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HUI LI et al, "Chemical synthesis and applications of colloidal metal phosphide nanocrystals", Frontiers in Chemistry, 2019, 6, Article 652

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(54) Title of the Invention: **Production of luminescent particles**
Abstract Title: **Production of luminescent particles**

(57) Metal phosphide nanoparticles or quantum dots e.g. of InP or InZnP are produced by reacting a precursor of the metal component with a phosphide precursor which is phosphine carboxamide ($PH_2C(O)NH_2$) or a compound of formula $H_2PCONR^1R^2$. The reaction may be carried out in solution e.g. in 1-octadecene containing a capping agent which may be hexadecylamine in an inert atmosphere at a temperature in the range 200-300°C . A shell e.g. of ZnS or ZnSe may be formed on the core, and the resulting nanoparticles may e.g. be incorporated into a QD-LED display, a QD-LED lamp or another article.
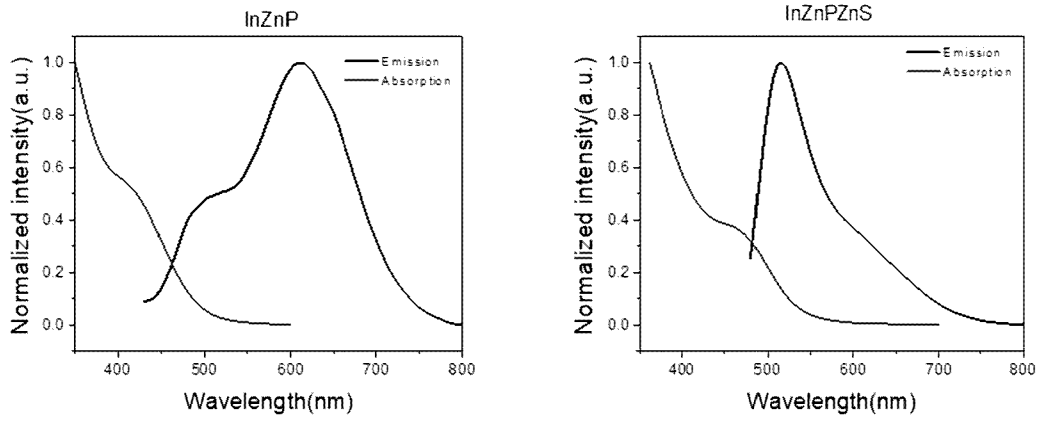
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Figure 1: Normalized absorption and PL spectra of InZnP (left, λex=420nm) and InZnP/ZnS (right, λex=470nm) nanoparticles.

PRODUCTION OF LUMINESCENT PARTICLES

FIELD OF THE INVENTION

The present invention relates to a process for the production of quantum dots which may be used, for example, in QD-LED displays or lamps, diode lasers and displays, image sensors, solar cells and other photovoltaic devices or other articles and in a variety of biological applications.

BACKGROUND TO THE INVENTION

Cadmium has been a standard material for formation of quantum dots, providing CdSe particles or particles of related alloys such as CdSeTe, capped with a ZnS shell – termed CdSe/ZnS core/shells. These materials have however become subject-to world-wide restriction on Cd based materials and Cd-free QDs are now the subject of intense commercial interest.

Indium phosphide-based quantum dots can provide a replacement, usually in the form InP particles capped with a ZnS shell - termed InP/ZnS core/shells. Use of InP for quantum dots is a well-developed technology and it is essentially one of the few materials where the emission is tuneable across the entire visible region, making it suitable for not only biological imaging but also display technology. However, the synthetic chemistry has barely developed in almost two decades. Only two precursors for phosphorous are, so far as the applicants are aware, routinely used, these being $P(SiMe_3)_3$ and $P(NMe_2)_3$, both of which are expensive and volatile air-sensitive liquids which are difficult to handle, $P(SiMe_3)_3$ being the more suitable.

Coating an additional shell provides extra means to manipulate the properties. Typically, type I core/shell NCs feature a strongly enhanced photoluminescence quantum yield (PLQY), such as InP/ZnS, and InP/ZnSe. Moreover, insert buffer layers (InP/GaP/ZnS) or adjust the lattice constant of core and shell (InZnP/ZnSeS) can minimize strain and alleviate interfacial defects, which is resulted from lattice

mismatch in core/shell NCs, see Li *et al.,* Chemical Synthesis and Applications of Colloidal Metal Phosphide Nanocrystals, *Front. Chem.,* 08 January 2019, Vol. 6, Article 652 where the subject of metal phosphide nanocrystals including InP and Zn_3P_2 is reviewed.

