(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 October 2016 (06.10.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/156266 A1

(51) International Patent Classification:
C09K 11/56 (2006.01) *C09K 11/02* (2006.01)
C09K 11/88 (2006.01)

(21) International Application Number:
PCT/EP2016/056705

(22) International Filing Date:
25 March 2016 (25.03.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/139,159 27 March 2015 (27.03.2015) US
15177407.2 17 July 2015 (17.07.2015) EP

(71) Applicant: **NEXDOT** [FR/FR]; 10 rue Vauquelin, 75005 Paris (FR).

(72) Inventors: **HEUCLIN, Hadrien**; c/o NEXDOT, 10 rue Vauquelin, 75005 Paris (FR). **NADAL, Brice**; c/o NEXDOT, 10 rue Vauquelin, 75005 Paris (FR). **GRAZON, Chloé**; c/o NEXDOT, 10 rue Vauquelin, 75005 Paris (FR). **MAHLER, Benoît**; c/o NEXDOT, 10 rue Vauquelin, 75005 Paris (FR). **LHUILLIER, Emmanuel**; c/o NEXDOT, 10 rue Vauquelin, 75005 Paris (FR).

(74) Agent: **ICOSA**; 83 avenue Denfert-Rochereau, 75014 Paris (FR).

(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).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2016/156266 A1

(54) Title: CORE-SHELL NANOPLATELETS FILM AND DISPLAY DEVICE USING THE SAME

(57) **Abstract**: The present invention relates to a population of semiconductor nanoplatelets, each member of the population comprising a nanoplatelet core including a first semiconductor material and a shell including a second semiconductor material on the surface of the nanoplatelet core, wherein the population exhibits fluorescence quantum efficiency at 100 °C or above that is at least 80% of the fluorescence quantum efficiency of the population at 20°C. The present invention also relates to a nanoplatelets film comprising said population of nanoplatelets, a backlight unit comprising said nanoplatelets film and a liquid crystal display comprising said backlight unit.

CORE-SHELL NANOPLATELETS FILM AND DISPLAY DEVICE USING THE SAME

FIELD OF INVENTION

The present invention relates to the field of nanoparticles and especially semiconductor nanocrystals. In particular, the present invention relates to nanoplatelets, nanoplatelets film and display device using said nanoplatelets film.

BACKGROUND OF INVENTION

To represent the colors in all their variety, one proceeds typically by additive synthesis of at least three complementary colors, especially red, green and blue. In a chromaticity diagram, the subset of available colors obtained by mixing different proportions of these three colors is formed by the triangle formed by the three coordinates associated with the three colors red green and blue. This subset constitutes what is called a gamut.

The majority of color display devices operate on this three-color principle: each pixel consists of three sub-pixels, one red, one green and one blue, whose mixture with different intensities can reproduce a colorful impression.

A luminescent or backlit display such as a computer LCD screen has to present the widest possible gamut for an accurate color reproduction. For this, the composing sub-pixels must be of the most saturated colors possible in order to describe the widest possible gamut. A light source has a saturated color if it is close to a monochromatic color. From a spectral point of view, this means that the light emitted by the source is comprised of a single narrow fluorescence band of wavelengths. A highly saturated shade has a vivid, intense color while a less saturated shade appears rather bland and gray.

It is therefore important to have light sources whose emission spectra are narrow and with saturated colors.

For example, in the case of a color display, the red, green and blue sub-pixels composing it must have a spectrum maximizing the gamut of the display system, and amounts exhibiting the narrowest possible emission from a spectral point of view.

Semiconductor nanoparticles, commonly called “quantum dots”, are known as emissive material. Said objects have a narrow fluorescence spectrum, approximately 30 nm full width at half maximum, and offer the possibility to emit in the entire visible spectrum as well as in the infrared with a single excitation source in the ultraviolet. They are currently used in display devices as phosphors. In this case an improvement of the gamut of polychromic displays requires a finesse of the emission spectra that is not accessible for quantum dots.

It is also known to use nanoplatelets to obtain great spectral emission finesse and a perfect control of the emission wavelength (see WO2013/140083).

However, said nanoplatelets of the prior art do not offer stability, especially the temperature stability, sufficient for long-term use in commercial display. Indeed, above 100°C, the fluorescence quantum efficiency of nanoplatelets of the prior art is divided by 2, preventing their use in commercial display.

It is therefore an object of the present invention to provide nanoplatelets and associated display devices exhibiting long-term high temperature stability.

SUMMARY

The present invention thus relates to a population of semiconductor nanoplatelets, each member of the population comprising a nanoplatelet core including a first semiconductor material and a shell including a second semiconductor material on the surface of the nanoplatelet core, wherein the population exhibits fluorescence quantum efficiency at 100 °C or above that is at least 80% of the fluorescence quantum efficiency of the population at 20°C. According to one embodiment, the temperature is in a range from 100 °C to 250°C.

According to one embodiment, the population of semiconductor nanoplatelets exhibits fluorescence quantum efficiency decrease of less than 50% after one hour under light illumination.

The present invention also relates to a nanoplatelets film, comprising a host material - preferably a polymeric host material- and emissive semiconductor nanoparticles embedded in said host material, wherein at least 20% of said emissive semiconductor nanoparticles are colloidal nanoplatelets according to the present invention.

According to one embodiment, the nanoplatelets film further comprises scattering elements dispersed in the host material.

The present invention also relates to an optical system comprising a light source having preferably a wavelength in a range from 400 to 470 nm such as for instance a gallium nitride based diode and a nanoplatelets film according to the present invention.

According to one embodiment, the nanoplatelets film is enclosed in a layer configured to reduce exposure of the nanoplatelets film to O_2 and H_2O.

The present invention also relates to a backlight unit comprising the optical system according to the invention and a light guide plate configured to guide the light exiting from the light source or the nanoplatelets film.

According to one embodiment, the backlight unit further comprises light recycling element configured to collimate the light in a given direction.

According to one embodiment, the nanoplatelets film is optically between the light source and the light guide plate.

According to one embodiment, the nanoplatelets film is optically between the light source and the light recycling element.

According to one embodiment, the light recycling element is optically between the light guide plate and the nanoplatelets film.

According to one embodiment, the backlight unit further comprises a light reflective material disposed on one surface of the light guide plate, wherein the surface onto which the reflector is disposed is substantially perpendicular to the surface facing the light source.

The present invention also relates to a liquid crystal display unit comprising a backlight unit according to the invention and a liquid crystal display panel having a set of red, blue and green color filters, wherein the nanoplatelets film is optically between the light source and the liquid crystal display panel.

The present invention also relates to a display device comprising the optical system, the backlight unit or the liquid crystal display unit according to the invention.

DEFINITIONS

In the present invention, the following terms have the following meanings:

- As used herein the singular forms "**a**", "**an**", and "**the**" include plural reference unless the context clearly dictates otherwise.
- The term "**about**" is used herein to mean approximately, roughly, around, or in the region of. When the term "about" is used in conjunction with a numerical range, it modifies that range by extending the boundaries above and below the numerical values set forth. In general, the term "about" is used herein to modify a numerical value above and below the stated value by a variance of 20 percent.
- "**Continuously emissive nanoplatelets**" over a predetermined period refer to nanoplatelets which exhibit, under excitation, fluorescence (or photoluminescence) intensity above a threshold over the predetermined period. The integration time is set to allow sufficient excitation events of the nanoplatelets and is superior or equal to 1 ms. According to the present invention, during a measurement (see examples), said threshold may be set at three times the noise.

- "**Fluorescence quantum efficiency or quantum yield**" refers to the ratio between the numbers of photons emitted by fluorescence divided by the number of absorbed photons.
- "**Display device**" refers to a device that display an image signal. Display devices include all devices that display an image such as, non-limitatively, a television, a computer monitor, a personal digital assistant, a mobile phone, a laptop computer, a tablet PC, an MP3 player, a CD player, a DVD player, a head mounted display, a smart watch, a watch phone or a smart device.
- "**Monolayer**" refers to a film or a continuous layer being of one atom thick.
- "**Nanoparticle or nanocrystal**" refers to a particle of any shape having at least one dimension in the 0.1 to 100 nanometers range.
- "**Nanoplatelet**", "**nanosheet**", "**nanoplate**" or "**2D-nanoparticle**" refers interchangeably to a nanoparticle having one dimension smaller than the two others; said dimension ranging from 0.1 to 100 nanometers. In the sense of the present invention, the smallest dimension (hereafter referred to as the thickness) is smaller than the other two dimensions (hereafter referred to as the length and the width) by a factor of at least 1.5, 2, 2.5, 3, 3.5, 4.5 or 5.
- "**Shell**" refers to a film or a layer of at least one atom thick covering the initial nanoplatelet on each faces (i.e. on the entire surface except, if the growth process is performed on a substrate, on the surface in contact with said substrate).
- "**Light recycling element**" refers to an optical element that recycles or reflects a portion of incident light. Illustrative light recycling element includes reflective polarizers, light polarizing film, prism film, micro-structured films, metallic layers, multi-layer optical film.
- "**Scattering element**" refers to an optical element that diffuses, spreads out or scatters light. Illustrative scattering element includes light scattering film, surface structuration, particulate-filled composite and combinations thereof.

DETAILED DESCRIPTION

This invention relates to a nanoplatelet comprising an initial nanoplatelet core and a shell.

According to a first embodiment, the initial nanoplatelet is an inorganic, colloidal, semiconductor and/or crystalline nanoplatelet.

According to one embodiment, the initial nanoplatelet has a thickness ranging from 0.3 nm to less than 500 nm, from 5 nm to less than 250 nm, from 0.3 nm to less than 100 nm, from 0.3 nm to less than 50 nm, from 0.3 nm to less than 25 nm, from 0.3 nm to less than 20 nm, from 0.3 nm to less than 15 nm, from 0.3 nm to less than 10 nm, or from 0.3 nm to less than 5 nm.

According to one embodiment, at least one of the lateral dimensions of the initial nanoplatelet is ranging from 2 nm to 1m, from 2 nm to 100 mm, from 2 nm to 10 mm, from 2 nm to 1 mm, from 2 nm to 100 µm, from 2 nm to 10 µm, from 2 nm to 1 µm, from 2 nm to 100 nm, or from 2 nm to 10 nm.

According to one embodiment, the material composing the initial nanoplatelet comprises a material MxEy, wherein:
M is selected from Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or a mixture thereof,
E is selected from O, S, Se, Te, N, P, As, F, Cl, Br, I, or a mixture thereof; and
x and y are independently a decimal number from 0 to 5.

According to an embodiment, the material MxEy comprises cationic element M and anionic element E in stoichiometric ratio, said stoichiometric ratio being characterized by values of x and y corresponding to absolute values of mean oxidation number of elements E and M respectively.

According to one embodiment, the faces substantially normal to the axis of the smallest dimension of the initial nanoplatelet consist either of M or E.

According to one embodiment, the smallest dimension of the initial nanoplatelet comprises an alternate of atomic layers of M and E.

According to one embodiment, the number of atomic layers of M in the initial nanoplatelet is equal to one plus the number of atomic layer of E.

According to an embodiment, the material composing the initial nanoplatelet comprises a material MxNyEz, wherein:

- M is selected from Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or a mixture thereof;
- N is selected from Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or a mixture thereof;
- E is selected from O, S, Se, Te, N, P, As, F, Cl, Br, I or a mixture thereof; and

x, y and z are independently a decimal number from 0 to 5, at the condition that when x is 0, y and z are not 0, when y is 0, x and z are not 0 and when z is 0, x and y are not 0.

According to a preferred embodiment, the material composing the initial nanoplatelet comprises a material MxEy wherein:

M is selected from group Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb, VIII or mixtures thereof;

E is selected from group Va, VIa, VIIa or mixtures thereof; and

x and y are independently a decimal number from 0 to 5.

According to one embodiment, the material composing the initial nanoplatelet comprises a semi-conductor from group IIb-VIa, group IVa-VIa, group Ib-IIIa-VIa, group IIb-IVa-Va, group Ib-VIa, group VIII-VIa, group IIb-Va, group IIIa-VIa, group IVb-VIa, group IIa-VIa, group IIIa-Va, group IIIa-VIa, group VIb-VIa, or group Va-VIa.

