperscript{a+}R\textsubscript{n}, wherein M is a metal, wherein n is at least 2, and wherein R is a hydrocarbon (i.e. the first type of capping molecules are metal organic molecules). Hence, the cation has a valence of two or higher. Examples of suitable cations are cations selected from the group of transition metals, especially of the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn, and Cd. Especially preferred are Zn, Mg, In, and Ga. The fact
that the valence n, which is preferably at least 2, such as 2, 3 or 4, also implies two or more hydrocarbon groups R does not imply that those hydrocarbon groups R are necessarily identical. Each hydrocarbon group R of the first type of capping molecule may be unique. For instance M^{n+}R_n may relate to \([H_2C=CH(CH_2)_3CO_2]Zn[CO_2(CH_2)_4CH_3]_, i.e. zinc decynenate hexanoate (thus with two different R groups). However, in a specific embodiment, all hydrocarbon groups R of the first type of ligand are identical. An example of a suitable first type of ligand is zinc undecynenate; i.e. \(M^{n+}R_n\) is \([H_2C=CH(CH_2)_3CO_2]Zn\). However, other (carboxylate) groups may also be applied, such as \([CH_3(CH_2)_{16}COO]_2Zn\), \([H_2C=C(CH_3)CO_2]Zn\), \((CF_2SO_2)_2Zn\), \(C_{18}H_{12}N_2O_2Zn\), \(C_{64}H_{56}N_8Zn\), etc. Hence, the metal-organic molecules, in the case of e.g. CdSe or CdS, may for instance be selected as zinc carboxylates. The first type of ligand coordinates to the anions at the surface of the quantum dot. Assuming e.g. CdSe, the first type will coordinate to Se anions. The first type of capping molecules may also be indicated as Lewis acid. The value of n is preferably (but not exclusively) 2.

Therefore, the first type of capping molecule comprises in an embodiment a first functional group, which may in an embodiment comprise a metal ion serving as a coordinating center, such as Zn (especially Zn\(^{2+}\), Ni (especially Ni\(^{2+}\)), In (like In\(^{3+}\)), Cd (like Cd\(^{2+}\)), Cu (like Cu\(^{+}\) or Cu\(^{2+}\)), which enables the coordination/connection with the anions - for instance S, Se, P - on the surface of a nano particle. Hence, the first functional group of the first type of capping molecule may comprise a metal ion with coordinating functionality. The first type of capping molecule or ligand may coordinate to an anion at the (outer) surface of the nano particle as the metal ion may have coordinating functionality.

The second type of capping molecule especially comprise an organic Lewis base. A Lewis base, is any species that donates a pair of electrons to a Lewis acid to form a Lewis adduct. For example, OH\(^-\) and NH\(_3\) are Lewis bases, because they can donate a lone pair of electrons. A Lewis acid is a molecule entity (and the corresponding chemical species) that is an electron-pair acceptor and therefore able to react with a Lewis base to form a Lewis adduct, by sharing the electron pair furnished by the Lewis base.

Therefore, the second type of capping molecule comprises in an embodiment a first functional group (of the second type of capping molecule), which may in an embodiment comprise an organic group, such as amine, acid, thiol, which enables the coordination/connection to the cations – for instance Cd, Zn, In, Cu, Mg, Ag, etc. – on the surface of a nano particle.
Hence, the coating with the capping molecules can be considered to be due to the fact that the capping molecules are coordination to the outer surface of the nano particle. This may be the outer surface of a bare nano particle or the outer surface of the coating (here inorganic, in general also semi conductor) coating of the nano particle. The capping molecules may thus attach to the outer surface.