As to the use of $P(SiMe_3)_3$, WO 2012/109046 (Ren et al., Kodak) describes a method for making a colloidal solution of indium phosphide semiconductor nanocrystals, comprising: (a) forming a first solution by combining solvents and ligands; and (b) heating the first solution e.g. based on 1-octadecene b.p. 314°C ± 5°C as solvent to a temperature equal to or higher than 290°C and while heating adding to the first solution a second solution containing trialkylindium, a phosphorus precursor and ligands so that a reaction takes place that forms a colloidal solution of indium phosphide semiconductor nanocrystals. The exemplified phosphorus precursor and trialkyl indium are tris(trimethylsilyl) phosphine (P(TMS)$_3$) and trimethyl indium, the eventual nanocrystals being of form InP/ZnSe. Other suggested precursors are tris(dimethylamino) phosphine, tricyclopentyl phosphine, tricyclohexyl phosphine, triallyl phosphine, di-2-norbornylphosphine, dicyclopentyl phosphine, dicyclohexyl phosphine, dibutyl phosphine, cyclohexyl phosphine, di-t-butylchloro phosphine, bis(dicyclohexyl-phosphino) methane, bis(dicyclohexylphosphino)ethane and benzyl-1-adamantyl phosphine. US 8679543 (Bartel *et al.*) is similar except that the resulting nanocrystals are of form InP/ZnS, the shell being applied without an interface layer.

US 9577149 (Lu *et al.,* Quantum Materials Corporation) discloses the continuous synthesis of InP/ZnS nanocrystals of high quantum yield in a micro-reaction system. The synthesis procedure is said to be more delicate compared to that of CdSe-based QDs partially due the highly sensitive phosphine precursors (Nann *et al. J.A.C.S..,* 2006, 128, 1054 and Nann *et al. J. Mater. Chem.,* 2008, 18, 2653). It is further explained that P(TMS)$_3$ is sensitive to oxidation and requires intensive degassing under an inert atmosphere before use and throughout the reaction process, so that handling during batch production is delicate, time consuming and costly.

US 8252205 (Jun *et al.,* Samsung) describes the preparation of metal phosphide nanocrystals which may be of AlP, InP, GaP, Zn_3P_2, Cd_3P_2, MnP, FeP, Fe_2P, Co_2P Ni_2P, or a combination thereof by wet chemical synthesis. A metal precursor solution is reacted with a phosphite compound of the formula $P(OR)_3$ wherein R is selected from a substituted or an unsubstituted C_1-C_{20} alkyl, aryl, ether, ethylene oxide, and propylene oxide, the use of triethyl phosphite being exemplified.

The use of Na_3P as a phosphorous precursor has also been reported with 4-ethylpyridine and trioctyl phosphine (TOP) as solvents, and $InCl_3$ as the indium precursor, K.-W. Jun, P. K. Khanna, K. B. Hong, J.-O. Baeg, Y.-D. Suh, *Mater. Chem. Phys.,* 2006, 96, 494. The resulting material was reportedly 5 nm in diameter and zinc blende in structure, exhibiting a clear excitonic peak in the absorption spectrum at approximately 580 nm, although no description of the emissive properties was provided.

Possibly the most successful alternative for silylated phosphines is tris(dimethylamino)phosphine, $P(NMe_2)_3$, which has been utilised as a precursor in the synthesis of TOPO capped InP at 365 °C, using $InCl_3$ as a starting material, see T. Matsumoto, S. Maenosono, Y. Yamaguchi, *Chem. Lett.,* 2004, 33, 1492. The resulting materials, approximately 6 nm in diameter with a large standard deviation of 50% exhibited a zinc blende core, with optical properties consistent with quantum confinement but without any excitonic feature in the absorption spectra and with broad emission.