According to one embodiment, the material composing the initial nanoplatelet comprises at least one semiconductor chosen among CdS, CdSe, CdTe, CdO, Cd_3P_2, Cd_3As_2, ZnS, ZnSe, ZnO, ZnTe, Zn_3P_2, Zn3As2, HgS, HgSe, HgTe, HgO, GeS, GeSe, GeTe, SnS, SnS_2, $SnSe_2$, SnSe, SnTe, PbS, PbSe, PbTe, GeS_2, $GeSe_2$, $CuInS_2$, $CuInSe_2$, CuS, Cu_2S, Ag_2S, Ag_2Se, Ag_2Te $AgInS_2$, $AgInSe_2$, FeS, FeS_2, FeO, Fe_2O_3, Fe_3O_4, Al_2O_3, TiO_2, MgO, MgS, MgSe, MgTe, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, In_2S_3,TlN, TlP, TlAs, TlSb, Bi_2S_3, Bi_2Se_3, Bi_2Te_3, MoS_2, WS_2, VO_2 or a mixture thereof.

According to a preferred embodiment, the initial nanoplatelet is selected from the group consisting of CdS, CdSe, CdSSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, $CuInS_2$, $CuInSe_2$, $AgInS_2$, $AgInSe_2$, CuS, Cu_2S, Ag_2S, Ag_2Se, Ag_2Te, FeS, FeS_2, PdS, Pd_4S, WS_2 or a mixture thereof.

According to one embodiment, the initial nanoplatelet comprises an alloy of the aforementioned materials.

According to one embodiment, the initial nanoplatelet comprises an additional element in minor quantities. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, the initial nanoplatelet comprises a transition metal or a lanthanide in minor quantities. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, the initial nanoplatelet comprises in minor quantities an element inducing an excess or a defect of electrons compared to the sole nanoplatelet. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, the initial nanoplatelet comprises in minor quantities an element inducing a modification of the optical properties compared to the sole nanoplatelet. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, the initial nanoplatelet consists of a core/shell nanoplatelet such as a core/shell nanoplatelet known by one skilled in the art or a core/shell nanoplatelet according to the present invention. According to one embodiment, the “core” nanoplatelets can have an overcoating or shell on the surface of its core.

According to a first embodiment, the final nanoplatelet (initial nanoplatelet + shell) is an inorganic, colloidal, semiconductor and/or crystalline nanoplatelet.

According to one embodiment, the final nanoplatelet has a thickness ranging from 0.5 nm to 10 mm, from 0.5 nm to 1 mm, from 0.5 nm to 100 µm, from 0.5 nm to 10 µm, from 0.5 nm to 1 µm, from 0.5 nm to 500 nm, from 0.5 nm to 250 nm, from 0.5 nm to 100 nm, from 0.5 nm to 50 nm, from 0.5 nm to 25 nm, from 0.5 nm to 20 nm, from 0.5 nm to 15 nm, from 0.5 nm to 10 nm or from 0.5 nm to 5 nm.

According to one embodiment, at least one of the lateral dimensions of the final nanoplatelet is ranging from 2 nm to 1m, from 2 nm to 100 mm, from 2 nm to 10 mm, from 2 nm to 1 mm, from 2 nm to 100 µm, from 2 nm to 10 µm, from 2 nm to 1 µm, from 2 nm to 100 nm, or from 2 nm to 10 nm.

According to one embodiment, the thickness of the shell is ranging from 0.2 nm to 10 mm, from 0.2 nm to 1 mm, from 0.2 nm to 100 µm, from 0.2 nm to 10 µm, from 0.2 nm to 1 µm, from 0.2 nm to 500 nm, from 0.2 nm to 250 nm, from 0.2 nm to 100 nm, from 0.2 nm to 50 nm, from 0.2 nm to 25 nm, from 0.2 nm to 20 nm, from 0.2 nm to 15 nm, from 0.2 nm to 10 nm or from 0.2 nm to 5 nm.

According to one embodiment, the material composing the shell comprises a material MxEy, wherein:
M is selected from Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or a mixture thereof,
E is selected from O, S, Se, Te, N, P, As, F, Cl, Br, I, or a mixture thereof,
and x and y are independently a decimal number from 0 to 5.

According to an embodiment, the material MxEy comprises cationic element M and anionic element E in stoichiometric ratio, said stoichiometric ratio being characterized by values of x and y corresponding to absolute values of mean oxidation number of elements E and M respectively.

According to one embodiment, the faces substantially normal to the axis of the smallest dimension of the shell consist either of M or E.

According to one embodiment, the smallest dimension of the shell comprises either an alternate of atomic layers of M and E.

According to one embodiment, the number of atomic layers of M in the shell is equal to one plus the number of atomic layer of E.

According to an embodiment, the material composing the shell comprises a material MxNyEz, wherein:

- M is selected from Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or a mixture thereof;
- N is selected from Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or a mixture thereof;
- E is selected from O, S, Se, Te, N, P, As, F, Cl, Br, I, or a mixture thereof; and

x, y and z are independently a decimal number from 0 to 5, at the condition that when x is 0, y and z are not 0, when y is 0, x and z are not 0 and when z is 0, x and y are not 0.

According to a preferred embodiment, the material composing the shell comprises a material MxEy wherein:

M is selected from group Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, VIII or mixtures thereof;

E is selected from group Va, VIa, VIIa or mixtures thereof; and

x and y are independently a decimal number from 0 to 5.

According to one embodiment, the material composing the shell comprises a semi-conductor from group IIb-VIa, group IVa-VIa, group Ib-IIIa-VIa, group IIb-IVa-Va, group Ib-VIa, group VIII-VIa, group IIb-Va, group IIIa-VIa, group IVb-VIa, group IIa-VIa, group IIIa-Va, group IIIa-VIa, group VIb-VIa, or group Va-VIa.

According to one embodiment, the material composing the shell comprises at least one semiconductor chosen among CdS, CdSe, CdTe, CdO, Cd_3P_2, Cd_3As_2, ZnS, ZnSe, ZnO, ZnTe, Zn_3P_2, Zn3As2, HgS, HgSe, HgTe, HgO, GeS, GeSe, GeTe, SnS, SnS_2, $SnSe_2$, SnSe, SnTe, PbS, PbSe, PbTe, GeS_2, $GeSe_2$, $CuInS_2$, $CuInSe_2$, CuS, Cu_2S, Ag_2S, Ag_2Se, Ag_2Te $AgInS_2$, $AgInSe_2$, FeS, FeS_2, FeO, Fe_2O_3, Fe_3O_4, Al_2O_3, TiO_2, MgO, MgS, MgSe, MgTe, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, In_2S_3,TlN, TlP, TlAs, TlSb, Bi_2S_3, Bi_2Se_3, Bi_2Te_3, MoS_2, WS_2, VO_2 or a mixture thereof.

According to one embodiment, the shell comprises an alloy or a gradient of the aforementioned materials.

According to a preferred embodiment, the shell is an alloy or a gradient the group consisting of CdS, CdSe, CdSSe, CdTe, ZnS, CdZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, $CuInS_2$, $CuInSe_2$, $AgInS_2$, $AgInSe_2$, CuS, Cu_2S, Ag_2S, Ag_2Se, Ag_2Te, FeS, FeS_2, PdS, Pd_4S, WS_2 or a mixture thereof.

According to one embodiment, the shell is an alloy of $Cd_xZn_{1-x}S$ with x ranging from 0 to 1. According to one embodiment, the shell is a gradient of CdZnS.

According to a preferred embodiment, the final core/shell nanoplatelet is selected from the group consisting of CdSe/CdS; CdSe/CdZnS; CdSe/ZnS; CdSeTe/CdS; CdSeTe/CdZnS; CdSeTe/ZnS; CdSSe/CdS; CdSSe/CdZnS; CdSSe/ZnS.

According to a preferred embodiment, the final core/shell nanoplatelet is selected from the group consisting of CdSe/CdS/ZnS; CdSe/CdZnS/ZnS; CdSeTe/CdS/ZnS; CdSeTe/CdZnS/ZnS; CdSeTe/ZnS; CdSSe/CdS/ZnS; CdSSe/CdZnS/ZnS; CdSSe/ZnS.

According to one embodiment, the final nanoplatelet is homostructured, i.e. the initial nanoplatelet and the shell are composed of the same material.

In one embodiment, the final nanoplatelet is heterostructured, i.e. the initial nanoplatelet and the shell are composed of at least two different materials.

According to one embodiment, the final nanoplatelet comprises the initial nanoplatelet and a sheet comprising at least one layer covering all of the initial nanoplatelet. Said layer being composed of the same material as the initial nanoplatelet or a different material than the initial nanoplatelet.

According to one embodiment, the final nanoplatelet comprises the initial nanoplatelet and a shell comprising 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 50 or more monolayers covering all of the initial nanoplatelet. Said layers being of same composition as the initial nanoplatelet or being of different composition than the initial nanoplatelet or being of different composition one to another.

According to one embodiment, the final nanoplatelet comprises the initial nanoplatelet and a shell comprising at least 5, 6, 7, 8, 9, 10, 15, 20, 25, 50 or more monolayers covering all of the initial nanoplatelet. Said layers being of same composition as the initial nanoplatelet or being of different composition than the initial nanoplatelet or being of different composition one to another.

According to one embodiment, the faces substantially normal to the axis of the smallest dimension of the final nanoplatelet consist either of M or E.

According to one embodiment, the smallest dimension of the final nanoplatelet comprises either an alternate of atomic layers of M and E.

According to one embodiment, the number of atomic layers of M in the final nanoplatelet is equal to one plus the number of atomic layer of E.

According to one embodiment, the shell is homogeneous thereby producing a final nanoplatelet.

According to one embodiment, the shell comprises a substantially identical thickness on each facet on the initial nanoplatelet.

The present invention relates to a process of growth of a shell on initial colloidal nanoplatelets.

According to one embodiment, the initial nanoplatelet is obtained by any method known from one skilled in the art.

According to one embodiment, the process of growth of a shell comprises the growth of a homogeneous shell on each facet of the initial colloidal nanoplatelet.

According to one embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the steps of injecting the initial colloidal nanoplatelets in a solvent at a temperature ranging from 200°C to 460°C and subsequently a precursor of E or M, wherein said precursor of E or M is injected slowly in order to control the shell growth rate; and wherein the precursor of respectively M or E is injected either in the solvent before injection of the initial colloidal nanoplatelets or in the mixture simultaneously with the precursor of respectively E or M.

According to one embodiment, the initial colloidal nanoplatelets are mixed with a fraction of the precursor's mixture before injection in the solvent.

According to one embodiment, the process of growth of a MxEy shell on initial colloidal nanoplatelets comprises the steps of injecting the initial colloidal nanoplatelets in a solvent at a temperature ranging from 200°C to 460°C and subsequently a precursor of E or M, wherein said precursor of E or M is injected slowly in order to control the shell growth rate; and wherein the precursor of respectively M or E is injected either in the solvent before injection of the initial colloidal nanoplatelets or in the mixture simultaneously with the precursor of respectively E or M; wherein x and y are independently a decimal number from 0 to 5.

According to one embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the following steps:

- heating a solvent at a temperature ranging from 200°C to 460°C;
- injecting in the solvent the initial colloidal nanoplatelets;
- injecting slowly in the mixture the precursor of E and the precursor of M;

- recovering the core/shell structure in the form of nanoplatelets.

According to another embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the following steps:

- heating a solvent at a temperature ranging from 200°C to 460°C;
- injecting a precursor of M in the solvent;
- injecting in the mixture the initial colloidal nanoplatelets;
- injecting slowly in the mixture the precursor of E;
- recovering the core/shell structure in the form of nanoplatelets.

According to another embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the following steps:

- heating a solvent at a temperature ranging from 200°C to 460°C;
- injecting a precursor of E in the solvent;
- injecting in the mixture the initial colloidal nanoplatelets;
- injecting slowly in the mixture the precursor of M;
- recovering the core/shell structure in the form of nanoplatelets.

