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(54) Title: LUMINESCENT PARTICLES

(57) Abstract: The present invention relates to luminescent particles, a process of their production and their 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 particle comprising a core and a shell, wherein the core comprises a plurality of nanocrystals of a compound of general formula (I): $E^a_xQ^b_yX_z$ wherein $a \cdot x + b \cdot y - z = 0$ is satisfied to provide electroneutrality, E^a is a cation with the positive charge a, Q^b is a metal in the oxidation state b with a d^0 or d^{10} electron configuration X is CI, Br, or I, and the shell is a conformal layer comprising an inorganic material.

Luminescent Particles

Description

The present invention relates to luminescent particles, a process of their production and their use as luminescent pigment in lighting devices such as light-emitting diodes, functional films, coatings, or photo resists.

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.

WO 2015 / 061 555 A1 disclose the use of perovskite-based materials as phosphors. These materials exhibit high luminescence quantum yields in combination with narrow emission spectra in comparison to traditionally used luminescent pigments. However, these perovskite materials suffer from low stability against air and moisture in the hot environment typically encountered in the proximity of a light source.

CN 104 861 958 disclose a method to increase the stability of the perovskite-based materials by embedding these materials in a polymeric matrix. However, this composite material is difficult to process and the stability is still insufficient for demanding applications.

Kim et al. disclose in Journal of Materials Chemistry A volume 3 (2015) pages 20092 – 20096 a solar cell with a perovskite layer and an overlayer formed by atomic layer deposition to increase the stability of the perovskite layer. However, this overlayer has to be prepared on the device which means that the perovskite has to be protected until the overlayer is formed. Also, such films cannot be applied to flexible objects and a slight damage in the overlayer can lead to destruction of the whole layer.

WO 2007 / 109 734 A2 discloses luminescent materials containing doped cesium metal halogenides which can be in form of particles surrounded by an outer layer containing for example aluminum oxide. However, these materials show insufficient stability under high thermal, mechanical and chemical stress, for example in lighting applications.

It was therefore an aim of the present invention to provide a luminescent material of increased stability against air and moisture in an environment of high thermal, mechanical and chemical stress. In addition, the luminescent material should be easily processed so to render maximum flexibility with regard to processing conditions during device fabrication. Another aim was to provide a luminescent material with decreased toxicity making the device fabrication safer.

These objects were achieved by a particle comprising a core and a shell, wherein the core comprises a plurality of nanocrystals of a compound of general formula (I): $E^a_xQ^b_yX_z$
wherein $a \cdot x + b \cdot y - z = 0$ is satisfied to provide electroneutrality,
E^a is a cation with the positive charge a,
Q^b is a metal in the oxidation state b with a d^0 or d^{10} electron configuration,
X is Cl, Br, or I, and
the shell is a conformal layer comprising an inorganic material.

The present invention further relates to a process for producing the particles according to the present invention comprising forming a shell around a core comprises a compound of general formula (I) by atomic layer deposition while the core is in motion.

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

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

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.

According to the present invention the particle comprises a core and a shell, wherein the core comprises a compound of general formula (I): $E^a_xQ^b_yX_z$ wherein $a \cdot x + b \cdot y - z = 0$ is satisfied to provide electroneutrality. E^a is a cation with the positive charge a. Preferably, a is 1 and E is an organic cation or alkali metal cation. Alkali cations include Li^+, Na^+, K^+, Rb^+ or Cs^+, preferably Rb^+ or Cs^+, in particular Cs^+. Preferred monovalent organic cations are ammonium cations in which one or more hydrogen atoms are exchanged by alkyl or acyl groups. Ammonium cations in which one or more hydrogen atoms are exchanged by alkyl groups include monoalkylammonium ions, dialkylammonium ions, trialkylammonium ions, tetraalkylammonium ions. Preferably, the alkyl group or groups are independent of each other C_1 to C_6 alkyl groups, in particular methyl or ethyl. Ammonium ions in which one or more hydrogen atoms are exchanged by acyl groups include amidinium ions and N-alkylamidinium, preferably amidinium ions. Preferably, the amidinium ion is derived from a C_1 to C_6 carboxamide, in particular from formamide or acetamide.

