



- (51) **International Patent Classification:**
C09K 11/02 (2006.01) *H01L 33/50* (2010.01)
C09K 11/08 (2006.01)
- (21) **International Application Number:** PCT/EP2016/070275
- (22) **International Filing Date:** 29 August 2016 (29.08.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:** 15183743.2 3 September 2015 (03.09.2015) EP
- (71) **Applicant:** BASF SE [DE/DE]; Carl-Bosch-Str. 38, 67056 Ludwigshafen am Rhein (DE).
- (72) **Inventors:** MARAIKE, Ahlf; Eichenweg 15, 69198 Schriesheim (DE). STEFAN, Dahmen; Karl-Raeder-Allee 22, 67098 Bad Duerkheim (DE). PETER, Leidinger; In der Kurzgewanne 29, 67259 Kleinniedesheim (DE). SANDRO, Pagano; Mandelring 132, 67433 Neustadt an der Weinstrasse (DE). RALPH, Rieger; Schwalbenweg 37, 67063 Ludwigshafen (DE).
- (74) **Agent:** BASF IP ASSOCIATION; BASF SE, ZRX - C6, 67056 Ludwigshafen (DE).
- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report (Art. 21(3))



WO 2017/036997 A1

(54) **Title:** PROCESS FOR FORMULATING QUANTUM DOTS

(57) **Abstract:** The present invention relates to a process for formulating quantum dots for the use as luminescent pigment in lighting devices such as light-emitting diodes, functional films, coatings, or photo resists. In particular, the present invention relates to a process for producing encapsulated quantum dots comprising (a) agglomerating quantum dots to form quantum dot agglomerates, and forming a shell around the quantum dot agglomerates by performing 3 to 80 cycles of an atomic layer deposition process while the quantum dot agglomerates are in motion.

PROCESS FOR FORMULATING QUANTUM DOTS

Description

5 The present invention relates to a process for formulating quantum dots for the use as luminescent pigment in lighting devices such as light-emitting diodes, functional films, coatings, or photo resists.

10 Generating white light is challenging, because light sources like light-emitting diodes (LED) often produce off-white light, for example blue light. A typical way of converting the off-white light into desirable white light is to use luminescent pigments which absorb part of the light and emit at a different wavelength such that the combination of the transmitted and the emitted light produces white light. Quantum dots are a promising class of luminescent nano pigments as they exhibit high luminescence quantum yields in combination with narrow emission spectra in comparison to traditionally used luminescent pigments (see for example WO 2011 / 020 098 A1).
15 The narrow emission enable higher color performance of displays and higher efficiency of warm-white lighting. However, quantum dots often suffer from low stability against air and moisture in the hot environment typically encountered in the proximity of a light source. An efficient encapsulation is therefore needed.

20 WO 2014 / 147 570 A1 discloses a method of encapsulating quantum dots by adsorbing them in a porous matrix and subsequent coating by atomic layer depositing. However, in this approach, self-quenching due to mutual contact of the quantum dots and difficulties upon processing remain a problem.

25 It was an object of the present invention to provide a process for the encapsulation of quantum dots in which self-quenching is reduced. Furthermore, it was aimed at a process which provides encapsulated quantum dots which can easily be processed in a light-source manufacturing process. The process should be more flexible to allow for an easy tuning of the refractive index of
30 the encapsulated quantum dots to match the embedding matrix in the light-source manufacturing process. Also, the product obtained by the process should be chemically and mechanically robust to allow maximum flexibility in the light-source manufacturing process.

35 These objects were achieved by a process for producing encapsulated quantum dots comprising

- (a) agglomerating quantum dots to form quantum dot agglomerates, and
- (b) forming a shell around the quantum dot agglomerates by performing 3 to 80 cycles of an atomic layer deposition process while the quantum dot agglomerates are in motion.

40 The invention further relates to a particle comprising a core and a shell, wherein the core comprises a plurality of quantum dots and the shell is a conformal layer comprising an inorganic material, wherein the shell has a thickness of 0.3 to 8 nm.

2

The invention further relates to the use of the particle according to the invention as conversion materials in light sources, functional films, coatings, or photo resists.

The invention further relates to a light source comprising a particle according to the invention.

5

Preferred embodiments of the present invention can be found in the description and the claims. Combinations of different embodiments fall within the scope of the present invention.

Quantum dots, sometimes also referred to as semiconductor nanocrystals or inorganic semiconductor nanocrystals, are nanometer sized crystalline particles containing an inorganic semiconductor. By choosing the particular composition, structure, and/or size, the optical properties of the quantum dots can be influenced over a wide range. Quantum dots typically have an average particle size of 1 to 1000 nm, preferably 2 to 100 nm, more preferably 3 to 50, in particular 4 to 20 nm, such as 5 to 10 nm. The size refers to the weight average particle size as obtained from laser diffraction, preferably analyzed by the Mie theory.