According to another embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the following steps:

- heating a solvent at a temperature ranging from 200°C to 460°C;
- injecting in the solvent the initial colloidal nanoplatelets, optionally mixed with a fraction of the precursors mixture;
- injecting slowly in the mixture the precursor of E and the precursor of M;
- recovering the core/shell structure in the form of nanoplatelets.

Herein the term "fraction of the precursors mixture" refers to a part of the total amount of precursors used in the reaction, i.e. from 0.001% to 50 %, preferably from 0.001% to 25%, more preferably from 0.01% to 10% of the total amount of the injected precursors mixture.

According to another embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the following steps:

- providing a solvent and a precursor of M;

- heating the mixture of the solvent and the precursor of M at a temperature ranging from 200°C to 460°C;
- injecting in the mixture the initial colloidal nanoplatelets;
- injecting slowly in the mixture the precursor of E;
- recovering the core/shell structure in the form of nanoplatelets.

According to another embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets comprises the following steps:

- providing a solvent and a precursor of E;
- heating the mixture of the solvent and the precursor of E at a temperature ranging from 200°C to 460°C;
- injecting in the mixture the initial colloidal nanoplatelets;
- injecting slowly in the mixture the precursor of M;
- recovering the core/shell structure in the form of nanoplatelets.

According to one embodiment, the initial colloidal nanoplatelets have a core/shell structure.

According to one embodiment, the process of growth of core/shell nanoplatelets comprising a ME shell on initial colloidal nanoplatelets further comprises the step of maintaining the mixture at a temperature ranging from 200°C to 460°C during a predetermined duration ranging from 5 to 180 minutes after the end of the injection of the second precursor.

According to one embodiment, the temperature of the annealing ranges from 200°C and 460°C, from 275°C to 365°C, from 300°C to 350°C or about 300°C.

According to one embodiment, the duration of the annealing ranges from 1 to 180 minutes, from 30 to 120 minutes, from 60 to 120 minutes or about 90 minutes.

According to one embodiment, the initial colloidal nanoplatelets are injected over a period of less than 10 minutes, less than 5 minutes, less than 1 minute, less than 30 seconds, less than 10 seconds, less than 5 seconds or less than 1 second. According to one embodiment, the initial colloidal nanoplatelets are injected at once.

According to one embodiment, the initial colloidal nanoplatelets are injected at a rate ranging from 1 mL/s to 1 L/s, from 1 mL/s to 100 mL/s, from 1 mL/s to 10 mL/s, from 2 to 8 mL/s or about 5 mL/s.

According to one embodiment, the injection of the precursor of E or the precursor of M of the shell is performed at a rate ranging from 0.1 to 30 mole/h/mole of M present in the initial nanoplatelet, preferably from 0.2 to 20 mole/h/mole of M present in the initial nanoplatelet, more preferably from 1 to 21 mole/h/mole of M present in the initial nanoplatelets.

According to one embodiment, the precursor of E or the precursor of M is injected slowly i.e. over a period ranging from 1 minutes to 2 hours, from 1 minute to 1 hour, from 5 to 30 minutes or from 10 to 20 minutes for each monolayer.

According to one embodiment, the precursor of E is injected slowly, i.e. at a rate ranging from 0.1 mL/h to 10 L/h, from 0.5 mL/h to 5 L/h or from 1 mL/h to 1 L/h.

According to one embodiment, the precursor of M is injected slowly, i.e. at a rate ranging from 0.1 mL/h to 10 L/h, from 0.5 mL/h to 5 L/h or from 1 mL/h to 1 L/h.

According to one embodiment, the precursor of E and the precursor of M are injected slowly in order to control the shell growth rate.

According to one embodiment wherein the precursor of M or the precursor of E is injected prior to the initial colloidal nanoplatelets, said precursor of M or said precursor of E is injected over a period of less than 30 seconds, less than 10 seconds, less than 5 seconds, less than 1 second. According to another embodiment wherein the precursor of M or the precursor of E is injected prior to the initial colloidal nanoplatelets, said precursor of M or said precursor of E is injected slowly, i.e. at a rate ranging from 0.1 mL/h to 10 L/h, from 0.5 mL/h to 5 L/h or from 1 mL/h to 1 L/h. According to one embodiment, the precursor of M or the precursor of E injected prior to the initial colloidal nanoplatelets is injected faster than the precursor of M or the precursor of E injected after the initial colloidal nanoplatelets.

According to one embodiment, the injection's rate of at least one of the precursor of E and/or the precursor of M is chosen such that the growth rate of the shell is ranging from 1 nm per second to 0.1 nm per hour.

According to one embodiment, the growth process is performed at temperature ranging from 200°C to 460°C, from 275°C to 365°C, from 300°C to 350°C or about 300°C.

According to one embodiment, the reaction is performed under an inert atmosphere, preferably nitrogen or argon atmosphere.

According to one embodiment, the precursor of E is capable of reacting with the precursor of M to form a material with the general formula ME.

According to one embodiment, the precursor of the shell to be deposited is a precursor of a material MxEy, wherein:
M is Zn, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V, Nd, Ta, Ti, Zr, Hf, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or a mixture thereof,
E is O, S, Se, Te, N, P, As, F, Cl, Br, I, or a mixture thereof,
and x and y are independently a decimal number from 0 to 5.

According to an embodiment, the precursor of the shell to be deposited is a material MxEy comprising cationic element M and anionic element E in stoichiometric ratio, said stoichiometric ratio being characterized by values of x and y corresponding to absolute values of mean oxidation number of elements E and M respectively.

According to a preferred embodiment, the precusrsor of the shell to be deposited is a precursor of a material MxEy wherein:
M is selected from group Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Vb, VIb, VIIb, VIII or mixtures thereof;
E is selected from group Va, VIa, VIIa or mixtures thereof; and
x and y are independently a decimal number from 0 to 5.

According to one embodiment, the precursor of the shell to be deposited is a precursor of a compound of group IIb-VIa, group IVa-VIa, group Ib-IIIa-VIa, group IIb-IVa-Va, group Ib-VIa, group VIII-VIa, group IIb-Va, group IIIa-VIa, group IVb-VIa, group IIa-VIa, group IIIa-Va, group IIIa-VIa, group VIb-VIa, or group Va-VIa.

According to one embodiment, the precursor of the shell to be deposited is a precursor of a material chosen among CdS, CdSe, CdTe, CdO, Cd_3P_2, Cd_3As_2, ZnS, ZnSe, ZnO, ZnTe, Zn_3P_2, Zn3As2, HgS, HgSe, HgTe, HgO, GeS, GeSe, GeTe, SnS, SnS_2, $SnSe_2$, SnSe, SnTe, PbS, PbSe, PbTe, GeS_2, $GeSe_2$, $CuInS_2$, $CuInSe_2$, CuS, Cu_2S, Ag_2S, Ag_2Se, Ag_2Te $AgInS_2$, $AgInSe_2$, FeS, FeS_2, FeO, Fe_2O_3, Fe_3O_4, Al_2O_3, TiO_2, MgO, MgS, MgSe, MgTe, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, In_2S_3,TlN, TlP, TlAs, TlSb, Bi_2S_3, Bi_2Se_3, Bi_2Te_3, MoS_2, WS_2, VO_2 or a mixture thereof.

According to a preferred embodiment, the precursor of the shell to be deposited is a precursor of a material selected from the group consisting of CdS, CdSe, CdSSe, CdTe, ZnO, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, $CuInS_2$, $CuInSe_2$, $AgInS_2$, $AgInSe_2$, CuS, Cu_2S, Ag_2S, Ag_2Se, Ag_2Te, FeS, FeS_2, PdS, Pd_4S, WS_2or a mixture thereof.

According to one embodiment, if E is a chalcogenide, the precursor of E is a compound containing the chalcogenide at the -2 oxidation state. According to one embodiment, if E is a chalcogenide, the precursor of E is formed in situ by reaction of a reducing agent with a compound containing E at the 0 oxidation state or at a strictly positive oxidation state.

According to one embodiment, if E is sulfur, the precursor of E is a thiol. According to one embodiment, if E is sulfur, the precursor of E is propanethiol, buanethiol, pentanethiol, hexanethiol, heptanethiol, octanethiol, decanethiol, dodecanethiol, tetradecanethiol or hexadecanethiol. According to one embodiment, if E is sulfur, the precursor of E is a salt containing S^{2-} sulfide ions. According to one embodiment, if E is sulfur, the precursor of E comprises bis(trimethylsilyl) sulfide (TMS_2S) or hydrogen sulfide (H_2S) or sodium hydrogen sulfide (NaSH) or sodium sulfide (Na_2S) or ammonium sulfide ($S(NH_4)_2$) or thiourea or thioacetamide. According to one embodiment, if E is sulfur, the precursor of E is sulfur dissolved in a suitable solvent. According to one embodiment, if E is sulfur, the precursor of E is sulfur dissolved in 1-octadecene. According to one embodiment, if E is sulfur, the precursor of E is sulfur dissolved in a phosphine. According to one embodiment, if E is sulfur, the precursor of E is sulfur dissolved in trioctylphosphine or tributylphosphine. According to one embodiment, if E is sulfur, the precursor of E is sulfur dissolved in an amine. According to one embodiment, if E is sulfur, the precursor of E is sulfur dissolved in oleylamine. According to one embodiment, if E is sulfur, the precursor of E is sulfur powder dispersed in a solvent. According to one embodiment, if E is sulfur, the precursor of E is sulfur powder dispersed in 1-octadecene.According to one embodiment, if E is selenium; the precursor of E comprises a salt containing Se^{2-} selenide ions. According to one embodiment, the precursor of E comprises bis(trimethylsilyl) selenide (TMS_2Se) or hydrogen selenide (H_2Se) or sodium selenide (Na_2Se) or sodium hydrogen selenide (NaSeH) or sodium selenosulfate (Na_2SeSO_3) or selenourea. According to one embodiment, if E is selenium, the precursor of E is a selenol. According to one embodiment, if E is selenium, the precursor of E is a diselenide, such as Diphenyl diselenide. According to one embodiment, if E is selenium, the precursor of E is selenium dissolved in a suitable solvent. According to one embodiment, if E is selenium, the precursor of E is selenium dissolved in 1-octadecene. According to one embodiment, if E is selenium, the precursor of E is selenium dissolved in a phosphine. According to one embodiment, if E is selenium, the precursor of E is selenium dissolved in trioctylphosphine or tributylphosphine. According to one embodiment, if E is selenium, the precursor of E is selenium dissolved in an amine. According to one embodiment, if E is selenium, the precursor of E is selenium dissolved in an amine and thiol mixture. According to one embodiment, if E is selenium, the precursor of E is selenium powder dispersed in a solvent. According to one embodiment, if E is selenium, the precursor of E is selenium powder dispersed in 1-octadecene.

According to one embodiment, if E is tellurium, the precursor of E is as salt containing Te^{2-} telluride ions. According to one embodiment, if E is tellurium, the precursor of E comprises bis(trimethylsilyl) telluride (TMS_2Te) or hydrogen telluride (H_2Te) or sodium telluride (Na_2Te) or sodium hydrogen telluride (NaTeH) or sodium tellurosulfate (Na_2TeSO_3) or tellurourea. According to one embodiment, if E is tellurium, the precursor of E is tellurium dissolved in a suitable solvent. According to one embodiment, if E is tellurium, the precursor of E is tellurium dissolved a phosphine. According to one embodiment, if E is tellurium, the precursor of E is tellurium dissolved in trioctylphosphine or tributylphosphine.

According to one embodiment, if E is oxygen, the precursor of E is the hydroxide ion (HO^-). According to one embodiment, if E is oxygen the precursor of E is a solution of sodium hydroxide (NaOH) or of potassium hydroxide (KOH) or of tetramethylammonium hydroxide (TMAOH). According to one embodiment, if E is oxygen, the precursor of E is generated in-situ by condensation between an amine and a carboxylic acid. According to one embodiment, if E is oxygen, the precursor of E is generated in-situ by condensation of two carboxylic acids.