Q^b is a metal in the oxidation state b with a d^0 or d^{10} electron configuration. Examples include Ge(II), Sn(II), Pb(II), Ti(IV), Zr(IV), Cu(I), Ag(I), Zn(II), Cd(II), preferably Ge(II), Sn(II), Pb(II).

Specific examples for compounds of general formula (I) include methyl ammonium lead halogenides, such methyl ammonium lead iodide ($CH_3NH_3PbI_3$) or $(CH_3NH_3)_2PbI_4$; formadinium lead halogenides like formamidinium lead iodide ($HC(NH_2)PbI_3$), formamidinium lead bromide ($HC(NH_2)PbBr_3$); formadinium tin halogenides like formamidinium tin chloride ($HC(NH_2)SnCl_3$),

formamidinium tin bromide ($HC(NH_2)SnBr_3$) or formamidinium tin iodide ($HC(NH_2)SnI_3$); cesium lead halogenides like cesium lead chloride ($CsPbCl_3$), cesium lead bromide ($CsPbBr_3$) or cesium tin iodide ($CsSnI_3$); or cesium tin halogenides like cesium tin bromide ($CsSnBr_3$) or cesium tin iodide ($CsSnI_3$); or layered perovskites like $(R_1NR_2R_3R_4)_2MI_4$ wherein R_1 is a C_3 to C_{12} alkyl or ammonium alkyl and R_2, R_3 and R_4 are independent of each other hydrogen or C_1 to C_{12} alkyl, for example $(C_4H_9NH_3)_2PbBr_4$ and $(H_3N\text{-}C_4H_8\text{-}NH_3)PbI_4$.

In the compound of general formula (I) E can be one alkali cation or ammonium cation in which one or more hydrogen atoms are exchanged by alkyl groups or it can be a mixture of more than one alkali cation or ammonium cation in which one or more hydrogen atoms are exchanged by alkyl groups. In the compound of general formula (I) Q can be one of Pb, Sn, or Ge, or two of them or even all three. In the compound of general formula (I) X can be one of Cl, Br, I, or two of them or even all of them. If E, Q, and/or X in the compound of general formula (I) are more than one species, the compound is preferably a solid solution. Examples are $CH_3NH_3Pb_{1-\alpha}Sn_\alpha I_3$ in which α is a number between 0 and 1, $CH_3NH_3PbBrI_2$, $HC(NH_2)PbCl_2I$, or $CsPbCl_2Br$.

Furthermore, the compound of general formula (I) can be doped. Examples for doping materials include alkali metals such as Li, Na, K, Rb, Cs; alkaline earth metals such as Be, Mg, Ca, Sr, Ba; transition metals such as Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os Ir, Pt, Au, Hg; group 13 elements such as B, Al, Ga, In, Tl; group 14 elements such as C, Si; group 15 elements such as N, P, As, Sb, Bi; group 16 elements such as O, S, Se, Te; group 17 elements such as F. Typical amounts of doping materials are 0.01 to 1000 ppm, preferably 0.1 to 100 ppm, in particular 1 to 10 ppm, wherein ppm stands for parts per million, referring to the ratio of the weight of the doping material to the weight of the compound of general formula (I).

The compound of general formula (I) is preferably crystalline. Preferably, the compound of general formula (I) crystallizes in a Perovskite crystal structure or a Perovskite-related crystal structure, in particular in a Perovskite crystal structure.

The compound of general formula (I) preferably absorbs light with a wavelength of 300 to 600 nm, more preferably of 400 to 500 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 emission coefficient in the emission spectrum. The absorption maximum can be outside of these values. The luminescence quantum efficiency is preferably at least 50 %, more preferably at least 75 %, in particular at least 90 %, such as at least 95 %. 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.

The particle according to the present invention comprises a core containing a plurality of nanocrystals of the compound of general formula (I). The nanocrystals preferably have a mass average diameter of 1 to 100 nm, more preferably 2 to 50 nm, such as 3 to 20 nm. Nanocrystals, in

particular those which are commercially available, often have stabilizers on the surface. Normally, these are hydrophobic. However, it is preferred to have hydrophilic stabilizers, in particular bifunctional hydrophilic stabilizers on the surface of the nanocrystals. Nanocrystals with hydrophilic stabilizers can be obtained from commercially available nanocrystals with hydrophobic stabilizers by stabilizer exchange, for example by removing any solvent if present and suspending the nanocrystals in the hydrophilic stabilizer. Examples for bifunctional stabilizers include dicarboxylic acids such as adipic acid; diamines like ethylenediamine; or dithiols like 1,4-benzenedithiol.