15

The quantum dot preferably contains a semiconductor material. Examples of such semiconductor materials include compounds containing an element of group 14 of the periodic table of the elements, for example C including diamond, Si, Ge, or Sn (sometimes referred to as IV-semiconductor derived from the former IUPAC nomenclature for groups in the periodic table of the elements); compounds containing an element of group 2 or 12 and an element of group 16, for example ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, CdTe, HgO, HgS, HgSe, HgTe, MgS, MgSe (sometimes referred to as II-VI-semiconductors); compounds containing an element of group 13 and an element of group 15, for example AlN, AlP, AlAs, AlSb, GaAs, GaN, GaP, GaSe, InN, InP, InAs, InSb, TiN, TiP, TiAs, TiSb (sometimes referred to as III-V-semiconductors); compounds containing an element of group 14 and an element of group 16, for example GeO₂, GeS₂, GeSe₂, GeTe₂, SnO₂, SnS₂, SnSe₂, SnTe₂, PbO, PbS, PbSe, PbTe (sometimes referred to as IV-VI-semiconductors); compounds containing an element of group 1 or 11 and an element of group 13 and an element of group 16, for example CuGaO₂, AgGaO₂, AgAlO₂, LiGaO₂ (sometimes referred to as I-III-VI-semiconductors); compounds containing an element of group 2 or 12 and an element of group 14 and an element of group 15, for example ZnSnP₂, ZnSnAs₂, CdSiAs₂, CdGeP₂ (sometimes referred to as II-IV-V-semiconductors). In many cases it is possible to partially replace one element by another element of the same group of the periodic system, as for example in CdS_xSe_{1-x} or In_xGa_{1-x}P or CuIn_xGa_{1-x}S_ySe_{1-y}, wherein x and y are 0 to 1.

25

It is possible that these semiconductors are doped by a small amount of another element for example 1 to 10 % of the total weight of the semiconductor. Furthermore, it is possible that the quantum dot is a core-shell particle in which the core contains one semiconductor as described above and the shell contains a different semiconductor. In these core-shell particles it is possible that the band gap of the semiconductor in the core is higher or lower than the band gap of the semiconductor in the shell. Examples of core-shell quantum dots are CdSe/CdZnS,

35

40

CdZnSe/CdZnS, CdS/CdZnS, InP/ZnS, wherein the first material denotes the core material and the second material denotes the shell material.

5 The quantum dots preferably absorb light with a wavelength of 200 to 500 nm, more preferably of 300 to 400 nm, and preferably emit at a wavelength of 450 to 800 nm, more preferably 510 to 650 nm. These values refer to the wavelength with the maximum absorption or emission coefficient in the absorption or emission spectrum. The luminescence quantum efficiency is preferably at least 50 %, more preferably at least 75 %, in particular at least 90 %, such as at least 95 %.

10 The full width at half maximum (FWHM) of the emission spectrum is preferably 100 nm or lower, more preferably 70 nm or lower, in particular 50 nm or lower, such as 35 nm or lower.

Quantum dots are often prepared by reacting precursors, for example metal-organic precursors, in solution or suspension at elevated temperatures (see for example Murray et al. in the Journal of the American Chemical Society, volume 115 (1993), pages 8706-8715). In this case, stabilizing ligands are often used, for example carboxylic acid such as oleic acid, or alkylphosphine oxides such as tri-n-octylphosphine oxide (TOPO). These stabilizing ligands usually cover the surface of the quantum dots and often a substantial part remains there in subsequent processing steps.

15 Preferably, the stabilizing ligands of the quantum dots which are required for their synthesis are at least in part exchanged by more polar stabilizers prior to further steps in the process according to the present invention. More polar stabilizers reduce aggregation in polar solvents which would detrimentally affect the luminescence characteristics of the quantum dots. Suitable polar ligands include carboxylates, thiols, hydroxides, phosphines, amines and phosphates.

25 According to the present invention, the quantum dots are agglomerated to form quantum dot agglomerates. The agglomeration is preferably performed by a sol-gel process, by a spray drying process, or by an emulsion process.

30 In a sol-gel process the quantum dots which are dispersed in an organic solvent are reacted with a soluble precursor which condenses and deposits around the quantum dots to form for example an inorganic oxide, an inorganic hydroxyide, an inorganic hydroxide, or an inorganic sulfide. Preferably, the precursor contains at least one metal or semimetal, in particular Al, Zr, Ti, Fe, Zn, Sn, Si or a rare earth metal, i.e. Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu. Suitable precursors include acetylacetonates like tris(acetylacetonato)silicon; alkoxides, in particular C₁ to C₄ alkoxides like tetra-isopropyltitanium or triethoxyaluminum; chalcogenides; halogenides like silicon tetrachloride; carboxylates; sandwich compounds like zincocene; or condensates like Li/Na/K water glass, Na/K metasilicate, polysilazanes or silicone. Silicon alkoxides are preferred including tetraalkylorthosilicates; trialkoxysilanes or triaryloxysilanes; dialkoxysilanes or diaryloxysilanes. It is possible to use one precursor or a mixture of more than one precursors, preferably one precursor is used.