According to one embodiment, if E is phosphorus, the precursor of E comprises phosphorus at the -3 oxidation state. According to one embodiment, the precursor of E comprises tris(trimethylsilyl) phosphine (TMS_3P) or phosphine (PH_3) or white phosphorus (P_4) or phosphorus trichloride (PCl_3). According to one embodiment, the precursor of E comprises a tris(dialkylamino)phosphine for example tris(dimethylamino)phosphine ($(Me_2N)_3P$) or tris(diethylamino)phosphine ($(Et_2N)_3P$). According to one embodiment, the precursor of E comprises a trialkylphosphine for example trioctylphosphine or tributylphosphine or triphenylphosphine.

According to one embodiment, if M is a metal, the precursor of M is a compound containing the metal at positive or 0 oxidation state. According to one embodiment, if M is a metal, the precursor of M comprises a metallic salt. In one embodiment, the metallic salt is a carboxylate of M, or a chloride of M, or a bromide of M, or a iodide of M, or a nitrate of M, or a sulfate of M, or a thiolate of M. According to one embodiment, the shell comprises a metal.

According to one embodiment, the shell to be deposited comprises a chalcogenide, a phosphide, a nitride, an arsenide or an oxide.

According to one embodiment, the initial nanosheet is dispersed in a solvent. According to one embodiment, the solvent is organic, preferably apolar or weakly polar. According to one embodiment, the solvent is a supercritical fluid or an ionic fluid. According to one embodiment, the solvent is selected from pentane, hexane, heptane, cyclohexane, petroleum ether, toluene, benzene, xylene, chlorobenzene, carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane, THF (tetrahydrofuran), acetonitrile, acetone, ethanol, methanol, ethyl acetate, ethylene glycol, diglyme (diethylene glycol dimethyl ether), diethyl ether, DME (1,2-dimethoxy-ethane, glyme), DMF (dimethylformamide), NMF (N-methylformamide), FA (Formamide), DMSO (dimethyl sulfoxide), 1,4-Dioxane, triethyl amine or mixture thereof.

According to one embodiment, the shell comprises an additional element in minor quantities. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, the shell comprises a transition metal or a lanthanide in minor quantities. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, the shell comprises in minor quantities an element inducing an excess or a defect of electrons compared to the sole film. The term “minor quantities” refers herein to quantities ranging from 0.0001% to 10% molar, preferably from 0.001% to 10% molar.

According to one embodiment, a reducing agent is introduced at the same time as at least one of the precursor of M and/or E. In one embodiment, the reducing agent comprises a hydride. Said hydride may be selected from sodium tetrahydroborate (NaBH4); sodium hydride (NaH), lithium tetrahydroaluminate (LiAlH4), diisobutylaluminum hydride (DIBALH). In one embodiment, the reducing agent comprises dihydrogen.

According to one embodiment, a stabilizing compound capable of stabilizing the final nanoplatelet is introduced in the solvent.

According to one embodiment, a stabilizing compound capable of stabilizing the final nanoplatelet is introduced in anyone of the precursor solutions.

According to one embodiment, the stabilizing compound of the final nanoplatelet comprises an organic ligand. Said organic ligand may comprise a carboxylic acid, a thiol, an amine, a phosphine, a phosphine oxide, a phosphonic acid, a phosphinic acid, an amide, an ester, a pyridine, an imidazole and/or an alcohol.

According to one embodiment, the stabilizing compound of the final nanoplatelet is an ion. Said ion comprises a quaternary ammonium.

According to one embodiment, the initial nanosheet is fixed on a least one substrate.

According to one embodiment, the fixation of the initial nanosheet on said substrate is performed by adsorption or chemical coupling.

According to one embodiment, said substrate is chosen among silica SiO_2, aluminum oxide Al_2O_3, indium-tin oxide ITO, fluorine-doped tin oxide FTO, titanium oxide TiO_2, gold, silver, nickel, molybdenum, aluminum, silicium, germanium, silicon carbide SiC, graphene and cellulose.

According to one embodiment, said substrate comprises a polymer.

According to one embodiment, the excess of precursors is discarded after the reaction.

According to one embodiment, the final nanoplatelet obtained after reaction of the precursors on the initial nanosheets is purified. Said purification is performed by flocculation and/or precipitation and/or filtration; such as for example successive precipitation in ethanol.

The present invention also relates to a population of semiconductor nanoplatelets, each member of the population comprising a nanoplatelet core including a first semiconductor material and at least one shell including a second semiconductor material on the surface of the nanoplatelet core, wherein after ligand exchange reaction the population exhibits a quantum yield decrease of less than 50%.

According to one embodiment, the population of semiconductor nanoplatelets of the present invention exhibit, after ligand exchange, a quantum yield decrease of less than 50%, less than 40%, less than 30%, less than 25%, less than 20%, less than 15% or less than 10%.

Especially, according to one embodiment, after transfer into an aqueous solution by ligand exchange reaction, the quantum yield of the population of nanoplatelets according to the present invention decrease of less than 50%, less than 40%, less than 30%, less than 25%, less than 20%, less than 15% or less than 10%.

According to one embodiment, the ligand is an organic ligand with a carbonated chain length between 1 and 30 carbons.

According to one embodiment, the ligand is a polymer.

According to one embodiment, the ligand is a hydrosoluble polymer.

According to one embodiment, the selected ligand may comprise a carboxylic acid, a thiol, an amine, a phosphine, a phosphine oxide, a phosphonic acid, a phosphinic acid, an amide, an ester, a pyridine, an imidazole and/or an alcohol.

According to one embodiment, the ligand is selected from myristic acid, stearic acid, palmitic acid, oleic acid, behenic acid, dodecanethiol, oleylamine, 3-mercaptopropionic acid.

According to one embodiment, the selected ligand may be any number of materials, but has an affinity for the semiconductor surface. In general, the capping agent can be an isolated organic molecule, a polymer (or a monomer for a polymerization reaction), an inorganic complex, and an extended crystalline structure.

According to one embodiment, the ligand exchange procedure comprises the step of treating a solution of nanoplatelets according to the invention with a ligand.

The present invention also relates to a population of semiconductor nanoplatelets wherein the population exhibits stable fluorescence quantum efficiency over time. According to one embodiment, the population of nanoplatelets, wherein each member of the population comprising a nanoplatelet core including a first semiconductor material and a shell including a second semiconductor material on the surface of the nanoplatelet core, exhibits fluorescence quantum efficiency decrease of less than 50%, less than 40%, less than 30% after one hour under light illumination with a photon flux of at least 1W.cm^{-2}, 5W.cm^{-2}, 10W.cm^{-2}, 12W.cm^{-2}, 15W.cm^{-2}.

According to one embodiment, the light illumination is provided by blue or UV light source such as laser, diode or Xenon Arc Lamp.

According to one embodiment, the photon flux of the illumination is comprised between 1mW.cm^{-2} and 100W.cm^{-2}, between 10mW.cm^{-2} and 50W.cm^{-2}, between 1W.cm^{-2} and 15W.cm^{-}2, or between 10mW.cm^{-2} and 10W.cm^{-2}.

According to one embodiment, the population of nanoplatelets, wherein each member of the population comprising a nanoplatelet core including a first semiconductor material and a shell including a second semiconductor material on the surface of the nanoplatelet core, exhibits fluorescence quantum efficiency decrease of less than 80%, less than 70%, less than 60%, less than 50%, less than 40%, less than 30%, less than 20% or less than 15% after 2 months after a ligand exchange.

According to one embodiment, the semiconductor nanoplatelets of the invention exhibit enhanced stability in time compared to quantum dots and nanoplatelets of the prior art.

According to one embodiment, the semiconductor nanoplatelets of the invention exhibit enhanced stability in temperature compared to quantum dots and nanoplatelets of the prior art.

According to one embodiment, the core/shell nanoplatelets according to the present invention exhibit stable fluorescence quantum efficiency in temperature. Especially, according to one embodiment, the population of semiconductor nanoplatelets according to the invention exhibits fluorescence quantum efficiency at 100 °C or above that is at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% of the fluorescence quantum efficiency of the population at 20°C. According to one embodiment, the temperature is in a range from 100°C to 250°C, from 100°C to 200°C, from 110°C to 160°C or about 140°C. According to one embodiment, the population of semiconductor nanoplatelets according to the invention exhibits fluorescence quantum efficiency at

200°C that is at least 50%, at least 60%, at least 70%, at least 80% or at least 90% of the fluorescence quantum efficiency of the population at 20°C.

According to one embodiment, the population of nanoplatelets according to the present invention exhibit emission spectra with a full width half maximum lower than 50, 40, 30, 25 nm or 20 nm.

The present invention also relates to nanoplatelets film exhibiting desirable characteristics for use in display devices, such as narrow full width at half maximum, high quantum yield and resistance to photo-bleaching.

According to one embodiment, the nanoplatelets film comprises a host material, preferably a polymeric host material and emissive semiconductor nanoparticles embedded in said host material, wherein at least 20% of said emissive semiconductor nanoparticles are colloidal nanoplatelets according the invention.

In one embodiment, at least 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% of said emissive semiconductor nanoparticles are colloidal core/shell nanoplatelets according to the present invention. In one embodiment, substantially all of said emissive semiconductor nanoparticles are colloidal core/shell nanoplatelets according to the present invention.

In one embodiment the nanoplatelets film comprises less than 50% in weight of emissive semiconductor nanoparticles, preferentially less than 10%.

In one embodiment the nanoplatelets film has a thickness between 30nm and 1cm, more preferably between 100nm and 1mm, even more preferably between 100nm and 500μm.

In one embodiment, the nanoplatelets film refers to a layer, sheet or film of host material that comprises a plurality of nanoplatelets.

In one embodiment, the nanoplatelets comprise an outer ligand coating and are dispersed in the host material, preferably a polymeric host material. In one embodiment, the host material is transparent in the visible range of wavelength.

In one embodiment the polymeric host material used to include the nanoplatelets is chosen among: silicone-based polymers, polydimethylsiloxanes (PDMS), polyethylene terephthalate, polyesters, polyacrylates, polymethacrylates, polycarbonate, poly(vinyl alcohol), polyvinylpyrrolidone, polyvinylpiridine, polysaccharides, poly(ethylene glycol), melamine resins, a phenol resin, an alkyl resin, an epoxy resin, a polyurethane resin, a maleic resin, a polyamide resin, an alkyl resin, a maleic resin, terpenes resins, copolymers forming the resins, polymerizable monomers comprising an UV initiator or thermic initiator.

In one embodiment the polymeric host material used to include the nanoplatelets is a polymerized solid made from an alkyl methacrylates or an alkyl acrylates such as acrylic acid, methacrylic acid, crotonic acid, acrylonitrile, acrylic esters substituted with methoxy, ethoxy, propoxy, butoxy, and similar derivatives for example, methyl acrylate, ethyle acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, lauryl acrylate, norbornyl acrylate, 2-ethyl hexyl acrylate, 2-hydroxyethyl acrylate, 4-hydroxybutyl acrylate, benzyl acrylate, phenyl acrylate, isobornyle acrylate, hydroxypropyl acrylate, fluorinated acrylic monomers, chlorinated acrylic monomers, methacrylic acid, methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethyl hexyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl methacrylate, benzyl methacrylate, phenyl methacrylate, lauryl methacrylate, norbornyl methacrylate, isobornyle methacrylate, hydroxypropyl methacrylate, fluorinated methacrylic monomers, chlorinated methacrylic monomers, alkyl crotonates, allyl crotonates, glycidyl methacrylate and related esters.

In one embodiment the polymeric host material may be a polymerized solid made from an alkyl acrylamide or alkyl méthacrylamide such as acrylamide, Alkylacrylamide, N-tert-Butylacrylamide, Diacetone acrylamide, N,N-Diethylacrylamide, N-(Isobutoxymethyl)acrylamide, N-(3-Methoxypropyl)acrylamide, N-Diphenylmethylacrylamide, N-Ethylacrylamide, N-Hydroxyethyl acrylamide, N-(Isobutoxymethyl)acrylamide, N-Isopropylacrylamide, N-(3-Methoxypropyl)acrylamide, N-Phenylacrylamide, N-[Tris(hydroxymethyl)methyl]acrylamide, N,N-Diethylmethacrylamide, N,N-Dimethylacrylamide, N-[3-(Dimethylamino)propyl]méthacrylamide, N-

(Hydroxymethyl)acrylamide, 2-Hydroxypropyl méthacrylamide, N-Isopropylmethacrylamide, Methacrylamide, N-(Triphenylmethyl)méthacrylamide and similar derivatives.

