

Synthesis of semiconductor nanoparticles using metal precursors comprising non- or weakly coordinating anions

The present invention relates to a method for the synthesis of semiconductor nanoparticles
5 using metal precursors comprising non- or weakly coordinating anions. It further relates to the consecutive process for the synthesis that includes first the preparation of a binary nanoparticle system then modified to make a ternary system which again can be further modified to make a quaternary system.

10 Fluorescing semiconducting nanoparticles (also called quantum dots) gain increasing commercial interest. They can be utilized as efficient fluorescent agents which are considered being more stable as well as able to cover the whole visible range including parts of the UV and Near IR when compared to organic dyes. Tuning can be achieved by modifying the chemical composition or varying particle size. It is known that due to quantum confinement
15 effects the variation of the particles size has a strong effect on the absorption and emission wavelengths which can be utilized to tune the emission colour considerably (100's of nanometers) to wavelengths below the one that corresponds to the bulk band gap. A further option to tune the absorption and emission wavelengths of semiconducting nanoparticles is an alloying process with a second material that has a different band gap than the first material.

20

Up to now the best performing materials still contain toxic elements like cadmium, lead or mercury which impedes a broad commercialization strongly. Alternative materials are being developed worldwide but there are no materials known yet those have a sufficient performance and can be produced economically. An alternative material with a very good performance is
25 therefore highly desired. Semiconducting core-shell nanoparticles based on ZnSe, ZnS, InP or a combination of IB, IIB, IIIA, VIA elements of the periodic classification which are represented e.g. by Cu_2S , CuInS_2 or $\text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2$ are, among others, promising candidates which are especially interesting for lighting applications when they are used as colour-converting phosphors in LEDs to convert blue light from a LED to green, yellow and/or red. As shell
30 material ZnS is mostly chosen due to the wide band gap of the material that encloses the excited states (Exciton) quite efficiently.

Bayer Technology Services GmbH already introduced a general process technology to synthesize semiconductor nanoparticles in a continuous way with micro reactor technology.
35 With this proprietary technology scale up of nanoparticle production can be done economically

to enable material quantum dot based applications like O(Q)LEDs, white LEDs for display and lighting, solar cells, anti-counterfeiting, light converters etc.

However the challenge for the synthesis of complex nanoparticles as described above is to find appropriate precursor materials and process parameters to synthesize nanoparticles with high
5 fluorescence efficiency, with a broad variability for the emission colour and with reasonable reaction times.

As already mentioned quantum dots with a composition that do not contain cadmium, lead or mercury are strongly needed for their commercial use in a broad field of material and life
10 science applications. Among others ternary systems like IB-III_A-VI_A (IB = Cu, Ag; III_A = In, Ga, Al; VI_A = S, Se, Te) or quaternary systems like IB-III_A-II_B-VI_A (IB = Cu, Ag; III_A = In, Ga, Al; II_B = Zn; VI_A = S, Se, Te) with different stoichiometry have been proposed to be promising candidates whereby CuInS₂ gained the largest interest recently due to its tunability of its fluorescence wavelength.

15

Since a high fluorescence quantum yield of quantum dots requires a very good crystallinity with a minimal number of lattice, point and surface defects the manufacture of ternary systems or even more of quaternary systems pose a great challenge compared to binary systems. The reason for this is that donor-acceptor defects like vacancies or anti-site defects of the cations
20 are generally more likely due to deviation from the ideal stoichiometry. Important consequences of those defects may include strong broadening of the fluorescence peak and quenching of photoluminescence. Whereas the former may be acceptable for certain applications like general lighting the latter has to be minimized to maintain a high fluorescence quantum yield. These facts are well known and especially true for CuInS₂. Addition of Zinc as
25 an additional cation is known to stabilize the CuInS₂-lattice which does not lead to a significant narrowing of the emission line but cause an increase of the fluorescence quantum yield compared to the pure CuInS₂ nanoparticles (H. Nakamura et al., Chem. Mater. 18 (2006) pp. 3330 and SG-Registration Number 20110XXXX-X). At the same time incorporation of Zinc into the CuInS₂ lattice, thereby forming a quaternary lattice, provides the opportunity to shift
30 the emission wavelength further to shorter wavelengths due to the widening of the band gap. In principle the formation of homogeneously alloyed nanocrystals is simplified if the crystalline-structure of the constituents matches with each other and if the lattice mismatch is small. In the case of CuInS₂ and ZnS both generally exist in a cubic (Zinc blende) or hexagonal (Wurtzite) phase, whereas CuInS₂ additionally can crystallize in a tetragonal phase (Chalcopyrite). Hence,
35 an alloyed system can be obtained by statistically replacing the Zn²⁺ sites of ZnS with Cu⁺ and

In^{3+} while maintaining the original crystalline symmetry. Since the lattice mismatch between ZnS and CuInS_2 is very small (approx. 2.2%) it is possible to synthesize homogeneously alloyed nanoparticles $\text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2$ or $(\text{CuInS}_2)_x(\text{ZnS})_{1-x}$, respectively (D. Pan et al.; Chem. Commun. (2009), pp. 4221) and not only heterogeneous crystals consisting of e.g. tetragonal phase
5 CuInS_2 -rich regions and cubic-phase ZnS-rich regions causing additional interface defects.

Furthermore, it is known that ZnS as a suited wide band gap material for an inorganic shell is necessary for almost all types of quantum dots to get high fluorescence quantum yields. This is also true for CuInS_2 nanoparticles and the position of valence and conduction band of ZnS
10 provides an effective confinement of the charge carriers' wave functions. Thus, ZnS efficiently passivates the surface traps and largely prevents a leakage of the created charge carriers and therefore their non-radiative recombination. Ideally, at the particle surface at least one layer consists of pure ZnS with the consequence that the quantum yield increases (e.g. R. Xie et al., J. Am. Chem. Soc. 131 (2009) pp. 5691; K. Kuo et al., Thin Solid Films 517 (2008) pp. 1257).

15 Due to the good compatibility of ZnS with CuInS_2 one would expect that a coating process of pre-synthesized CuInS_2 nanoparticles with ZnS leads to fully or partly (i.e. with a gradient of the Zn concentration with a lower concentration at the particle centre and a higher at the surface) alloyed particles. In contrast to the growth of a ZnS shell with a well-defined interface
20 to the core that commonly generates a slight red shift of the fluorescence, the alloyed particles should be recognized by a substantial blue shift of the fluorescence wavelength due to both, the widening of the band gap during the alloying process and the stronger confinement of the residual smaller becoming CuInS_2 core. The blue shift should be the stronger the more Zinc is added to the CuInS_2 nanoparticles. It is also obvious that homogeneously alloyed nanoparticles
25 can be easier prepared by applying the coating method where Zn-ions diffuse into the existing homogeneous CuInS_2 lattice than by a synthesis route at which all metal-ions are introduced at the beginning.

In practice, the blue shift was actually observed upon Zn-addition but it stopped in the yellow-orange wavelength region independent on the amount of Zinc that is added (SG-Registration
30 Number 20110XXXX-X). A possible reason may be that the usual Zinc precursors are hindered by ligands, decomposed precursor or other components of the synthetic broth to deeply penetrate into the CuInS_2 nanoparticles. As a matter of fact ligands are well known to show a strong influence on the growth kinetics and finally also on the particle composition (J. Feng et al., Chem. Commun. 47 (2011) pp. 6422).

35 It is known that the synthesis of a ternary or even quaternary nanoparticle systems like IB-III A-

VIA (IB = Cu, Ag; IIIA = In, Ga, Al; VIA = S, Se, Te) relies on precursor materials that have, in a certain process parameter window, a controlled reactivity to ensure that the nanoparticle's stoichiometry is formed as required. Further it is necessary that suited coordinating ligands are included to control the particle formation, particle composition, limit the growth process and secure a stable dispersion of the particles (J. Feng et al., Chem. Commun. 47 (2011) pp. 6422). For ternary systems like CuInS₂ or even for quaternary sulphides nanoparticles like Cu_xIn_yZn_{2-x-y}S₂ long chain alkane thiols like dodecane thiol which act both as sulphur source and coordinating ligand for the particle at the same time are known to be advantageous. Cationic long-chain (unsaturated) surfactants like oleylamine or anionic long-chain (unsaturated) surfactants like oleic acid are further potential ligands which are often coexisting in the reaction solution.

It was already shown that under certain synthesis conditions the ZnS coating process results in a diffusion of Zinc-ions into the CuInS₂-core resulting in a smaller becoming core of pure CuInS₂ during an annealing process. A detailed description of the necessary processing steps was given (SG-Registration Number 20110XXXX-X). This treatment with Zinc results in a blue shift of the fluorescence due to the then smaller core which results in a particle shell composed of Cu_xIn_yZn_{2-x-y}S₂ wherein $0 < x$ and $y < 1$ with a gradual increase of x and y from the particle surface to the remaining core of CuInS₂. In case of a not yet fully alloyed particle the gradient layer Cu_xIn_yZn_{2-x-y}S₂ works further as buffer layer in-between CuInS₂ and ZnS minimizing the lattice mismatch and the surface/interface defect density even more. The fluorescence quantum yield was therefore strongly increased. The observed blue shift, however, starting from the red-infrared stopped in the yellow orange spectral region even though a large excess of Zn-precursor material was added to the reaction solution.