The core preferably also contains a binder. The binder can be a ceramic or a polymer. A preferred ceramic is silica. Suitable polymers include modified cellulose, polyethylene oxide, polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals, polycarbonate, poly(meth)acrylates; resins like polyurethane resins, polyamide resins, maleic acid resins or silicon resins.

Preferably, the core further comprises scattering particles which often increase the external luminescence quantum yield. 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 scattering particles typically have a size of 0.1 to 5 µm, preferably 0.2 to 2 µm.

Preferably, the core further contains a layer of a functionalized organic compound on the surface, for example a monolayer. These can increase the stability of the compound of general formula (I) as well as the adhesion of the shell to the core. Functionalized organic compounds include organic amines, carboxylic acids, or organic thiols. Preferably, the functionalized organic compound contains 4 to 32 carbon atoms, more preferably 8 to 24. Preferably, the organic compound contains at least one carbon-carbon double bond. Examples for functionalized organic compounds include oleic acid, oleylamine. Even more preferably, the functionalized organic compound contains at least two functional groups. Examples are sebacic acid, or dodecanedioic diamine, ethylene-dithiol, or 1,4-benzene-dithiol.

According to the present invention, the particle further comprises a shell as a conformal layer comprising an inorganic material. Inorganic in the context of the present invention refers to materials which contain at least 1 wt.-% of at least one metal or semimetal, preferably at least 2 wt.-%, more preferably at least 5 wt.-%, in particular at least 10 wt.-%.

Inorganic materials include inorganic oxides, inorganic nitrides, inorganic carbides, perovskite oxides, garnets, pyrochlors, transparent conductors and II-VI compounds. Inorganic oxides are preferred. Typically, the inorganic material contains a metal or semimetal. In particular, 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. Preferred metals or semimetals are B, Al, Si, Ti, Zn, Y, Zr, La, in particular Al.

Examples for inorganic oxides including earth alkaline metal oxides such as BeO, MgO, CaO, SrO, BaO; main group metal oxides such as Al_2O_3, SiO_2, Ga_2O_3, GeO_2, In_2O_3, SnO_2, Tl_2O, PbO, PbO_2, Bi_2O_3; transition metal oxides such as Sc_2O_3, TiO_2, V_2O_5, CrO_2, MnO, Mn_2O_3, FeO, Fe_3O_4, Fe_2O_3, CoO, Co_2O_3, NiO, Ni_2O_3, Cu_2O, CuO, ZnO, Y_2O_3, ZrO_2, Nb_2O_5, MoO, MoO_2, Tc, RuO_2, Rh_2O, PdO, Ag_2O, CdO, HfO_2, Ta_2O_5, WO_3, ReO_3, OsO_4, IrO_2, PtO_2, AuO, Hg_2O; lanthanoid oxides such as La_2O_3, Ce_2O_3, CeO_2, Pr_2O_3, Nd_2O_3, Pm_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3. Preferred are B_2O_3, Al_2O_3, SiO_2, La_2O_3, Y_2O_3, ZnO, ZrO_2, in particular Al_2O_3. Often, oxides in thin layers according to the present invention are hydrated to some extent. These hydrates nevertheless count as oxides represented by a formula above in the context of the present invention. Alternatively, the oxide Al_2O_3, for example, can be represented by the more general formula $AlO_x(OH)_y$, wherein $0 \le x \le 1.5$; $0 \le y \le 3$ and $2x + y = 3$, preferably $1 \le x \le 1.5$; $0 \le y \le 1$ and $2x + y = 3$.