Herein, the Lewis base (and Lewis acid) are organic molecules, i.e. a hydrocarbon having a Lewis base moiety. Especially, the second capping molecule may be selected from the group consisting of RCN (nitrile), RNH2 (primary amine), R2NH (secondary amine), RSH (thiol), and RCOOH (carboxylic acid), and amino acid wherein R in the second type of capping molecules comprises a hydrocarbon. Again, the fact that in some embodiments there may be two or more hydrocarbon groups R in the second capping molecule does not imply that those hydrocarbon groups R are necessarily identical. Each hydrocarbon group R of the second type of capping molecule may be unique. However, in a specific embodiment (wherein more than one hydrocarbon group is present in the second capping molecule), all hydrocarbon groups R of the second type of ligand are identical. An example of a suitable second type of ligand is hexadecylamine, however, also other ligands may be applied, such as terphenyl thiol C13H4S, Arginine-glycine-aspartic acid peptide, etc.

This dual-surfactants modification method provides a close to 1:1 cover (or coating) of the cations and anions ions exposed on the surface of QDs, e.g. Cd- and Se- on CdSe surface and prevents the dangling bonds on the QDs surfaces. In this case, the surface coating is similar as the inorganic ZnS coated surface of the QDs and provides close enhancement to QDs as the ZnS coating. With the carefully selected stable organic molecules and organometallic molecules, the surface modified QDs have shown highly improved quantum yields and photo chemcial stability. Furthermore, the air-stable organic molecules could be chosen as dual-surfactants to offer additional enhanced surface protection and air stability for even ZnS coated quantum dots. Since the organic coating process may be through a ligands exchange process without the problem of lattice mismatch, the method could be applied for any shape of the quantum dots, offering this method a much more general application than the inorganic coating. For example, after the treatment with this as-described method, the quantum efficiency of one CdSe/CdS rods has risen from 45% to 85% (higher than the reported CdSe/CdS/ZnS rods with a Max QE of 75%) and the photo chemical stability also been strongly improved >10 times than the CdSe/CdS/ZnS rods prepared following conventional processes. Especially, the molar ratio of the first of capping molecules to the second type of capping molecules is in the range of 0.8-1.2 (i.e. 8:10-12:10),
even more especially 0.9-1.1, yet even more especially 0.95-1.05. For instance, 1.05 mole of zinc undecylenate and 1 mole of hexadecylamine give a molar ratio of 1.05.

In yet a further specific embodiment, R in M^{n+}(R)_n is selected from the group of carboxylates, and wherein the second type of capping molecule comprises a hydrocarbon selected from the group consisting of RCN, RNI₂, R₂NH, RSH, and RCOOH, wherein R in the second type of capping molecules comprise a hydrocarbon, wherein the hydrocarbon chain comprise a repeated hydrocarbon (CH or CH₂) with a number of 2-100, for instance the hydrocarbon chain comprise a repeated hydrocarbon with a number of 4-20, like for instance CH₃(CH₂)₅COOH or CH₃(C₂H₅)₅CH₂SH.

In yet a further aspect, the invention also provides a method for the production of ligand coated (or organic molecule capped) semiconductor based luminescent nano particles, the method comprising synthesizing semiconductor based luminescent nano particles and applying to an outer surface of the quantum dots a first type of capping molecules and a second type of capping molecules, wherein the first type of capping molecule comprises M^{n+}R, wherein M is a metal, wherein n is at least 2, and wherein R is a hydrocarbon, and wherein the second type of capping molecule comprise an organic Lewis base. This may be a one-pot synthesis, but the quantum dots may also be produced in a sequential process. Hence, in an embodiment during synthesis of the semiconductor based luminescent nano particles the first type of capping molecules and the second type of capping molecules are present. In such process, the quantum dots are made and coated in one go. However, in another embodiment, which may preferably be applied after synthesis of the semiconductor based luminescent nano particles, the semiconductor based luminescent nano particles are contacted with the first type of capping molecules and the second type of capping molecules. In such embodiment, during synthesis of the quantum dots, the surface thereof may be coated with other types of ligands, such as TOP. However, when applying those quantum dots to the combination of the first capping molecule and the second capping molecule, the original ligands may at least partially (or in an embodiment entirely) be replaced by the ligands of the combination.