Therefore there is a need for a method for the preparation of semiconducting nanoparticles wherein Zinc precursors are able to penetrate under reasonable low temperatures and short time scales deeply into a CuInS₂ core so a blue shift beyond yellow orange spectral region can be obtained.

This would be very advantageous for practical applications like the use of those particle systems in LED lighting where green colors are necessary.

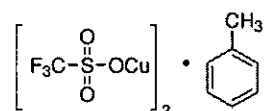
In the method of the present invention it was found that the fluorescence quantum yield and the range of accessible colours can be further increased when the nanoparticles are synthesized according to the process described in SG-Registration Number 20110XXXX-X when

particular precursors are used for core synthesis and / or shell formation. It was shown that these particular precursor class of non- or weakly coordinating anions play a special advantageous role for core synthesis and for the coating with a shell. Those anions readily release their respective cations like Zn^{2+} , Cu^+ or In^{3+} for fast reaction with the relevant precursors present in the reaction solution. An alloying process of the particles was shown even when the inventive anions are added after the core synthesis. This can even be done in more than one consecutive step with a single or even different type of the inventive ions to change a starting binary to a ternary and even to a quaternary nanoparticle system. At the same time the quantum yield (QY) is very high indicating that quenching defects are efficiently eliminated and the surface states are well saturated. Preferably when the last step is done with same type of the inventive ions as second last step, the stability of the QY can be strongly improved, Using CuInS_2 nanoparticles as an example it could be demonstrated that by using these precursors the accessible colour range could be extended from deep red and near IR to blue-green compared to deep red and near IR to orange-yellow when using the classical precursor materials for the metal ions like e.g. acetates or carbamates (e.g. zinc diethyldithiocarbamate). It could even be demonstrated that after first synthesizing a copper(I) sulfide nanoparticles that only very weakly luminesce in the near infrared the luminescence could be strongly increased and blue shifted after treatment with the inventive ions containing indium (In). This trend was further continued when a treatment followed with the inventive ions containing Zinc (Zn). For example if Zinc Bis(trifluoromethanesulfonyl)imide (TSFI) is used the variation of the amount of TSFI can tune the color easiliy from blue-green (approx.. 520 nm) to red (approx. 670 nm) The metal complexes based on the anions mentioned below can be used as precursors to synthesize the mentioned binary, ternary or even quaternary nanoparticle systems. Metal complexes in the sense of the present invention can include elements of the transition metal - group IIIB, IVB, VB, VIB, VIII, IB, IIB -, main group metals - IA, IIA, IIIA, IVA, VA. Preferred, the preparation of the metal complexes will start from lithium or sodium salts of the anions selecting from the group of non- or weakly coordinating anions comprising:

- Simple anions, like fluorides (F^-), cyanides (CN^-)
- Sulphates, sulfonates, phosphates, acetates of formula:

R-SO_4^- , Triflates, R-SO_3^- ,

Especially Copper(I) trifluoromethanesulfonate toluene complex



$\text{R}_2\text{-PO}_4^+$, R-PO_4^{2-} , PO_4^{3-} , R-COO^- ,

wherein $\text{R} = \text{C}_n\text{F}_{2n+1}$ (fluorinated branched or non-branched alkyl) or $\text{R} = \text{C}_n\text{F}_{2n-1}$

(fluorinated aryl)

- Borates, aluminates, antimonates, arsenites, and phosphates selected from the group consisting of:

Tetrafluoroborate (BF_4^-),

5 Hexafluorophosphate (PF_6^-),

Tetrafluoroaluminate (AlF_4^-),

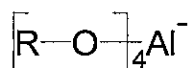
Tetrachloroaluminate (AlCl_4^-),

Hexafluoroantimonate (SbF_6^-),

Hexafluoroarsenite (AsF_6^-),

10

- Aluminates of formula:

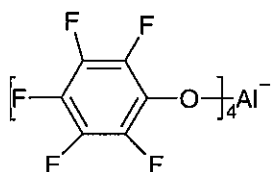


wherein $\text{R} = \text{C}_n\text{F}_{2n+1}$ (fluorinated branched or non-branched alkyl) or $\text{R} = \text{C}_n\text{F}_{2n-1}$ (fluorinated aryl)

15

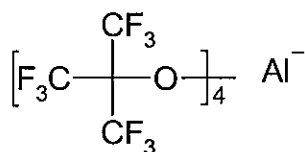
Especially:

Tetrakis [2, 3, 4, 5, 6-pentafluorophenolato] aluminate(1-)



20

Tetrakis [1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-2-propanolato] aluminate(1-)



- Borates of formula

R_4B^- wherein $\text{R} = \text{CN}$, $\text{C}_n\text{F}_{2n+1}$ (fluorinated branched or non-branched alkyl) or $\text{R} = \text{C}_n\text{F}_{2n-1}$ (fluorinated aryl)

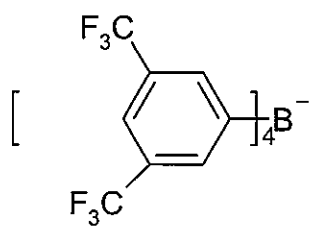
25

Especially:

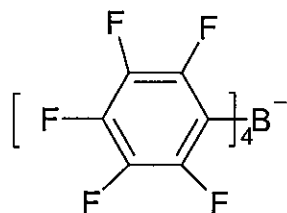
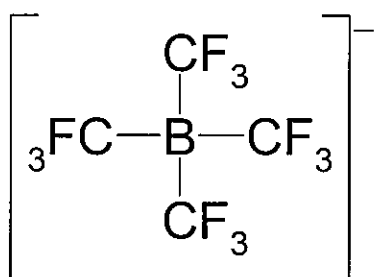
Tetra(cyano)borate

$\text{B}(\text{CN})_4^-$

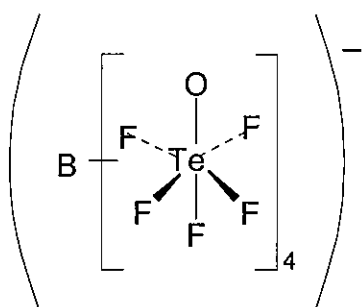
Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate



Tetrakis (pentafluorophenyl) borate

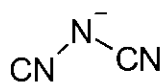
Tetrakis(trifluoromethyl)borate $[\text{B}(\text{CF}_3)_4]^-$ 

5

Teflate-Borate $[\text{B}(\text{OTeF}_5)_4]^-$ 

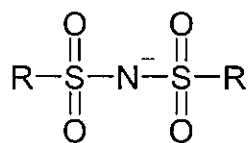
- Amides and imides selected from the group of:

Dicyanamide



10

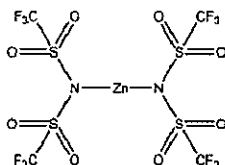
Bis-sulfonyl-imides of formula:



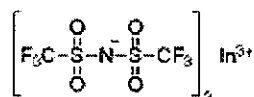
with R= F, CN, C_nF_{2n+1} (fluorinated branched or non-branched alkyl) or R = C_nF_{2n-1} (fluorinated aryl)

Especially:

5 Zinc Bis(trifluoromethanesulfonyl)imide (made out of the Lithium salt purchased from 3M)



Indium Tris(trifluoromethanesulfonimide)



10 Copper trifluoromethanesulfonimide (according structure)

- Carboranes of formula XCB₁₁R₁₁⁻ wherein R=H, F and X= H; alkyl,
- Carborates (e.g. T. Kueppers, PHD Thesis: "Beiträge zur Chemie der schwach koordinierenden Anionen [B(CN)₄]⁻ und [1-R-CB₁₁F₁₁]⁻ mit R = H, C₂H₅", Universitaet Wuppertal, 2007, p. 47 – 52)

15 The process for preparing the particles is essentially according to SG-Registration Number 20110XXXX-X and typically comprises the following steps:

- 1.) Precursors for the core and shell are separately prepared. Precursors for the core or shell are dissolved in solvent mixture further comprising one or more ligand or surfactant, resp. and at a temperature that is still beneath the threshold at which nucleation takes place being typically from room temperature to 190 °C, preferably from 50 °C to 180 °C so a core reaction mixture and a shell reaction mixture are prepared. The terms ligand and surfactant are used synonymously in the following. In the method of the present invention at least one of the core or shell metal precursors comprises at least one of the above mentioned non- or weakly coordinating anions.
- 25 In case a ternary core is used the molecular ratio of metal precursors in the core reaction mixture usually is close to the stoichiometric ratio of the according bulk material and varies preferred by a factor of ≤ 9 , preferred by a factor ≤ 3 , most preferred by a factor of ≤ 1.3 . This means for example in the case of CuInS₂ (CIS) that the molecular ratio of the Cu- and In-precursor ranges preferably from (1 - 9):(1 - 9), more preferable (1 - 5):(1 - 5), most preferably 1 - 2 b:(1 - 2). The molar content of the anion precursor is preferable in excess of the molar content of the metal salt. In case the anion precursor is also ligand a molar ratio
- 30 from (100-1.5):1 for anion:cation are usually used, preferred from (50-2):1, most preferred

from (20-10):1. It is preferred that core solution mixture comprises a total amount of cation salts (i.e. Copper, Indium, Silver and Gallium) in a concentration from 0.0005 M to 1 M, preferably from 0.001 M to 0.5 M, and more preferably from 0.005 to 0.1 M in at least one solvent.