Examples for inorganic nitrides include BN, AlN, Si_3N_4, Ti_3N_4, TaN, NbN, WN, MoN, GaN, Zr_3N_4, InN, and Hf_3N_4, preferably BN, AlN, Si_3N_4, Ti_3N_4, Zr_3N_4. Examples for inorganic carbides include B_4C_3, SiC, ZrC. Examples for perovskite oxides include $BaTiO_3$, $SrTiO_3$, $LaNiO_3$, and $LaCoO_3$. Examples for garnets include $Fe_3Al_2(SiO_4)_3$, $Mg_3Al_2(SiO_4)_3$, and $Mn_3Al_2(SiO_4)_3$. Examples for pyrochlores include $La_2Zr_2O_7$, $Gd_{1.9}Ca_{0.1}Ti_2O_{6.9}$, $Dy_2Ti_2O_7$, and $Y_2Mo_2O_7$. Examples for transparent conductors include Sn-doped In_2O_3, Sb-doped SnO_2, F-doped SnO_2, Al-doped ZnO. Examples for II-VI compounds are ZnS, ZnSe, ZnTe, CaS, SrS, BaS, CdS, CdTe, CdSe. Furthermore, mixed oxides and/or nitrides are possible such as AlON, SiAlON.

It is possible that the shell contains only one inorganic material or more than one, for example two. If the shell contains more than one inorganic material it is preferable that these are located in separate layers to form, in case of two inorganic materials, an inner and an outer shell, for example an inner shell containing Al_2O_3 and an outer shell containing ZrO_2. Furthermore, the shell can contain one or more organic layers, preferably molecular monolayers. It is expected that these increase the mechanical stability of the shell, i.e. better retains the barrier properties of the shell upon application of mechanical stress or strain.

According to the present invention, the shell is conformal. As typically used in the technical field, a conformal shell has the same or substantially the same thickness at any place it covers the core. Substantially usually means, that the thickness at the place of the lowest thickness is at least 50 % the thickness at the thickest place, more preferably at least 70 %, in particular at least 90 %. The shell is preferably obtainable by atomic layer deposition as described below. Preferably, the shell covers at least 95 % of the surface of the core, more preferably at least 99 %, in particular completely or substantially completely.

The shell preferably has a thickness of 0.3 to 100 nm, more preferably 1 to 50 nm, in particular 2 to 20, such as 3 to 8 nm or 12 to 18 nm. The thickness and the conformity of the shell can for example be determined by freezing a sample in a matrix, e.g. solid ethylene, fracturing the sample and analyze it by scanning electron microscopy (SEM).

Preferably, the particle further contains an additional outer shell of a soft material. Soft materials include waxes, polymers and soft resins, for example silicone. 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 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 particle according to the present invention preferably has a particle size of 0.1 to 500 µm, more preferably 0.5 to 100 µm, in particular 1 to 20 µm.

One of the advantages of the particle according to the present invention is its flexibility in the device fabrication. For example, the particles can be processed in an ink or a paste containing any conventional solvent. Due to the inorganic shell, the core does not dissolve or is affected in any other way, for example by water in the solvent. Also, particles can be processed into mechanically flexible objects in contrast to pristine films which would break upon mechanical stress. Furthermore, particles containing different compounds of general formula (I) can be mixed to obtain certain color effects while the individual particles of general formula (I) stay separated from each other maintaining their high luminescence quantum yield and their narrow emission spectrum.

The present invention further relates to a process for making the particles according to the present invention. This process comprises forming a shell around a core comprising a plurality of nanocrystals of the compound of general formula (I). The core is as described above.

If the core comprises a plurality of particles of the compound of general formula (I) embedded in a binder, the particles of the compound of general formula (I) are preferably agglomerated with the binder to form an agglomerate, for example by a sol-gel process, by a spray drying process, or by an emulsion process.

In a sol-gel process the particles of the compound of general formula (I) which are dispersed in an organic solvent are reacted with a soluble precursor which condenses and deposits around the particles of the compound of general formula (I) to form for example an inorganic oxide, 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 C_1 to C_4 alkoxides like tetraisopropyltitanium 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.

