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(12) **United States Patent**
Talapin et al.

(10) **Patent No.:** **US 9,346,998 B2**
(45) **Date of Patent:** **May 24, 2016**

(54) **MATERIALS AND METHODS FOR THE PREPARATION OF NANOCOMPOSITES**

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(2), (4) Date: **Jan. 19, 2012**

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PCT Pub. Date: **Oct. 28, 2010**

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(51) **Int. Cl.**

C01B 19/00 (2006.01)
C09K 11/56 (2006.01)
B82Y 30/00 (2011.01)
B82Y 40/00 (2011.01)
C09K 11/02 (2006.01)
C09K 11/88 (2006.01)
C30B 7/00 (2006.01)
C30B 29/40 (2006.01)
C30B 29/46 (2006.01)
C30B 29/60 (2006.01)
H01L 35/16 (2006.01)

(52) **U.S. Cl.**

CPC **C09K 11/562** (2013.01); **B82Y 30/00** (2013.01); **B82Y 40/00** (2013.01); **C01B 19/002** (2013.01); **C01B 19/007** (2013.01); **C09K 11/025** (2013.01); **C09K 11/565** (2013.01); **C09K 11/883** (2013.01); **C30B 7/00** (2013.01); **C30B 29/40** (2013.01); **C30B 29/46** (2013.01); **C30B 29/60** (2013.01); **H01L 35/16** (2013.01); **C01P 2002/52** (2013.01); **C01P 2002/72** (2013.01); **C01P 2002/84** (2013.01); **C01P 2002/85** (2013.01); **C01P 2004/03** (2013.01); **C01P 2004/04** (2013.01); **C01P 2004/16** (2013.01)

(58) **Field of Classification Search**

USPC 438/95, 93; 204/59; 252/502; 423/508
See application file for complete search history.

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Primary Examiner — Monique Peets

(74) *Attorney, Agent, or Firm* — Marshall, Gerstein & Borun LLP

(57) **ABSTRACT**

Disclosed herein is an isolable colloidal particle comprising a nanoparticle and an inorganic capping agent bound to the surface of the nanoparticle, a solution of the same, a method for making the same from a biphasic solvent mixture, and the formation of structures and solids from the isolable colloidal particle. The process can yield photovoltaic cells, piezoelectric crystals, thermoelectric layers, optoelectronic layers, light emitting diodes, ferroelectric layers, thin film transistors, floating gate memory devices, imaging devices, phase change layers, and sensor devices.

7 Claims, 32 Drawing Sheets

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FIG. 1

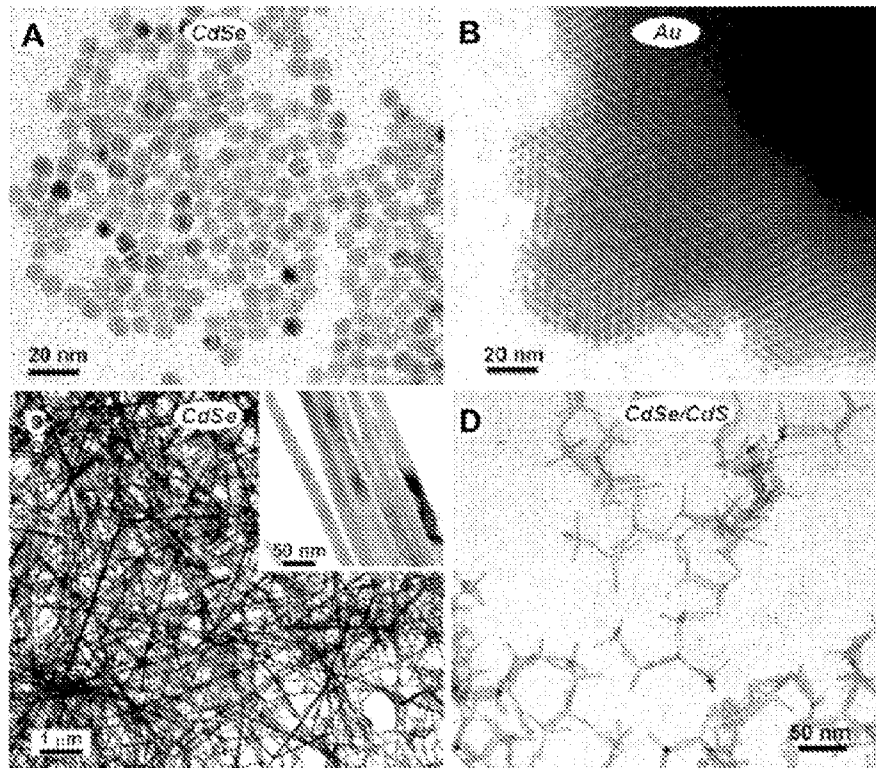


FIG. 2

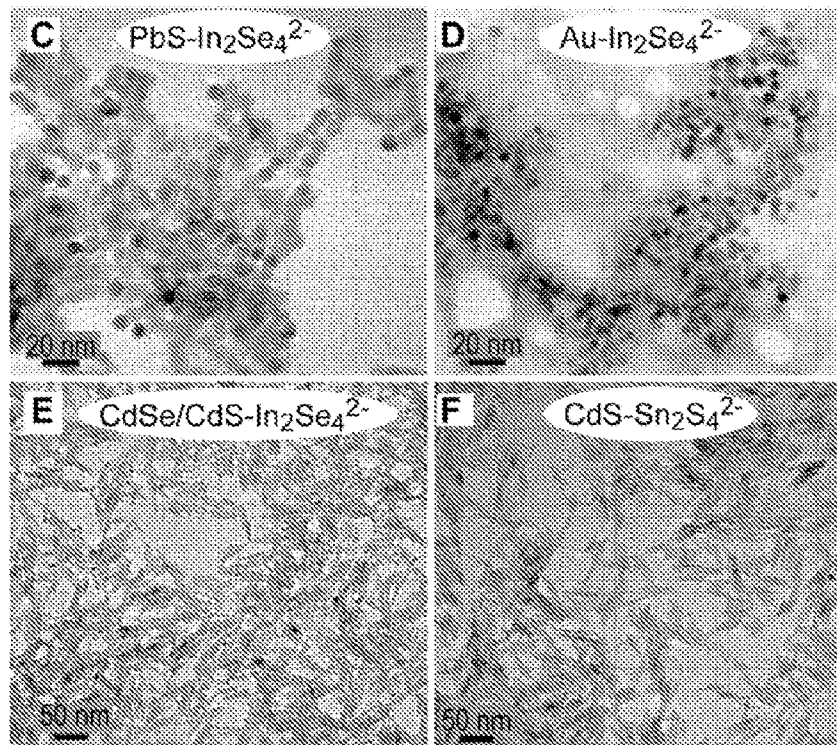




FIG. 3

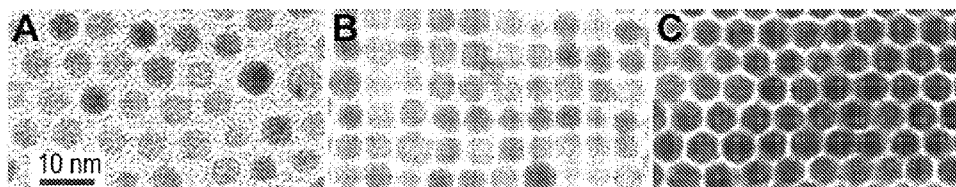


FIG. 4

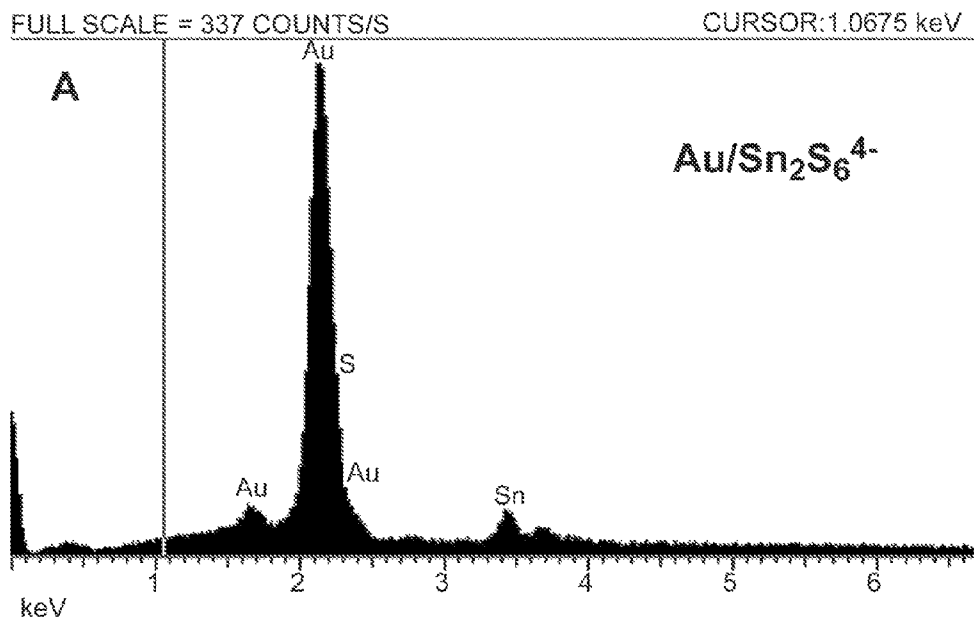
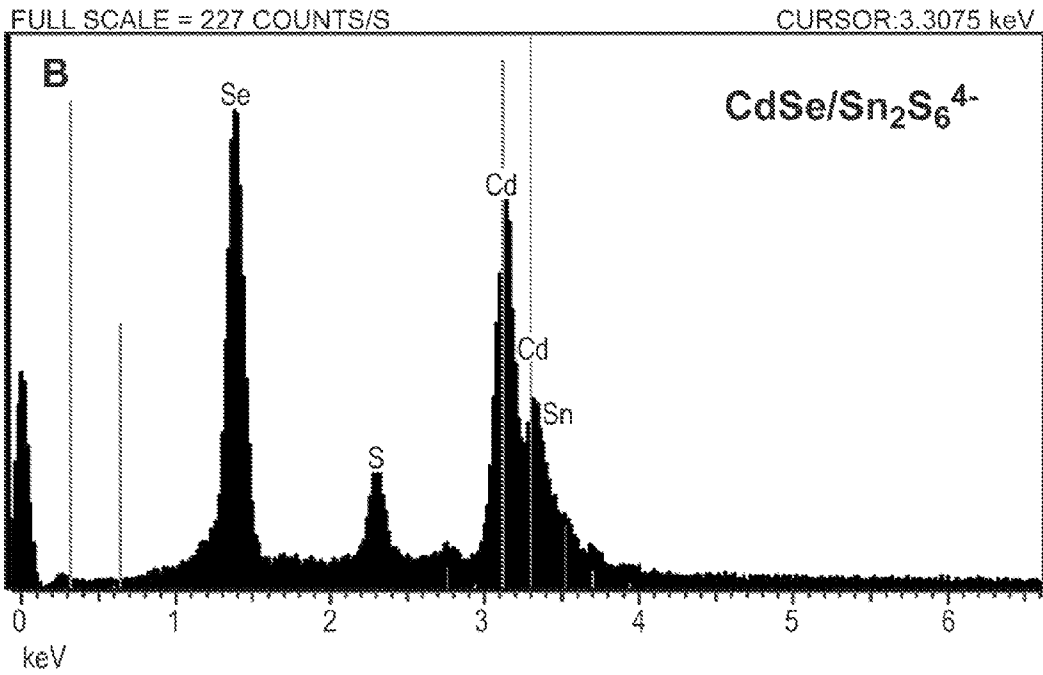