5 Preferably core reaction mixture and a shell reaction mixture are clear and flowable solutions with a viscosity below 50 mPas preferably below 10 mPas homogeneity.

2.) Core reaction mixture is heated above nucleation threshold temperature typically from 100°C to 350°C, preferably from 180°C to 300°C, most preferably from 200°C to 270°C and then kept at the reaction temperature for core nucleation. The heating procedure should
10 be preferably done with a heating rate of > 1 K/s, preferably with a heating rate of > 10 K/s and most preferably with a heating rate of > 100 K/s, wherein preferred procedure is that the reaction mixture is pumped through a micro-heat exchanger to heat up the mixture with the highest possible heating rate. The temperature is kept for a time period of preferably between 1 minutes and 10 hours, more preferably between 3 minutes and 1 hour. Preferably
15 the heated reaction mixture flows into a residence microreactor with micro heat exchanger to adjust and hold the above given temperatures.

3.) Optionally and for larger particles or for better particle quality the heated reaction mixture is then kept at a temperature being well suited for core growth but lower than the nucleation temperature wherein a second injection of the core reaction mixture can be done. The
20 temperature range is from 100°C to 270°C, preferred from 150°C to 250°C and most preferred from 180°C to 240°C and can thereby be adjusted by heating oil. The temperature is kept for a time period of preferably between 1 minutes and 10 hours, more preferably between 3 minutes and 1 hour. Preferably the heated reaction mixture flows into a residence micro-reactor with micro heat exchanger to adjust and hold the above given temperatures.

25 Optionally, this step can be repeated as it is appropriate for best results.

4.) Shell reaction mixture containing precursors of shell material is added to the reaction mixture for shell coating of the core nanoparticles prepared in step 2.) or 3.) respectively.

4a.) In a first embodiment of the method of the present invention this step is conducted drop-wise.

30 4b.) Alternatively the reaction solution containing the core material is cooled down and the additional reaction mixture containing precursors of shell material is added and mixed at temperatures below 100°C, preferred at room temperature. Then the reaction mixture containing the core and precursors of shell material is heated up again. Step 4 is then preferably conducted in a micro-mixer.

35 4c.) Alternatively the reaction solution containing the core material is cooled down, mixed with

the shell precursor materials and heated to a temperature from 100°C to 200°C, preferred from 140°C to 180°C for at least 1 min, preferred from 3 min to 60 min and most preferred from 5 min to 20 min. Preferably this alternative is conducted in a micro-mixer and a residence micro-reactor, optionally with micro heat exchanger, to adjust and hold the above given temperatures.

- 5.) The reaction mixture is heated and/or hold to a shell growth temperature from 100°C to 260°C, preferred from 150°C to 250°C and most preferred from 180°C to 230°C usually for a time period of preferably from 1 minutes to 10 hours, more preferably from 3 minutes to 3 hours and most preferred from 5 min to 90 min. The reaction temperature can thereby be adjusted using heating oil bath. In a preferred embodiment a residence reactor with heat exchanger is used to grow the shell material under the conditions given above. Most preferably the reaction mixture flows through a residence micro-reactor, optionally connected to a micro heat exchanger, to grow the shell material under the conditions given above. Optionally the residence micro-reactor system can be segmented into a micro-reactor and an attached conventional tube system which diameter is usually ≤ 2 mm but not restricted thereto.

It is preferred that the outer shell of step 5) shows a thickness from 0.3 to 4 nm of shell material that is with a percentage of at least 80%. Preferably whole or part of step 4.) and 5.) are repeated in to obtain the outer shell of desired thickness and composition.

- 6.) Reaction mixture is then cooled down to prevent further particle growth preferably by flowing into a second micro heat-exchanger or capillary tube to cool the reaction solution.

7) Usually the nanoparticles are then separated by adding anti-solvents and dried.

Typically the core of the nanoparticles of the present inventions is a nanoparticle comprising elements of the group:

- IB such as Cu, Ag or combination thereof,
- IIB in particular Zn,
- IIIA such as Al, Ga, In, or combinations thereof

further referred to as metal precursors and

- VIA such as S, Se, Te or combinations thereof, further referred to as anion precursor,
- wherein the composition of the nanoparticles is selected from the group consisting of I-VI, II-VI, III-VI, I-III-VI or I-II-IV-VI, II-III-VI or II-IV-V or mixtures thereof.

I-VI group semiconductors in the sense of the present invention are in particular CuS_2 .

II-VI group semiconductors in the sense of the present invention are e. g. ZnS , ZnSe or ZnTe .

- III-VI group semiconductors in the sense of the present invention are In_2S_3 .

I-III-VI group semiconductors in the sense of the present invention are CuInS_2 , AgInS_2 , CuInSe_2 , AgInSe_2 , CuGaS_2 , CuGaSe_2 , AgGaS_2 , AgGaSe_2 , CuInGaS , CuAgInS , CuInGaSe , CuAgInSe , AgInGaS , AgInGaSe , CuAgGaS , CuAgGaSe . Preferably, I-III-VI group
5 semiconductors in present invention are CuInS_2 (CIS), AgInS_2 , CuInSe_2 , AgInSe_2 , CuGaS_2 , CuInGaS , CuAgInS , AgInGaS . Most preferably, I-III-VI group semiconductors in present invention are CuInS_2 , AgInS_2 because of lower toxicity.

II-IV-V group semiconductors in the sense of the present invention are e.g. ZnSiP_2 , ZnGeP_2 , ZnSnP_2 , ZnSiN_2 , ZnGeN_2 , ZnSnN_2 .

10 II-III-VI group semiconductors in the sense of the present invention are e.g. ZnX_2Y_4 ($\text{X} = \text{Al}$, Ga , In ; $\text{Y} = \text{S}$, Se , Te).

I-II-IV-VI group semiconductors in the sense of the present invention are e.g. $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnGeS}_4$, $\text{Cu}_2\text{ZnSnS}_4$.
15

Typically the shell of the present invention is a II-VI shell in particular a ZnS , ZnSe , ZnTe shell.

Se source can be selected from Selenium and bis(trimethylsilyl) selenide, or any mixture of
20 them. Potential S-source may be S or S-containing compounds such as Thiourea, Bis(trimethylsilyl) sulphide or alkanethiol, etc. The alkanethiols can be mercaptans having one or more sulfhydryl functional groups, or a mixture of the mercaptans having one or more sulfhydryl functional groups. The mercaptan having one sulfhydryl functional group is preferably octyl mercaptan, iso-octyl-mercaptan, dodecyl mercaptan, hexadecanethiol or
25 octadecanethiol, etc. The mercaptans having more sulfhydryl functional groups are preferably 1,8-dioctyl mercaptans or 1,6-dioctyl mercaptans, etc.

The nanoparticles of the present inventions can have various shapes, morphologies (spherical particles, rods, plates, tetrapods, etc) and sizes. The nanoparticles of the present
30 invention show a characteristic average particle size of up to 40 nm, in a preferred embodiment of from 0.5 to 20 nm, and in a very particularly preferred embodiment particles with characteristic dimensions of from 1 to 10 nm, characteristic dimension meaning the property-determining dimension, for example the diameter of rods or the diameter of tetrapod arms. The particle size distribution which can be achieved has usually a standard
35 deviation of ± 10 nm, preferably of ± 5 nm and particularly preferably of ± 2 nm. A particle size distribution may be established and evaluated, for example, by a statistical analysis of transmission electron microscopy images.

The size and morphology of particles in particular core size and shell thickness can be varied by adjusting concentration and concentration ratios of precursor materials, ligand types and solvents as well as process parameters like temperature, temperature ramps, order and dynamics of addition of precursors and so on.