The use of $P(NMe_2)_3$ has been extended to the synthesis of InP, 2-4 nm in diameter, in an autoclave, using $InCl_3$ and DDA (as a capping agent), and toluene as a solvent, see C. Li, M. Ando, H. Enomoto, N Murase, *J. Phys. Chem.* C., 2008, 112, 20190. The reaction proceeded at 180°C for 24 hours before the sample was isolated by size selective precipitation, and etched with HF giving particles with emission quantum yields of up to 58 %, before the addition of a wide band gap shell. Notably, trap emission was observed after size selective precipitation, which was attributed to the formation of a surface oxide. This explanation is in contrast with earlier reports that

suggested the oxide layer was actually essential to forming an emissive species. In this case, the ZnS shell was, unusually, added after the phase transfer step, in water. This was improved by adding the shell in a second autoclave step, H.-J. Byun, W.-S. Song, H. Yang, *Nanotechnology*, 2011, 22, 235605.

In an interesting amendment to the synthesis of anisotropic InP, Dorn *et al.* prepared nanowires using InI_3, and $P(NMe_2)_3$ in OAm, which was injected into a flask of TOP (285 °C) under nitrogen into which electrodes, coated with bismuth catalysts had been placed, termed electrically controlled solution-liquid-solution (EC-SLS) growth (figure 4), A. Dorn, P. M. Allen, M. G. Bawendi, *ACS Nano*, 2009, 3, 3260. The polycrystalline nanowires, with an amorphous 5 nm oxide layer, were rapidly grown between the gaps on the electrode, with the degree of growth controlled by the bias. Notably the bridging of the wires could be monitored by measuring the conductivity.

Other solution-based phosphines have been reported as potential precursors for InP nanofiber synthesis, such as tri(m-tolyl)phosphine ($P(PhMe)_3$), although this precursor was utilised in a sealed ampule synthesis at 370 °C, with no capping agent and using indium nanoparticles as precursors, J. Wang, Q. Yang, Z. Zhang, T. Li, S. Zhang, *Dalton Trans.*, 2010, 39, 227.

White phosphorous, P_4, has also been used as a precursor and reacted with In particles yielding InP particles, although no optical properties were reported S. Carenco, M. Demange, J. Shi, C. Boissière, C. Sanchez, P. Le Floch, N. Mézailles, *Chem. Commun.*, 2010, 46, 5578.

It is possible to produce InP quantum dots by generating PH_3 in situ by adding HCl to Ca_3P_2 under an argon atmosphere, then bubbling the nascent gas through a reaction flask containing 1-octadecene (ODE), $InCl_3$ and myristic acid at 250°C. The phosphine delivery was strongest in the first few minutes, but was maintained throughout the reaction, although at a lower output allowing size focusing of the particle size, yielding particles with excellent optical properties and narrow size distributions of ca. 10%. This continuous delivery also overcame phosphorous depletion problem associated

with P(SiMe$_3$)$_3$. The resulting particles, between 3 and 6 nm in diameter exhibited a zinc blende core, with no evidence of oxide side products observed. The resulting nanoparticles exhibited a clear excitonic peak which could be tuned between 650 and 700 nm, with emission between 675 and 720 nm by varying precursor ratios. The emission quantum yield was low, below 1 % but could be improved using a shelling technique to give InP/ZnS quantum dots. Use of phosphine gas for producing quantum dots is described e.g. in US 9,343,301 (Nanoco).

Notwithstanding the effort which has been put into the production of metal phosphide nanomaterial production, the problem remains of providing effective production processes based on a phosphorus precursor that is non-volatile and air-stable.

SUMMARY OF THE INVENTION

In an embodiment, the invention provides a process for production of metal phosphide quantum dots or cores thereof which may be of AlP, InP, GaP, Zn$_3$P$_2$, Cd$_3$P$_2$, MnP, FeP, Fe$_2$P, Co$_2$P Ni$_2$P, or a combination thereof.

The process comprises the step of forming a quantum dot or quantum dot core by reacting a precursor of the metal component with a phosphide precursor which is phosphine carboxamide (PH$_2$C(O)NH$_2$). Alternatively there may be used a compound of formula H$_2$PCONR$_1$R$_2$ wherein R$_1$ may represent hydrogen or an organic residue and R$_2$ represents an organic residue which may be the same as or different from R$_1$, the organic residue or residues e.g. being C$_1$-C$_4$ alkyl, e.g. methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 of the accompanying drawings shows plots of normalized emission and absorption intensity against wavelength for InZnP and InZnP/Zns nanoparticles.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present synthetic method makes the synthesis of InP based nanomaterial much simpler and safer, reducing the need for specialist glassware and scale up equipment.