FIG. 5

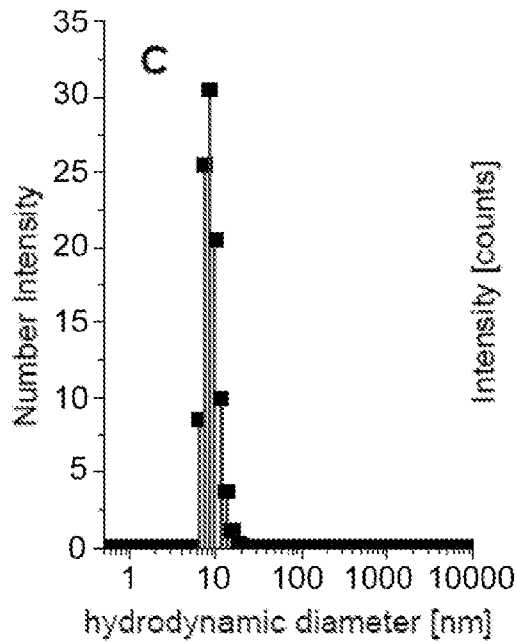
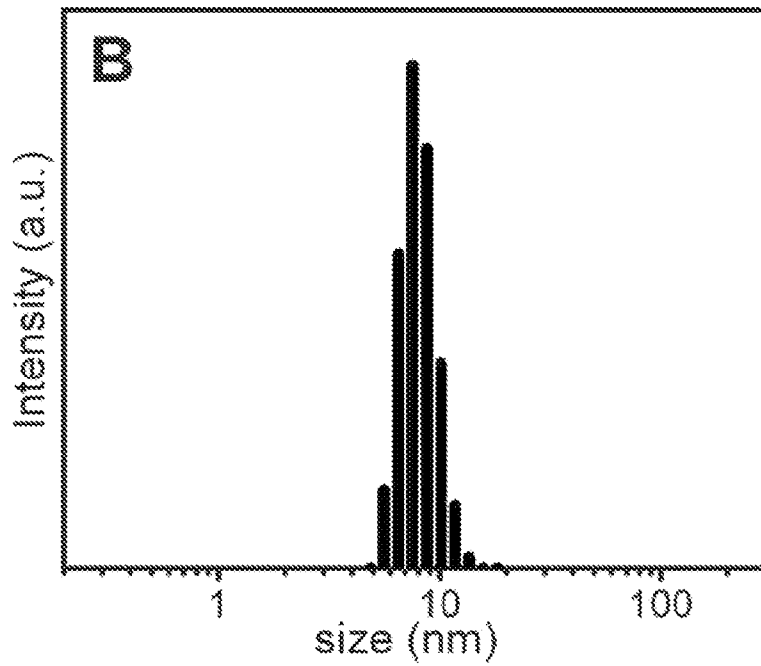


FIG. 6

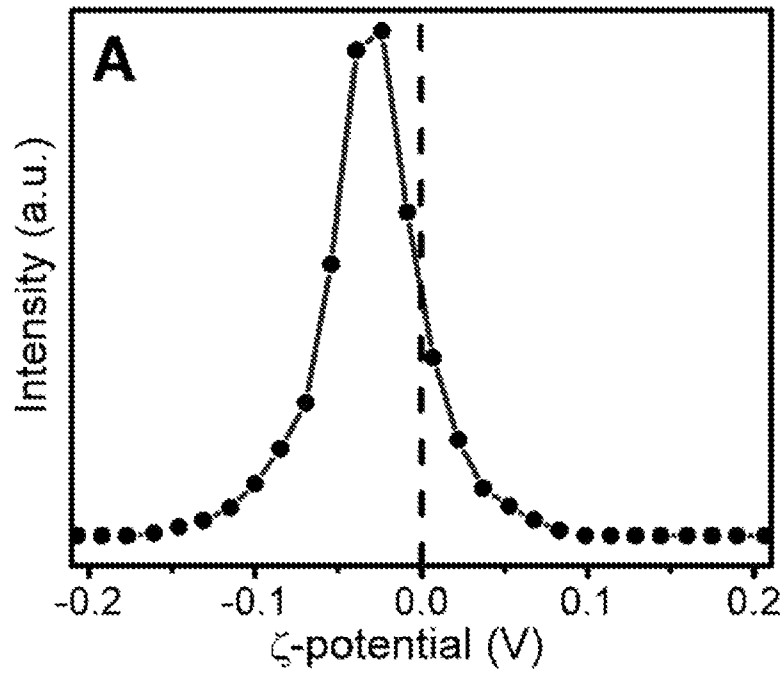


FIG. 7

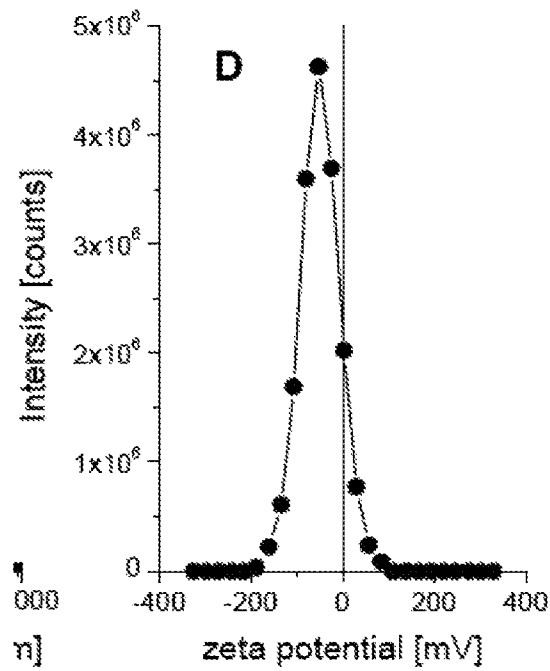
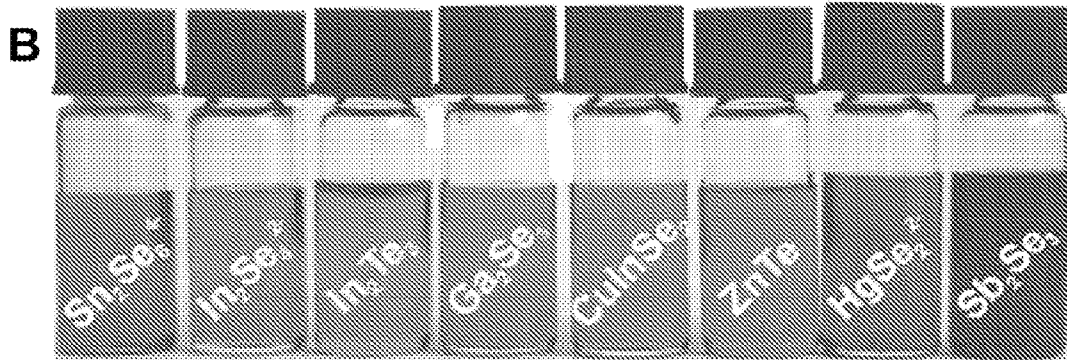