In one embodiment the polymeric host material used to include the nanoplatelets comprises PMMA, Poly(lauryl methacrylate), glycolized poly(ethylene terephthalate), Poly(maleic anhydride –alt-octadecene) and mixtures thereof.

In one embodiment the polymeric host material used to include the nanoplatelets is a polymerized solid made from allyl methacrylate, benzyl methyl acrylate, 1,3- butanediol dimethacrylate, 1,4-butanediol dimethacrylate, butyl acrylate, n-butyl methacrylate, ethyl methacrylate, 2-ethyl hexyl acrylate, 1,6-hexanediol dimethacrylate, 4- hydroxybutyl acrylate, hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- hydroxypropyl acrylate, isobutyl methacrylate, lauryl methacrylate, methacrylic acid, methyl acrylate, 2,2,3,3 ,4,4,5,5-octafluoropentyl acrylate, pentaerythritol triacrylate, 2,2,2- trifluoroethyl 2-methyl acrylate, trimethylolpropane triacrylate, acrylamide n,n,-methylene- bisacryl-amide phenyl acrylate, and divinyl benzene.

In one embodiment the polymeric host material used to include the nanoplatelets is a polymerized solid made from alpha-olefins, dienes such as butadiene and chloroprene; styrene, alpha-methyl styrene, and the like; heteroatom substituted alpha-olefins, for example, vinyl acetate, vinyl alkyl ethers for example, ethyl vinyl ether, vinyltrimethylsilane, vinyl chloride, tetrafluoroethylene, chlorotrifiuoroethylene, cyclic and polycyclic olefin compounds for example, cyclopentene, cyclohexene, cycloheptene, cyclooctene, and cyclic derivatives up to C20; polycyclic derivates for example, norbornene, and similar derivatives up to C20; cyclic vinyl ethers for example, 2, 3-dihydrofuran, 3,4-dihydropyran, and similar derivatives; allylic alcohol derivatives for example, vinylethylene carbonate, disubstituted olefins such as maleic and fumaric compounds for example, maleic anhydride, diethylfumarate, and the like, and mixtures thereof.

In one embodiment the polymeric host material used to include the nanoplatelets is deposited under its final form tanks to spincoating, dipcoating, electrophoretic deposition, dropcasting. In one embodiment the polymeric host material is mixed with the nanoplatelets thanks to an extrusion process.

According to one embodiment, the nanoplatelets film further comprises scattering elements dispersed in the host material.

In one embodiment, the nanoplatelets film comprises at least one population of nanoplatelets. In the present application a population of nanoplatelets is defined by the maximum emission wavelength.

In one embodiment the nanoplatelets film comprises two populations of nanoplatelets with different colors. In one embodiment, the nanoplatelets film consists of nanoplatelets which emit green light and red light upon down-conversion of a blue light source. Thus, the blue light from the light source(s) pass through the nanoplatelets film, where predetermined amounts of green and red light are mixed with the remaining blue light to create the tri-chromatic white light.

In one embodiment, the nanoplatelets film comprises two populations of nanoplatelets, a first population with a maximum emission wavelength between 500 nm and 560 nm, more preferably between 515 nm and 545 nm and a second population with a maximum emission wavelength between 600 nm and 700 nm, more preferably between 610 nm and 650 nm.

In one embodiment the nanoplatelets film comprises two populations of core/shell nanoplatelets with different color. In one embodiment the nanoplatelets film comprises two populations of core/shell nanoplatelets one is green and one is red, see figure 5.

In one embodiment the nanoplatelets films comprises a blend of two populations of core/shell nanoplatelets with different colors.

In one embodiment the nanoplatelets films is splitted in several area each of them comprise a different population having different color of core/shell nanoplatelets.

In one embodiment the nanoplatelets film is made of a stack of two films, each of them comprises a different population of nanoplatelets having a different color.

In on embodiment, the nanoplatelets film is encapsulated into a multi-layered system. In one embodiment, the encapsulated nanoplatelets film is made of at least three layers. According to one embodiment, the two external layers provide scattering properties.

In one embodiment, the nanoplatelets film is covered by at least one insulating layer or sandwiched by at least two insulating layers, see figure 1. In one embodiment, the nanoplatelets film is enclosed in an O_2 and/or H_2O non-permeable layer. In one embodiment, the O_2 and/or H_2O insulating layer can be made of glass, PET, PDMS… According to one embodiment, the nanoplatelets film is enclosed in a layer configured to reduce exposure of the nanoplatelets film to O_2 and H_2O, such as glass, PET, PDMS... In one embodiment, the insulating layer includes but is not limited to glass, PET (Polyethylene terephthalate), PDMS (Polydimethylsiloxane), PES (Polyethersulfone), PEN (Polyethylene naphthalate), PC (Polycarbonate), PI (Polyimide), PNB (Polynorbornene), PAR (Polyarylate), PEEK (Polyetheretherketone), PCO (Polycyclic olefins), PVDC (Polyvinylidene chloride), Nylon, ITO (Indium tin oxide), FTO (Fluorine doped tin oxide), cellulose, Al_2O_3, AlO_xN_y, SiO_xC_y, SiO_2, SiO_x, SiN_x, SiC_x, ZrO2, TiO_2, ceramic, organic modified ceramic and mixture thereof.

In one embodiment, the encapsulated nanoplatelets film also comprises at least one transparent substrate.

In one embodiment the polymer host material comprising the nanoplatelets is protected from air by an additional layer. In one embodiment the polymer host material comprising the nanoplatelets is protected from air by UV curable polymer. In one embodiment the host material comprising the nanoplatelets is protected from air by UV curable resin. In one embodiment the polymer host material comprising the nanoplatelets is protected from air by a mixture of bisphenol A glycerolate, lauryl methacrylate and an UV initiator such as benzophenone or 3,4 dimethylbenzophenone.

In one embodiment the core/shell nanoplatelets have a polarized emission. According to one embodiment, the polarized emission of core/shell nanoplatelets is used to build a 3D display.

In one embodiment the nanoplatelets film is illuminated using UV light with a wavelength ranging from 200 to 400 nm. In one embodiment the nanoplatelets film is illuminated using a blue LED with a wavelength ranging from 400nm to 470nm such as for instance a gallium nitride based diode. In one embodiment the nanoplatelets films is deposited on a blue LED with a wavelength ranging from 400nm to 470nm. In one embodiment the nanoplatelets films is deposited on a LED with an emission peak at about 405 nm. In one embodiment the nanoplatelets films is deposited on a LED with an emission peak at about 447 nm. In one embodiment the nanoplatelets films is deposited on a LED with an emission peak at about 455 nm. In one embodiment the material encapsulating the nanoplatelets is illuminated by a photon flux between 1 $\mu W.cm^{-2}$ and 1 $kW.cm^{-2}$ and more preferably between 1 $mW.cm^{-2}$ and 100 $W.cm^{-2}$, and even more preferably between between $1mW.cm^{-2}$ and $10W.cm^{-2}$. In one embodiment the material encapsulating the nanoplatelets is illuminated by a photon flux of 12 $W.cm^{-2}$. In one embodiment the core/shell nanoplatelets are used to downshift the light from a blue or UV source. In one embodiment, the term light source may also relate to a plurality of light source.

In one embodiment the LED used to illuminate the nanoplatelets film is a GaN diode, a InGaN diode, a GaAlN diode, a GaAlPN diode, a AlGaAs diode, a AlGaInP diode, a AlGaInN diode. In one embodiment the encapsulated nanoplatelets film is directly deposited on the blue LED. In one embodiment the material comprising the encapsulated nanoplatelets film is directly deposited on the blue LED by spaycoating, dip-coating.

In one embodiment the nanoplatelets film is not in contact with the blue or UV source of light.

In one embodiment, the nanoplatelets film further comprises scattering elements dispersed in the host material. In one embodiment a scattering system is used between the blue or UV LED and the encapsulated nanoplatelets film.

In one embodiment a scattering system is used to scatter the light downshifted by the system composed of a blue or UV light and the material including the core/shell nanoplatelets.

In one embodiment the material encapsulating the nanoplatelets is operated at a temperature between -50°C and 150°C and more preferably between -30°C and 120°C. In one embodiment the material encapsulating the nanoplatelets is operated at a temperature between -50°C and 150°C and more preferably between 20°C and 110°C. In one embodiment the material encapsulating the nanoplatelets is cooled by a air fan. In one embodiment the material encapsulating the nanoplatelets is cooled by water. In one embodiment the material encapsulating the nanoplatelets is not cooled by any active system. In one embodiment the material encapsulating the nanoplatelets is connected to a heat diffusing system. In one embodiment the material encapsulating the nanoplatelets is illuminated thanks to a two photon absorption. In one embodiment the material encapsulating the nanoplatelets is illuminated thanks to a multiphoton absorption.

In one embodiment the nanoplatelets film comprises additives in addition to the core/shell nanoplatelets, see Figure 2. In one embodiment the nanoplatelets film comprises additives which have optical properties. In one embodiment the nanoplatelets film comprises additives which scatter light in the visible range of wavelength. In one embodiment the nanoplatelets film comprises additives which are particles which size is included between 10nm and 1mm and more preferably between 100nm and 10µm. In one embodiment the nanoplatelets film comprises additives which are particles which weight ratio is between 0 and 20% and more preferably between 0.5% and 2%. In one embodiment the nanoplatelets film comprises additives which are particles made of TiO_2, SiO_2, ZrO_2.

In one embodiment the nanoplatelets film comprises additives such as hydrophobic montmorilonite. In one embodiment the nanoplatelets film comprises additives such as metallic particles with plasmonic properties. In one embodiment the nanoplatelets film comprises additives such as metallic nanoparticles with plasmonic properties, preferably made of Ag or Au.

In one embodiment the material encapsulating the nanoplatelets has a tubular or a rectangular shape.

In one embodiment the material encapsulating the nanoplatelets is used as a waveguide.

According to one embodiment, as depicted on figure 1, the encapsulated nanoplatelets film 9 comprises a nanoplatelets film 3 disposed on a transparent substrate 4. A layer configured to reduce exposition to O_2 and H_2O 2 is disposed on the nanoplatelets film 3. A transparent substrate 1 is also disposed on the layer 2. A light source 5 is connected to the transparent substrate 4.

In one embodiment, the nanoplatelets film 3 further comprises scattering elements 6 dispersed in the host material, see figure 2.

According to one embodiment, as depicted in figure 3, a light guide plate 7 is optically between the encapsulated nanoplatelets film 9 and the light source 5. According to one embodiment, the light guide plate 7 further comprises light recycling element 8 configured to collimate the light in a given direction.

According to one embodiment, as depicted in figure 4, the encapsulated nanoplatelets film 9 is optically between the light source 5 and the light guide plate 7.

The present invention also relates to an optical system comprising a light source having preferably a wavelength in a range from 400 to 470nm such as for instance a gallium nitride based diode and a nanoplatelets film or an encapsulated nanoplatelets film according to the invention.

In one embodiment the material encapsulating the nanoplatelets has a tubular or a rectangular shape. In one embodiment the material encapsulating the nanoplatelets is used as a waveguide or light guide plate.

The present invention also relates to a backlight unit comprising an optical system according to the invention and a light guide plate configured to guide the light exiting from the light source or the nanoplatelets film.

According to one embodiment, the backlight unit further comprises light recycling element configured to collimate the light in a given direction.

According to one embodiment, in the backlight unit, the nanoplatelets film is optically between the light source and the light guide plate. According to one embodiment, in the backlight unit, the nanoplatelets film is optically between the light source and the light recycling element. According to one embodiment, in the backlight unit, the light recycling element is optically between the light guide plate and the nanoplatelets film.

