

QUANTUM DOT FOR PHOSPHOR FILM

FIELD

This invention relates to a quantum dot for a phosphor film, a method of forming the quantum dot and a method of forming the phosphor film.

BACKGROUND

Use of down conversion phosphor (i.e. from UV to visible light) has been shown to improve solar cell efficiency by up to 2%. However, while quantum dots are good candidates for forming down conversion phosphor, intense UV light exposure results in intense heat which leads to instability of the quantum dots. There is thus a need to provide a quantum dot phosphor that provides high emission yield while having high temperature stability and long shelf life.

SUMMARY

A stable and efficient solution-processed phosphor thin film is fabricated using a metal chalcogenide colloidal quantum dot. The thin film is processed to be optimal as a down conversion phosphor to improve the efficiency of solar cells, and possesses properties of high emissivity, stable operation at high temperature and long operation lifetime.

According to a first aspect, there is provided quantum dot comprising: a core comprising a gradient alloy of at least one metal chalcogenide; a shell around the core; and thermally combustible ligands on the shell; the quantum dot being soluble in a polar solvent having a higher vapour pressure than water.

The gradient alloy may have the formula I:



where values of x and y decrease radially from a centre to a circumference of the core; and wherein the shell comprises a layer of ZnS around the core.

Thickness of the shell may range from 0.3nm to 1.5nm.

The thermally combustible ligands may comprise tetramethylammonium hydroxide (TMAH) bound to 3-mercaptopropionic acid (3-MPA).

According to a second aspect, there is provided a method of forming the quantum dot of the first aspect, the method comprising the steps of:

- (a) adding 3-MPA to a solution of a preliminary quantum dot having native ligands in an organic solvent to obtain a first suspension;
- (b) centrifuging the first suspension to obtain the preliminary quantum dot having surface bound 3-MPA ligands in solid form;
- (c) adding a polar solvent to the preliminary quantum dot having surface bound 3-MPA ligands to form a second suspension;
- (d) adding TMAH to the second suspension to form a solution of the quantum dot having thermally combustible ligands in the polar solvent;
- (e) adding a non-polar solvent to the solution obtained in step (d) to obtain a third suspension; and
- (f) centrifuging the third suspension to obtain the quantum dot having thermally combustible ligands in solid form.

The method may further comprise the step of (g) dissolving the quantum dot having thermally combustible ligands in solid form in a polar solvent having a higher vapour pressure than water.

For both aspects, the polar solvent may be ethanol.

According to a third aspect, there is provided a phosphor film comprising: an inert substrate; a coating comprising micro voids and the quantum dot of the first aspect without the thermally combustible ligands on the inert substrate; and a layer of Al_2O_3 conformally deposited on the coating.

According to a fourth aspect, there is provided a method of forming the phosphor film of the third aspect, the method comprising the steps of:

- (a) coating the inert substrate with quantum dots of the first aspect via solution processing using a solution of the quantum dots in a polar solvent having a higher vapour pressure than water; and
- (b) performing atomic layer deposition of Al_2O_3 on the coating.

In step (b), the thermally combustible ligands may be decomposed to form the micro voids in the coating.

BRIEF DESCRIPTION OF FIGURES

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments of the present invention, the description being with reference to the accompanying illustrative drawings.

FIG. 1 is a schematic illustration of an exemplary quantum dot formed from a preliminary quantum dot.

FIG. 2 is a schematic illustration of formation of an exemplary phosphor film formed from the quantum dot of FIG. 1.

FIG. 3 is a plot of normalised photoluminescence vs wavelength of the exemplary phosphor film of FIG. 2 at different temperatures.

FIG. 4 is a plot of normalised photoluminescence vs wavelength of a phosphor film formed from as-prepared quantum dots at different temperatures.

FIG. 5 is a flow chart of an exemplary method of forming the quantum dot of FIG. 1.

FIG. 6 is a flow chart of an exemplary method of forming the phosphor film shown in FIG. 2.

DETAILED DESCRIPTION

Exemplary embodiments of a quantum dot 10 for a phosphor film 20, a method of forming the quantum dot 100 and a method of forming the phosphor film 200 will be described below with reference to FIGS. 1 to 6. The same reference numerals are used throughout the figures for the same or similar parts.

In general, as shown in FIG. 1, the quantum dot 10 has a core-shell structure with thermally combustible ligands 13. In an exemplary embodiment, the core 11 comprises a metal chalcogenide gradient alloy having the formula I:



where values of x and y decrease radially from a centre to a circumference of the core 11. In the exemplary embodiment, the shell 12 comprises a layer of ZnS around the core 11. The shell 12 may have a thickness ranging from 0.3 nm to 1.5 nm, which corresponds to 1 to 5 monolayers of ZnS, with 1.5nm being an exemplary optimum thickness. In other embodiments, the quantum dot 10 may comprise core/shell nanocrystals of other gradient alloys of at least one metal chalcogenide, such as PbS/CdS, InP/ZnS and CuInS₂/ZnS. The quantum dot 10 also has thermally combustible ligands 13 provided on the shell 13, allowing the quantum dot 10 to be soluble in a polar solvent with a lower boiling point and higher vapour pressure than water, such as ethanol, isopropanol and methanol. In this way, a solution of the quantum dot 10 in the polar solvent may be used to form a down conversion phosphor films using solution-processed coating techniques such as spin coating or dip coating to improve the efficiency of solar cells, as will be described in greater detail below. In the exemplary embodiment, the thermally combustible ligands 13 comprise tetramethylammonium hydroxide (TMAH) bound to 3-mercaptopropionic acid (3-MPA). Other exemplary combustible ligands may include short chain acids such as formic acid.