FIG. 8

3.6 nm CdSe NCs + various metal chalcogenide ligands



Sn₂S₆⁴⁻ ligand + various inorganic NCs

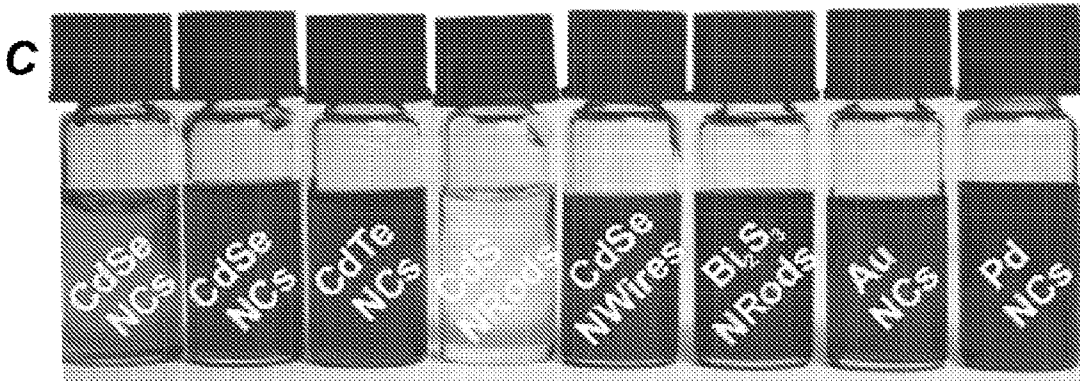


FIG. 9

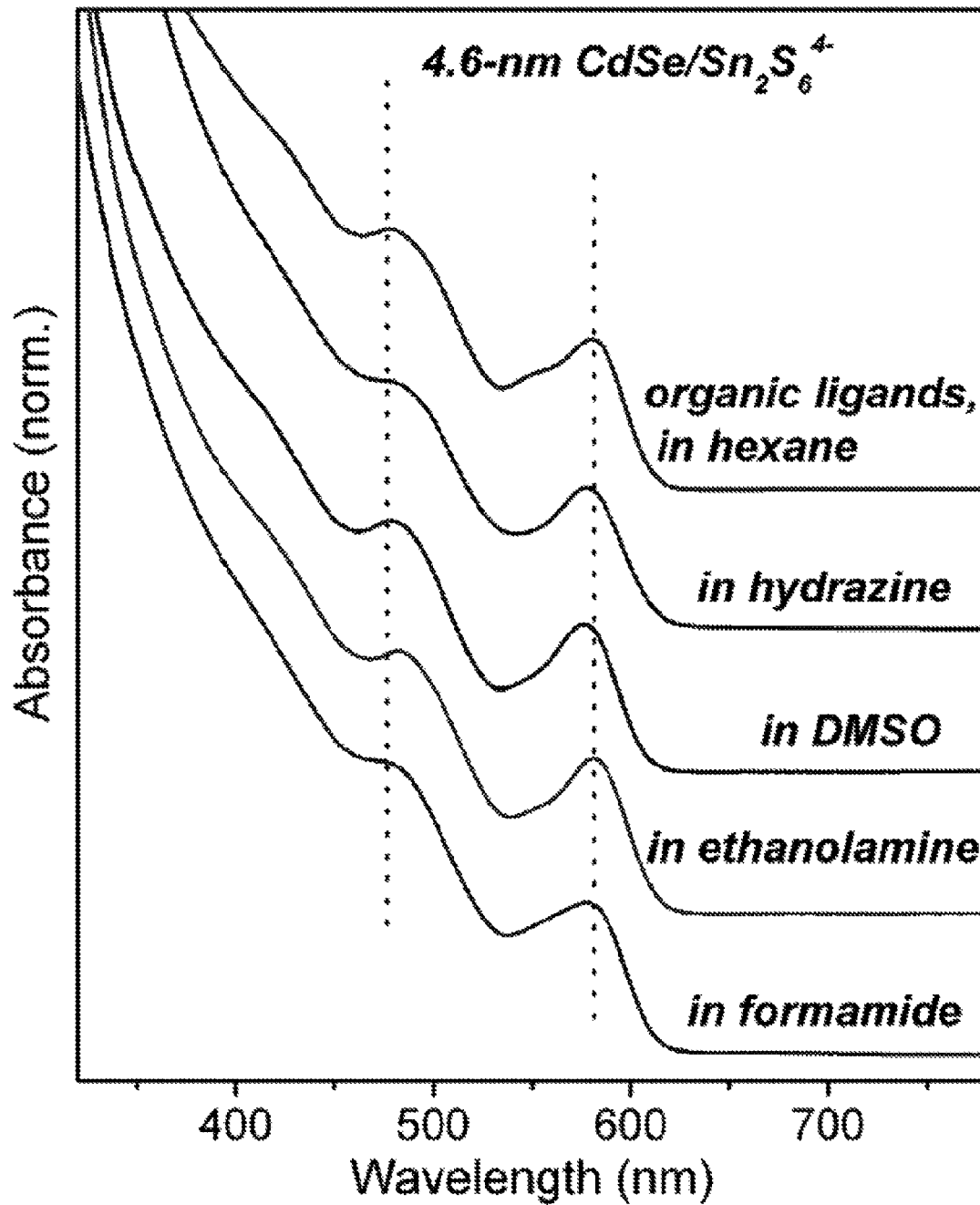


FIG. 10

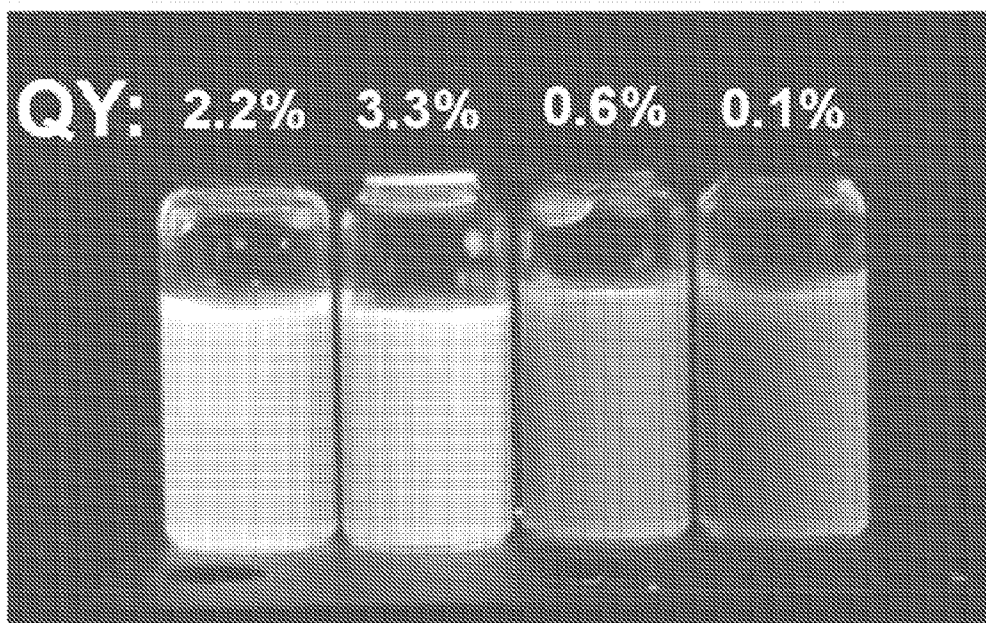


FIG. 11

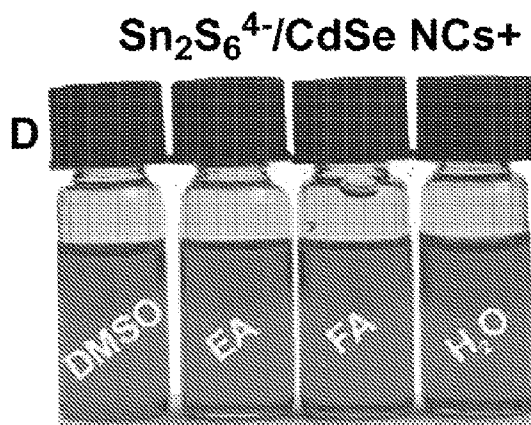
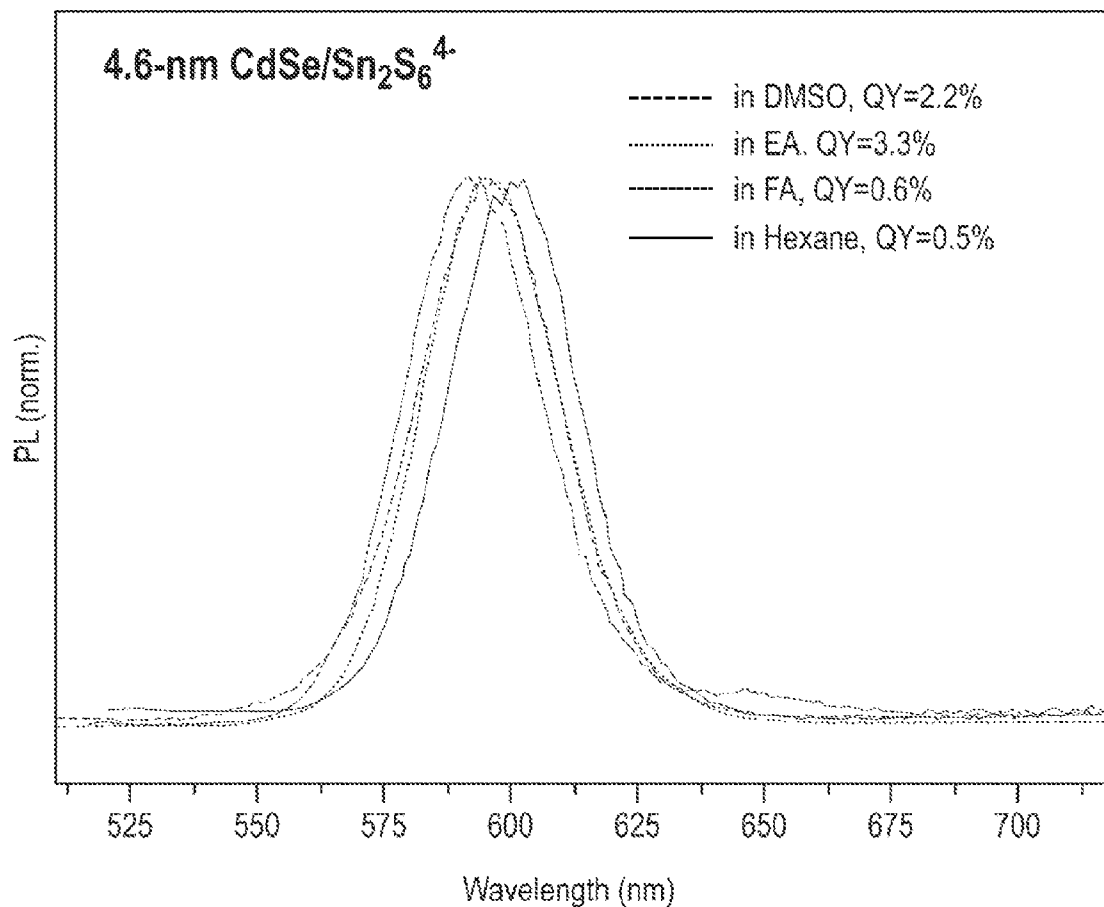


FIG. 12

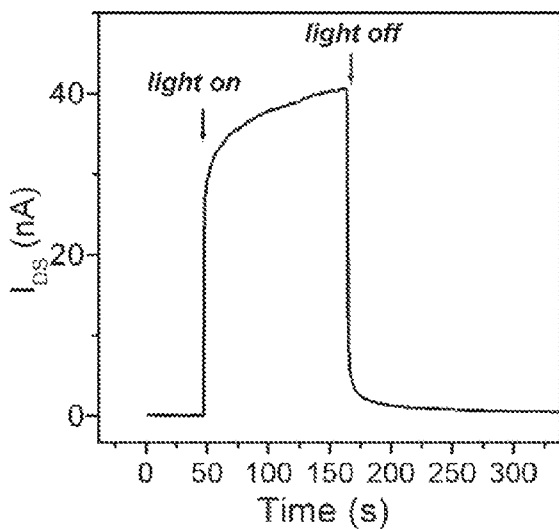
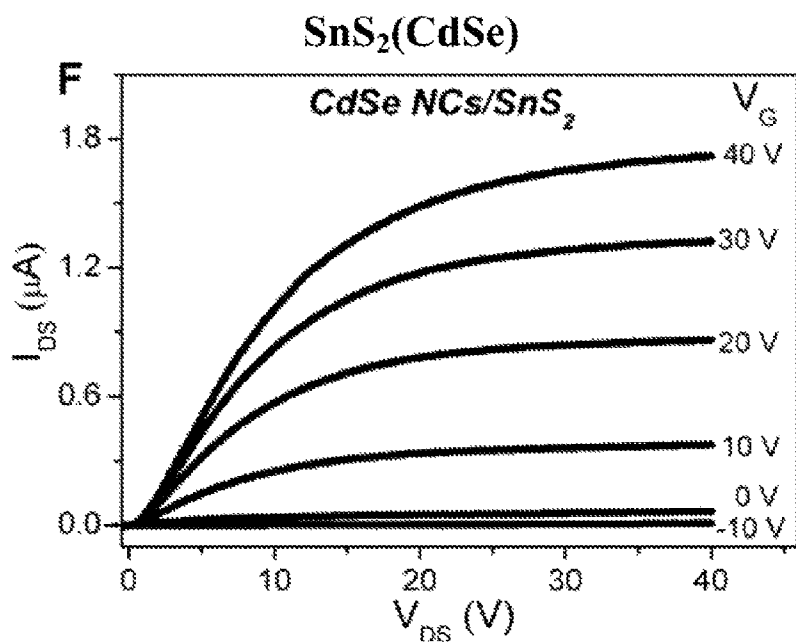
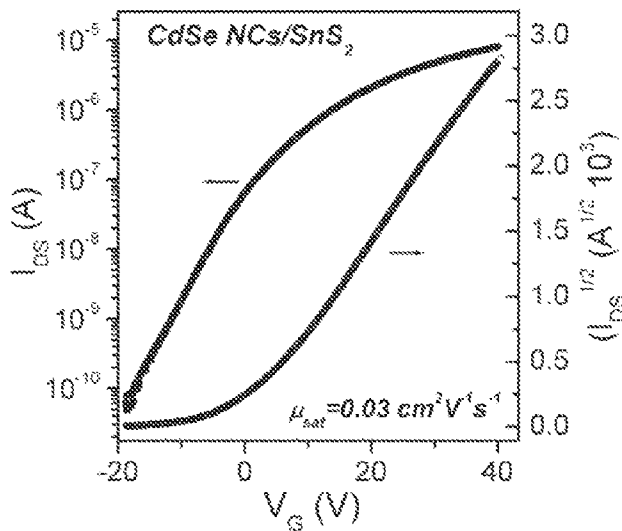