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 trimethoxmetylsilane, triethoxymethylsilane, tripropoxymethylsilane, triphenyloxymethylsilane, trimethoxyethylsilane, triethoxyethylsilane, tripropoxyethylsilane, triphenyloxyethylsilane, trimethoxypropylsilane, triethoxypropylsilane, tripropoxypropylsilane, triphenyloxypropylsilane, trimethoxyphenylsilane, triethoxyphenylsilane, tripropoxyphenylsilane, triphenyloxyphenylsilane

Preferred examples for dialkoxysilanes or diaryloxysilanes are dimethoxy-dimetylsilane, 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; aromatic hydrocarbons like toluene or xylene; heteroaromatics like pyridine; chlorinated solvents like chloroform; aliphatic hydrocarbons like hexane or octane. Preferred solvents are those which dissolve the compound of general formula (I) to a very low extend, for example less than 10 g/l, preferably less than 1 g/l, in particular less than 0.1 g/l, for example aromatic or aliphatic hydrocarbons. As some compounds of general formula (I) 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 particles of the compound of general formula (I) are activated prior to the sol-gel process to increase the reactivity and/or the connectivity of the surface of the particles of the compound of general formula (I). 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-(carbamoylazo)isobutyronitrile, 4,4-azobis(4-cyanovaleric acid). Alternatively, activation can be performed by treatment with styrene, vinyltoluene, ethylene, butadiene, vinylacetate, vinylchloride, vinylidenchloride, acrylonitrile, acrylamide, methacrylamide; C_1-C_{20}-alkyl or C_3-C_{20}-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 C_1-C_{10}-hydroxyalkyl(meth)acrylates such as hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, glycidyl(meth)acrylate; acides 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)methyldimethoxysilane, (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 particles of the compound of general formula (I). While the reaction proceeds, several of the particles of the compound of general formula (I) with a shell form an aggregate, in which the particles of the compound of general formula (I) are separated by each other through the initially formed shell. Such an agglomeration is obtained if the concentration of the precursor and/or the particles of the compound of general formula (I) 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 particles of the compound of general formula (I) 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 particles of the compound of general formula (I) can be a traditional spray drying process in which agglomerates are formed from a suspension containing the particles of the compound of general formula (I), a solvent and a binder 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 binders 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 particles of the compound of general formula (I) and the binder in the solvent should be chosen to render a suspension of sufficiently low viscosity to enable atomization. Preferably, the weight ratio of binder to particles of the compound of general formula (I) 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 particles of the compound of general formula (I) 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, vinylester 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 agglomerates are preferably collected by a cyclone.

For an emulsion process employed to agglomerate the particles of the compound of general formula (I) 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) or preferably a two component (2K) silicone with a viscosity of 500 to 10000 mPa·s, preferably 1000 to 5000 mPa·s. 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-sheer mixing, by using high pressure homogenizer, by ultrasound, or by passing through microfluidic channels. 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 agglomerates are obtained by removing the solvent, for example by filtering or centrifugation.

In case the core further comprises a scattering material, these are included in the agglomeration process. The scattering particles are described above.

It is also possible that the core of the particle according to the present invention is formed by loading a porous matrix material with the compound of general formula (I), for example by dissolving the compound of general formula (I) in a solvent, adding the porous matrix material, and evaporating the solvent. In this case, the porous matrix material acts as the binder in the particle obtained in the process. Suitable porous matrix materials have pores with an average pore diameter of 0.1 to 500 µm, preferably 0.5 to 200 µm, in particular 1 to 100 µm. Porous matrix materials include zeolites, metal-organic frameworks, porous resin or polymer particles. Zeolites are preferred.

In some cases it is advantageous if the core of the particle according to the present invention is sintered prior to the shell formation. Typically, sintering means heating to a temperature of 50 to 300 °C, preferable 80 to 200 °C, in particular 100 – 150 °C for a period of time of 1 min to 6 hours, preferably 20 min to 3 hours, in particular 30 to 90 min.

Preferably, prior to forming the shell the core is treated with an oxidant like ozone or a plasma, like oxygen or ozone plasma to increase the reactivity of the surface of the core.

According to the present invention, the shell is formed 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. Therefore, a (semi)metal-containing compound is employed as a precursor. Any (semi)metal-containing compound which can be brought into the gaseous state is suitable. 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-pentane-opentylat or bisimidazolidinylenrutheniumchloride; (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 C_1 to C_4 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 (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2) or hydrogen peroxide; to reducing agents like hydrogen, alcohols, hydrazine 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-butanediole, 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.