Currently, CdSe based nanoparticles are prepared by air stable solids – no such chemistry currently exists for InP. The nanomaterials or quantum dots made by the present method resemble those made by previous methods, are typically are of size 2-100nm and have a discrete quantized energy spectrum. Small quantum dots, such as colloidal semiconductor nanocrystals, can be as small as 2 to 10nm, corresponding to 10 to 50 atoms in diameter and a total of 100 to 100,000 atoms within the quantum dot volume. Self-assembled quantum dots are typically between 10 and 50 nm in size. Small quantum dots of size 2-3 nm emit shorter wavelengths with colours in the red and green, whereas larger quantum dots of size 5-6 nm tend to emit in the orange or red, although precise colours depend on the composition and structure of the quantum dot. Shell thicknesses may be >0.5 nm, e.g. about 1 nm.

The metal component precursor may be of any material known for solution phase formation of metal phosphide nanomaterial or quantum dot cores which may be in turn e.g. AlP, InP, GaP, Zn_3P_2, Cd_3P_2, MnP, FeP, Fe_2P, Co_2P Ni_2P, or a combination thereof. Cores of InP or InZnP need no interface layer between the core and shell to achieve the desired properties, although such an interface layer may be provided if desired. A ZnS shell is thus applied directly onto and in contact with the InP or InZnP core. Avoiding the need for an interface layer simplifies preparation of the nanocrystal and makes it easier to produce a desired nanocrystal consistently, because it removes a source of potential defects such as lattice mismatches.

Metal component precursors may be of any In or InZn or other metal compound or salt which is compatible with the solvent and phosphorus precursors and will react therewith. Organic acid salts may be used, or simple halides such as indium or zinc

chlorides. Indium salts that have been suggested will normally be trivalent and include indium acetate, indium nitrate, or indium chloride.

As previously explained, the reaction may be carried out using phosphine carboxamide ($PH_2C(O)NH_2$) as phosphide precursor. Jupp *et al.*, *J. Am. Chem. Soc.*, 2013, 135, 51, 19131–19134 reported that reaction of 2-phosphaethynolate (PCO^-) e.g. sodium 2-phosphaethynolate with ammonium salts quantitatively yielded phosphinecarboxamide ($PH_2C(O)NH_2$). This phosphorus-containing analogue of urea was said to be a rare example of an air-stable primary phosphine. Beddoe *et al.*, *Dalton Trans.*, 2018, 47, 9221 disclosed the use of phosphinecarboxamide as a phosphorus precursor alongside zinc acetate for the chemical vapour deposition (CVD) of adherent and crystalline zinc phosphide Zn_3P_2 films. Phosphinecarboxamide was said to be a safer and more efficient precursor than the highly toxic, corrosive and flammable phosphine used in previous CVD syntheses. However, the use of phosphinecarboxamide in the field of quantum dot production has not previously been reported.

In a modification, appropriate organic ammonium salts might be used as starting materials for phosphinecarboxamide derivatives useful as phosphorus precursors. Such saltsmay be of formula $R_1R_2NH_2X$ wherein R_1 and R_2 are independently hydrogen or organic substituents e.g. alkyl or cycloalkyl, e.g. C_1-C_4 alkyl such as methyl. Thus the reaction may be represented as follows

$$R_1R_2NH_2Cl + NaOCP \rightarrow R_1R_2NH + HOCP + NaCl \rightarrow H_2PCONR_1R_2$$

wherein R_1 and R_2 are as defined above and Na may be replaced by another appropriate metal. Thus, products that may be useful for the present purpose include $H_2PCONHCH_3$ and $H_2PCON(CH_3)_2$.

An advantage of phosphine carboxamide is that it may be used to create nanocrystals or quantum dots under conditions generally similar to those previously employed using other reagents e.g. $P(SiMe_3)_3$ and $P(NMe_2)_3$.

Nanocrystal or quantum dot formation may be by colloidal synthesis from solution of the starting materials in an organic solvent or mixture of solvents. Solvents that may be employed may be similar to those employed by Kodak (above). Examples of suggested non-coordinating or weakly coordinating solvents include, but are not limited to, cis-2-methyl-7-octadecene, squalene, ethers such as 1- tetradecenedioctylether, dodecyl ether, hexadecyl ether, dihexyl ether, butyl phenyl ether and benzyl phenyl ether, esters $CH_3(CH_2)_nC(0)0(CH_2)_mCH_3$ wherein n = 4-18 and m = 1-8, such as methyl myristate, octyl octanoate, or hexyl octanoate. Examples of suggested non-coordinating solvents include, but are not limited to, squalane, octadecane, or any other saturated hydrocarbon compounds. Mixture of two or more solvents can also be used. In some embodiment, the solvent is selected from unsaturated high boiling point hydrocarbons $CH_3(CH_2)_nCH=CH_2$ wherein n = 7-30, conveniently a C 12-20 alpha-olefin, such as 1-nonadcene, 1-octadecene, 1-heptadecene, 1-pentadecene, or 1-eicosene. 1-Octadecene has been employed as solvent in a number of publications and is employed in the present examples.