FIG. 13



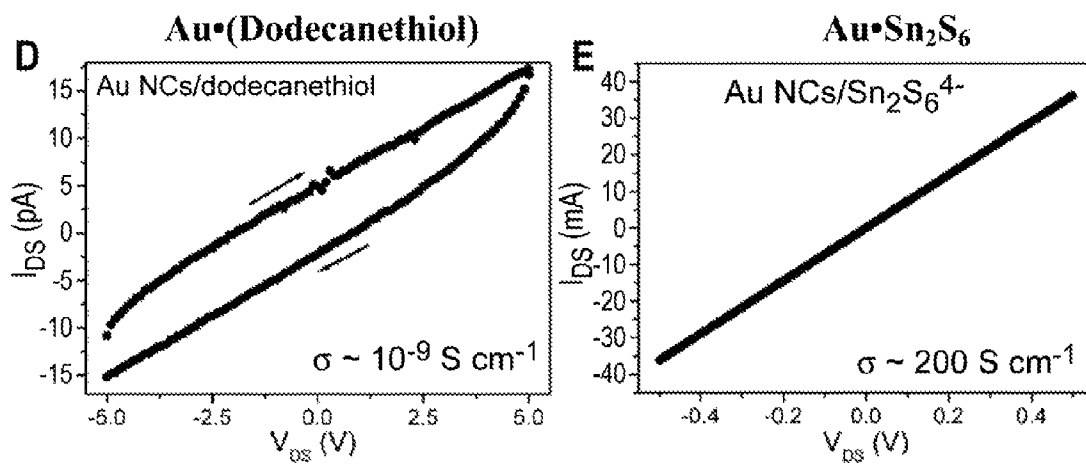


FIG. 14

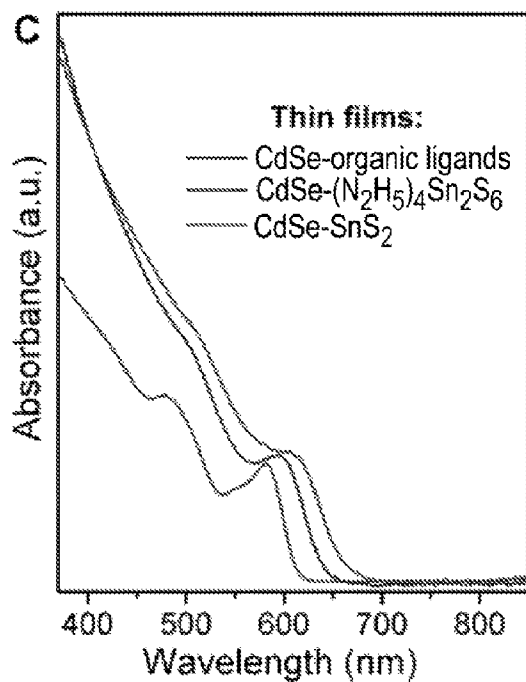


FIG. 15

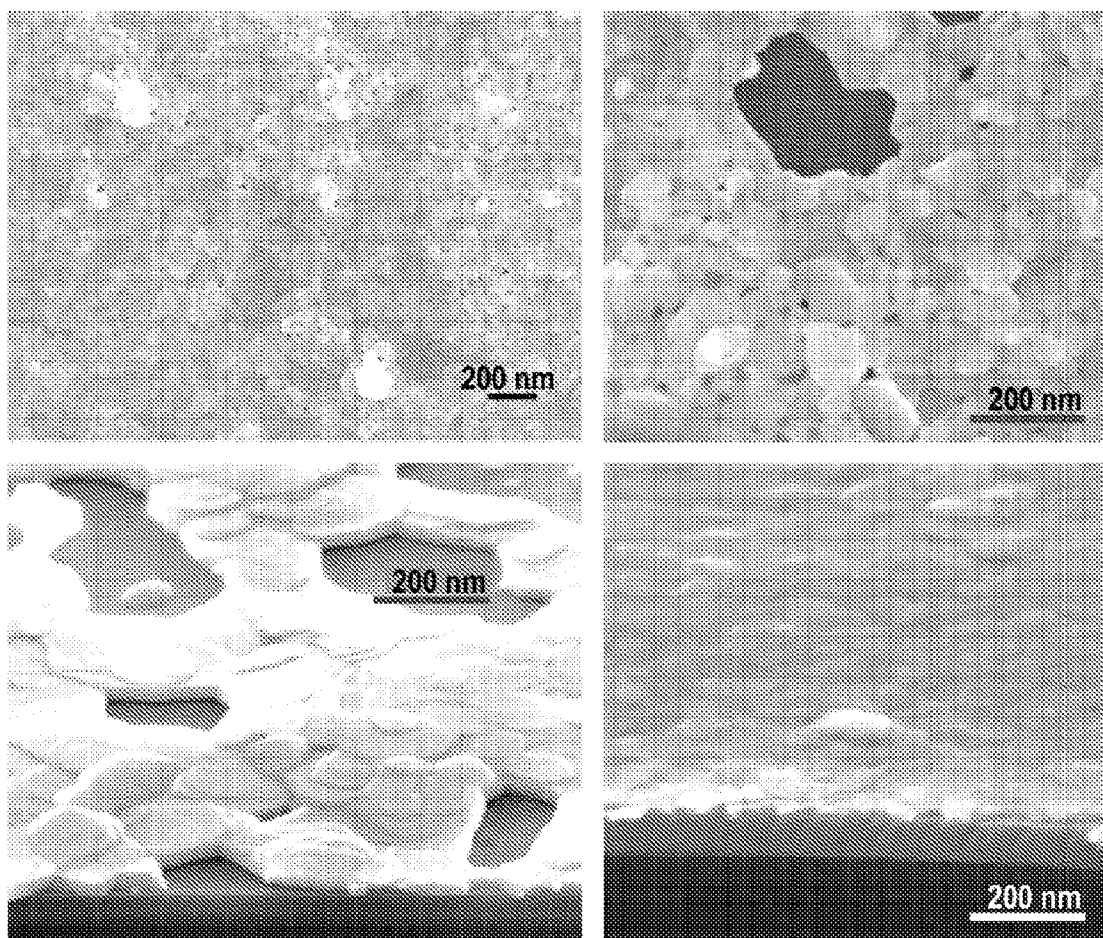


FIG. 16

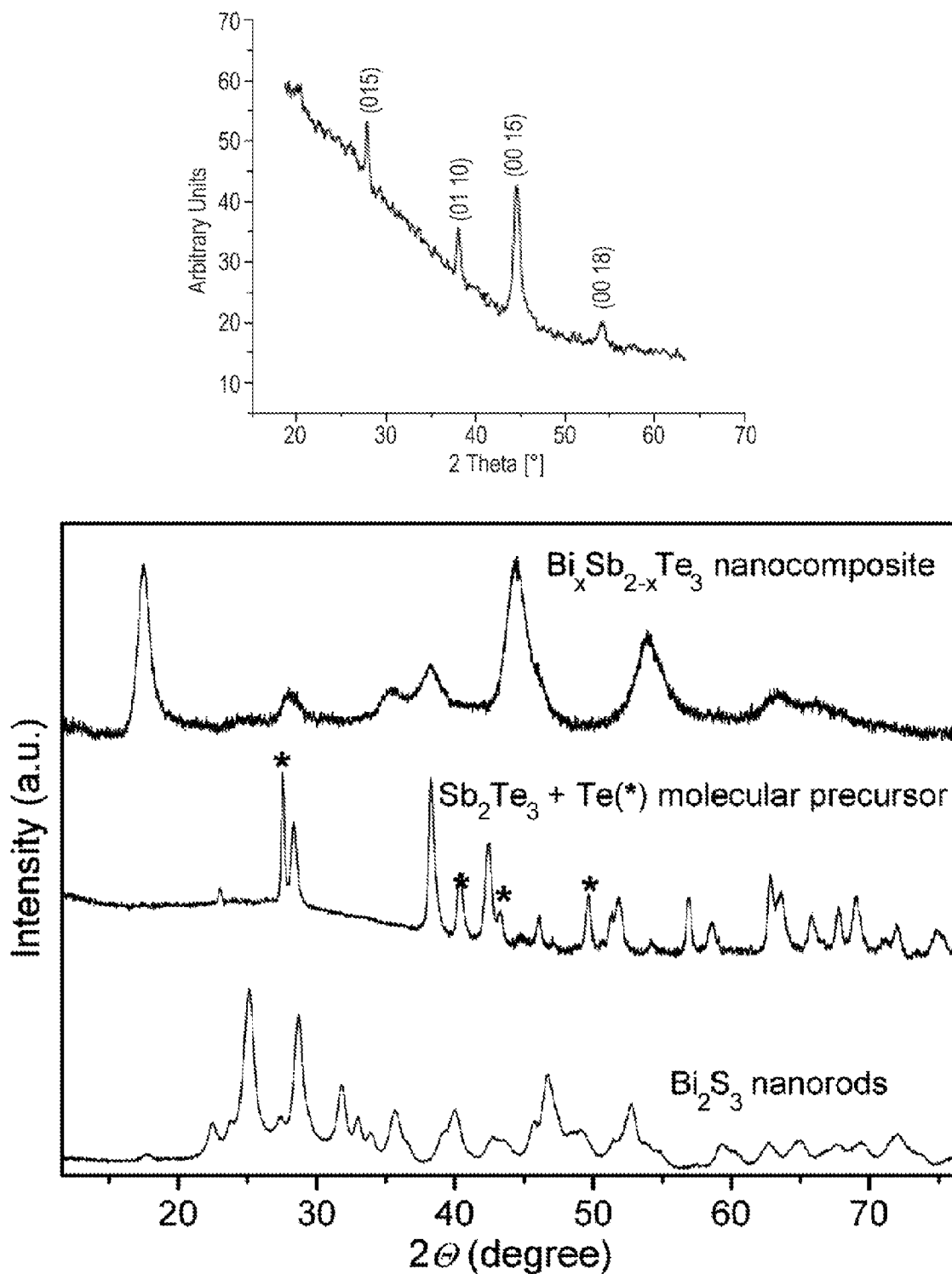