5

Solvent can be any non-coordinating long chain molecules (10 or more than 10 C) preferably non polar or low polar. The polarity index can vary from 4 to 0, preferably 1.5 to 0, most preferably 0.8 to 0, based on the polarity index of water being 9, according to the polarity scale (V.J. Barwick, Trends in Analytical Chemistry, vol. 16, no. 6, 1997, p.293ff, Table 5). The solvent is a high boiling point solvent, preferably without any double bond in the chain to prevent any side reaction. The organic solvents, during the reaction temperature, should be stable and degrade as little as possible. Preferably the boiling point of organic compound is above 200 °C, more preferably above 240 °C. Among others suitable solvents are octadecene, 1-hexadecene, 1-eicosene, paraffin wax, diphenyl ether, benzyl ether, dioctyl ether, squalane, trioctylamine, heat transfer fluids or any solvent mixture thereof,

Ligands can be phosphine (oxide), phosphonic acid, phosphinic acid, alkyl, amine, thiol and carboxylic acid. Suitable ligands are oleylamine, oleic acid, trioctylphosphine, trioctylphosphine oxide, myristic acid, low molecular weight thiols (from 8 to 18 C) such as dodecanethiol, tetradecanethiol, hexadecanethiol, as well as mixture thereof. For better luminescence quantum yield in the production of CuInS₂ thiols are preferred and dodecanethiol, tetradecanethiol and hexadecanethiol are most preferred.

The properties of nanoparticles such as particle size and particle morphology are characterized using transmission electron microscopy (TEM, Philips CM 20). The photoluminescence of nanoparticles are tested by UV / VIS absorption (Jena Analytics, Specord) and photoluminescence spectroscopy (Fluorolog 3, Jobin Yvon).

Characterization further includes Thermogravimetric Analysis-Mass Spectroscopy (TGA-MS), X-Ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD) and Photoluminescence (PL). Quantum yield were measured by comparison with sulforhodamine B according to the method described in "A Guide to Recording Fluorescence Quantum Yields", Jobin Yvon Horiba, http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Fluorescence/quantumyield_strad.pdf, retrieved October 5th, 2011.

35

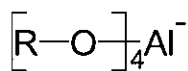
A first object of the present invention therefore a method for the preparation of

semiconducting core-shell nanoparticles comprising elements of the groups IB, IIB, IIIA, IVA, VA or VIA of the periodic classification wherein the composition of the core nanoparticle is selected from the group consisting of IB-VIA, IIB-VIA, IIIA-VIA, IB-IIIA-VIA or IB-IIB-IVA-VIA, IIB-IIIA-VIA or IIB-IVA-VA or mixtures thereof, and at least one shell comprises elements of the groups IIB and VIA, wherein in case the core composition is IIB-VIA the shell comprises at least a further element selected from the groups IB, IIIA, IVA or VA,, comprising the following steps:

- a.) Core reaction mixture comprising at least one cation metal precursors and an anion precursor is dissolved in a ligand and solvent mixture at a temperature that is still beneath the threshold at which nucleation takes place,
- b.) Core reaction mixture is heated above nucleation threshold temperature and then kept at the reaction temperature for core nucleation,
- c.) Optionally the heated reaction mixture is kept at a temperature well suited for core growth but lower than the nucleation temperature,
- d.) Shell reaction mixture prepared separately comprising at least one cation metal precursors and an anion precursor and heated at a temperature that is still beneath the threshold at which nucleation takes place is added to the reaction mixture of step b) or c) for shell coating of the core nanoparticles,
- e.) reaction mixture of step d) is heated and hold to a shell growth temperature,
- f.) reaction mixture is then cooled down to prevent further particle growth.

Wherein at least one of the metal precursor of step a) or d) comprises at least one non- or weakly coordinating anion selected from the group comprising:

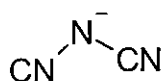
- fluorides (F⁻), cyanides (CN⁻)
- Sulphates, sulfonates, phosphates, acetates of formula: R-SO₄⁻, Triflates, R-SO₃⁻, R₂-PO₄⁴⁻, R-PO₄²⁻, PO₄³⁻, R-COO⁻, wherein R = C_nF_{2n+1} or R = C_nF_{2n-1},
- BF₄⁻, PF₆⁻, AlF₄⁻, AlCl₄⁻, SbF₆⁻, AsF₆⁻,
- Aluminates of formula:



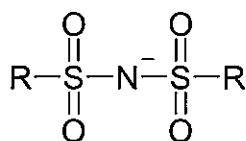
wherein R = C_nF_{2n+1} or R = C_nF_{2n-1}

- Borates of formula R₄-B⁻ wherein R = CN, C_nF_{2n+1} or R = C_nF_{2n-1}
- Amides and imides selected from the group of:

Dicyanamide



Bis-sulfonyl-imides of formula:



5 with R= F, CN, C_nF_{2n+1} (fluorinated branched or non-branched alkyl) or R = C_nF_{2n-1} (fluorinated aryl)

- Carboranes of formula XCB₁₁R₁₁- wherein R=H, F and X= H; alkyl,

Carborates

In particular a method wherein semiconducting core-shell nanoparticles are luminating at a colour range which is varied by way of adjusting concentration and concentration ratios of the non- or weakly coordinating anion.

The method of the present invention can be extended for the preparation of nanoparticles with different composition. For example, it can include binary copper sulphide or indium sulfide, ternary copper indium sulphide or quaternary copper indium zinc sulphide or doped/alloyed copper indium sulphide so composition is Cu_xIn_yZn_zS_n. According selenides or tellurides can also be prepared. Various morphologies like dots, ellipsoids, rods, tetrapods or multibranched can be achieved using the method of the present invention.

In a preferred embodiment a II-VI core is used. In this case typically a core/shell/shell nanoparticle is prepared wherein inner shell is made of a ternary or quaternary system and outer shell is a II-VI shell in particular a ZnS, ZnSe or ZnTe.

As an example the method of the invention allows to start with a pure ZnS core followed by the growth of a first CuInS₂ shell before the above proposed ZnS treatments and subsequent annealing are followed. This process would lead to "reverse type I particles, ZnS@CIS@ZnS," with gradient interfaces to widen the accessible colour range. This procedure may ensure a larger band gap inner core which after the above described annealing induced diffusion processes, would provide blue and green fluorescing nanoparticles with high quantum yield.

30 Important for a commercial application is the adaptation of synthesis conditions to a continuous production process. Most of known syntheses of CuInS₂ nanoparticles and its related structures are based on the batch route, which inevitably meet the difficulties of heat and mass transfer. The recently introduced microfluidic methods can realize operation in closed systems, and the

precise control of synthetic conditions offered by the strengthened heat and mass transfer makes the reproducible reaction achievable. Thus, we demonstrated the synthesis of ternary or quaternary nanoparticles with the composition IB-III A-VIA (IB = Cu, Ag; III A = In, Ga, Al; VIA = S, Se, Te) and using the inventive precursor materials by a continuous route based on
5 micro-reaction technology showing advantages being similar as previously described.

In a particular embodiment the synthesis of nanoparticles with precursors according to this invention is conducted in a microreactor system comprising elements selected from the group comprising for step a) and d) micromixers, for step b), c) and e) residence
10 microreactors, and for step f) a micro heat exchanger, wherein micromixers and residence reactors also comprise micro heat exchangers and elements are connected with each other so the reaction mixture flows continuously from one to the next element.

Using the inventive precursor materials and applying the described procedure resulted in a broader achievable colour range. In particular it could be demonstrated that the synthesis of
15 green fluorescing particles was easier to achieve if e.g. Zinc Bis(trifluoromethanesulfonyl)imide was used as Zinc precursor for the shell material. Advantages include a wider color tunability (due to a broader tunable band gap), narrower FWHM, shorter reaction time, high quantum yield and better stability. One time injection of Zinc Bis(trifluoromethanesulfonyl)imide with various ratio can tune the color of the system
20 from blue-green to red and even to the infrared. The full width half maximum (FWHM) can be tuned between 50 and 200 nm. The reaction time can be shortened to 5-15 mins. Quantum yields of 70% for in green color luminating nanoparticles (with an emission maximum at wavelengths around 520-540 nm) could be achieved with the new method and more than 80% for orange-yellow color luminating nanoparticles (with an emission maximum at wavelengths
25 around 580-600 nm) with improved reproducibility compared to the method of SG-Registration Number 20110XXXX-X. The stability was proved to be good with only little decrease of relatively less than 10% after 2 months.

A further object of the present invention is therefore a semiconducting core-shell
30 nanoparticle comprising elements of the groups IB, IIB, III A, IVA, VA or VIA of the periodic classification wherein:

- the composition of the core nanoparticle is selected from the group consisting of
IB-VIA, IIB-VIA, III A-VIA, IB-III A-VIA or IB-IIB-IVA-VIA, IIB-III A-VIA or
35 IIB-IVA-VA or mixtures thereof, and

- at least one shell comprises elements of the groups IIB and VIA, wherein in case the core composition is IIB-VIA the shell comprises at least a further element selected from the groups IB, IIIA, IVA or VA,

- having an emission maximum at wavelengths around 400-560 nm and a quantum yield $\geq 60\%$,
in particular green colour luminating nanoparticles with an emission maximum at wavelengths around 520-540 nm and / or in particular having a full width half maximum from 50 to 200 nm.