The reaction is advantageously carried put in the presence of an organic capping agent which may be a Lewis base compound diluted in an inert solvent such as a hydrocarbon. Highly reactive non-fully coordinated atoms "dangling bond" on the surface of a developing nanoparticle particle tend to cause the particles to agglomerate. This problem can be overcome by passivating (capping) the "bare" surface atoms with protecting organic groups. The outer most layer of organic material (capping agent) helps to inhibit particle aggregation and also further protects the nanoparticles or quantum dots from their surrounding chemical environment. Capping agents which have been suggested include TOP, TOPO, HDA, or long chain organic acids such as myristic acid (tetradecanoic acid), long chain amines, or functionalised polyethylene glycol (PEG) chains. Hexadecylamine and octylamine are suitable for this purpose.

Reaction temperatures for core formation may conveniently be in the range 200-300°C. Reaction temperatures for shell formation on the formed cores e.g. from a dialkyldithiocarbamate are somewhat higher, e.g. in the region of 300°C, conveniently

still below the boiling point of 1-octadecene at atmospheric pressure, the same solvent conveniently being used for both procedures.

A single shell e.g of ZnS may be deposited on the core e.g. from zinc diethyldithiocarbamate as described below.

In an alternative, cores prepared as described above may be converted into three-layer core/inner shell/outer shell quantum dots following the procedure described by Won *et al.,* Highly efficient and stable InP/ZnSe/ZnS quantum dot light-emitting diodes, *Nature*, Vol 575, 28 November 2019 at p. 634, https://doi.org/10.1038/s41586-019-1771-5. The authors explain that preparation of a uniform InP core can be followed by a highly symmetrical core/shell quantum dot with a quantum yield of approximately 100%. In particular, hydrofluoric acid is added to etch out any oxidative InP core surface during the growth of the initial ZnSe shell and then high-temperature ZnSe growth is enabled at 340°C. The engineered shell thickness suppresses energy transfer and Auger recombination in order to maintain high luminescence efficiency, and the initial surface ligand is replaced with a shorter one for better charge injection. The optimized InP/ZnSe/ZnS QD-LEDs show a high external quantum efficiency, high brightness and long lifetime, providing a performance comparable to that of state-of-the-art Cd-containing QD-LEDs, see also Efros, Quantum dots realize their potential, *Nature*, Vol 575, 28 November 2019 at p. 604. The Won procedure is believed applicable to cores of both In and InZn.

How the invention may be put into effect will now be described, by way of illustration only, in the following examples.

Example 1

Synthesis of InZnP and InZnP/ZnS quantum dots using Phosphine carboxamide ($PH_2C(O)NH_2$) as phosphide precursor

To form the InZnP core, 0.075g InCl$_3$ (3.4×10^{-4}mol) were added into a three-necked flask with 0.43g zinc stearate (6.8×10^{-4}mol), 0.105g PH$_2$C(O)NH$_2$ (6.8×10^{-4}mol), 1.5g hexadecylamine (HAD, capping agent), then to this was added 20mL 1-octadecene (solvent) under a nitrogen atmosphere. The reagents were degassed at 120°C for 180 minutes, then the flask back-filled with nitrogen. The flask was then heated up to 220°C and left for 30 minutes, during which time the solution turned from clear red to clear saffron orange.

For the ZnS shell deposition, we then added 0.3 mL pre-prepared 0.1M ZDEC (361.93mg zinc diethyldithiocarbamate/10mL 1-octadecene) into InZnP solution, then heated up rapidly to 300°C for 10 minutes whilst still under the nitrogen atmosphere. The emission wavelength of InZnP and InZnP/ZnS were 610 nm and 510 nm (see Fig. 1).

Example 2

Purification and re-dispersion of nanoparticles

A mixed solvent of hexane and methanol (volume ratio 1:1) was added into the reaction solutions of Example 1 at room temperature. The mixed solution was shaken for 30 seconds, then centrifuged for 3 minutes at 3000 rpm to form a pellet of solid nanoparticles.