40

Tetraalkylorthosilicates are preferred. Preferred examples are tetramethylorthosilicate (TMOS), tetraethylorthosilicate (TEOS), tetrapropylorthosilicate, tetrabutylorthosilicate, tetrapentylorthosilicate, tetraphenylorthosilicate, trimethyl-monoethylorthosilicate, dimethyl-diethylorthosilicate, triethyl-monomethylorthosilicate, trimethyl-monopropylorthosilicate, monomethyl-tributylorthosilicate, monomethyl-tripentylorthosilicate, monomethyl-triphenyloxyorthosilicate, dimethyl-dipropylorthosilicate, tripropyl-monomethylorthosilicate, trimethyl-monobutylorthosilicate, dimethyl-dibutylorthosilicate, triethyl-monopropylorthosilicate, diethyl-dipropylorthosilicate, tributyl-monopropylorthosilicate, dimethyl-monoethyl-monobutylorthosilicate, diethyl-monomethyl-monobutylorthosilicate, diethyl-monopropyl-monobutylorthosilicate, dipropyl-monomethyl-monoethylorthosilicate, dipropyl-monomethyl-monobutylorthosilicate, dipropyl-monoethyl-monobutylorthosilicate, dibutyl-monomethyl-monoethylorthosilicate, dibutyl-monoethyl-monopropylorthosilicate, monomethyl-monoethyl-monopropyl-monobutylorthosilicate.

Preferred examples for trialkoxysilanes or triaryloxysilanes are trimethoxymethylsilane, triethoxymethylsilane, tripropoxymethylsilane, triphenyloxymethylsilane, trimethoxyethylsilane, triethoxyethylsilane, tripropoxyethylsilane, triphenyloxyethylsilane, trimethoxypropylsilane, triethoxypropylsilane, tripropoxypropylsilane, triphenyloxypropylsilane, trimethoxyphenylsilane, triethoxyphenylsilane, tripropoxyphenylsilane, triphenyloxyphenylsilane

Preferred examples for dialkoxysilanes or diaryloxysilanes are dimethoxy-dimethylsilane, diethoxy-dimethylsilane, dipropoxy-dimethylsilane, diphenyloxy-dimethylsilane, dimethoxy-diethylsilane, diethoxy-diethylsilane, dipropoxy-diethylsilane, diphenyloxy-diethylsilane, dimethoxy-dipropylsilane, diethoxy-dipropylsilane, dipropoxy-dipropylsilane, diphenyloxy-dipropylsilane, dimethoxy-diphenylsilane, diethoxy-diphenylsilane, dipropoxy-diphenylsilane, diphenyloxy-diphenylsilane.

Suitable organic solvents include alcohols like methanol, ethanol, isopropanol, ethylene glycol, diethylene glycol; ketones like acetone, methylethylketone, cyclohexanone; acyclic ethers like diethyl ether, di-n-butylether; cyclic ethers like tetrahydrofurane, dioxane, trioxane; amides like dimethylformamide, dimethylacetamide, N-methyl pyrrolidone; nitrils like acetonitrile; heteroaromatics like pyridine. Alcohols, ketones and cyclic ethers are preferred, in particular ethanol, isopropanol, or acetone. As some quantum dots are sensitive towards water it is preferred to use solvents with a low water content or water-free solvents. Preferably, the water content of the solvent is less than 1000 ppm, more preferably less than 100 ppm, in particular less than 10 ppm, wherein ppm stands for parts per million. A well suited method to determine the water content of an organic solvent is the direct titration according to Karl Fischer, for example described in detail in DIN 51777-1 part 1 (1983).

Preferably, the quantum dots are activated prior to the sol-gel process to increase the reactivity and/or the connectivity of the quantum dot surface. Activation can be performed by treatment with an oxidant like peroxides or azo compounds. Examples for peroxides are hydrogenperoxide, dibenzoylperoxide, dicyclohexylperoxodicarbonate, dilauroylperoxide, methylethylketone