According to one embodiment, the backlight unit further comprises a light reflective material disposed on one surface of the light guide plate, wherein the surface onto which the reflector is disposed is substantially perpendicular to the surface facing the light source.

The present invention also relates to a liquid crystal display unit comprising a backlight unit according to the invention and a liquid crystal display panel having a set of red, blue and green color filters, wherein the nanoplatelets film is optically between the light source and the liquid crystal display panel.

The present invention also relates to a display device comprising an optical system according to the invention, a backlight unit according to the invention or a liquid crystal display unit according to the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a scheme of an encapsulating strategy according to the invention, wherein the nanoplatelets are encapsulated in a transparent host material which is itself protected from O_2 by a UV polymerizable polymer and by insulating substrate.

Figure 2 shows a scheme of an encapsulating strategy according to the invention, wherein the nanoplatelets are encapsulated in a transparent host material which is itself protected from O_2 by a UV polymerizable polymer and by insulating substrate. Somme additive have been added in the host material containing the NPL in order to scatter the light.

Figure 3 shows a strategy for the illumination of the encapsulated nanoplatelets film according to the invention. A blue LED light is scattered all over the illuminating system by a transparent scatter which surface is further functionalized by additional scattering center.

Figure 4 shows a strategy for the illumination of the encapsulated nanoplatelets film according to the invention. The film is first illuminated by the blue LED and the produced white light is scattered all over the illuminating system by a transparent scatter which surface is further functionalized by additional scattering center.

Figure 5 shows the emission spectrum of a film including green and red nanoplatelets illuminated by a 455 nm blue diode.

Figure 6 shows the measurement of the normalized fluorescence quantum efficiency coming from film of CdSe/CdZnS nanoplatelets according to the invention, quantum dots of the prior art or CdSe/CdZnS nanoplatelets of the prior art deposed on microscope glass slides. Films are excited using a Hg lamp, and the emitted light is collected with an oil objective (100x, NA = 1.4) and adapted filters (550 nm short-pass filter for the excitation and 590 nm long-pass filter for the emission).

Figure 7 shows the measurement of the normalized fluorescence quantum efficiency coming from a layered material comprising CdSe/CdZnS nanoplatelets of the invention, quantum dots of the prior art or CdSe/CdZnS nanoplatelets of the prior art under blue LED excitation operated at 160mA, (see photobleaching measurements after encapsulation) corresponding to an illumination with a photon flux of $12W.cm^{-2}$.

Figure 8 shows the measurement of the normalized flurorescence quantum efficiency coming from CdSe/ZnS nanoplatelets according to the invention, CdSe/CdZnS nanoplatelets according to the invention, CdSe/CdS/ZnS quantum dots according to the prior art and CdSe/CdZnS nanoplatelets according to the prior art deposed on a glass slide in function of temperature. Films are excited with a laser at 404 nm.

REFERENCES

1. Transparent substrate
2. Layer configured to reduce exposition to O_2 and H_2O
3. Host material comprising the nanoplatelets
4. Transparent substrate
5. Light source, e.g. blue LED
6. Scattering element
7. Light guide plate
8. Light recycling element
9. Encapsulated nanoplatelets film

EXAMPLES

Example 1

A solution of CdSe-ZnS nanoplatelets is first precipitated in air free glove box by addition of ethanol. After centrifugation the formed pellet is redispersed in chloroform solution. Meanwhile a solution at 30 % in weight of Poly(maleic anhydride –alt-octadecene) (MW=40kg.mol-1) in chloroform is prepared. Then the nanoplatelets solution is mixed with the polymer solution in a 1:1 volume ratio and the solution is further stirred. On a 02 insulating substrate (glass or PET) the solution nanoplatelets-polymer mixture is brushed and let dried for 30min. Then UV polymerizable oligomer made of 99% of lauryl methacrylate and 1% of benzophenone is deposited on the top of the nanoplatelets film. A top substrate (same as the bottom substrate) is deposited on the system. The film is the polymerized under UV for 4 min. The layered material is then glued thanks to a PMMA solution dissolved in chloroform on a 455nm LED from Avigo technology. The LED is operated under a constant current ranging from 1mA to 500mA.

Example 2

A solution of CdSe-ZnS nanoplatelets is first precipitated in air free glove box by addition of ethanol. After centrifugation the formed pellet is redispsered in chloroform solution.

Meanwhile a solution at 30 % in weight of PMMA (MW=120kg.mol-1) in chloroform is prepared. Then the nanoplatelets solution is mixed with the polymer solution in a 1:1 volume ratio and the solution is further stirred. On a 02 insulating substrate (glass or PET) the solution nanoplatelets-polymer mixture is brushed and let dried for 30min. Then nail varnish is deposited on the top of the nanoplatelets film. A top substrate (same as the bottom substrate) is deposited on the system. The film is the polymerized under UV for 4 min.

Example 3

A red solution of CdSe-ZnS nanoplatelets is first precipitated in air free glove box by addition of ethanol. After centrifugation the formed pellet is redispsered in chloroform solution. Similarly a solution of green core/shell nanoplatelets made of CdSSe-CdZnS core/shell nanoplatelets is precipitated and dispersed in chloroform. Meanwhile a solution at 30 % in weight of Poly(maleic anhydride–alt-octadecene) in chloroform is prepared. The three solutions are then mixed. The concentration of particles is determined by the desired final color gamut. We then add to the mixture 1% in weight of 1µm size TiO2 particles. The mixture is further stirred for 10minutes. This solution is spin coated on a PDMS substrate. We then spin coat a mixture of UV polymerizable oligomer. The latter mixture is made of 99% of lauryl methacrylate and 1% of benzophenone. A top substrate made of PDMS is then deposited. The final film is illuminated under UV for 5min and let rest for 1h.

Example 4

A solution of CdSe-ZnS nanoplatelets is first precipitated in air free glove box by addition of ethanol. After centrifugation the formed pellet is redispersed in chloroform. Meanwhile a solution at 20 % in weight of Poly(maleic anhydride–alt-octadecene) (MW=40kg.mol-1) in chloroform is prepared. A dispersion in chloroform of hydrophobic montmorilonite (NANOCLAY, NANOMER I.28E) at 1% in weight is prepared by ultrasonication for 10 minutes. Equal volumes of the nanoplatelets, polymer and nanoclay solutions are mixed together and the solution is further stirred. On a 02 insulating substrate (glass or PET) the solution nanoplatelets-polymer mixture is brushed and let dried for 30min. Then nail varnish is deposited on the top of the nanoplatelets film. A top substrate (same as the bottom substrate) is deposited on the system. The film is the polymerized under UV for 4 min.

Photobleaching measurements in air

The NPLs or QDs in hexane solution are diluted in a mixture of 90% hexane/10% octane and deposited by drop-casting on a glass substrate. The sample is visualized using an inverted fluorescent microscope. An area of the sample containing NPLs or QDs as a concentration still allowing distinguishing single nanocrystals is excited using a Hg lamp, and the emitted light is collected with an oil objective (100x, NA = 1.4) and adapted filters (550 nm short-pass filter for the excitation and 590 nm long-pass filter for the emission). The emitted light of the sample can be observed on a CCD camera (Cascade 512B, Roper Scientific). An image of the illuminated field is taken every minute and the mean intensity of the film is normalized with the initial intensity, allowing to plot the mean intensity variations over time (see figure 6).

Photobleaching measurements after encapsulation

The layered material glued to a LED as described above is excited using the LED emission under 160mA operation corresponding to an illumination with a photon flux of 12W.cm^{-2}. The fluorescence of the layered material as well as a fraction of the blue light from the LED is acquired using an optical fiber spectrometer (Ocean-optics usb 2000). The stability of the fluorescence over time is obtained by normalizing the integrated fluorescence from the layered material by the integrated fluorescence from the blue LED. This fluorescence quantum efficiency is then normalized to the initial ratio and plotted over time for direct comparisons purposes (Figure 7).

Fluorescence stability versus temperature measurement

The layered material preparation is described above. The layered material is heated via a hot plate at the desired temperature ranging from 20°C to 200°C and the fluorescence is measured using an optical fiber spectrometer (Ocean-optics usb 2000) under excitation with a laser at 404nm. The measurements are taken after temperature stabilization (see figure 8).

Nanoplatelets cores preparations

Synthesis of CdSe 460 nanoplatelets (NPLs)

240 mg of Cadmium acetate ($Cd(OAc)_2$) (0,9mmol), 31 mg of Se 100 mesh, 150µL oleic acid (OA) and 15mL of 1-octadecene (ODE) are introduced in a three neck flask and are degassed under vacuum. The mixture is heated under argon flow at 180°C for 30 min.

Synthesis of CdSe 510 NPLs

170mg of cadmium myristate ($Cd(myr)_2$) (0,3mmol), 12mg of Se 100 mesh and 15mL of ODE are introduced in a three neck flask and are degassed under vacuum. The mixture is heated under argon flow at 240°C, when the temperature reaches 195°C, 40mg of $Cd(OAc)_2$ (0,15mmol) are introduced. The mixture is heated for 10 minutes at 240°C.

Synthesis of CdSe 550 NPLs

170mg of $Cd(myr)_2$ (0,3mmol) and 15mL of ODE are introduced in a three neck flask and are degassed under vacuum. The mixture is heated under argon flow at 250°C and 1mL of a dispersion of Se 100 mesh sonicated in ODE (0,1M) are quickly injected. After 30 seconds, 80mg of $Cd(OAc)_2$ (0,3mmol) are introduced. The mixture is heated for 10 minutes at 250°C.

Synthesis of CdTe 428 NPLs

A three neck flask is charged with 130 mg of cadmium proprionate ($Cd(prop)_2$) (0.5 mmol), 80 µL of OA (0.25 mmol), and 10 mL of ODE, and the mixture is stirred and degassed under vacuum at 95°C for 2 h. The mixture under argon is heated at 180°C and 100 µL of a solution of 1 M Te dissolved in trioctylphosphine (TOP-Te) diluted in 0.5 mL of ODE are swiftly added. The reaction is heated for 20 min at the same temperature.

When 428 NPLs are prepared using $Cd(OAc)_2$, TOP-Te 1 M is injected between 120 and 140°C.

Synthesis of CdTe 500 NPLs

A three-neck flask is charged with 130 mg of $Cd(prop)_2$ (0.5 mmol), 80 µL of OA (0.25 mmol), and 10 mL of ODE, and the mixture is stirred and degassed under vacuum at 95°C for 2 h. The mixture under argon is heated at 210°C, and 100 µL of a solution of 1 M TOP-Te diluted in 0.5 mL of ODE is swiftly added. The reaction is heated for 30 min at the same temperature.

When Cd(OAc)2 was used as cadmium precursor, TOP-Te is injected between 170 and 190°C.

Synthesis of CdTe 556 NPLs

133 mg of $Cd(OAc)_2$ (0.5 mmol), 255 µL of OA (0.8 mmol), and 25 mL of ODE are charged into a three-neck flask, and the mixture is stirred and degassed under vacuum at 95°C for 2 h. The flask is filled with argon and the temperature is increased to 215°C. Then, 0.05 mmol of stoichiometric TOP-Te (2.24 M) diluted in 2.5 mL ODE is injected with a syringe pump at a constant rate over 15 min. When the addition is completed, the reaction is heated for 15 min.

Synthesis of CdS 375 NPLs

In a three neck flask 160 mg of $Cd(OAc)_2$ (0.6mmol), 190 µL (0.6mmol) of OA, 1.5 mL of sulfur dissolved in 1-octadecene (S-ODE) 0.1M and 13.5 mL of ODE are introduced and degassed under vacuum for 30 minutes. Then the mixture is heated at 180°C under Argon flow for 30 minutes.

Synthesis of CdS 407 NPLs

In a three neck flask 160 mg of $Cd(OAc)_2$ (0.6mmol), 190 µL (0.6mmol) of OA, 1.5 mL of S-ODE 0.1M and 13.5 mL of octadecene are introduced and degassed under vacuum for 30 minutes. Then the mixture is heated at 260°C under Argon flow for 1 minute.