The nanoparticles were then dissolved in hexane, and an upper-layer of mixture which contained the nanoparticles was collected. Then the process was repeated four more times. Ethanol was added into the solutions which were shaken well for 30 seconds, and then centrifuged for 3 minutes at 4500 rpm. The nanoparticles were precipitated, washed four more times with ethanol and methanol and then dried overnight under atmospheric conditions. The nanoparticles were re-dissolved in toluene and stored under room temperature in a sample vial. The InZnP and InZnP/ZnS nanoparticles illuminated under a 365 nm UV lamp displayed bright visible fluorescence, respectively of an orange-red and of a yellow colour, their normalized absorption and photoluminescence spectra being shown in Fig 1. It is expected that further research will increase the range of

quantum dot sizes (which give different colours) and different structures which may make the materials brighter.

Example 3

Synthesis of InZnP/ZnSe/ZnS quantum dots

Following the procedure of Won *et al.* the procedure of Examples 1 and 2 is followed up to completion of the centrifugation step, after which a thick inner shell of zinc selenide is formed by re-dispersing the core pellet in toluene, injecting the InP core material in toluene into zinc acetate $Zn(OAc)_2$ in trioctylamine. Immediately after core injection, diluted hydrofluoric acid in acetone is added, after which shell growth is by selenium in trioctylphosphine, the shell formation being at 340°C for 1 hour. An outer shell is then formed by adding a lesser amount of zinc acetate and sulfur in trioctylphosphine. The reaction mixture is then cooled to room temperature, the quantum dots are precipitated with ethanol and recovered by centrifugation.

CLAIMS

1.   A process for production of metal phosphide nanoparticles or quantum dots which may be of AlP, InP, GaP, Zn_3P_2, Cd_3P_2, MnP, FeP, Fe_2P, Co_2P Ni_2P, or a combination thereof, wherein the process comprises the step of forming the quantum dots cores thereof by reacting a precursor of the metal component with a phosphide precursor which is phosphine carboxamide $(PH_2C(O)NH_2)$ or a compound of formula $H_2PCONR_1R_2$ wherein R_1 may represent hydrogen or an organic residue and R_2 represents an organic residue which may be the same as or different from R_1, the organic residue or residues e.g. being C_1-C_4 alkyl, e.g. methyl or cycloalkyl.

2.   The process of claim 1, wherein the metal component is indium optionally together with an alloy-forming component.

3.   The process of any preceding claim, wherein the cores formed are of InP or InZnP.

4.   The process of claim 1, 2 or 3, wherein the reaction is carried out in solution.

5.   The process of claim 4, wherein the solvent is a C_{12}-C_{20} alpha-olefin.

6.   The process of claim 5, wherein the solvent is 1-octadecene.

7.   The process of any preceding claim, wherein the solution further comprises a capping agent which is a long chain alpha-amine.

8.   The process of claim 7, wherein the amine is hexadecylamine.

9.   The process of any preceding range wherein the core-forming reaction is carried out in an inert atmosphere at a temperature in the range 200-300°C.

10.   The process of any preceding claim, further comprising forming a shell, or inner and outer shells, on the core.

11.   The process of claim 9, wherein the core is of In or InZn and the shell is e.g. of ZnS or ZnSe.

12.   The process of claim 11, wherein the shell is of ZnS and is formed by thermal decomposition of a dialkyldithiocarbamate in a solvent.

13.   The process of claim 12, wherein the dialkyldithiocarbamate is diethyldithiocarbamate.

14.   The process of claim 12 or 12, wherein the solvent is 1-octadecene and the decomposition temperature is about 300°C.

15.   The process of any preceding claim, further comprising incorporating the quantum dots into a QD-LED display, a QD-LED lamp, a diode laser, an image sensor, a solar cell a photovoltaic device or another article

Intellectual Property Office

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	HUI LI et al, "Chemical synthesis and applications of colloidal metal phosphide nanocrystals", Frontiers in Chemistry, 2019, 6, Article 652

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC
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The following online and other databases have been used in the preparation of this search report
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International Classification:

Subclass	Subgroup	Valid From
C09K	0011/70	01/01/2006
C01B	0025/08	01/01/2006
C09K	0011/08	01/01/2006
C09K	0011/62	01/01/2006