peroxide, di-tert-butylperoxide, acetylacetone peroxide, tert-butylhydrogenperoxide, cumolhydrogenperoxide, tert-butylperneodecanoate, tert-amylperpivalate, tert-butylperpivalat, tert-butylperneohexanoate, tert-butylper-2-ethylhexanoate, tert-butyl-perbenzoate, lithium, sodium, potassium or ammonium peroxodisulfate. Examples for azo compounds are azodiisobutyronitrile, 2,2'-azobis(2-amidinopropane)dihydrochloride, 2-(carbamoilazo)isobutyronitrile, 4,4'-azobis(4-cyanovaleric acid). Alternatively, activation can be performed by treatment with styrene, vinyltoluene, ethylene, butadiene, vinylacetate, vinylchloride, vinylidenechloride, acrylonitrile, acrylamide, methacrylamide; C₁-C₂₀-alkyl or C₃-C₂₀-alkenylester of acrylic or methacrylic acid such as methacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, butylacrylate, butylmethacrylate, 2-ethylhexylacrylate, 2-ethylhexylmethacrylate, benzylacrylate, benzylmethacrylate, laurylacrylate, laurylmethacrylate, oleylacrylate, oleylmethacrylate, palmitylacrylate, palmitylmethacrylate, stearylacrylate, stearylmethacrylate; hydroxyl-containing monomers, in particular C₁-C₁₀-hydroxyalkyl(meth)acrylates such as hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, glycidyl(meth)acrylate; acids such as acrylic acid, methacrylic acid, acryloxypropionic acid, methacryloxypropionic acid, acryloxyacetic acid, methacryloxyacetic acid, crotonic acid, aconitic acid, itaconic acid, monomethylmaleate, maleic acid, monomethylitaconate, maleic acid anhydride, fumaric acid, monomethylfumarate, itaconic acid anhydride, oleic acid, linoleic acid, linolic acid, castor oil acid, palmitoleic acid, elaidic acid, vaccenic acid, icosenic acid, cetoleic acid, erucaic acid, nervic acid, arachidonic acid, timnodic acid, clupanodonic acid; silane monomers, for example vinylalkoxysilanes such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriisopropoxysilane, vinyltriphenoxysilane, vinyltris(dimethylsiloxy)silane, vinyltris(2-methoxyethoxy)silane, vinyltris(3-methoxypropoxy)silane, vinyltris(trimethylsiloxy)silane, or acryloxysilanes such as 2-(acryloxyethoxy)trimethylsilane, acryloxymethyltrimethylsilane, (3-acryloxypropyl)dimethyl-methoxysilane, (3-cryloxypropyl)methylbis(trimethylsiloxy)silane, (3-acryloxypropyl)methyl-dimethoxysilane, (3-acryloxypropyl)trimethoxysilane, (3-Acryloxypropyl)tris(trimethylsiloxy)silane, or methacryloxysilanes such as (3-methacryloxypropyl)trimethoxysilane, (3-methacryloxypropyl)methyl-dimethoxysilane, (3-methacryloxypropyl)dimethylmethoxysilane, (3-methacryloxypropyl)triethoxysilane, (methacryloxymethyl)methyldiethoxysilane, (3-methacryloxypropyl)methyldiethyloxysilane.

In the initial stage of the sol-gel process, a thin shell is formed around the quantum dots. While the reaction proceeds, several of the quantum dots with a shell form an aggregate, in which the quantum dots are separated by each other through the initially formed shell. Such an agglomeration is obtained if the concentration of the precursor and/or the quantum dots is sufficiently high and/or the reaction proceeds at a sufficiently high rate. Suitable precursor concentrations depend on the precursor, but are generally 0.0001 to 10 mol/l, preferably 0.001 to 5 mol/l, more preferably 0.01 to 2 mol/l, in particular 0.1 to 1 mol/l. Preferable concentrations of quantum dots are 0.1 to 200 g/l, more preferably 0.2 to 100 g/l, even more preferably 0.5 to 50 g/l, in particular 1 to 20 g/l. The reaction rate can be influenced by the temperature and/or a catalyst. Preferable reaction temperatures are 30 to 150 °C, more preferably 50 to 100 °C. Preferable catalysts include organic acids such as acetic acid or oxalic acid; or bases such as ammonia or potassium hydroxide.

A spray drying process employed to agglomerate the quantum dots can be a traditional spray drying process in which agglomerates are formed from a suspension containing the quantum dots, a solvent and a matrix material which dissolves in the solvent. Suitable solvents should have a high volatility, for example alkanes like hexane; halogenated hydrocarbons like dichloromethane; alcohols like methanol, ethanol, iso-propanol; ketones like acetone; esters like ethylacetate; aromatic hydrocarbons like toluene. The solvents should preferably have a low water content as described above. Suitable matrix materials include polymers like modified cellulose, polyethylene oxide, polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals, polycarbonate, poly(meth)acrylates; resins like polyurethane resins, polyamide resins, maleic acid resins; salts like potassium acetate, ammonium chloride, sodium lactate; sugars like glucose. The concentration of the quantum dots and the matrix material in the solvent should be chosen to render a suspension of sufficiently low viscosity to enable atomization. Preferably, the weight ratio of matrix material to quantum dots in the suspension is 0.01 to 1, more preferably 0.1 to 0.5.

Alternatively, the agglomerates are formed by a reactive spray drying process. In such a process, a suspension is atomized containing quantum dots and at least one precursor which solidifies due to a chemical reaction during the spray drying process. Solidification can be effected in various ways, for example by heat, UV or electron beam curing, or a hardener which is co-sprayed. Suitable precursors which solidify by heating include resins like acrylate resins, epoxide resins, silicone resins, polyimide resins, polysulfone resins. It is also possible to use precursors as described for the sol-gel process above, for example tetraethoxyorthosilicate. In this case, the suspension further comprises a catalyst as described above. Suitable precursors which solidify upon UV or electron beam curing include mono-, bi-, or polyfunctional (meth)acrylic monomers like methylmethacrylate, n-butylacrylate, vinylacrylate; mono-, bi-, or polyfunctional aromatic monomers like styrene, divinylbenzene; curable resins like acrylic resins, epoxy resins, vinyl ester resins, silicone resins, polyimide resins, polysulfone resins. Often a UV-initiator is added, for example one of the Irgacure® series. UV curing can be performed with light of various wavelength, for example with UV-A (315 - 380 nm), UV-B (280 - 315 nm), UV-C (200 - 280 nm), preferably UV-B. Suitable precursors which solidify in the presence of a hardener include salts like calcium chloride which is hardened by a soluble carbonate such as sodium carbonate; polyelectrolytes like polyacrylic acid which are hardened by multivalent ions such as aluminum or polyelectrolytes of opposite charge such as polyvinylammonium chloride.