As indicated above, the first type of capping molecule and the second type of capping molecule are preferably presented to the surface of the quantum dot in a substantially 1:1 ratio. Hence, in an embodiment of the method, the first type of capping molecules and the second type of capping molecules are applied to the outer surface of the semiconductor based luminescent nano particles in a the molar ratio of the first of capping molecules to the second type of capping molecules in the range of 0.8-1.2 (see also above).
In yet a further aspect, the invention also provides a lighting unit comprising (i) a light source configured to generate light source light and (ii) a light converter configured to convert at least part of the light source light into converter light, wherein the light converter comprises the luminescent material as described herein or obtainable according to the method as described herein. It may be advantageous, in view of efficiency and/or stability, to arrange the quantum dots at a non-zero distance from the light source. Hence, in an embodiment, the light converter material may be configured at a non-zero distance of the light source. For instance, the light converter material, or especially the luminescent material, may be applied to or may be comprised by a window of the lighting unit. In case the light source is configured to provide blue light, the luminescent material may be configured to convert only part of the light source light. The blue light of the light source and the luminescent material light of the luminescent nano particles based luminescent material together may in an embodiment provide white lighting unit light.

In a further embodiment, the light source comprise a solid state light source, such as a solid state light emitting device or solid state laser. The term light source may also relate to a plurality of light sources.

In yet another embodiment, the luminescent material is embedded in another material. For instance, the coated quantum dots may be embedded in a polymeric material.

The term white light herein, is known to the person skilled in the art. It especially relates to light having a correlated color temperature (CCT) between about 2000 and 20000 K, especially 2700-20000 K, for general lighting especially in the range of about 2700 K and 6500 K, and for backlighting purposes especially in the range of about 7000 K and 20000 K, and especially within about 15 SDCM (standard deviation of color matching) from the BBL (black body locus), especially within about 10 SDCM from the BBL., even more especially within about 5 SDCM from the BBL.

The terms “violet light” or “violet emission” especially relates to light having a wavelength in the range of about 380-440 nm. The terms “blue light” or “blue emission” especially relates to light having a wavelength in the range of about 440-490 nm (including some violet and cyan hues). The terms “green light” or “green emission” especially relate to light having a wavelength in the range of about 490-560 nm. The terms “yellow light” or “yellow emission” especially relate to light having a wavelength in the range of about 560-590 nm. The terms “orange light” or “orange emission” especially relate to light having a wavelength in the range of about 590-620. The terms “red light” or “red emission” especially relate to light having a wavelength in the range of about 620-750 nm. The terms “visible”
light or “visible emission” refer to light having a wavelength in the range of about 380-750 nm.

The term “substantially” herein, such as in “substantially all emission” or in “substantially consists”, will be understood by the person skilled in the art. The term “substantially” may also include embodiments with “entirely”, “completely”, “all”, etc. Hence, in embodiments the adjective substantially may also be removed. Where applicable, the term “substantially” may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. The term “comprise” includes also embodiments wherein the term “comprises” means “consists of”.

Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

The devices herein are amongst others described during operation. As will be clear to the person skilled in the art, the invention is not limited to methods of operation or devices in operation.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. Use of the verb "to comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. In the device claim enumerating several means, several of these means may be embodied by one and the same item of hardware. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

The invention further applies to a device comprising one or more of the characterising features described in the description and/or shown in the attached drawings. The invention further pertains to a method or process comprising one or more of the characterising features described in the description and/or shown in the attached drawings.
The various aspects discussed in this patent can be combined in order to provide additional advantages. Furthermore, some of the features can form the basis for one or more divisional applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Figs. 1a-1d schematically depict some aspects of the invention. The drawings are not necessarily on scale;

Fig 2a-b TEM figures of quantum dots.