FIG. 17

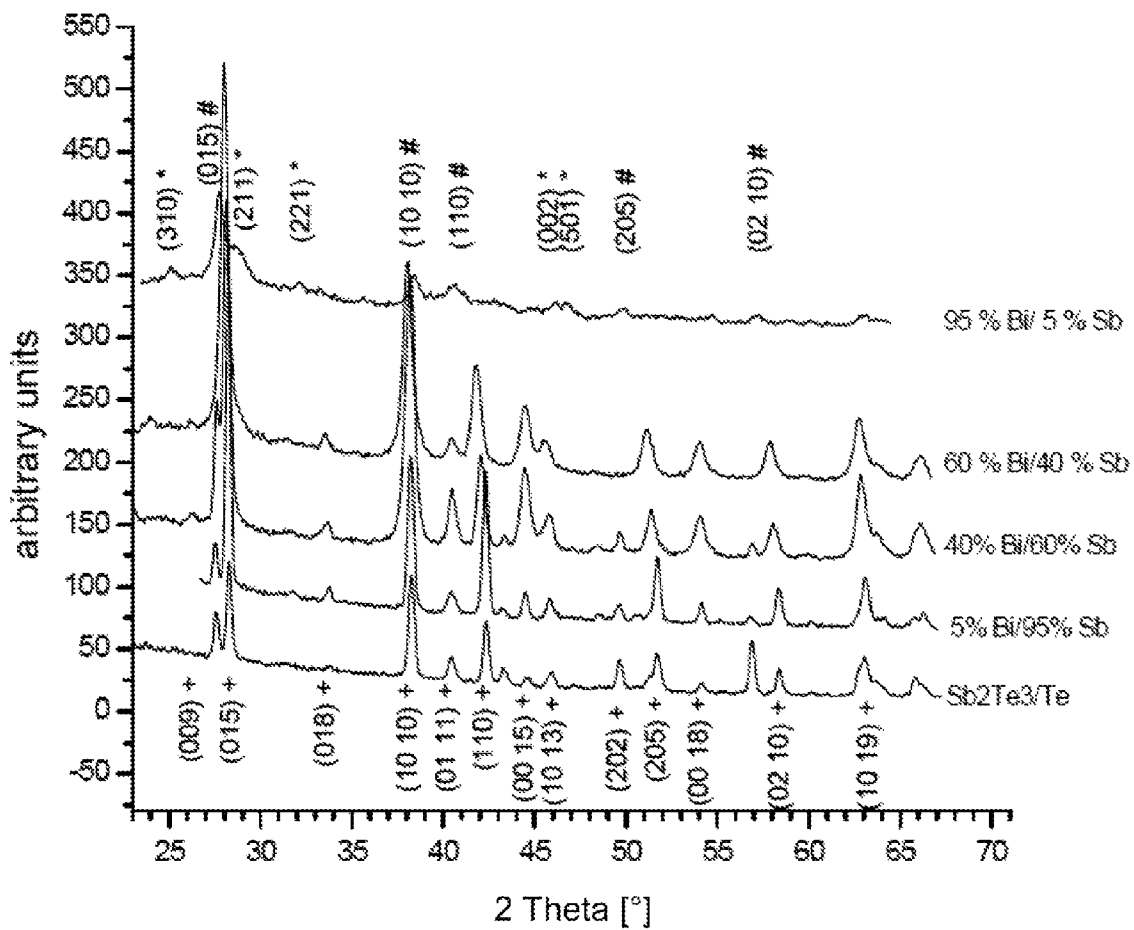


FIG. 18

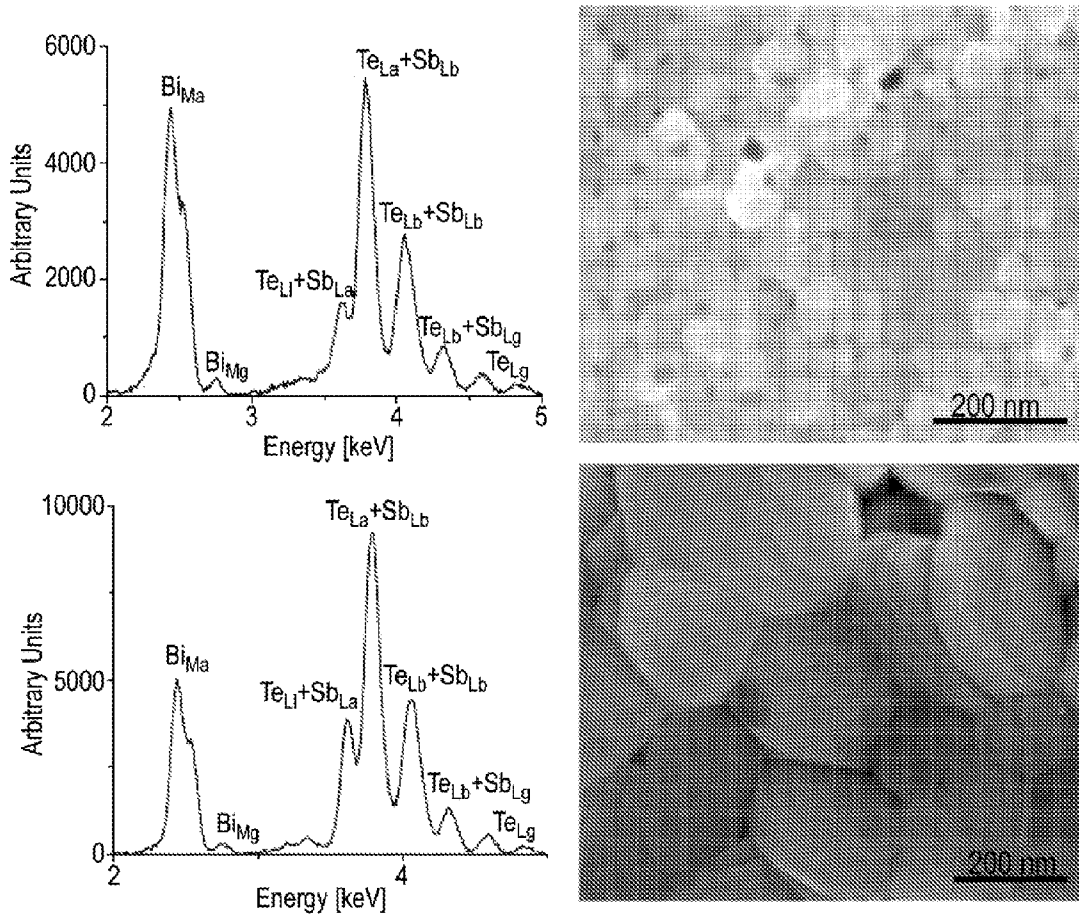


FIG. 19

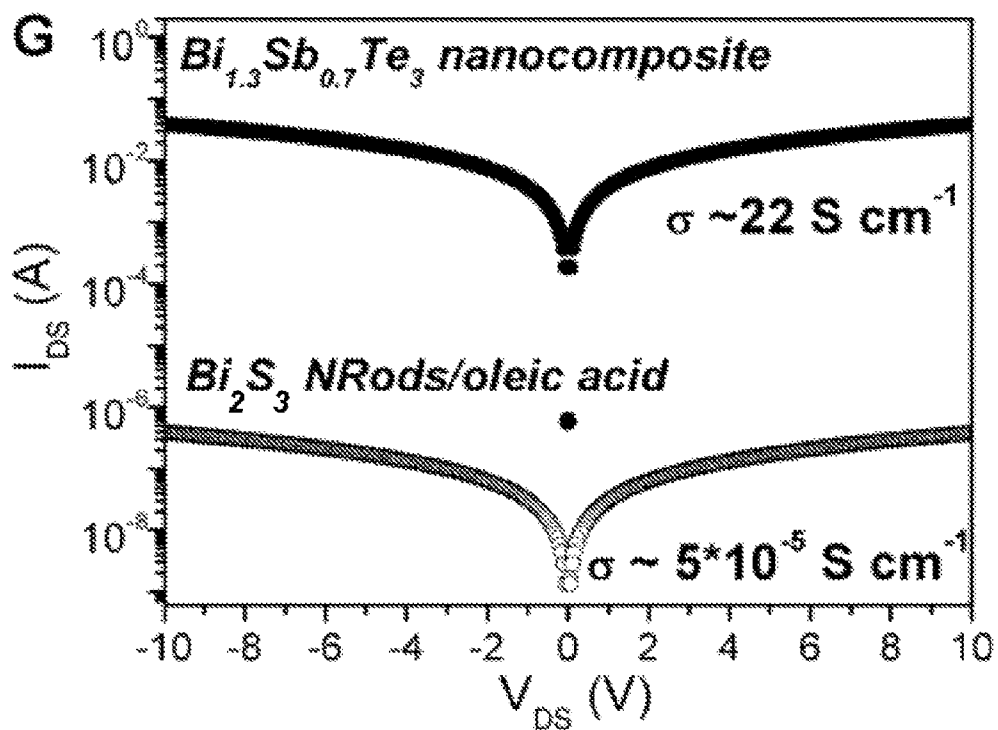


FIG. 20

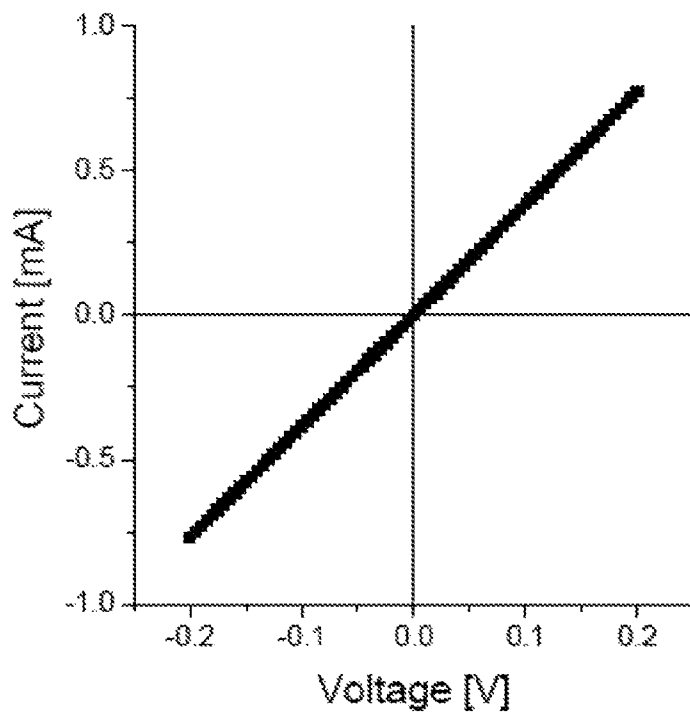