Synthesis of Core/Crown CdSe/CdS NPLs

In a three neck flask, 320 mg of $Cd(OAc)_2$ (1.2 mmol), 380 µL of OA (1.51 mmol) and 8 mL of octadecene are degassed under vacuum at 65°C for 30 minutes. Then CdSe nanoplatelets cores in 4 mL of ODE are introduced under Argon. The reaction is heated at 210 °C and 0.3 mmol of S-ODE 0.05M are added drop wise. After injection, the reaction is heated at 210°C for 10 minutes.

Synthesis of Core/Crown CdSe/CdTe NPLs

In a three neck flask, CdSe nanoplatelets cores in 6 mL of ODE are introduced with 238 µL of OA (0.75 mmol) and 130 mg of $Cd(prop)_2$. The mixture is degassed under vacuum for 30 minutes then, under argon, the reaction is heated at 235°C and 50 µL of TOP-Te 1M in 1 mL of ODE is added drop wise. After the addition, the reaction is heated at 235°C for 15 minutes.

Synthesis of CdSeS alloyed NPLs

170mg of $Cd(myr)_2$ (0,3mmol) and 15mL of ODE are introduced in a three neck flask and are degassed under vacuum. The mixture is heated under argon flow at 250°C and 1mL of a dispersion of Se 100 mesh sonicated in S-ODE and ODE (total concentration of selenium and sulfur 0,1M) are quickly injected. After 30 seconds, 120mg of $Cd(OAc)_2$ (0,45mmol) are introduced. The mixture is heated for 10 minutes at 250°C.

Shells growth

CdS shell growth with octanethiol

In a three neck flask, 15 mL of trioctylamine (TOA) are introduced and degassed under vacuum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in ODE are swiftly injected followed by the injection of 7 mL of 0.1 M octanethiol solution in ODE and 7 mL of 0.1M $Cd(OA)_2$ in ODE with syringe pumps at a constant rate over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

CdS shell growth with butanethiol

In a three neck flask, 15 mL of trioctylamine (TOA) are introduced and degassed under vacuum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in ODE are swiftly injected followed by the injection of 7 mL of 0.1 M butanethiol solution in ODE and 7 mL of 0.1M $Cd(OA)_2$ in ODE with syringe pumps at a constant rate over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

ZnS shell growth with octanethiol

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vacuum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in octadecene are swiftly injected followed by the injection of 7 mL of 0.1 M octanethiol solution in octadecene and 7 mL of 0.1M zinc oleate $(Zn(OA)_2{}^)$ in octadecene with syringe pumps at a constant rate over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

ZnS shell growth with butanethiol

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vacuum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in octadecene are swiftly injected followed by the injection of 7 mL of 0.1 M butanethiol solution in octadecene and 7 mL of 0.1M zinc oleate $(Zn(OA)_2)$ in octadecene with syringe pumps at a constant rate over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

CdZnS gradient shell growth with octanethiol

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vaccum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in octadecene are swiftly injected followed by the injection of 7 mL of 0.1 M octanethiol solution in octadecene with syringe pumps at a constant rate and 3.5 mL of 0.1M $Cd(OA)_2$ in octadecene and 3.5 mL of 0.1M $Zn(OA)_2$ in octadecene with syringe pumps at variables rates over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

CdZnS gradient shell growth with butanethiol

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vaccum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in octadecene are swiftly injected followed by the injection of 7 mL of 0.1 M butanethiol solution in octadecene with syringe pumps at a constant rate and 3.5 mL of 0.1M $Cd(OA)_2$ in octadecene and 3.5 mL of 0.1M $Zn(OA)_2$ in octadecene with syringe pumps at variables rates over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

CdxZn1-xS alloys shell growth with octanethiol

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vaccum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in octadecene are swiftly injected followed by the injection of 7 mL of 0.1 M octanethiol solution in octadecene, 3.5 mL of 0.1M $Cd(OA)_2$ in octadecene and 3.5 mL of 0.1M $Zn(OA)_2$ in octadecene with syringe pumps at a constant rate over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

CdxZn1-xS alloys shell growth with butanethiol

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vaccum at 100°C. Then the reaction mixture is heated at 300°C under Argon and 5 mL of core nanoplatelets in octadecene are swiftly injected followed by the injection of 7 mL of 0.1 M butanethiol solution in octadecene, (x)*3.5 mL of 0.1M $Cd(OA)_2$ in octadecene and (1-x)*3.5 mL of 0.1M $Zn(OA)_2$ in octadecene with syringe pumps at a constant rate over 90 min. After the addition, the reaction is heated at 300°C for 90 minutes.

CdZnS shell growth (manufactured according to the prior art: ambient temperature Mahler et al. JACS. 2012, 134(45), 18591-18598)

1 mL of CdSe 510 NPLs in hexane is diluted in 4 mL of chloroform, then 100 mg of thioacetamide (TAA) and 1 mL of octylamine are added in the flask and the mixture is sonicated until complete dissolution of the TAA (about 5 min). The color of the solution changed from yellow to orange during this time. 350 μL of a solution of Cd(NO3)2 0.2 M in ethanol and 150 μL of a solution of Zn(NO3)2 0.2 M in ethanol are then added to the flask. The reaction was allowed to proceed for 2 h at 65°C. After synthesis, the core/shell platelets were isolated from the secondary nucleation by precipitation with a few drops of ethanol and suspended in 5 mL of chloroform. Then 100 μL of Zn(NO3)2 0.2 M in ethanol is added to the nanoplatelets solution. They aggregate steadily and are resuspended by adding 200 μL oleic acid.

ZnS alternative shell growth

In a three neck flask, 15 mL of trioctylamine are introduced and degassed under vacuum at 100°C. Then the reaction mixture is heated at 310°C under Argon and 5 mL of core nanoplatelets in octadecene mixed with 50μL of precursors mixture are swiftly injected followed by the injection of 2 mL of 0.1M zinc oleate ($Zn(OA)_2$) and octanethiol solution in octadecene with syringe pump at a constant rate over 80 min.

CLAIMS

1. A population of semiconductor nanoplatelets, each member of the population comprising a nanoplatelet core including a first semiconductor material and a shell including a second semiconductor material on the surface of the nanoplatelet core, wherein the population exhibits fluorescence quantum efficiency at 100 °C or above that is at least 80% of the fluorescence quantum efficiency of the population at 20°C.

2. The population of semiconductor nanoplatelets according to claim **1**, wherein the population exhibits fluorescence quantum efficiency decrease of less than 50% after one hour under light illumination.

3. A nanoplatelets film, comprising a host material, preferably a polymeric host material and emissive semiconductor nanoparticles embedded in said host material, wherein at least 20% of said emissive semiconductor nanoparticles are colloidal nanoplatelets according to claim **1** or claim **2**.

4. A nanoplatelets film according to claim **3** further comprising scattering elements dispersed in the host material.

5. An optical system comprising a light source having preferably a wavelength in a range from 400 to 470 nm such as for instance a gallium nitride based diode and a nanoplatelets film according to claim **3** or claim **4**.

6. The optical system according to claim **5**, wherein the nanoplatelets film is enclosed in a layer configured to reduce exposure of the nanoplatelets film to O_2 and H_2O.

7. A backlight unit comprising the optical system according to claim **5** or **6**, and a light guide plate configured to guide the light exiting from the light source or the nanoplatelets film.

8. The backlight unit according to claim **7**, further comprising light recycling element configured to collimate the light in a given direction.

9. The backlight unit according to claim **7** or claim **8**, wherein the nanoplatelets film is optically between the light source and the light guide plate.

10. The backlight unit according to claim **7**, wherein the nanoplatelets film is optically between the light source and the light recycling element.

11. The backlight unit according to claim **7**, wherein the light recycling element is optically between the light guide plate and the nanoplatelets film.

12. The backlight unit according to claim **10** or **11**, further comprising a light reflective material disposed on one surface of the light guide plate, wherein the surface onto which the reflector is disposed is substantially perpendicular to the surface facing the light source.

13. Liquid crystal display unit comprising a backlight unit according to anyone of claims **7** to **12** and a liquid crystal display panel having a set of red, blue and green color filters, wherein the nanoplatelets film is optically between the light source and the liquid crystal display panel.

14. A display device comprising the optical system according to claims **5** or **6**, the backlight unit according to anyone of claims **7** to **12** or the liquid crystal display unit according to claim **13**.