In particular the semiconducting core-shell nanoparticle of the present invention has the general formula:

- $ABC_2@A_xB_yZn_{2-x-y}C_2$ or
- $A_xB_yZn_{2-x-y}C_2@ZnC$ or
- $ABC_2@A_xB_yZn_{2-x-y}C_2@ZnC$ or
- $ZnC@ABC_2@A_xB_yZn_{2-x-y}C_2@ZnC$
- $ZnC@A_xB_yZn_{2-x-y}C_2@ABC_2@A_xB_yZn_{2-x-y}C_2@ZnC$

wherein A = one or more element of the group IB such as Cu, Ag or a combination thereof, B = one or more element of the group IIIA such as Al, Ga, In, or a combinations thereof or IC = one or more element of the group VIA such as S, Se, Te or a combinations thereof and

wherein x and y is $0 < x$ and $y < 1$ with no preference on the value for $|x - y|$ with a gradual increase of x and y from the particle surface to the remaining core.

In particular semiconducting core-shell nanoparticle wherein A=Cu, B=In and C=S.

Most preferred are nanoparticles obtainable by the method of the invention in particular ternary, quaternary or higher nanoparticle system obtained from a starting binary system.

Further objects of the present inventions are formulation or device comprising the semiconducting core-shell nanoparticle of the present invention, in particular electronic devices.

Examples:

Following particles were prepared to illustrate the applicability of the method of the present invention.

Example 1: Preparation of red luminating Quantum Dots (QD) $CuInS_2$ core particles

12.6 mg Copper(I)acetate (97%), 29.2 mg Indium(III)acetate (99.99%), 14.23 ml 1-Octadecene (90%) and 0.36 ml Dodecanethiole (98%) were added in a 3-neck round bottomed flask (RBF), degassed for 30 min and purged with N₂. The solution was rapidly heated up to 190°C under N₂ for 45 min and cooled down to room temperature (RT). Then the solution was rapidly heated up to 240°C for 30mins. The fluorescence emission peak of the dispersion was located at 710 nm with a full width half maximum (FWHM) of 130 nm. The quantum yield is 11% based on sulforhodamine B as reference.

10 Example 2: Preparation of red luminating QD CuInS₂ core particles with Max. Emission 735-780 nm

15.1 mg Copper(I)acetate (97%), 34.8 mg Indium(III)acetate (99.99%), 16 ml 1-Octadecene (ODE, 90%) and 1.74 ml Dodecanethiole (98%) were added in a 3-neck round bottomed flask (RBF), degassed for 30 min and purged with N₂. The solution was rapidly heated up to 160°C under N₂ for 10 min and cooled down to room temperature (RT). The mixture turns viscous. 1.39 ml ODE, 0.43 ml oleylamine (OLA) and 0.43 ml TOP was added so that the mixture became clear with a tea-like yellow color. Then the solution was heated up to 75°C and maintained for 5 min before cooled down to RT. Then the solution was rapidly heated up to 230°C and left there for 60 mins before cooled down slowly to RT. The fluorescence emission peak of the dispersion was located at 730 nm with a full width half maximum (FWHM) of 115 nm. The quantum yield is 6% based on sulforhodamine B as reference.

Example 3: Preparation of green color luminating QD CuInS₂@Cu_xIn_yZn_{2-x-y}S₂ core - gradient shell particles

The obtained core solution described in example 1 was kept under N₂ at RT (Precursor 1). Then 249.5 mg Zinc Bis(trifluoromethanesulfonyl)imide (99.99%), 5 ml TOP (90%) were added into a 3-neck round bottomed flask (RBF) and heated up to 70°C to dissolve chemicals until an almost transparent solution was formed (Precursor 2). Precursor 2 was then injected into precursor 1 at RT. The mixture solution was rapidly heated up to 200°C under N₂ 90 min before cooled slowly to room temperature. The fluorescence emission peak of the dispersion was located at 525 nm with a full width half maximum (FWHM) of 86 nm. The quantum yield was 70 % based on sulforhodamine B as reference. All sensitive precursor materials should be carefully handled to prevent exposure to air and moisture.

Comparative Example 3: Preparation of green color luminating QD $\text{CuInS}_2@ \text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2$ core - gradient shell particles according to the method of SG-Registration Number 20110XXXX-X.

76 mg Copper(I)acetate (97%), 175 mg Indium(III)acetate (99.99%), 15 ml 1-Octadecene (90%) and 3 ml Dodecanethiole (98%) (70%) were added in a 3-neck round bottomed flask (RBF), degassed for 30 min and purged with N_2 (Precursor 1). The solution was heated to 220 °C (10 mins). Then 1.7554 g Zinc acetate (99.99%), 24 ml 1-Octadecene (90%), 12 ml Dodecanethiole (98%), 8 ml Oleylamine (70%) and 8 ml TOP were added into a sample vial and heated to 50 °C in an oil bath to dissolve chemicals until a transparent solution was formed (Precursor 2). Precursor 1 temperature was rapidly cooled to 50 °C from 220 °C (in 2 mins) using the water bath. At 50 °C Precursor 2 was injected into reaction. Reaction was left to mix at 50 °C for 5 mins and the temperature was raised to 240 °C. Reaction was carried out 240 °C for 30min. In the further overcoating synthesis, 28 ml of obtained $\text{CuInS}_2@ \text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2$ described above was added in to a 3-neck RBF, degassed for 30 min and purged with N_2 . Then separately 2 batches were prepared with each containing 220 mg Zinc acetate (99.99%), 6 ml 1-Octadecene (90%), 3 ml Dodecanethiole (98%) and 2 ml Oleylamine (70%) which were added into a sample vial and heated to 100 °C in an oil bath to dissolve chemicals until a transparent or almost transparent solution was formed (Precursor 3). First batch of precursor 3 was injected into 28 ml of obtained $\text{CuInS}_2@ \text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2$ reaction solution at 220 °C using a syringe pump (11 ml at 1 ml/min). Then after 1st injection, let it react for 30 min. Then the second batch was injected at 220 °C using a syringe pump (11 ml at 1 ml/min). Then the reaction solution was held at 220 °C for another 30 min. The fluorescence emission peak of the dispersion was located at 545 nm with a “full width of half maximum” (FWHM) at about 115 nm. The quantum yield was 33 %.

25

Example 4: Preparation of orange color luminating QD $\text{CuInS}_2@ \text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2$ core - gradient shell-particles

The obtained core solution described in example 2 was kept under N_2 at RT (Precursor 1). Then 249.5 mg Zinc Bis(trifluoromethanesulfonyl)imide (99.99%), 5 ml TOP (90%) and 0.19 ml DDT were added into a 3-neck round bottomed flask (RBF) and heated up to 70 °C to dissolve chemicals until a transparent solution was formed (Precursor 2). Precursor 2 was then injected into precursor 1 at RT. The mixture solution was rapidly heated up to 200 °C under N_2 90 min before cooled slowly to room temperature. The fluorescence emission peak of the dispersion was located at 638 nm with a full width half maximum (FWHM) of 170 nm. The

30

quantum yield was 82 % based on sulforhodamine B as reference. Stability tests showed that there is no decrease of the quantum yield within 1-3 months.

Example 5: Preparation of orange-yellow luminescent QD $\text{CuInS}_2@ \text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2@ \text{ZnS}$ core shell particles

Precursor 1: 15.1 mg Copper (I) acetate (97 %) and 34.8 mg of Indium (III) acetate (99.99 %) were added in a 3-necked round bottom flask (RBF) inside the glove box, degassed for 10 min and purged with N_2 . 1.74 ml of Dodecanethiol (DDT, 98%) and 14 ml of Dioctyl ether (DOE, 99%) were added in a Schlenk flask, degassed for 10 min and purged with N_2 . Inject Dodecanethiol (DDT, 98%) and Dioctyl ether (DOE, 99%) mixture into the 3-necked round bottom flask (RBF) containing copper(I) acetate and Indium(III) acetate, degassed for 10 min and purge with N_2 . The solution was rapidly heated to 160°C under N_2 and maintained for 10 min before cooled down to room temperature (RT). A bright yellow viscous solution was formed. 1.94 ml of Dioctyl ether (DOE, 99%), 0.43 ml of Oleylamine (OLA, 70%) and 0.43 ml of Trioctylphosphine (TOP, 97%) was added so that the mixture became clear with tea-like yellow color. The reaction was heated up to 230°C and maintained for 60 min before cooled down to room temperature (RT). The fluorescence emission peak of the dispersion was located at 748 nm with a full width half maximum (FWHM) of 136 nm. The quantum yield was 6 % based on sulforhodamine B as reference.

Precursor 2: 125.1 mg of Zinc di[bis(trifluoromethylsulfonyl)imide (99.99 %) and 5 ml of Trioctylphosphine (TOP, 97%) were added into a 3-necked round flask (RBF) and heated to 70°C to dissolve chemicals until an almost transparent solution was formed. Precursor 2 was then injected into precursor 1 at RT. The mixture was rapidly heated up to 200°C under N_2 for 90 min before cooled slowly to RT. The fluorescence emission peak of the dispersion was located at 620 nm with a full width half maximum (FWHM) of 150 nm. The quantum yield was 79 % based on sulforhodamine B as reference.