FIG. 21

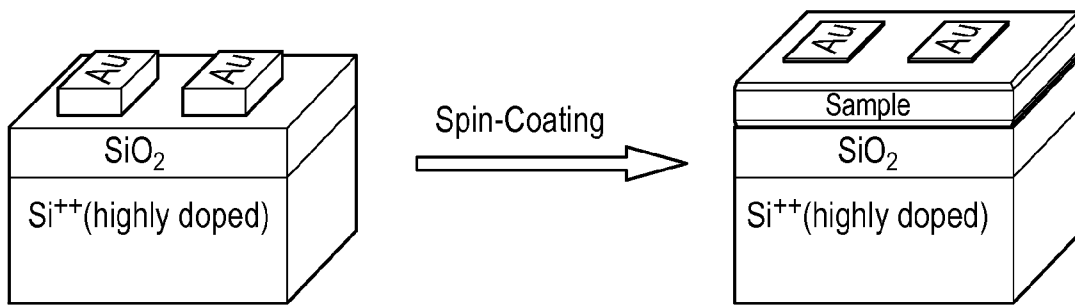


FIG. 22

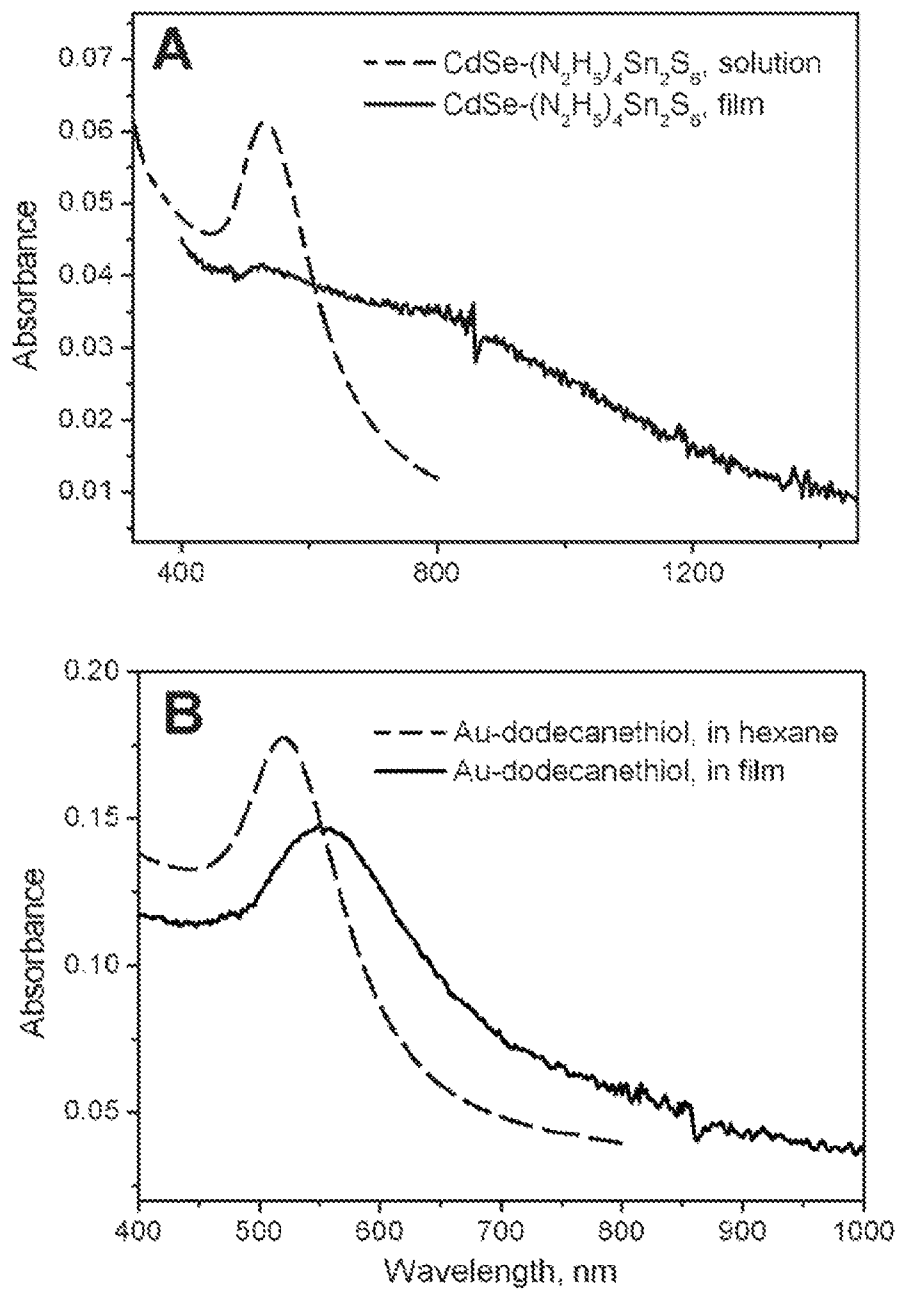


FIG. 23

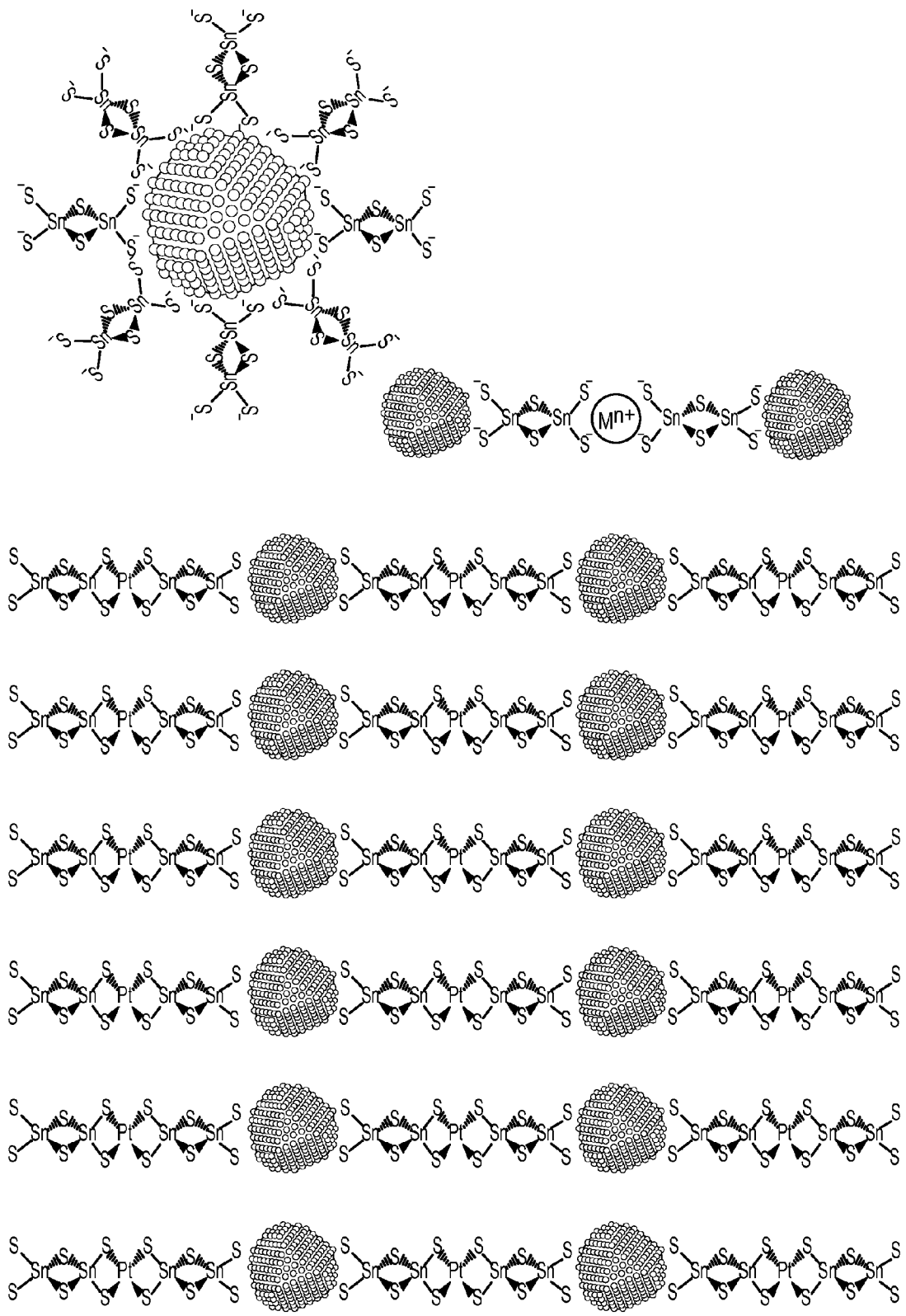
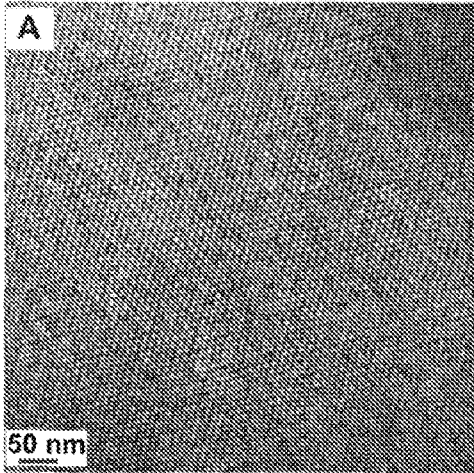