DETAILED DESCRIPTION OF THE EMBODIMENT

Fig. 1a schematically depicts a quantum dot (particle) or nano particle 10, in this embodiment based on CdS. This implies that at the surface of the QD particle 10, indicated with reference 11, cadmium and sulfur ions are present. The nano particle 10 is capped with capping molecules or ligands 200. The first type ligand 200, $M^{n+}R_n$, is indicated with reference 1. Here, M is zinc (Zn), and R3 and R4 are used to indicate that the two hydrocarbons R may be different. However, R3 and R4 may also be identical. The second type of capping molecule 200 comprise an organic Lewis base, and is indicated with reference 2. Here, an amine is used, with R1, R2 and H. Instead of H, also a further hydrocarbon may chosen. The first type ligand coordinates to sulfur; the second coordinates to cadmium. In this way, a capping molecules coated / capped semiconductor based luminescent nano particle is provided, which is indicated with reference 100. Note that reference 10 refers to the "bare" quantum dot (with or without a shell), and the reference 100 refers to the coated quantum dot, i.e. the quantum dot (particle) or nano particle including the capping molecules 200 at the outer surface 11.

Fig. 1b schematically depicts the same embodiment of the capping molecules coated semiconductor based luminescent nano particle 100 as depicted in fig. 1a, with the difference that the quantum dot 10 is now a core-shell quantum dot. The core is indicated with reference 12; the shell is indicated with reference 13. The core 12 may for instance be CdSe and the shell 13 may for instance be CdS.

Fig. 1c schematically depicts a plurality of ligand coated semiconductor based luminescent nano particle, i.e. a luminescent material 30.
This luminescent material may be applied in a lighting unit 5, as schematically depicted in Fig. 1d. Here, lighting unit 5 comprises a light source 20, configured to generate light source light 21, and a converter 40, configured to convert at least part of the light source light 21 into converter light 41. To this end, the converter may comprise (including in an embodiment consist) the luminescent material 30, which may essentially consist of the ligand coated semiconductor based luminescent nano particles 100. Optionally, the converter 40 may comprise further material 42. For instance, the converter may be a polymeric foil or plate, embedding the luminescent material 30. The converter 40 may especially be arranged at a non-zero distance d from the light source 20, which may for instance be a light emitting diode, although the distance d may also be zero, for instance when the luminescent material 30 is applied on a LED die or embedded in a (silicone) cone on the LED die. The converter may optionally allow at least part of the light source light 21 penetrate through the converter. In this way, downstream of the converter, a combination of converter light 41 and light source light 21 may be found. The light downstream of the light converter is indicated a lighting unit light 51.

In addition to the ligand coated semiconductor based luminescent nano particles 100, the luminescent material 30 may optionally comprise also other types of luminescent materials, for instance to tune the color of the lighting unit light 51, to increase the color rendering, to tune the color temperature, etc.

The terms “upstream” and “downstream” relate to an arrangement of items or features relative to the propagation of the light from a light generating means (here the especially the first light source), wherein relative to a first position within a beam of light from the light generating means, a second position in the beam of light closer to the light generating means is “upstream”, and a third position within the beam of light further away from the light generating means is “downstream”.

EXPERIMENTAL

The structure and optical properties of the quantum dot products can be easily detected. The structure could be characterized through the characterization methods of TEM, EDXS, XRD, ICPMS and XPS for the shape, type of components, crystal structure of components and ratio of the components. The species and ratio of the surface capping molecules could be analyzed directly by IR, NMR or analyzed as the free molecules in solution after ligands exchange.
Below we show an example experiment to obtain the surface modified CdSe/CdS rods with the described method as well as the structure and optical characterization for the as-prepared material.

**Example 1**

Ligands exchange for a Cd-rich CdSe/CdS QRs: The CdSe/CdS rods are pre-synthesized according to literature (L. Carbone, et al. “Synthesis and micrometer-scale assembly of colloidal CdSe/CdS nanorods prepared by a seeded growth approach” *Nano Lett.*, **2007**, 7 (10), 2942-2950). After synthesis, the QRs (quantum rods) are purified and re-dissolved in toluene to form a 2.5E-08 M/ml solution.

Dissolved are 2.5E-09 mol CdSe/CdS rods, 0.2 mmol zinc undecylanate, and 1 ml hexyldecylamine into 5ml trioctylphosphor oxide. The mixture is heated to 150 °C under N2 with stirring; 0.05 mmol dimethyilsilylsulfide is injected. The mixture is kept at 150 °C for 30 min then cooled down to room temperature. The QDs are washed with ethanol and toluene for 3 times and re-dispersed in 3 ml toluene.