Precursor 3 was prepared as precursor 2. Precursor 3 was then injected into precursor 1 and 2 at RT. The mixture was rapidly heated up to 200°C under N_2 for 5 min before cooled slowly to RT. The fluorescence emission peak of the dispersion was located at 599 nm with a full width half maximum (FWHM) of 128 nm. The quantum yield was 78 % based on sulforhodamine B as reference.

There is a further blue shift of the maximum emission peak due to the addition of a second Zn-containing shell. Before and after purification, there is no change for QY. The stability was proven to be good since there is no decrease of QY within 3 months.

Example 6: Preparation of luminating $\text{CuInS}_2@(\text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2)@\text{ZnS}$ core shell particles with CuI as core metal precursor

19 mg Copper(I)iodide (98%), 29.2 mg Indium(III)acetate (99.99%), 14.35 ml 1-Octadecene (90%) and 0.24 ml Dodecanethiols (98%) were added in a 3-neck round bottomed flask (RBF),
5 degassed for 30 min and purged with N_2 . The solution was rapidly heated up to 220 °C under N_2 for 45 min and cooled down to room temperature (Precursor 1). Then 249.5 mg Zinc Bis(trifluoromethanesulfonyl)imide (99.99%), 5 ml TOP (90%) were added into a 3-neck round bottomed flask (RBF) and heated up to 70 °C to dissolve chemicals until an almost transparent solution was formed (Precursor 2). Precursor 2 was quickly injected into precursor
10 1, degassed and heated to 200 °C for 90 min. The mixture was then cooled to room temperature. The fluorescence emission peak of the dispersion was located at 542 nm with a full width half maximum (FWHM) of 91 nm. The quantum yield was 5.7 % based on sulforhodamine B as reference.

15 Example 7: Preparation of luminating QD $\text{CuInS}_2@(\text{ZnS})@\text{ZnS}$ core shell particles from $\text{Cu}_2\text{S} \rightarrow \text{CIS} \rightarrow \text{CuInS}_2@(\text{ZnS})$ route

Precursor 1: 31.5 mg Copper(I)acetate (97%), 18 ml 1-Octadecene (90%) and 1.8 ml Dodecanethiol (98%) were added in a 3-neck round bottomed flask (RBF), degassed for 10 min and purged with N_2 . The solution was rapidly heated up to 160 °C under N_2 and the orange-
20 brown turbid liquid was formed and hold for 2 min. Then the solution was heated up to 170 °C and maintained for 4 min before cooled down to RT. 10 ml 1-Octadecene (90%) was injected to the above solution, heated up to 140 °C and maintained for 2 min before cooled down to RT. Then 8 ml 1-Octadecene (90%) was injected to the above solution, heated up to 240 °C and maintained for 30 min before cooled down to RT. The clear dark brown solution was
25 formed. 10 ml of the above obtained Cu_2S particle solution (Precursor 1) was used for the following Indium(III) tris(trifluoromethanesulfonimide) and Zinc Bis(trifluoromethanesulfonyl)imide injection.

Precursor 2: 95.5 mg Indium(III) tris(trifluoromethanesulfonimide), 3.1 ml Trioctylphosphine and 1.9 ml Dodecanethiol were mixed. Precursor 2 was injected into 10 ml of the precursor 1
30 reaction solution at room temperature. The reaction solution was degassed for 5 min, then heated up to 240 °C and maintained for 10 min. The reaction was cooled to room temperature after 10 mins. The clear dark red solution was fluorescing in red color.

Precursor 3: 249.5 mg Zinc Bis(trifluoromethanesulfonyl)imide and 5 ml Trioctylphosphine
Precursor 3 was injected into the above obtained CuInS_2 particle solution at room temperature.
35 The reaction solution was degassed for 5 min, then heated up to 200 °C and maintained for 60

min. The reaction mixture was cooled to room temperature after 10 mins. The fluorescence emission peak of the dispersion was located at 699 nm with a full width half maximum (FWHM) of 150 nm and a quantum yield of 30 %. This example proved the transformation from Cu_2S to CuInS_2 and then to $\text{CuInS}_2@\text{ZnS}$.

5

Example 8: Preparation of luminating QD $\text{CuInS}_2@\text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2@\text{ZnS}$ core shell particles with $\text{Zn}(\text{TFSI})_2$ as Zn precursor and dioctyl ether as solvent

Precursor 1: 15.1 mg Copper (I) acetate (97%) and 34.8mg of Indium (III) acetate (99.99%) were added in a 3-necked round bottom flask (RBF) inside the glove box, degassed for 10 min and purged with N_2 . 1.74 ml of Dodecanethiol (DDT, 98%) and 14 ml of Dioctyl ether (DOE, 99%) were added in a Schlenk flask, degassed for 10min and purged with N_2 . Dodecanethiol (DDT, 98%) and Dioctyl ether (DOE, 99%) mixture was then injected into the 3-necked round bottom flask (RBF) containing copper(I) acetate and Indium(III) acetate, degassed for 10 min and purged with N_2 . The solution was rapidly heated to 160°C under N_2 and maintained for 10 min before cooled down to room temperature (RT). A bright yellow viscous solution was formed. 1.94 ml of Dioctyl ether (DOE, 99%), 0.43 ml of Oleylamine (OLA, 70%) and 0.43 ml of Trioctylphosphine (TOP, 97%) was added so that the mixture became clear with tea-like yellow color. The reaction was heated up to 230°C and maintained for 60 min before cooled down to room temperature. The fluorescence emission peak of the dispersion was located at 761 nm with a full width half maximum (FWHM) of 134 nm. The quantum yield was 7 % based on sulforhodamine B as reference.

Precursor 2: 125.1 mg of Zinc di[bis(trifluoromethylsulfonyl)imide (99.99 %) and 5 ml of Trioctylphosphine (TOP, 97%) were added into a 3-necked round flask (RBF) and heated to 70°C to dissolve chemicals until an almost transparent solution was formed. Precursor 2 was then injected into precursor 1 at RT. The mixture was rapidly heated up to 200°C under N_2 for 90 min before cooled slowly to RT. The fluorescence emission peak of the dispersion was located at 678 nm with a full width half maximum (FWHM) of 205 nm. The quantum yield was 65 % based on sulforhodamine B as reference. All sensitive precursor materials should be carefully handled to prevent exposure to air and moisture. The obtained sample is easier to be purified and more stable compared with samples synthesized by ODE as solvent.

30

Example 9: Preparation of luminating QD $\text{CuInS}_2@\text{Cu}_x\text{In}_y\text{Zn}_{2-x-y}\text{S}_2@\text{ZnS}$ core shell particles with $\text{CuAc}:\text{InAc}_3=1:3$ ratio and $\text{Zn}(\text{TFSI})_2$ as Zn precursor

Precursor 1: 12.6 mg Copper (I) acetate (97%) and 87.6 mg of Indium (III) acetate (99.99%) were added in a 3-necked round bottom flask (RBF) inside the glove box, degassed for 10 min

35

and purged with N₂. 0.36 ml of Dodecanethiol (DDT, 98%) and 14.23 ml of 1-Octadecene (ODE, 90%) were added in a Schlenk flask, degassed for 10 min and purged with N₂. Dodecanethiol (DDT, 98%) and 1-Octadecene (ODE, 90%) mixture was injected into the 3-necked round bottom flask (RBF) containing copper(I) acetate and Indium(III) acetate, degassed for 10 min and purged with N₂. The solution was rapidly heated to 190°C under N₂ and maintained for 45 min before cooled down to room temperature (RT). A clear intense red solution was formed. The reaction heated up to 240°C and maintained for 10 min before cooled down to RT. The fluorescence emission peak of the dispersion was located at 697 nm with a full width half maximum (FWHM) of 155 nm. The quantum yield was 35 % based on sulforhodamine B as reference.

Precursor 2: 249.5 mg of Zinc di[bis(trifluoromethylsulfonyl)imide (99.99%) and 5 ml of Trioctylphosphine (TOP, 97%) were added into a 3-necked round flask (RBF) and heated to 70°C to dissolve chemicals until an almost transparent solution was formed. Precursor 2 was then injected into precursor 1 at RT. The mixture was rapidly heated up to 200°C under N₂ for 5 min before cooled slowly to room temperature (RT). The fluorescence emission peak of the dispersion was located at 543 nm with a full width half maximum (FWHM) of 100 nm. The quantum yield was 57 % based on Fluorescein as reference. All sensitive precursor materials should be carefully handled to prevent exposure to air and moisture

Example 10: Preparation of luminating OD CuInS₂@Cu_xIn_yZn_{2-x-y}S₂@ZnS core shell particles with CuAc:InAc₃=1 :4 ratio and Zn (TFSI)₂ as Zn precursor

Precursor 1: 12.6 mg Copper (I) acetate (97%) and 116.8 mg of Indium (III) acetate (99.99%) were added in a 3-necked round bottom flask (RBF) inside the glove box, degassed for 10 min and purged with N₂. 0.36 ml of Dodecanethiol (DDT, 98%) and 14.23 ml of 1-Octadecene (ODE, 90%) were added in a Schlenk flask, degassed for 10 min and purged with N₂. Dodecanethiol (DDT, 98%) and 1-Octadecene (ODE, 90%) mixture was injected into the 3-necked round bottom flask (RBF) containing copper(I) acetate and Indium(III) acetate, degassed for 10 min and purged with N₂. The solution was rapidly heated to 190°C under N₂ and maintained for 45 min before cooled down to room temperature (RT). A clear intense red solution was formed. The reaction heated up to 240°C and maintained for 5 min before cooled down to RT. The fluorescence emission peak of the dispersion was located at 679 nm with a full width half maximum (FWHM) of 135 nm. The quantum yield was 15% based on sulforhodamine B as reference.