In any of these spray drying processes, atomization is usually performed by a spray nozzle, preferably a two-component jet, wherein one component is an inert gas which facilitates the atomization process. The atomized suspension is exposed to a stream of a dry gas, preferably an inert gas such as nitrogen or argon. The temperature of the gas before coming in contact with the atomized suspension is preferably 50 to 300 °C, more preferably 100 to 250 °C. The quantum dot agglomerates are preferably collected by a cyclone.

For an emulsion process employed to agglomerate the quantum dots the quantum dots are dispersed in a liquid which can be emulsified in a solvent and can be solidified. Typically, polymerizable monomers are used for such liquids. Examples include (meth)acrylic monomers like methylmethacrylate; aromatic vinyl monomers like styrene; vinyl ethers such as methyl vinyl ether; N-vinyl amides like N-vinyl formamide or N-vinyl pyrrolidone; or silicones like dimethyl-dichlorosilane or acetyl-functionalized oligo(dimethylsiloxane). The solvent forming the continuous phase can be water, but preferably it is a water-free solvent, for example acetonitrile, perfluorinated solvents, or ionic liquids. The emulsion usually needs stabilization, for example by a surfactant, by small particles (Pickering) or polymers. Emulsification can be effected in various ways, for example by high-shear mixing, by using high pressure homogenizer, or by ultrasound. After emulsification, the disperse phase is solidified by heating and/or by UV curing. Typically, an initiator is used, for example a peroxide like tert-butyl peroxide; azoinitiators like azo-isobutyronitrile (AIBN); or Irgacure® initiators. When heating a temperature of preferably 50 to 150 °C, more preferably 70 to 95 °C is used. Preferably, the heating and/or UV curing is done under an inert atmosphere, for example nitrogen or argon. Heating and/or UV curing are typically performed at a pressure of normal pressure to 100 bar, preferably at 1.5 to 10 bar. The heating and/or UV curing is preferably performed for 1 to 10 h, more preferably 2 to 5 h. UV curing can be performed with light of various wavelength, for example with UV-A (315 - 380 nm), UV-B (280 - 315 nm), UV-C (200 - 280 nm), preferably UV-B. After hardening the disperse phase, the quantum dot agglomerates are obtained by removing the solvent, for example by filtering or centrifugation.

The quantum dot agglomerates obtained in the process according to the present invention preferably have a weight average particle size of 10 to 500 µm, more preferably 25 to 200 µm, in particular 40 to 100 µm. The particle size is preferably determined by laser diffraction. The quantum dot agglomerates are preferably spherically shaped which means that largest dimension of any particle on average is not more than 50 % larger than the smallest dimension of the same particle, preferably not more than 30 %, in particular not more than 10 %.

According to the present invention, a shell is formed around the quantum dot agglomerates by atomic layer deposition. Atomic layer deposition (ALD) is a process in which compounds from a gas phase react with surface in a self-limiting way to form a layer which ideally consists of a single molecular layer. This layer can either be decomposed or be reacted with a different compound from the gas phase. This cycle can be repeated to build up thicker layers. Equivalent expressions for ALD are molecular layer deposition (MLD) or atomic layer epitaxy (ALE). The ALD process is described in detail by George (Chemical Reviews 110 (2010), 111-131).

The shell formed by ALD preferably contains a metal or semimetal, subsequently abbreviated (semi)metal. Metals are Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Bi. Semimetals are B, Si, As, Ge, Sb. More preferably, the shell contains B, Al, Si, Ti, Zn, Y, Zr, La, in particular Al.

Any (semi)metal-containing compound which can be brought into the gaseous state is suitable as precursor in the ALD process. Preferably, the (semi)metal-containing compound is a (semi)metal organic compound. These compounds include alkyl (semi)metals such as dimethyl zinc, trimethylaluminum or dibutyl tin; (semi)metal alkoxylates such as tetramethoxy silicon or tetra-isopropoxy zirconium; cyclopentadiene adducts like ferrocene or titanocene; (semi)metal carbenes such as tantalum-pentaneopentylat or bisimidazolinylenrutheniumchloride; (semi)metal halogenides such as germanium tetrabromide or titanium tetrachloride; carbon monoxide complexes like chromium hexacarbonyl or nickel tetracarbonyl. More preferably, the (semi)metal-containing compound is an alkyl (semi)metal, in particular a C₁ to C₄ alkyl (semi)metal. A particularly preferred precursor is trimethyl aluminum.

It is possible to deposit only one (semi)metal-containing compound in one ALD cycle or to use more than one (semi)metal-containing compound in one ALD cycle. If more than one (semi)metal-containing compound in one ALD cycle is used, it is possible to deposit them simultaneously or to deposit them one after the other in case the subsequent compound can react with a surface covered with the preceding compound.