**Example 2**

Ligands exchange for a In-rich InP QDs. The InP QDs are pre-synthesized according to literature (S. Xu, S. Kumar, T. Nann, “Rapid synthesis of high quality InP nanocrystals” *J. Am. Chem. Soc.* **2006**, 128, 1054-1055). After synthesis, the QDs are purified and re-dissolved in toluene to form a 2.5E-08 M/ml solution.

Dissolved are 5E-08 mol InP dots, 0.2 mmol zinc undecylanate, 1 ml hexyldecylamine into 5ml octadecane. The mixture is heated to 150 °C under N2 with stirring; 0.1 mmol dimethyilsilylsulfide is injected. The mixture is kept at 150 °C for 30 min then cooled down to room temperature. The QDs are washed with ethanol and toluene for 3 times and re-dispersed in 3 ml toluene.

**Example 3**

Ligands exchange for a S-rich CdSe/CdS/ZnS QDs. The CdSe/CdS/ZnS are pre-synthesized according to literature (D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, H. Weller, “Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine-trioctylphosphine oxide-trioctylphospine mixture” *Nano Lett.* **2001**, 1, 207-211.) After synthesis, the QDs are purified and re-dissolved in toluene to form a 2.5E-08 M/ml solution.
Dissolved are $5 \times 10^{-9}$ mol CdSe/CdS/ZnS QDs, 0.2 mmol zinc undecylamine, 1 ml hexyldecaline into 5 ml octadecene. The mixture is heated to 150 °C under N$_2$ with stirring; 0.05 mmol diethylzinc is injected then followed with 0.04 mmol dimethylsilylsulfide. The mixture is kept at 150 °C for 30 min then cooled down to room temperature. The QDs are washed with ethanol and toluene for 3 times and re-dispersed in 3 ml toluene.

**Characterizations:**

From ICPMS and XPS measurements, the Zn contained on the surface is a 48% fraction of the surface coverage by all molecules on the surface. As the characterization from photoluminescence measurements, the emitting peak of the surface modified CdSe/CdS rods show no different from the raw CdSe/CdS rods. The quantum yields increases from 50% to 85%.

TEM images of the surface modified CdSe/CdS rods and raw rods show no evidence of ZnS lattice on the surface of CdSe/CdS rods, and no evidence of any ZnS particle and clusters. Fig. 2a shows the QD before surface modification and fig. 2b after surface modification.

The luminescence lifetime under continue radiation of the surface modified CdSe/CdS rods show high photochemical stability. There is no substantial decrease in intensity with time (> 100 h).

FTIR measurements show that the surface is capped with the amine and zinc carboxylate.
CLAIMS:

1. A luminescent material (30) comprising semiconductor based luminescent nano particles, wherein the nano particles have an outer surface coated with a first type of capping molecules and a second type of capping molecules, wherein the first type of capping molecule comprises $M^{n+}R_n$, wherein $M$ is a metal, wherein $n$ is at least 2, and wherein $R$ is a hydrocarbon, and wherein the second type of capping molecule comprises an organic Lewis base.

2. The luminescent material according to claim 1, wherein the semiconductor based luminescent nano particles comprise II-VI quantum dots.

3. The luminescent material according to any one of the preceding claims, wherein the semiconductor based luminescent nano particles are selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, CdSeS, CdSeTe, CdSTe, ZnSeS, ZnSeTe, ZnSTe, HgSeS, HgSeTe, HgSTe, CdZnS, CdZnSe, CdZnTe, CdHgS, CdHgSe, CdHgTe, HgZnS, HgZnSe, HgZnTe, CdZnSeS, CdZnSeTe, CdZnSTe, CdHgSeS, CdHgSeTe, CdHgSTe, HgZnSeS, HgZnSeTe and HgZnSTe.

4. The luminescent material according to any one of the preceding claims, wherein the semiconductor based luminescent nano particles are selected from the group consisting of CdS, CdSe, CdSe/CdS and CdSe/CdS/ZnS.