Preferably, 3 to 1000 ALD cycles are performed, more preferably 10 to 500, in particular 20 to 200, for example 30 to 80 or 120 to 180.

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.

According to the present invention the core is 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 core, more preferably 0.1 to 10 l/h per gram core. 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.

In case the particle comprises a further shell of a soft material, this shell can be formed 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 typically evaporated during the coating process.

The particles according to the present invention can be used as luminescent pigments in light sources, functional films, coatings, photo resists, or imaging. Therefore, the present invention relates to the use of the particles in light sources, functional films, coatings, photo resists, or imaging. Functional films include security applications, such as markers for banknotes, stamps or important documents. Imaging includes bioimaging in which the luminescent particles are absorbed in biomaterials to make structural features visible by photoluminescence.

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 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.

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 suspension, 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.

Examples

Example 1: Preparation of a compound of general formula (I)

The synthesis of $CsPbX_3$ (X = Cl, Br, I) according to Angewandte Chemie International Edition volume 54 (2015), page 15424 was followed. All syntheses were done in an inert atmosphere of argon or nitrogen using Schlenk techniques.

Exemplary description of $CsPbBr_3$ nanocrystal synthesis: A mixture of $PbBr_2$ (0.07 g, 0.19 mmol) in 5 mL degassed 1-octadecene (ODE) was mixed in a 25 mL three-necked flask and degassed oleic acid (0.5 mL) and oleylamine, (0.5 mL) were added. The mixture was stirred at 120 °C. After 30 min the $PbBr_2$ was fully dissolved and the mixture was heated to 180 °C. A 0.125 M Cs-oleate solution in 1-octadecene was pre-heated to 100 °C and 0.4 mL of this solution rapidly injected in the previous described mixture. The flask with the resulting greenish solution was quenched using an ice bath and 5 mL of tert-butanol were added. The mixture with the precipitated nanocrystals was centrifuged (5000 rpm) for 10 min and the resulting pellet redispersed in 5 mL of toluene. Size of the particles was in the range of 5-20 nm as determined by transmission electron microscopy.

For measuring the emission intensity, a toluene dispersion containing nanoparticles of the compound of general formula (I) in a polystyrene matrix was prepared which was doctorbladed and dried under vacuum. The nanoparticle concentration in the film was 1 wt.-% and the dried film thickness was 100-200 µm.

Example 2: Preparation of crystals of the compound of general formula (I)

A mixture of $PbBr_2$ (5.00 g, 13.6 mmol) and CsBr (2.90 g, 13.6 mmol) was sealed in an evacuated quartz ampoule and heated to 500 °C for 3 h. After cooling to room temperature the obtained ingot was powdered with a mortar.

For the measurement of the emission intensity of the particles a silicone film on a glass plate was prepared. 1 wt.-% of particles were mixed with 2K silicone resin (Wacker Elastosil RT 604) using a speedmixer (DAC 400 FVZ, Hauschild). The films were prepared using a doctor blade (300 µm) and cured at 70 °C for 1 h. The resulting film thickness was 200-250 µm. The resulting material did not show any luminescence by excitation at 450nm.

Example 3: ALD coating of nanocrystals of the compound of general formula (I)

Attempts of coating the nanocrystals of the compound of general formula (I) as obtained in example 1 by ALD directly have been unsuccessful due to the nature of nanoparticles. By drying the nanoparticle suspension an oily powder was obtained which makes it impossible to coat single nanoparticles by ALD.

Example 4: Nanocrystals of the compound of general formula (I) in an organic binder

Polystyrene (PS 168N, Styrolution) or Zeonex (PS 168N, Zeon) was added to the toluene dispersion obtained in example 1, wherein the concentration of the compound of general formula (I) in the dispersion was 5 %. The dispersion was loaded into Büchi B-290 spray-drying tower and sprayed using the following parameters: Nozzle 0.5-0.7 mm, 120-140 °C inlet temperature and 40-70 °C outlet temperature, feed rate 1 L/h and N_2 gas. The right viscosity for trouble-free spray drying was adjusted by using further toluene. The material was collected as a dry powder and stored under nitrogen.