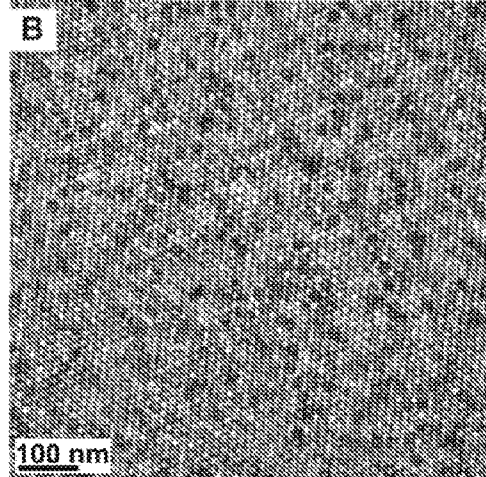
FIG. 24

FIG. 25

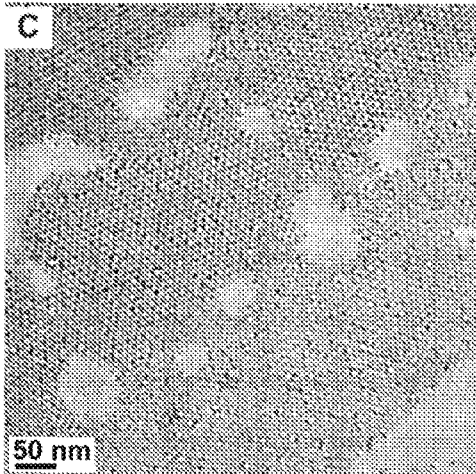
PbS-AsS₃³⁻-DDAB nanocrystals



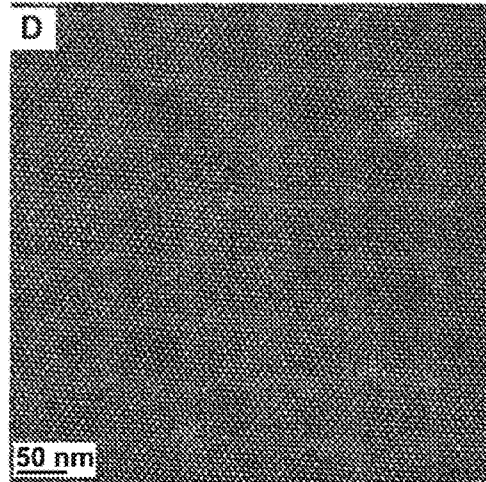
CdSe-AsS₃³⁻-DDAB nanocrystals



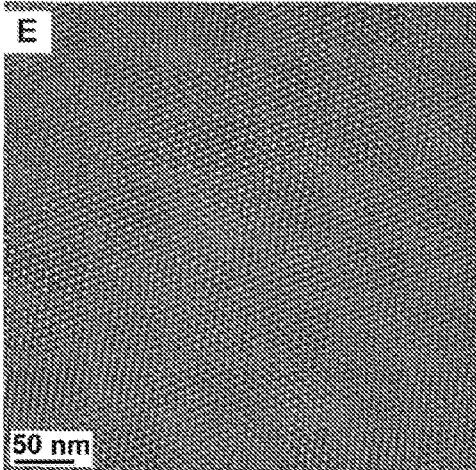
PbSe-AsS₃³⁻-DDAB NCs



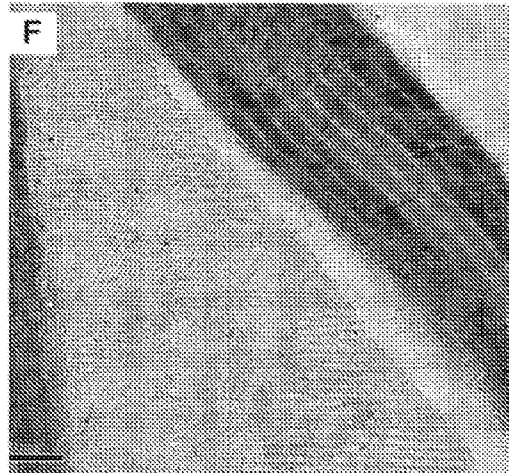
Au-AsS₃³⁻-DDAB NCs

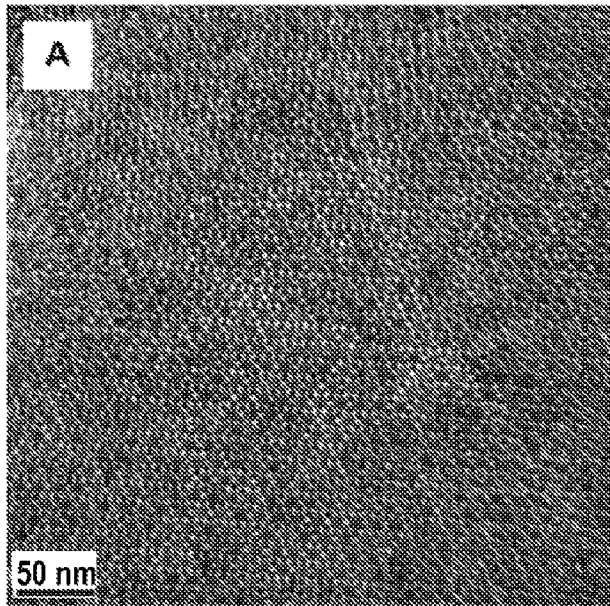


Pd-AsS₃³⁻-DDAB NCs, MCC144



CdSrods-AsS₃³⁻-DDAB

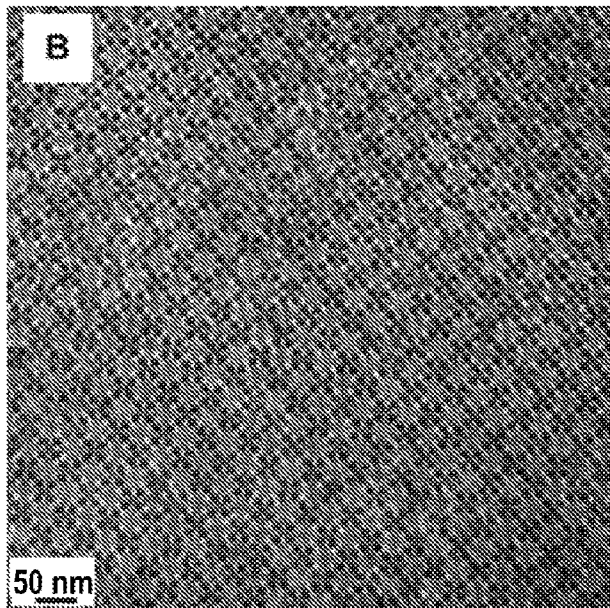
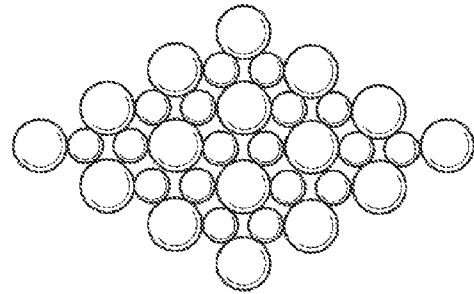




CdSe NCs + Au NCs

AlB₂ type structure

MCC101



PbS NCs + Au NCs

NaZn₁₃ type structure

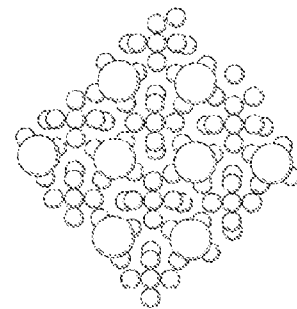


FIG. 26

FIG. 27

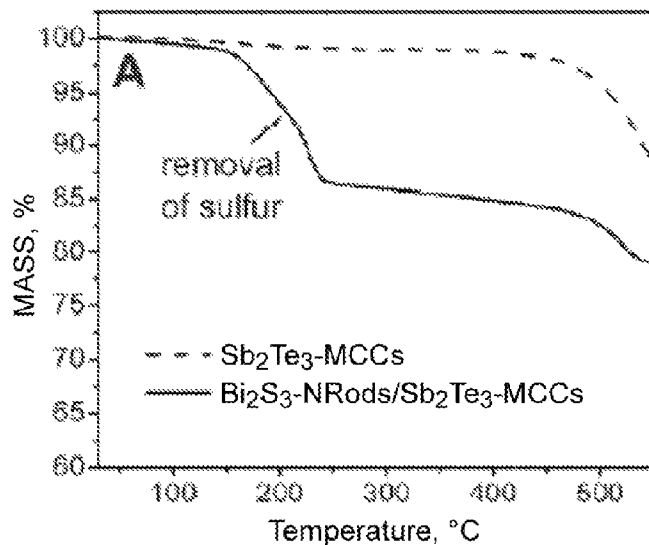
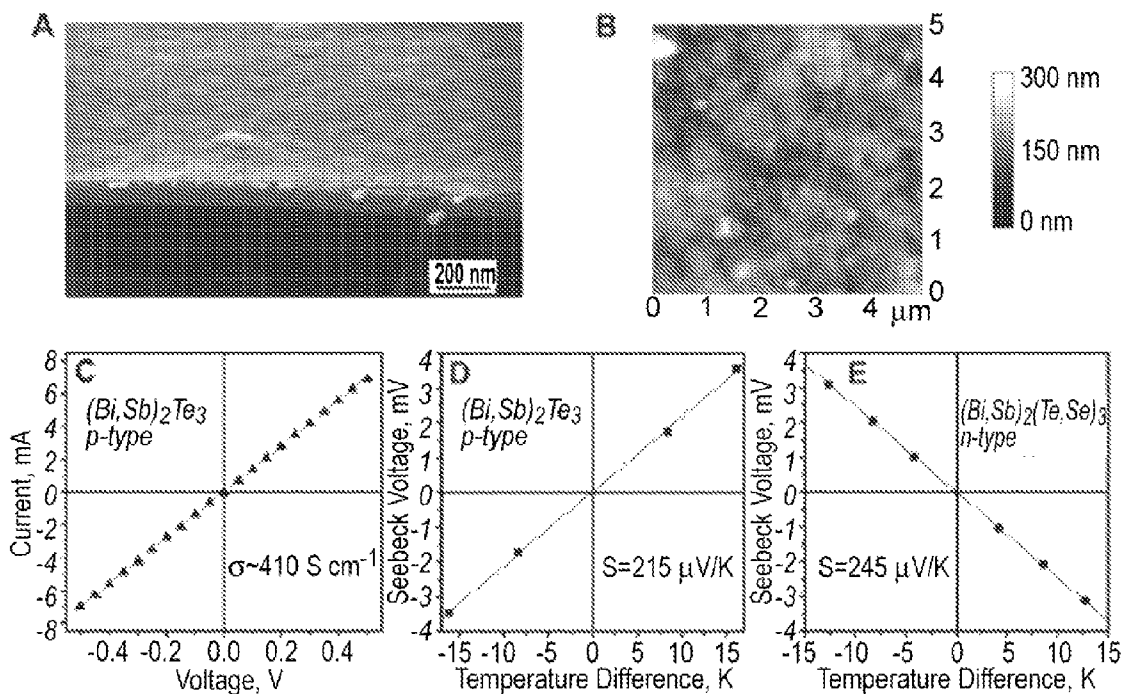