To form the quantum dot 10 with thermally combustible ligands 13, a preliminary quantum dot 80 is used, as shown in FIGS. 1 and 5. The preliminary quantum dot 80 may be synthesized by first synthesizing a core 11 that comprises an alloyed basic quantum dot with a gradient composition of at least one metal chalcogenide. In an exemplary embodiment, the gradient alloy has the formula $Cd_xZn_{1-x}Se_yS_{1-y}$, where the values of x and y are higher in value in the core regions 11 and smaller nearer the circumference. A further synthesis step introduces a certain thickness of a ZnS shell material around the basic quantum dot or core 11, thus synthesizing the shell 12, which confers a higher photoluminescence quantum yield due to increased surface passivation and chemical stability. Synthesis of the core 11 and shell 12 may be performed using known methods [1, 2], resulting in formation of a preliminary quantum dot 80 having native ligands 83 on the shell 12, as shown in FIG. 1, where the native ligands may comprise oleic acid ligands, for example.

In the exemplary method 100 of forming the quantum dot 10, the preliminary quantum dot (that is dissolved in an organic solvent such as hexane, toluene, chloroform or octane), is reacted with 3-MPA to obtain a first suspension comprising a dispersion of the preliminary quantum dot (103). For example, to 5ml of 10 mg/ml of a solution of the preliminary

quantum dot in hexane, 0.2 ml of 3-MPA may be added. Reaction of the gradient alloyed preliminary quantum dot with 3-MPA results in precipitation of the preliminary quantum dot from the hexane, which can be separated and the preliminary quantum dot collected by centrifugation. Immediate flocculation of the preliminary quantum dot upon addition of the 3-MPA is due to ligand exchange of long native stabilizing ligands of the preliminary quantum dot with short 3-MPA ligands.

Accordingly, the first suspension is centrifuged to obtain the preliminary quantum dot having surface-bound 3-MPA ligands in solid form (104). The supernatant, containing excess 3-MPA ligands and native ligands, is discarded. A polar solvent is then added to the obtained preliminary quantum dot with 3-MPA ligands to form a second suspension (105): for example, 5ml of ethanol may be added to the solid preliminary quantum dot obtained from the centrifugation and agitated to form the second suspension (105).

TMAH is next added dropwise to the second suspension with stirring, thereby forming a solution of the quantum dots 10 having ligands 13 of TMAH bound to 3-MPA in the polar solvent (106), as shown in FIG. 1. This may be achieved by agitating the vessel in which the second suspension is contained by stirring, and concurrently, adding drops of methanolic TMAH (i.e., TMAH in methanol) to the second suspension until the mixture turns from turbid to the clear solution. TMAH binds to surface bound 3-MPA via acid-base reaction to form a new ionic ligand 13 that is thermally combustible and also allows the quantum dot 10 to be soluble in polar solvents with a lower boiling point and higher vapour pressure than water.

A washing step is then employed to remove excess TMAH, in which a non-polar solvent (such as toluene) is added to the solution to obtain a third suspension comprising the quantum dot dispersed in the solution (107). In the washing step, the toluene is added until the solution turns turbid, indicating formation of the third suspension. The third suspension is then centrifuged to obtain the quantum dot in solid form (108). This may be achieved by centrifugation and collecting the solid, discarding the supernatant and drying the collected solid to obtain the quantum dot in dried solid form. The obtained quantum dot 10 in solid form may subsequently be dissolved in a polar solvent such as ethanol for use in phosphor film 20 formation.

To form the phosphor film 20, as shown in FIG. 2, first, a coating comprising a thin film 20 of the quantum dots 10 may be formed on a substrate 21 via a solution processing technique (201) such as spin coating or dip coating, using the quantum dot 10 dissolved in a high vapour pressure polar solvent such as ethanol. The substrate 21 may be made of glass or silicon, for example.