For the measurement of the emission intensity of the thus obtained particles a silicone film on a glass plate was prepared. The particles were mixed with 2K silicone resin (Wacker Elastosil RT 604) using a speedmixer (DAC 400 FVZ, Hauschild) to obtain a mixture containing 20 wt.-% of particles. The films were prepared using a doctor blade (300 µm) and cured at 70 °C for 1 h. The resulting film thickness was 200-250 µm.

Example 5: ALD coating of nanocrystals of the compound of general formula (I) in an organic binder

The particles obtained in example 4 were coated with Al_2O_3 by vacuum ALD. The samples were loaded into the ALD reaction chamber and the system was purged with an inert carrier gas. Alternating exposure to trimethyl aluminium and water vapor at a process pressure range of 0.1-2 mbar and a substrate temperature between 60 and 150 °C results in a uniform cycle by cycle growth of alumina. The reactant pulsed were controlled by pneumatic ALD valves. The pulse length can vary between 10 ms and has no upper limit because of the self-limiting nature of this coating process. The deposited film thickness was monitored by *in situ* microbalance measurement.

For the measurement of the emission intensity the coated particles where mixed with 2K silicone resin (Wacker Elastosil RT 604) using a speedmixer (DAC 400 FVZ, Hauschild) to obtain a particle concentration of 20 wt.-%. Films therof were prepared using a doctor blade (300 µm) and cured at 70 °C for 1 h. The resulting film thickness was 200-250 µm.

Example 6: Nanocrystals of the compound of general formula (I) in an inorganic binder

Template assisted synthesis of $CsPbX_3$ (X = Cl, Br, I) according to Nanoletters volume 16 (2016), page 5866. Commercial silica gel (Davisil Grade 643, Sigma Aldrich) with a pore size of 150 Å and a particle size distribution of 35-70 mm was dried at 150° C for 12 h under vacuum. 5.0 mg of the obtained silica was impregnated with 75 µL of 0.1 M solution of $CsPbBr_3$ in N-methylformamide. After impregnation, the excess solution was removed by damping with filter paper. The as-obtained powder was sandwiched between two glass slides and heated up to 150 °C in a vacuum oven for 40 minutes. Afterwards, the powder was allowed to cool to 80 °C under vacuum and then to room temperature in air. For the measurement of the emission intensity of the thus obtained particles a silicone film on a glass plate was prepared. The particles

were mixed with 2K silicone resin (Wacker Elastosil RT 604) using a speedmixer (DAC 400 FVZ, Hauschild) to obtain a particle concentration of 2.6 wt.-%. The films were prepared using a doctor blade (300 µm) and cured at 70 °C for 1 h. The resulting film thickness was 200-250 µm.

Example 7: ALD coating of nanocrystals of the compound of general formula (I) in an inorganic binder

The particles obtained in example 6 were coated with Al_2O_3 by vacuum ALD. The samples were loaded into the ALD reaction chamber and the system was purged with an inert carrier gas. Alternating exposure to trimethylaluminium and water vapor at a process pressure range of 0.1-2 mbar and a substrate temperature between 60 and 150 °C results in a uniform cycle by cycle growth of alumina. The reactant pulsed were controlled by pneumatic ALD valves. The pulse length can vary between 10 ms and has no upper limit because of the self-limiting nature of this coating process. The deposited film thickness was monitored by *in situ* microbalance measurement.

For the measurement of the emission intensity of the thus obtained particles were mixed with 2K silicone resin (Wacker Elastosil RT 604) using a speedmixer (DAC 400 FVZ, Hauschild) to obtain a particle concentration of 20 wt.-%. Films thereof were prepared using a doctor blade (300 µm) and cured at 70 °C for 1 h. The resulting film thickness was 200-250 µm.

Measurement of emission intensity

The quantum yields and emission spectra of the films were measured using a calibrated quantum yield detection system (Hamamatsu, model C9920-02). The films were put on a modified Philips Fortimo blue LED lamp for degradation tests. The Philips Fortimo were controlled to yield a stable 450 nm emission with a flux of 100 mW/cm^2. The samples heat up to 30-50 °C during the illumination. After the films were illuminated for 24 h using the Fortimo device, the emission intensity was measured. The emission intensity was divided by the initial emission intensity to yield the decrease in emission intensity in percent. Individual samples of the same experiment exhibited a broad distribution of +/- 20 % in emission intensity after 24 h. Three samples have been measured for each experiment, all obtained values had to fall in the range of emission intensity after 24 h described in Table 1. This is the reason why a range is given instead of individual results.