5. The luminescent material according to any one of the preceding claims, wherein the semiconductor based luminescent nano particles comprise core-shell quantum dots.

6. The luminescent material according to any one of the preceding claims, wherein the semiconductor based luminescent nano particles comprise dots-in-rods nano particles.
7. The luminescent material according to any one of the preceding claims, wherein the molar ratio of the first of capping molecules to the second type of capping molecules is in the range of 0.8-1.2.

8. The luminescent material according to any one of the preceding claims, wherein M is selected from the group of transition metals, wherein R in \( M^{n+}(R) \) is selected from the group of carboxylates, and wherein the second type of capping molecule comprises a hydrocarbon selected from the group consisting of RCN, R\( \text{NH}_2 \), R\( \text{NHN} \), RSH, and RCOOH, wherein R in the second type of capping molecules comprise a hydrocarbon.

9. A method for the production of ligand coated semiconductor based luminescent nano particles, the method comprising synthesizing semiconductor based luminescent nano particles and applying to an outer surface of the quantum dots a first type of capping molecules and a second type of capping molecules, wherein the first type of capping molecule comprises \( M^{n+}R \), wherein M is a metal, wherein n is at least 2, and wherein R is a hydrocarbon, and wherein the second type of capping molecule comprise an organic Lewis base.

10. The method according to claim 9, wherein during synthesis of the semiconductor based luminescent nano particles the first type of capping molecules and the second type of capping molecules are present.

11. The method according to claim 9, wherein after synthesis of the semiconductor based luminescent nano particles, the semiconductor based luminescent nano particles are contacted with the first type of capping molecules and the second type of capping molecules.

12. The method according to any one of claims 9-11, wherein the first type of capping molecules and the second type of capping molecules are applied to the outer surface of the semiconductor based luminescent nano particles in a the molar ratio of the first of capping molecules to the second type of capping molecules in the range of 0.8-1.2.

13. A lighting unit (5) comprising (i) a light source (20) configured to generate light source light (21) and (ii) a light converter (40) configured to convert at least part of the
light source light into converter light (41), wherein the light converter comprises the 
luminescent material (30) according to any one of claims 1-8 or obtainable according to the 
method of any one of claims 9-12.

14. The lighting unit according to claim 13, wherein the light converter material is 
configured at a non-zero distance of the light source and wherein the light source comprise a 
solid state light source.

15. The lighting unit according to any one of claims 13-14, wherein the 
luminescent material is embedded in another material.
A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K11/02  C09K11/56  C09K11/70  C09K11/88
ADD. H01L33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K  H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 2011/017951 A1 (RYOWA TATSUYA [JP]) 27 January 2011 (2011-01-27) claims 1-10; figure 1; table 1</td>
<td>1,5-15</td>
</tr>
<tr>
<td>X</td>
<td>US 2011/272668 A1 (TAYLOR PETER NEIL [GB] ET AL) 10 November 2011 (2011-11-10) claims 1-33; figure 9; examples 1-12</td>
<td>1,5-15</td>
</tr>
</tbody>
</table>

☐ Further documents are listed in the continuation of Box C.  ☑ See patent family annex.

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

Date of the actual completion of the international search: 10 June 2013
Date of mailing of the international search report: 17/06/2013

Name and mailing address of the ISA/Authorized officer:
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 040-2040,
Fax: (+31-70) 340-3016
Mehdaoui, Imed
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KR 20110039156 A</td>
<td>15-04-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2011084250 A1</td>
<td>14-04-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2011026472 A</td>
<td>10-02-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2011017951 A1</td>
<td>27-01-2011</td>
</tr>
<tr>
<td>US 2011272668 A1</td>
<td>10-11-2011</td>
<td>CN 102292411 A</td>
<td>21-12-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2467161 A</td>
<td>28-07-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2012515803 A</td>
<td>12-07-2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2011272668 A1</td>
<td>10-11-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2010085002 A1</td>
<td>29-07-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2008206565 A1</td>
<td>28-08-2008</td>
</tr>
</tbody>
</table>