Post-processing via atomic layer deposition (ALD) of alumina (Al_2O_3) 23 on the matrix 21 coated with the quantum dots 10 is then performed in a heated chamber (202), for example, at a temperature ranging from 150 °C to 200 °C). In the post-processing, the combustible ligands 13 on the quantum dots 10 are combusted by heating to leave behind micro voids 22 in the quantum dot coating 15 due to decomposition of the combustible ligands 13, while alumina 23 is layered directly onto the film of quantum dots without ligands 15 as well as the voids 22, resulting in in-situ infilling of the voids 22 with alumina 23 and forming the phosphor film 20. The layer of alumina 23 protects and stabilises the phosphor film 20 against environmental factors such as oxygen and humidity, thus assisting in lengthening shelf life of the phosphor film 20. In an exemplary embodiment, a total of 25 nm of Al_2O_3 is deposited via ALD. In other embodiments, the layer of deposited alumina may range from 20 to 50 nm.

Notably, decomposition of the combustible ligands 13 during the post-processing creates micro voids 25 which creates unevenness that scatters light. Creating a roughened surface on the quantum dot coating thus helps to minimize specular reflection. As ALD is a conformal coating technique, the coating of alumina preserves this microporous or rough surface structure which reduces the need for an anti-reflection coating to be implemented on top of the quantum dot phosphor coating when the phosphor film 20 is used as down converters in solar cells.

It was also found that the alumina coated phosphor film 20 made with ligand-exchanged quantum dots 10 dissolved in ethanol has the ability to survive high temperature conditions and with little drop in emission intensity. As can be seen in FIG. 3 in which high temperature in-situ normalized photoluminescence (PL) vs wavelength of the phosphor film 20 was plotted for the phosphor film 20 under room temperature, 50 °C, 100 °C, 150 °C and 200 °C, the drop in PL when temperature increased is significantly less (from 1.0 to above 0.6) when

compared to FIG. 4 which plots PL vs wavelength for phosphor films made using as-prepared preliminary quantum dots in a hexane solution without ligand exchange (from 1.0 to below 0.4).

The above description thus discloses a semiconductor quantum dot 10 and method 100 of its forming 20 that allows the quantum dot 10 to be soluble in a polar solvent such as ethanol, thereby allowing a phosphor film 20 to be formed using a method 200 comprising solution processing and post-processing with ALD of alumina that results in a phosphor film 20 of maximum stability and yet retaining a high photoluminescence efficiency even after ligand exchange and solution in ethanol of the quantum dot 10.

Whilst there has been described in the foregoing description exemplary embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations and combination in details of design, construction and/or operation may be made without departing from the present invention.

REFERENCES

1. Y. Wei, J. Yang and J.Y. Ying, Chem. Commun., 2010, 46, 3179–3181.
- S. Jun, E. Jang, J. E. Lim, Nanotechnology, 2006, 17, 3892.

CLAIMS

1. A phosphor film comprising:
 - an inert substrate;
 - a coating comprising micro voids and a quantum dot comprising:
 - a core comprising a gradient alloy of at least one metal chalcogenide;
 - a shell around the core; and
 - the quantum dot being soluble in a polar solvent having a higher vapour pressure than water;
 - wherein the micro voids are formed from decomposition of thermally combustible ligands on the shell, such that the inert substrate is without the thermally combustible ligands; and
 - a layer of Al_2O_3 conformally deposited on the coating.
2. The phosphor film of claim 1, wherein the gradient alloy has the formula I:

$$\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y} \quad \text{I}$$
 where values of x and y decrease radially from a centre to a circumference of the core;
 - and wherein the shell comprises a layer of ZnS around the core.
3. The phosphor film of claim 1 or 2, wherein thickness of the shell ranges from 0.3nm to 1.5nm.
4. The phosphor film of any preceding claim, wherein the thermally combustible ligands comprise tetramethylammonium hydroxide (TMAH) bound to 3-mercaptopropionic acid (3-MPA).
5. The phosphor film of any preceding claim, wherein the polar solvent is ethanol.
6. A method of forming a phosphor film of any preceding claim, the method comprising the steps of:
 - (a) coating the inert substrate with the quantum dots via solution processing techniques using a solution of the quantum dots in a polar solvent having a higher

- vapour pressure than water; and
- (b) performing atomic layer deposition of Al_2O_3 on the coating.
7. The method of claim 6, wherein in step (b), the thermally combustible ligands are decomposed to form the micro voids in the coating.
8. The method of claim 6 or 7, wherein the quantum dots are formed from a method comprising the steps of:
- adding 3-MPA to a solution of a preliminary quantum dot having native ligands in an organic solvent to obtain a first suspension;
 - centrifuging the first suspension to obtain the preliminary quantum dot having surface bound 3-MPA ligands in solid form;
 - adding a polar solvent to the preliminary quantum dot having surface bound 3-MPA ligands to form a second suspension;
 - adding TMAH to the second suspension to form a solution of the quantum dot having thermally combustible ligands in the polar solvent;
 - adding a non-polar solvent to the solution obtained in step (d) to obtain a third suspension; and
 - centrifuging the third suspension to obtain the quantum dot having thermally combustible ligands in solid form.
9. The method of claim 8, further comprising dissolving the quantum dot having thermally combustible ligands in solid form in a polar solvent having a higher vapour pressure than water.
10. The method of claim 9, wherein the polar solvent is ethanol.