Example	Concentration of the compound of general formula (I) in the film	ALD treatment	emission intensity after 24 h
1	1%	-	< 20 %
2	1%	-	< 20 %
3	-	-	-
4	1%	-	< 20 %
5	1%	50 cycles, Al_2O_3	> 20 %
6	1%	-	< 20 %
7	1%	50 cycles, Al_2O_3	> 20 %

Table 1: Summary of examples described above. Showing that particles coated with an additional ALD barrier layer show higher emission intensity after irradiation for 24 h with 100 mW/cm^2 blue LED light.

Claims

1. A particle comprising a core and a shell, wherein the core comprises a plurality of nanocrystals of a compound of general formula (I): $E^a_xQ^b_yX_z$
wherein $a \cdot x + b \cdot y - z = 0$ is satisfied to provide electroneutrality,
E^a is a cation with the positive charge a,
Q^b is a metal in the oxidation state b with a d^0 or d^{10} electron configuration,
X is Cl, Br, or I, and
the shell is a conformal layer comprising an inorganic material.

2. The particle according to claim 1, wherein the nanocrystals have a stabilizer on the surface.

3. The particle according to claim 1 or 2, wherein the core contains a binder.

4. The particle according to any of the claims 1 to 3, wherein the binder is silica or a polymeric binder.

5. The particle according to any of the claims 1 to 4, wherein E^a is Cs^+.

6. The particle according to any of the claims 1 to 5, wherein the shell has a thickness of 2 to 20 nm.

7. The particle according to any of the claims 1 to 6, wherein the particle has a size of 1 to 50 µm.

8. The particle according to any of the claims 1 to 7, wherein the core contains scattering particles.

9. The particle according to any of the claims 1 to 8, wherein the shell comprises alumina.

10. A process for producing the particles according to claims 1 to 9 comprising forming a shell around a core comprises a plurality of nanocrystals of a compound of general formula (I) by atomic layer deposition while the core is in motion.

11. The process according to claim 10 wherein the atomic layer deposition process employs trimethyl aluminum.

12. The process according to claims 10 or 11 wherein the atomic layer deposition process is performed at a temperature of 50 to 200 °C.

13. The process according to any of the claims 10 to 12 wherein the particles are kept in motion by a fluidized bed apparatus.

14. Use of the particle according to any of the claims 1 to 9 as luminescent pigments in light sources, functional films, coatings, photo resists, or imaging.

15. A light source comprising a particle according to any of the claims 1 to 9.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/053757

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/02
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

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	WO 2007/109734 A2 (ULTRADOTS INC [US]; VARADARAJAN JOHN [US]; RESAN MIRNA [US]; WU FANXIN) 27 September 2007 (2007-09-27)	1,3-7,9, 14,15
Y	paragraphs [0041], [0062] - [0085]; examples 2, 29-36	2,8, 10-13
Y	US 2007/172580 A1 (FAN CHEN-WEN [US] ET AL) 26 July 2007 (2007-07-26)	2,8, 10-13
A	paragraphs [0002], [0018] - [0021]; claims 1-18	1,3-7, 14,15
Y	US 4 585 673 A (SIGAI A GARY [US]) 29 April 1986 (1986-04-29) column 1, line 40 - column 2, line 34; claims 1-28	1-15
Y	DE 29 52 436 A1 (HEIDRICH KARL DR RER NAT) 2 July 1981 (1981-07-02) page 4, lines 1-15; claims 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	Date of mailing of the international search report
19 April 2017	28/04/2017

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

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2017/053757

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-15(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continuation of Box II.2

Claims Nos.: 1-15(partially)

Present claim 1 relates to an extremely large number of possible compounds. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds on the basis of the examples on pages 13-17 of the application. The particle according claim 1 is referring to a large number of metals, although in the example only "Pb" is mentioned in combination with Cs and X being Cl, Br, I (example 1), namely CsPbBr3 (example 2). The shell is defined as any inorganic material, although in the example only Al2O3 is demonstrated.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/053757

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