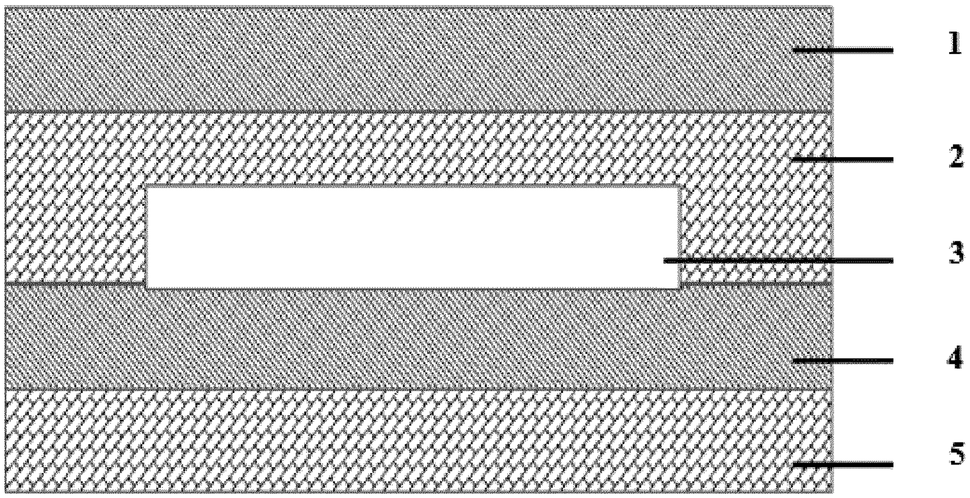

FIG. 1

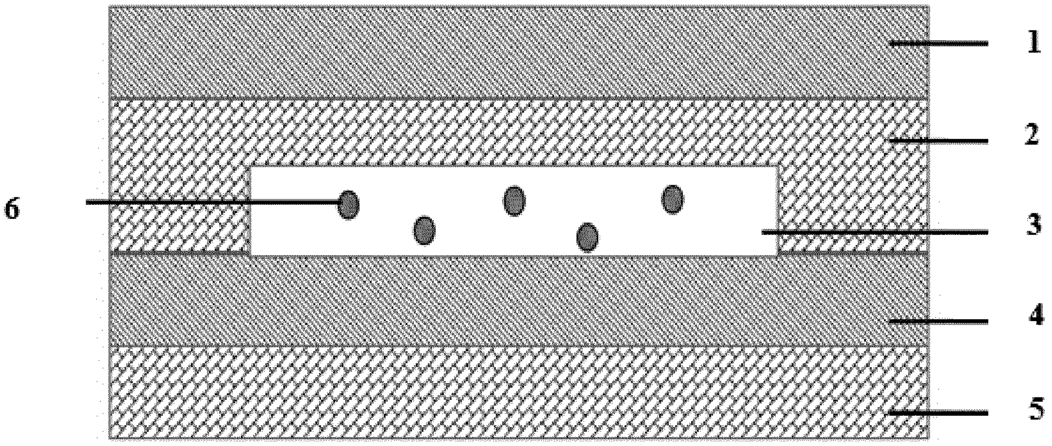

FIG. 2

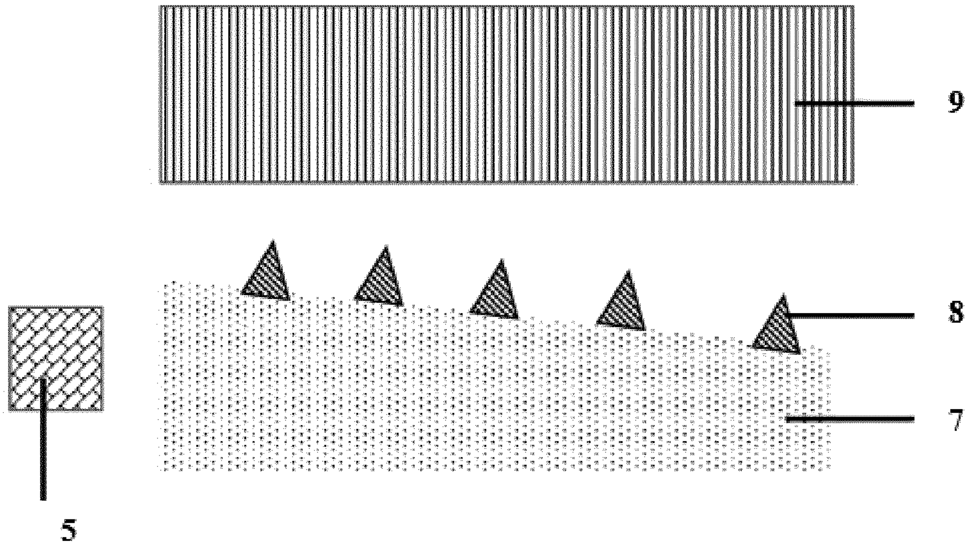

FIG. 3

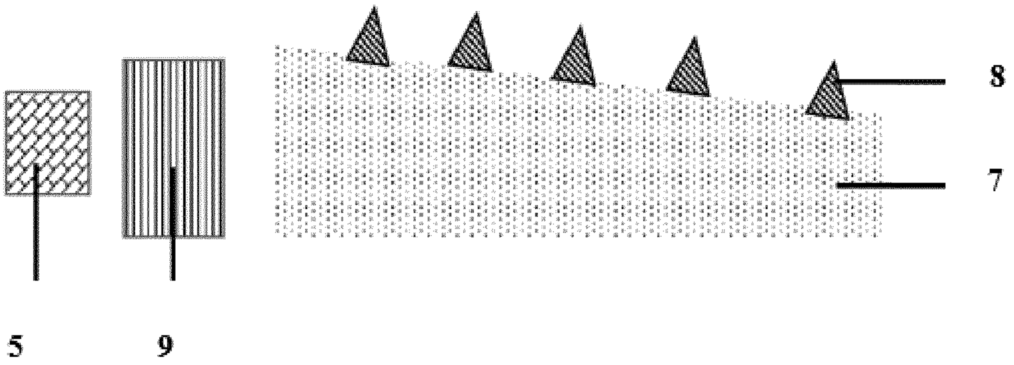

FIG. 4

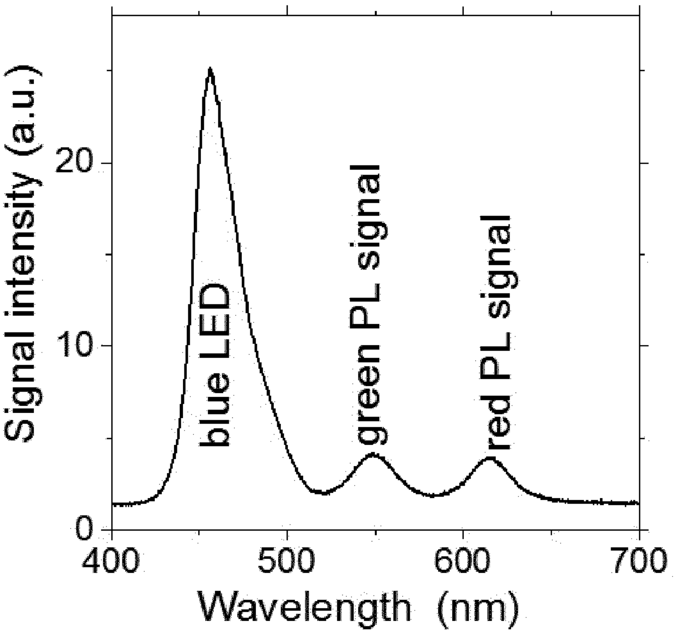
Signal intensity (a.u.)
0
10
20
400
500
600
700
Wavelength (nm)
blue LED
green PL signal
red PL signal

FIG. 5

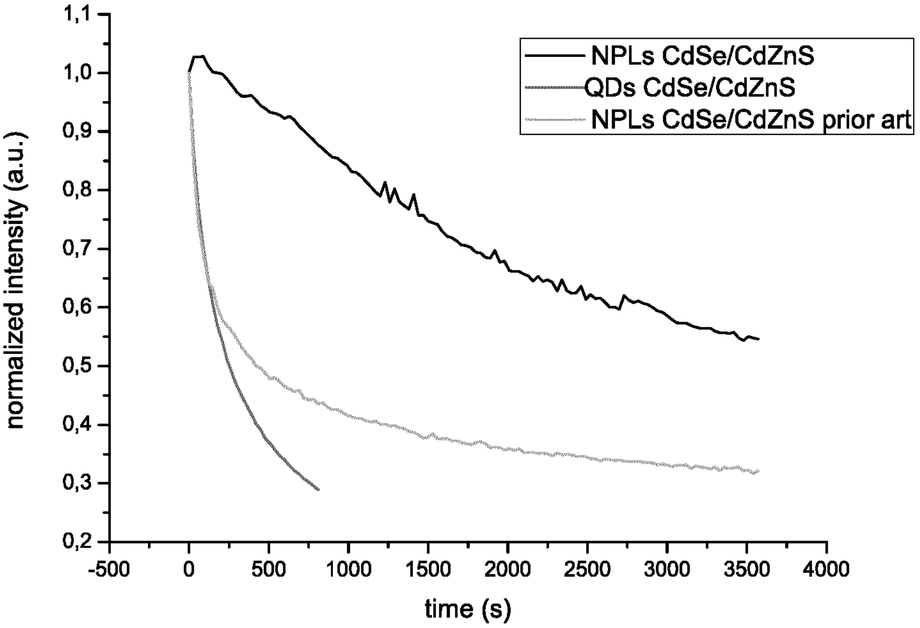
normalized intensity (a.u.)
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
-500
0
500
1000
1500
2000
2500
3000
3500
4000
time (s)
NPLs CdSe/CdZnS
QDs CdSe/CdZnS
NPLs CdSe/CdZnS prior art

FIG. 6

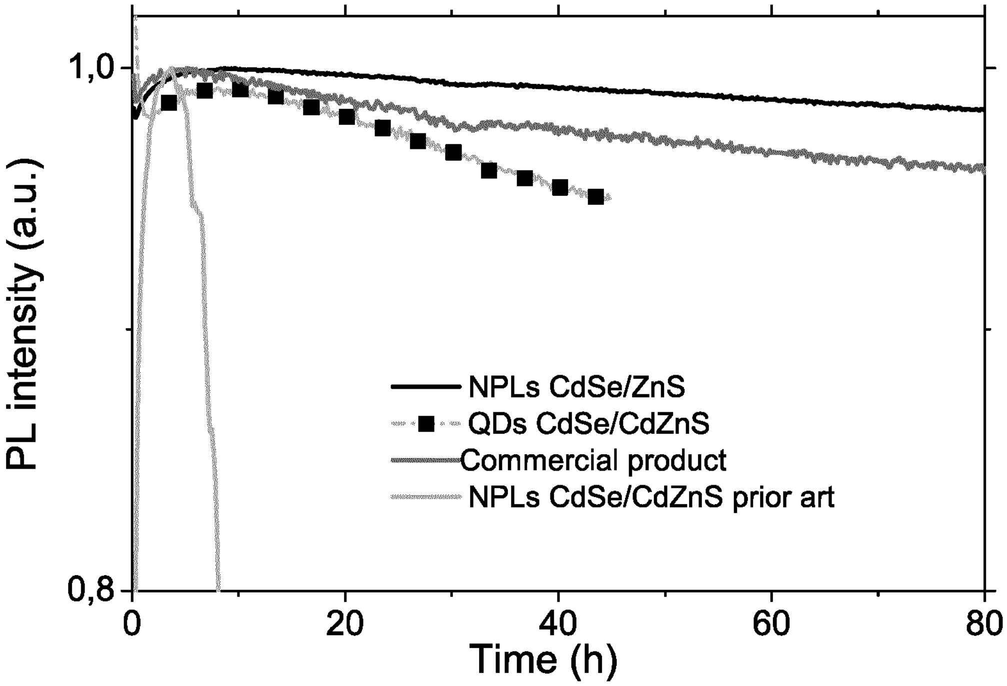
1,0
0,8
PL intensity (a.u.)
0
20
40
60
80
Time (h)
NPLs CdSe/ZnS
QDs CdSe/CdZnS
Commercial product
NPLs CdSe/CdZnS prior art

FIG. 7

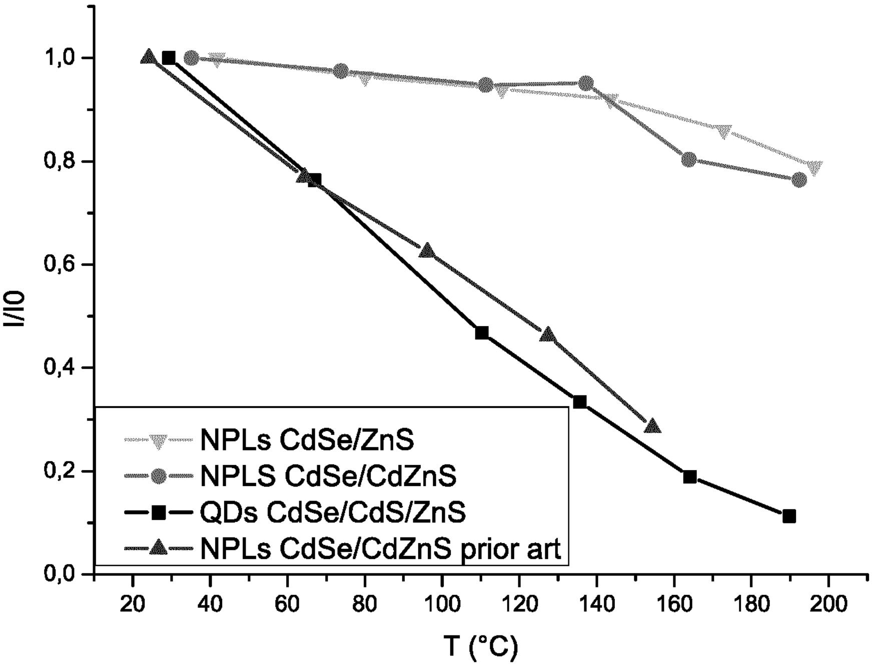
1,0
0,8
0,6
0,4
0,2
0,0
I/I0
20
40
60
80
100
120
140
160
180
200
T (°C)
NPLs CdSe/ZnS
NPLS CdSe/CdZnS
QDs CdSe/CdS/ZnS
NPLs CdSe/CdZnS prior art

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/056705

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/56 C09K11/88 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 2013/162646 A1 (QD VISION INC [US]) 31 October 2013 (2013-10-31) pages 8,30,32,; claims 1-3; figures 4,5; examples	1-14
X	SILVIA PEDETTI ET AL: "Type-II CdSe/CdTe Core/Crown Semiconductor Nanoplatelets", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 136, no. 46, 19 November 2014 (2014-11-19), pages 16430-16438, XP055276571, US ISSN: 0002-7863, DOI: 10.1021/ja509307m Introduction; figures	1-14

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☒ 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

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"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 9 June 2016	Date of mailing of the international search report 17/06/2016
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 Baldé, Kaisa

1

International application No
PCT/EP2016/056705

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MICKAËL D. TESSIER ET AL: "Efficient Exciton Concentrators Built from Colloidal Core/Crown CdSe/CdS Semiconductor Nanoplatelets", NANO LETTERS, vol. 14, no. 1, 8 January 2014 (2014-01-08), pages 207-213, XP055276573, US ISSN: 1530-6984, DOI: 10.1021/nl403746p the whole document -----	1-14
X	WO 2013/057270 A1 (SOLARWELL [FR]; LEWINER JACQUES [FR]; MAHLER BENOIT [FR]) 25 April 2013 (2013-04-25) claims 1-6; examples -----	1,2

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/056705

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013162646 A1	31-10-2013	NONE	
WO 2013057270 A1	25-04-2013	EP 2769403 A1	27-08-2014
		US 2014255316 A1	11-09-2014
		WO 2013057270 A1	25-04-2013