Besides depositing one or more than one (semi)metal-containing compounds an ALD cycle comprises decomposing the deposited (semi)metal-containing compound. This decomposition can be effected in various ways. The temperature of the substrate can be increased above the decomposition temperature of the (semi)metal-containing compound.

Furthermore, it is possible to expose the deposited (semi)metal-containing compound to a plasma like an oxygen plasma or a hydrogen plasma; to oxidants like oxygen, oxygen radicals, ozone, nitrous oxide (N₂O), nitric oxide (NO), nitrogendioxide (NO₂) or hydrogenperoxide; to reducing agents like hydrogen, alcohols, hydroazine or hydroxylamine, or solvents like water. It is preferable to use oxidants, plasma or water to obtain a layer of a metal oxide or a semimetal oxide. Exposure to water, an oxygen plasma or ozone is preferred. Exposure to water is particularly preferred.

As an alternative to decomposition of the (semi)metal-containing compound, it is possible to react the deposited (semi)metal-containing compound with a compound bearing at least two functional groups which can react with the (semi)metal-containing compound. Such compounds react with the surface and represent anchor groups for further deposition reactions of a (semi)metal-containing compound in a subsequent ALD cycle. Examples of such compounds include diols like ethylene glycol, 1,4-butanediol, or p-hydroquinone; dithiols like 1,4-butanedithiol or 1,4-mercaptobenzene; hydroxythiols like mercaptoethanol or 4-hydroxymethylthiobenzene; diamines like ethylene diamine or p-phenylene-diamine; hydroxylamine like ethanolamine or 4-aminobenzylic alcohol; thioamines like aminothioethanol.

Typical pressures at which the ALD process is performed range from 1500 to 10⁻⁵ mbar, preferably from 100 to 10⁻³ mbar, more preferably from 10 to 0.1 mbar. It is therefore preferable to run

the process in an apparatus in which the pressure can be adjusted such as in a vacuum chamber. Alternatively, the reaction is run at or around normal pressure, i.e. 500 to 1500 mbar, preferably 800 to 1200 mbar. As most compounds to be deposited by ALD have a vapor pressure below the pressure of the process, it is preferable to mix the vapor with an inert gas, for example nitrogen or argon. The temperature for the ALD process is in the range of -20 to 500 °C, preferably 0 to 300 °C, in particular 50 to 200 °C, such as 80 to 150 °C. Typically, the surface is exposed to the (semi)metal-containing compound in one ALD cycle for 1 ms to 30 s, preferably 10 ms to 5 s, in particular 50 ms to 1 s. It is preferable to purge the substrate with an inert gas in between exposing the surface to the (semi)metal-containing compound or any other compound of different chemical structure, normally for 0.1 s to 10 min, preferably for 1 s to 3 min, in particular for 10 s to 1 min.

According to the present invention, the shell is formed by 3 to 80 ALD cycles, preferably 4 to 70, more preferably 5 to 60, even more preferably 7 to 50, in particular 10 to 40, such as 15 to 30. Typically, a thickness of 0.3 to 8 nm is thereby achieved, preferably 0.4 to 7 nm, more preferably 0.5 to 6 nm, even more preferably 0.7 to 5 nm, in particular 1 to 4 nm, such as 1.5 to 3 nm. A shell of this thickness has a sufficiently low air and water vapor transmission rate. In addition, it has been surprisingly found out that a shell of this thickness renders particles which can be easily processed without losing their barrier properties.

Preferably, in every third to 20th ALD cycle the deposited (semi)metal-containing compound is reacted with a compound bearing at least two functional groups, more preferably in every fourth to 15th ALD cycle, even more preferably in every fifth to 12th ALD cycle, in particular in every sixth to tenth ALD cycle. In the remaining ALD cycles the deposited (semi)metal-containing compound is decomposed. Each ALD cycle can employ the same (semi)metal-containing compound or different ones, preferably at least two different (semi)metal-containing compounds are employed, in particular at least two compounds containing different metals.

In case at least one ALD cycle contains reacting the deposited (semi)metal-containing compound with a compound bearing at least two functional groups, it is often useful to make thicker shells. Therefore, the thickness of the shell formed by ALD is in this case 0.3 to 50 nm, preferably 0.4 to 40 nm, more preferably 0.5 to 30 nm, even more preferably 0.6 to 20 nm, in particular 0.8 to 15, such as 1 to 8 nm.

According to the present invention the quantum dot agglomerates are in motion during the atomic layer deposition. The motion can be generated by rotating or vibrating the reaction vessel or gas stream. A gas stream is preferred. The gas stream is preferably the gas containing the (semi)metal-containing compound and optionally an inert gas. Preferably, the gas stream is at a rate of 0.01 to 100 l/h per gram quantum dot agglomerates, more preferably 0.1 to 10 l/h per gram quantum dot agglomerates. Conventional fluidized-bed reactors are suitable for the process according to the present invention. A particularly well suitable apparatus is described in

WO 2010 / 100 335 A1. A rotary kiln which is particularly modified for ALD processes is also preferred.