Precursor 2: 249.5 mg of Zinc di[bis(trifluoromethylsulfonyl)imide (99.99%) and 5 ml of Trioctylphosphine (TOP, 97%) were added into a 3-necked round flask (RBF) and heated to

70°C to dissolve chemicals until an almost transparent solution was formed. Precursor 2 was then injected into precursor 1 at RT. The mixture was rapidly heated up to 200°C under N₂ for 5 min before cooled slowly to room temperature (RT). The fluorescence emission peak of the dispersion was located at 541 nm with a full width half maximum (FWHM) of 94 nm. The quantum yield was 53 % based on fluorescein as reference. All sensitive precursor materials should be carefully handled to prevent exposure to air and moisture.

Example 11: Preparation of luminating yellow color CuInS₂@Cu_xIn_yZn_{2-x-y}S₂@ZnS core shell particles with Zn (TFSI)₂ as Zn precursor

10 Precursor 1: 63.2 mg Copper (I) acetate (97%) and 146 mg of Indium (III) acetate (99.99%) were added in a 3-necked round bottom flask (RBF) inside the glove box, degassed for 10 min and purged with N₂. 1.82 ml of Dodecanethiol (DDT,98%) and 71.15 ml of 1-Octadecene (ODE,90%) were added in a Schlenk flask, degassed for 10 min and purged with N₂. Dodecanethiol (DDT, 98%) and 1-Octadecene (ODE, 90%) mixture was injected into the 15 necked round bottom flask (RBF) containing copper(I) acetate and Indium(III) acetate, degassed for 10 min and purged with N₂. The solution was rapidly heated to 190°C under N₂ and maintained for 45 min before cooled down to room temperature (RT). A clear intense red solution was formed. The reaction heated up to 240°C and maintained for 30 min before cooled down to room temperature (RT). The fluorescence emission peak of the dispersion was located 20 at 710 nm with a full width half maximum (FWHM) of 106 nm. The quantum yield was 5% based on sulforhodamine B as reference.

Precursor 2: 625.7 mg of Zinc di[bis(trifluoromethylsulfonyl)imide (99.99%) and 25 ml of Trioctylphosphine (TOP, 97%) were added into a 3-necked round flask (RBF) and heated to 70°C to dissolve chemicals until an almost transparent solution was formed. Precursor 2 was 25 then injected into precursor 1 at room temperature (RT).The mixture was rapidly heated up to 200°C under N₂ for 90 min before cooled slowly to RT. The fluorescence emission peak of the dispersion was located at 585 nm with a full width half maximum (FWHM) of 97 nm. The quantum yield was 82 % based on sulforhodamine B as reference. All sensitive precursor materials should be carefully handled to prevent exposure to air and moisture

30

Example 12: Variation of the amount of Zinc Bis(trifluoromethanesulfonyl)imide

Preparation was conducted as described in example 11 with different amount of Zinc Bis(trifluoromethanesulfonyl)imide. Color was easiliy tuned from blue-green (520 nm) to red (670 nm)

35

Precursor Ratio	Core-Shell Particles	
CIS : ZnTFSI	Lamda _{max} (nm)	QY (%)
2:1	634	14.20
1:1	595	34.98
1:2	585	82.30
1:4	526	70.58

Example 13: Preparation of yellow color luminating QD CuInS₂@ZnS core shell particles using continuous method <with Dioctyl ether and ZnTFSI, Cu:In = 1:3>

5 Precursor 1: 119.9 mg Copper(I)iodide (98%), 540.2 mg Indium(III)acetate (99.99%), 90 ml dioctyl ether and 6.0 ml Dodecanethiol (98%) were added in a 3-neck round bottomed flask (RBF), degassed for 10 min and purged with N₂. The solution was rapidly heated up to 170 °C under N₂ and hold for 25 min until a reddish-orange, clear solution is formed. The solution was
10 then cooled down to RT. 84 ml dioctyl ether was injected to the above solution. The mixture was degassed for 10 min, followed by purging with N₂ for 10 min. The mixture was injected into the micro-reactor at a flow-rate of 3 mL/min, under a temperature of 260 °C for the synthesis of CuInS₂ (CIS) core. The resulting product emits orange light under UV excitation (peak emission wavelength ~ 630 nm, QY~10%). 30 mL of the core solution was placed in a RBF and degassed for 5min, followed by purging with N₂ for 5 min. The mixture was then
15 heated to and maintained at 40 °C.

Precursor 2: 249.5 mg Zinc di[bis(trifluoromethylsulfonyl)imide], 5 ml Trioctylphosphine and 0.19 ml Dodecanethiol were mixed and sealed. The mixture is stirred and heated to 70 °C until it becomes a clear, tea-colored solution. Precursor 2 was injected the 30 mL of CIS core formed earlier in the micro-reactor in RBF. The resulting mixture is maintained at 40 °C while being
20 stirred continuously for about 10 min. The above mixture was then injected into the micro-reactor at a flow-rate of 6 mL/min at 260 °C for the formation of ZnS shell over the CIS core. The resulting product emitted a peak emission wavelength (588 nm, QY~32 %) that is blue-shifted by about 40 nm compared with the wavelength of peak emission of the CIS core.

25 Example 14: Preparation of orange colour luminating QD CuInS₂@ZnS core shell particles using continuous method <with ODE and ZnTFSI Cu:In = 1:3>

Precursor 1: 23.6 mg Copper(I)acetate (97%), 163.6 mg Indium(III)acetate (99.99%), 54.5 ml 1-Octadecene (90%) and 1.36 ml Dodecanethiol (98%) were added in a 3-neck round bottomed

flask (RBF), degassed for 10 min and purged with N₂. The solution was rapidly heated up to 170 °C under N₂ and hold for 40 min until tea-like, yellow, clear solution is formed. The solution was then cooled down to RT. 31.8 ml 1-Octadecene (90%) was injected to the above solution, and the mixture was degassed for 10 min, followed by purging with N₂ for 10 min.

- 5 The mixture was injected into the micro-reactor at a flow-rate of 6 mL/min, under a temperature of 270 °C for the synthesis of CIS core. The resulting product emitted red light under UV excitation (peak emission wavelength ~ 668 nm, QY = 14%).

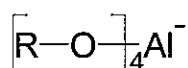
- Precursor 2: 249.5 mg Zinc di[bis(trifluoromethylsulfonyl)imide], 5 ml Trioctylphosphine and 0.19 ml Dodecanethiol were mixed and sealed. The mixture is stirred and heated to 70 °C until
10 it becomes a clear, tea-colored solution. Precursor 2 was injected the 18 mL of CIS core formed earlier in the micro-reactor in RBF and mixed by stirring under N₂ flow for 10 min. The above mixture was then injected into the micro-reactor at a flow-rate of 6 mL/min at 240 °C for the formation of ZnS shell over the CIS core. The resulting product emitted at a peak emission wavelength (608nm, QY = 30%) that was blue-shifted by about 60 nm compared with the
15 wavelength of peak emission of the CIS core.

Claims

1. Method for the preparation of semiconducting core-shell nanoparticles comprising elements of the groups IB, IIB, IIIA, IVA, VA or VIA of the periodic classification wherein the composition of the core nanoparticle is selected from the group consisting of IB-VIA, IIB-VIA, IIIA-VIA, IB-IIIA-VIA or IB-IIB-IVA-VIA, IIB-IIIA-VIA or IIB-IVA-VA or mixtures thereof, and at least one shell comprises elements of the groups IIB and VIA, , wherein in case the core composition is IIB-VIA the shell comprises at least a further element selected from the groups IB, IIIA, IVA or VA, said method comprising the following steps:
 - a.) Core reaction mixture comprising at least one cation metal precursors and an anion precursor is dissolved in a ligand and solvent mixture at a temperature that is still beneath the threshold at which nucleation takes place,
 - b.) Core reaction mixture is heated above nucleation threshold temperature and then kept at the reaction temperature for core nucleation,
 - c.) Optionally the heated reaction mixture is kept at a temperature well suited for core growth but lower than the nucleation temperature,
 - d.) Shell reaction mixture prepared separately comprising at least one cation metal precursors and an anion precursor and heated at a temperature that is still beneath the threshold at which nucleation takes place is added to the reaction mixture of step b) or c) for shell coating of the core nanoparticles,
 - e.) reaction mixture of step d) is heated and hold to a shell growth temperature,
 - f.) reaction mixture is then cooled down to prevent further particle growth.