5 Preferably, after applying the shell by ALD a second shell out of a soft material is formed around the particles. Soft materials include waxes, polymers and soft resins, for example silicone. The shell of soft materials can be applied by conventional coating techniques, for example in a fluidized-bed reactor. The soft materials can either be melted or dissolved in a solvent. In the latter case, the solvent is evaporated during the coating process. The coating can be a uniform shell or it can cover only a substantial part of the surface, for example at least 70 %, in particular at
10 least 90 %. A second shell of a soft material further increases the mechanical robustness of the particles allowing even harsh processing conditions without any damage to the particles.

The particles obtained by the process according to the present invention comprise a core and a shell, wherein the core comprises a plurality of quantum dots and the shell is a conformal layer
15 comprising an inorganic material, wherein the shell has a thickness of 0.3 to 8 nm. Preferably, the shell has a thickness of 0.4 to 7 nm, more preferably 0.5 to 6 nm, even more preferably 0.7 to 5 nm, in particular 1 to 4 nm, such as 1.5 to 3 nm. Conformal typically means that the thickness of the shell at the thinnest position is more than 50 % of the thickness at the thickest position, preferably more than 70 %, in particular more than 90 %, in particular more than 95 %. Further details of the core and the shell are as described above, wherein the core is formed by the
20 quantum dot agglomerate.

The particles obtained in the process according to the present invention preferably have a weight average particle size of 20 to 500 μm , more preferably 30 to 200 μm , in particular 40 to
25 100 μm . The particle size is preferably determined by laser diffraction. The particles are preferably spherically shaped which means that largest dimension of any particle on average is not more than 50 % larger than the smallest dimension of the same particle, preferably not more than 30 %, in particular not more than 10 %. The spherical shape can be analyzed by optical microscopy. The particles have a low surface area, their BET surface is preferably 0.1 to 100
30 m^2/g , more preferably 0.2 to 50 m^2/g , even more preferably 0.5 to 30 m^2/g , in particular 1 to 20 m^2/g .

The particles according to the present invention can be used as luminescent pigments in light sources, functional films, coatings or photo resists. Therefore, the present invention relates to
35 the use of the particles in light sources, functional films, coatings or photo resists. The present invention further relates to light sources comprising the particles according to the present invention. Preferably, the light source is a light-emitting diode (LED), in particular a phosphor-converted LED. The LED comprises semiconductors, preferred examples are InGaN, ZnSe, GaN, AlGaP, AlGaInP or GaP. The particles are preferably used as phosphor in a light source, for example as downconversion material. Even more preferably, the particles are used as remote
40

phosphor, i.e. as phosphor in distance to a light source. Also, the particles according to the present invention can be used in functional films, coatings or photo resists where they act for example as color converter or as color filter.

5 Usually, the particles according to the present invention are embedded in a matrix which forms a layer through which the light beam of the light source passes. The matrix is a transparent material including polymers, resins or glasses. A preferred resin is silicone resin. The matrix including the particles according to the present invention can be made by depositing a suspension of the particles in a liquid precursor, for example an alkylchlorosilane mixture, and curing this sus-
10 pension, for example by exposing to water vapor. Alternatively, the layer can be produced by melting the matrix, mixing with the particles according to the present invention and applying this mixture to the light source.

In some cases it is advantageous to add further scattering particles into the matrix containing
15 the particles according to the present invention. Scattering particles include metal or metal oxide particles, air bubbles, and glass and polymeric beads. Metal oxide particles are preferred, in particular TiO_2 , ZrO_2 , SiO_2 , BaTiO_3 , BaSO_4 or ZnO . The particles typically have a size of 0.1 to 5 μm , preferably 0.2 to 2 μm . The particles according to the present invention scatter light by themselves, such that less additional scattering particles are needed, in some cases no addi-
20 tional scattering particle are needed at all.

For the generation of white light a portion of the blue light from the light source is converted into green and red light by green and red emitting quantum dots. Due to the broad absorption spectra of quantum dots red quantum dots also absorb light emitted by the green quantum dots. This
25 reabsorption phenomena of quantum dots reducing external quantum efficiency can be reduced by this invention if particle according to the present invention comprising only red quantum dots and particles according to the present invention comprising only green quantum dots are produced separately. By adjusting the ratio of these two particles in the blue light beam white light can be produced with higher external quantum efficiency in comparison to arbitrarily mixed
30 quantum dots in a matrix. The size and surface properties of the particles according to the present invention is very similar to traditional phosphors for light source. Therefore, these phosphors can be replaced by the particles of the present invention without major changes to the light source manufacturing process.

Claims

1. A process for producing encapsulated quantum dots comprising
 - (a) agglomerating quantum dots to form quantum dot agglomerates, and
 - (b) forming a shell around the quantum dot agglomerates by performing 3 to 80 cycles of an atomic layer deposition process while the quantum dot agglomerates are in motion.
2. The process according to claim 1 wherein the agglomeration is done by a sol-gel process, by a spray drying process, or by an emulsion process.
3. The process according to claim 1 or 2 wherein the quantum dot agglomerates have a weight average particle size of 20 to 500 μm .
4. The process according to any of the claims 1 to 3 wherein the shell has a thickness of 1 to 5 nm.
5. The process according to any of the claims 1 to 4 wherein the atomic layer deposition process employs trimethyl aluminum.
6. The process according to any of the claims 1 to 5 wherein the atomic layer deposition process is performed at a temperature of 50 to 200 $^{\circ}\text{C}$.
7. The process according to any of the claims 1 to 6 wherein the atomic layer deposition process employs precursors with at least two different metals.
8. The process according to any of the claims 1 to 7 wherein the quantum dot agglomerate is kept in motion by a fluidized bed apparatus.
9. A particle comprising a core and a shell, wherein the core comprises a plurality of quantum dots and the shell is a conformal layer comprising an inorganic material, wherein the shell has a thickness of 0.3 to 8 nm.
10. The particle according to claim 9, wherein the particle has a size of 20 to 500 μm .
11. The particle according to claim 9 or 10, wherein the core further comprises silica or a polymeric binder.
12. The particle according to any of the claims 9 to 11, wherein the shell comprises alumina.

13. The particle according to any of the claims 9 to 12, wherein the shell has a thickness of 0.7 to 5 nm.
14. Use of the particle according to any of the claims 9 to 12 as luminescent pigments in light sources, functional films, coatings, or photo resists.
15. A light source comprising a particle according to any of the claims 9 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/070275

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/02 C09K11/08 H01L33/50
ADD.
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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/264196 A1 (WERNER MATTHEW [GB] ET AL) 18 September 2014 (2014-09-18)	1,3-15
Y	paragraph [0135]; example 1 page 0149 page 0067 page 0079 page 0081 page 0050 paragraph [0001]	1-15
Y	US 2015/179900 A1 (PICKETT NIGEL [GB] ET AL) 25 June 2015 (2015-06-25) claims 1-6 examples 1-5	1-15

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

"&" document member of the same patent family

Date of the actual completion of the international search 16 September 2016	Date of mailing of the international search report 28/09/2016
--	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Poole, Robert
--	-------------------------------------

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/070275

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/068321 A1 (PICKETT NIGEL [GB] ET AL) 24 March 2011 (2011-03-24) paragraph [0087]; claims 1,32-39; examples 1-8 -----	1-15
A	US 2007/172580 A1 (FAN CHEN-WEN [US] ET AL) 26 July 2007 (2007-07-26) claims 7-16 -----	1-15
A	WO 2014/128676 A1 (KONINKL PHILIPS NV [NL]; PHILIPS DEUTSCHLAND GMBH [DE]) 28 August 2014 (2014-08-28) claims 1,14,15 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/070275

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2014264196	A1	18-09-2014	CN 105051152 A	11-11-2015
			EP 2970762 A2	20-01-2016
			HK 1212724 A1	17-06-2016
			JP 2016518468 A	23-06-2016
			KR 20150126961 A	13-11-2015
			TW 201503419 A	16-01-2015
			US 2014264196 A1	18-09-2014
			WO 2014140936 A2	18-09-2014
US 2015179900	A1	25-06-2015	AU 2010299633 A1	12-04-2012
			CA 2774839 A1	31-03-2011
			CN 102668143 A	12-09-2012
			EP 2481101 A1	01-08-2012
			IL 218708 A	31-08-2015
			JP 2013505347 A	14-02-2013
			KR 20120063525 A	15-06-2012
			TW 201120112 A	16-06-2011
			US 2011068322 A1	24-03-2011
			US 2015179900 A1	25-06-2015
			WO 2011036447 A1	31-03-2011
US 2011068321	A1	24-03-2011	AU 2010299632 A1	12-04-2012
			CA 2774838 A1	31-03-2011
			CN 102648536 A	22-08-2012
			EP 2481100 A1	01-08-2012
			IL 218709 A	31-08-2015
			JP 5759995 B2	05-08-2015
			JP 2013505346 A	14-02-2013
			KR 20120062902 A	14-06-2012
			KR 20150039127 A	09-04-2015
			TW 201141985 A	01-12-2011
			US 2011068321 A1	24-03-2011
			US 2015048311 A1	19-02-2015
			WO 2011036446 A1	31-03-2011
US 2007172580	A1	26-07-2007	CA 2631729 A1	02-08-2007
			CN 101360803 A	04-02-2009
			EP 1976648 A2	08-10-2008
			JP 5384945 B2	08-01-2014
			JP 2009524736 A	02-07-2009
			KR 20080089337 A	06-10-2008
			US 2007172580 A1	26-07-2007
			WO 2007087480 A2	02-08-2007
WO 2014128676	A1	28-08-2014	CN 105073946 A	18-11-2015
			EP 2958974 A1	30-12-2015
			JP 2016515145 A	26-05-2016
			KR 20150123887 A	04-11-2015
			US 2015362150 A1	17-12-2015
			WO 2014128676 A1	28-08-2014