Wherein at least one of the metal precursor of step a) or d) comprises at least one non- or weakly coordinating anion selected from the group comprising:

- fluorides (F⁻), cyanides (CN⁻)
- Sulphates, sulfonates, phosphates, acetates of formula: R-SO₄⁻, Triflates, R-SO₃⁻, R₂-PO₄⁴⁻, R-PO₄²⁻, PO₄³⁻, R-COO⁻, wherein R = C_nF_{2n+1} or R = C_nF_{2n-1} ,
- BF₄⁻, PF₆⁻, AlF₄⁻, AlCl₄⁻, SbF₆⁻, AsF₆⁻,
- Aluminates of formula:

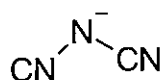


wherein R = C_nF_{2n+1} or R = C_nF_{2n-1}

- Borates of formula R₄-B⁻ wherein R = CN, C_nF_{2n+1} or R = C_nF_{2n-1}

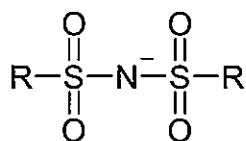
- Amides and imides selected from the group of:

Dicyanamide



Bis-sulfonyl-imides of formula:

5



with R= F, CN, C_nF_{2n+1} (fluorinated branched or non-branched alkyl) or R = C_nF_{2n-1} (fluorinated aryl)

- Carboranes of formula XCB₁₁R₁₁- wherein R=H, F and X= H; alkyl,

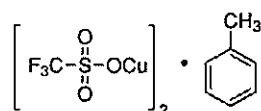
10

- Carborates

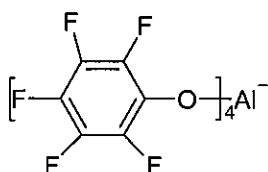
2. Method according to claim 1 wherein the non- or weakly coordinating anion is selected from the group comprising:

Copper(I) trifluoromethanesulfonate toluene complex

15

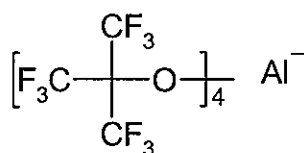


Tetrakis [2, 3, 4, 5, 6-pentafluorophenolato] aluminate(1-)



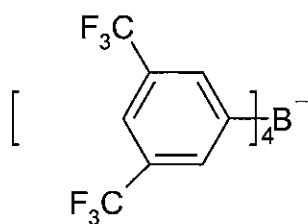
Tetrakis [1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-2-propanolato] aluminate(1-)

20

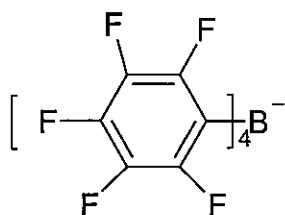


Tetra(cyano)borate B(CN)₄⁻

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate



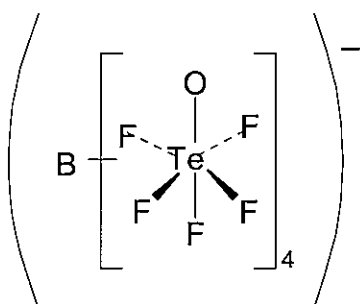
Tetrakis (pentafluorophenyl) borate



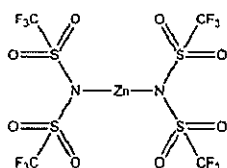
Tetrakis(trifluoromethyl)borate $[B(CF_3)_4]^-$

5

Teflate-Borate $[B(OTeF_5)_4]^-$



Zinc Bis(trifluoromethanesulfonyl)imide



10

Indium or copper Tris(trifluoromethanesulfonimide).

15

3. Method according to one of the claims 1 or 2 wherein semiconducting core-shell nanoparticles are luminating at a colour range which is varied by way of adjusting concentration and concentration ratios of the non- or weakly coordinating anion.

4. Method according to one of the claims 1 to 3 wherein semiconducting core-shell nanoparticles are prepared in more than one consecutive step with single or different types of the non- or weakly coordinating anion ions to change a starting binary to a ternary, quaternary or higher nanoparticle system.

20

5. Method according to one of the claims 1 to 4 conducted in a microreactor system comprising elements selected from the group comprising for step a) and d) micromixers, for step b), c) and e) residence microreactors, and for step f) a micro heat exchanger, wherein micromixers and residence reactors also comprise micro heat exchangers and elements are connected with each other so the reaction mixture flows continuously from one to the next element.
6. Semiconducting core-shell nanoparticle comprising elements of the groups IB, IIB, IIIA, IVA, VA or VIA of the periodic classification wherein:
 - the composition of the core nanoparticle is selected from the group consisting of IB-VIA, IIB-VIA, IIIA-VIA, IB-IIIA-VIA or IB-IIB-IVA-VIA, IIB-IIIA-VIA, IIB-IVA-VA or mixtures thereof, and
 - at least one shell comprises elements of the groups IIB and VIA, , wherein in case the core composition is IIB-VIA the shell comprises at least a further element selected from the groups IB, IIIA, IVA or VA,
 - having an emission maximum at wavelengths around 400-560 nm and a quantum yield ≥ 60 %.
7. Semiconducting core-shell nanoparticle according to claim 6 having a full width half maximum from 50 to 200 nm.
8. Semiconducting core-shell nanoparticle according to one of the claim 6 or 7 with the general formula:
 - $ABC_2@A_xB_yZn_{2-x-y}C_2$ or
 - $A_xB_yZn_{2-x-y}C_2@ZnC$ or
 - $ABC_2@A_xB_yZn_{2-x-y}C_2@ZnC$ or
 - $ZnC @ABC_2@A_xB_yZn_{2-x-y}C_2@ZnC$
 - $ZnC@A_xB_yZn_{2-x-y}C_2@ABC_2@A_xB_yZn_{2-x-y}C_2@ZnC$
 wherein A = one or more element of the group IB, B = one or more element of the group IIIA or C = one or more element of the group VIA, and

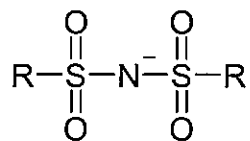
wherein x and y is $0 < x$ and $y < 1$ with no preference on the value for $|x - y|$ with a gradual increase of x and y from the particle surface to the remaining core
9. Semiconducting core-shell nanoparticle according to claim 8 wherein A = Cu, Ag or a combination thereof, B = Al, Ga, In, or a combinations thereof or C = S, Se, Te or a combinations thereof,

10. Semiconducting core-shell nanoparticle according to claim 9 wherein A=Cu, B=In and C=S.
11. Semiconducting core-shell nanoparticle according to one of the claims 6 to 10
5 obtainable by the method according to one of the claims 1 to 5.
12. Semiconducting core-shell nanoparticle according to claim 11 wherein a binary system is used as a core material for the preparation of ternary, quaternary or higher nanoparticle system.
- 10 13. Formulation comprising the semiconducting core-shell nanoparticle according to one of the claim 6 to 12.
14. Device comprising the semiconducting core-shell nanoparticle according to one of the
15 claim 6 or 12.
15. Device according to claim 14 wherein the device is an electronic device.
16. Use of metal precursor comprising at least one non- or weakly coordinating anion selected
20 from the group comprising:
 - fluorides (F⁻), cyanides (CN⁻)
 - Sulphates, sulfonates, phosphates, acetates of formula: R-SO₄⁻, Triflates, R-SO₃⁻, R₂-PO₄⁴⁻, R-PO₄²⁻, PO₄³⁻, R-COO⁻, wherein R = C_nF_{2n+1} or R = C_nF_{2n-1},
 - BF₄⁻, PF₆⁻, AlF₄⁻, AlCl₄⁻, SbF₆⁻, AsF₆⁻,
 - 25 • Aluminates of formula:

$$\left[\text{R}-\text{O} \right]_4 \text{Al}^-$$
 wherein R = C_nF_{2n+1} or R = C_nF_{2n-1}
 - Borates of formula R₄-B⁻ wherein R = CN, C_nF_{2n+1} or R = C_nF_{2n-1}
 - Amides and imides selected from the group of:

30 Dicyanamide

$$\text{CN}-\text{N}^--\text{CN}$$
 Bis-sulfonyl-imides of formula:



with R= F, CN, C_nF_{2n+1} (fluorinated branched or non-branched alkyl) or R = C_nF_{2n-1} (fluorinated aryl)

- Carboranes of formula XCB₁₁R₁₁- wherein R=H, F and X= H; alkyl,
 - Carborates
- for the preparation of semi-conducting nanoparticles.