FIG. 28



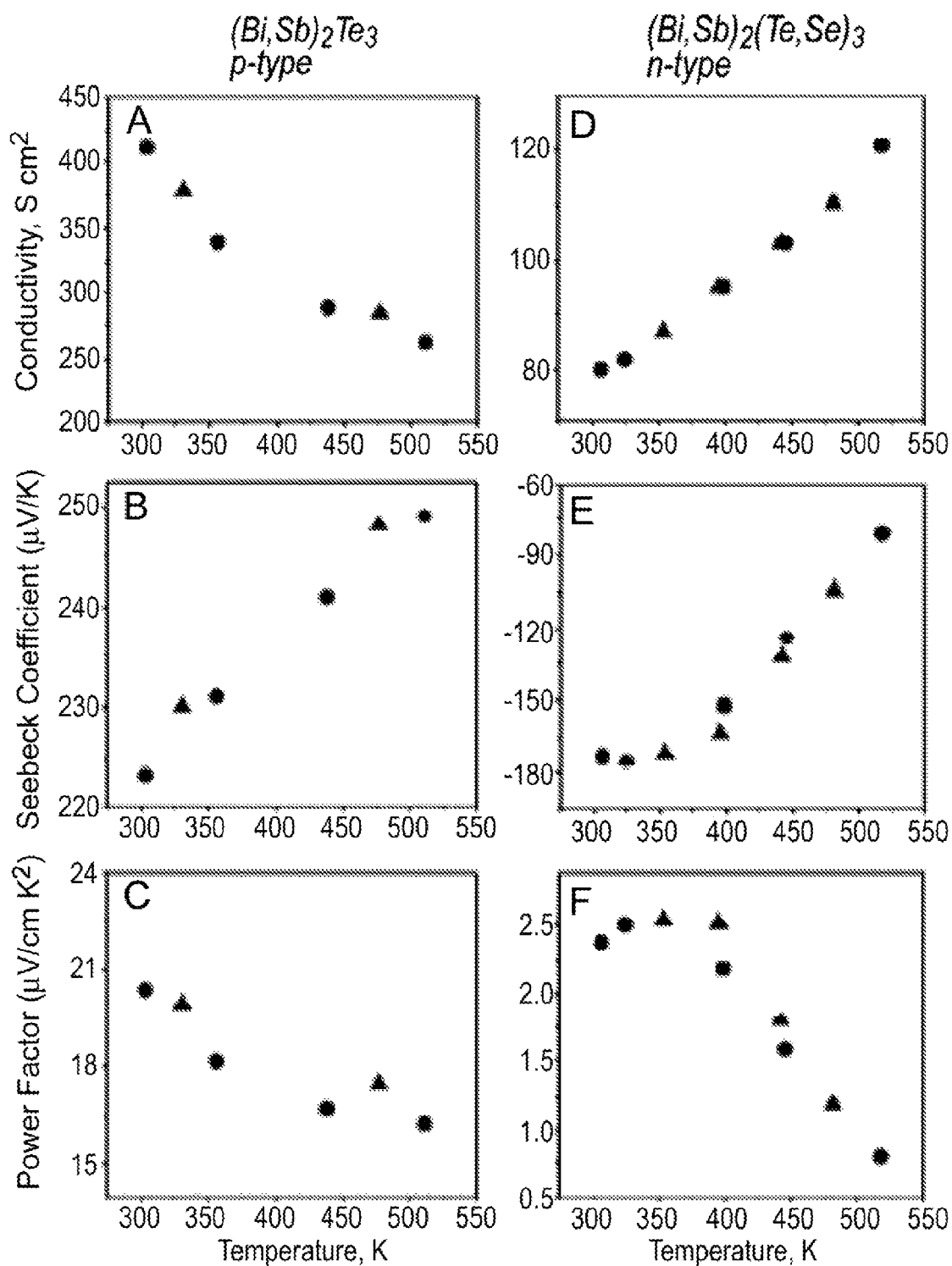


FIG. 29

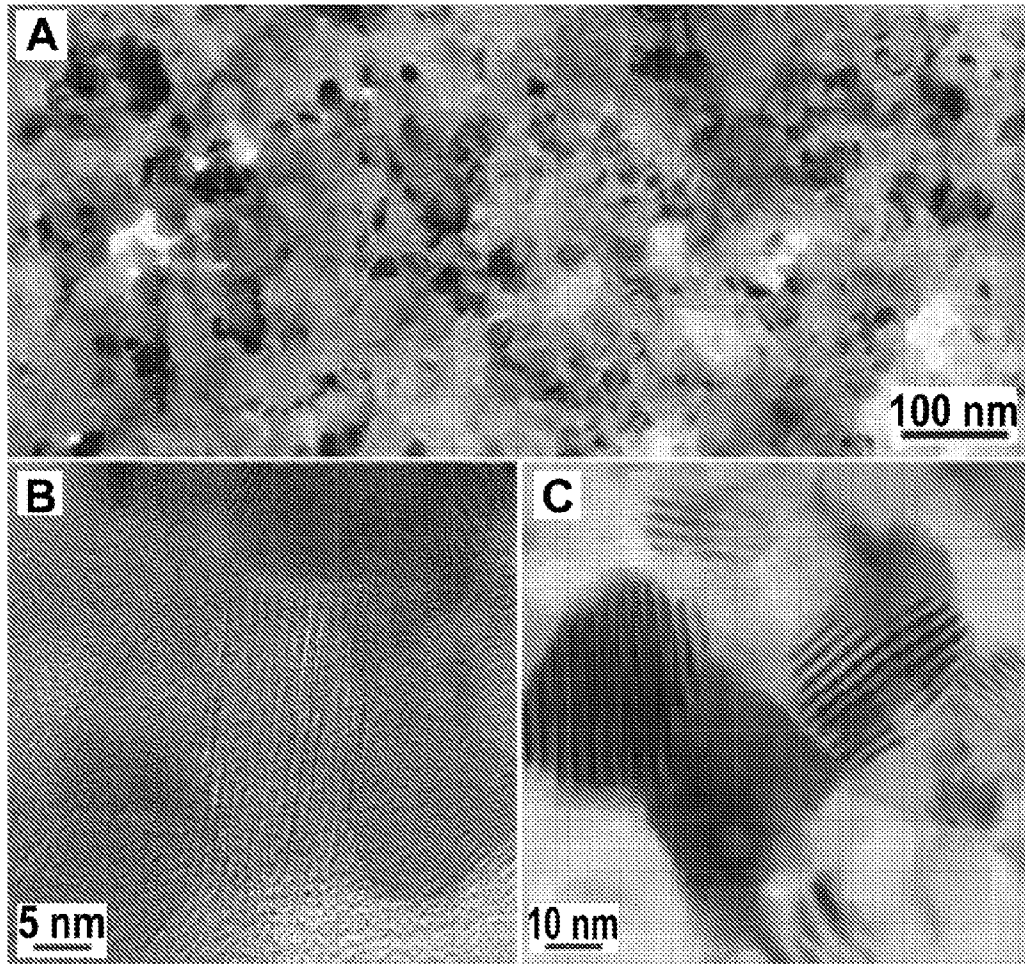


FIG. 30

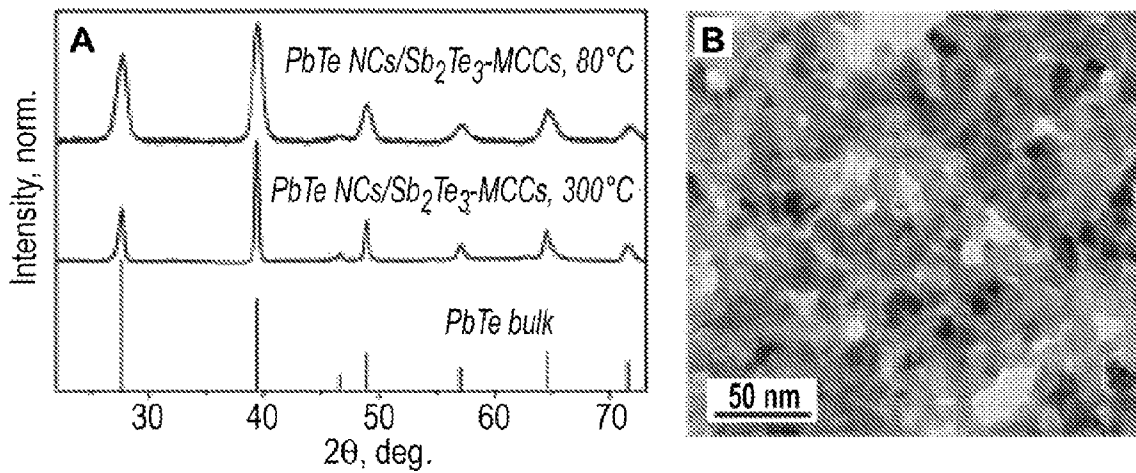


FIG. 31

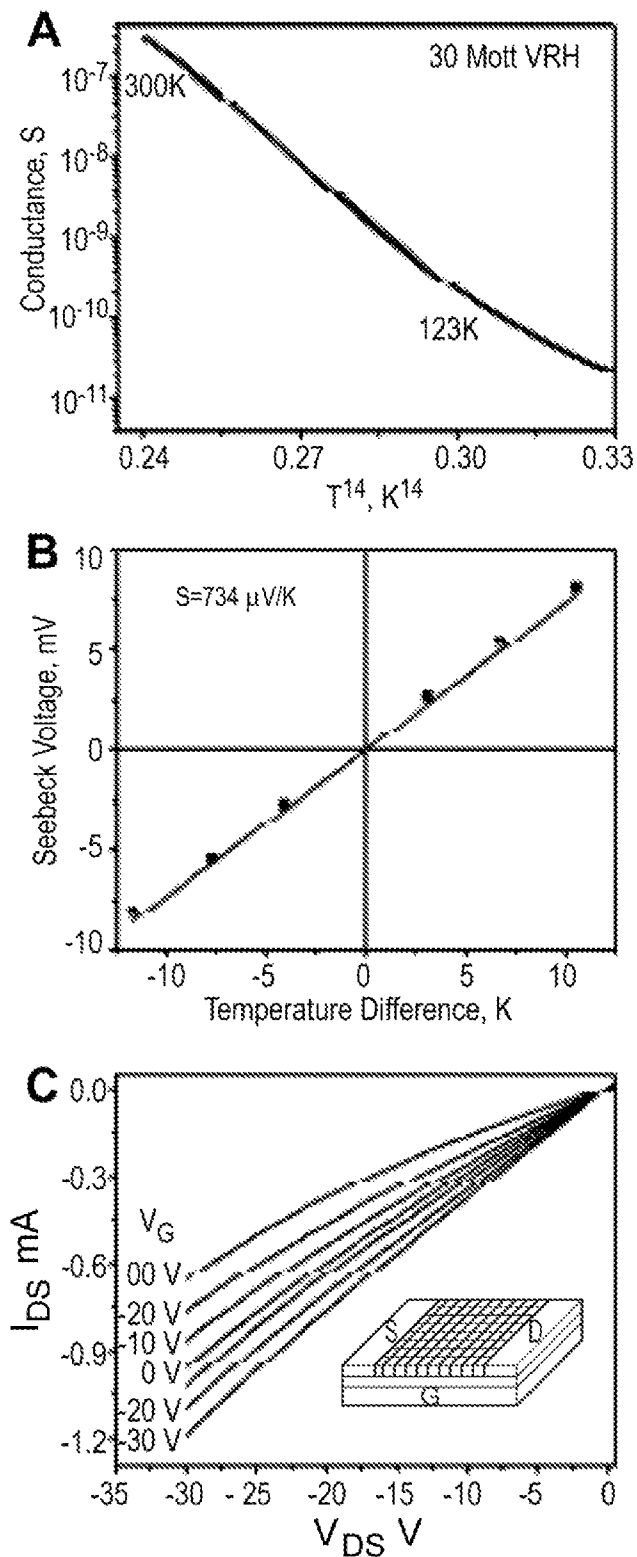


FIG. 32

FIG. 34

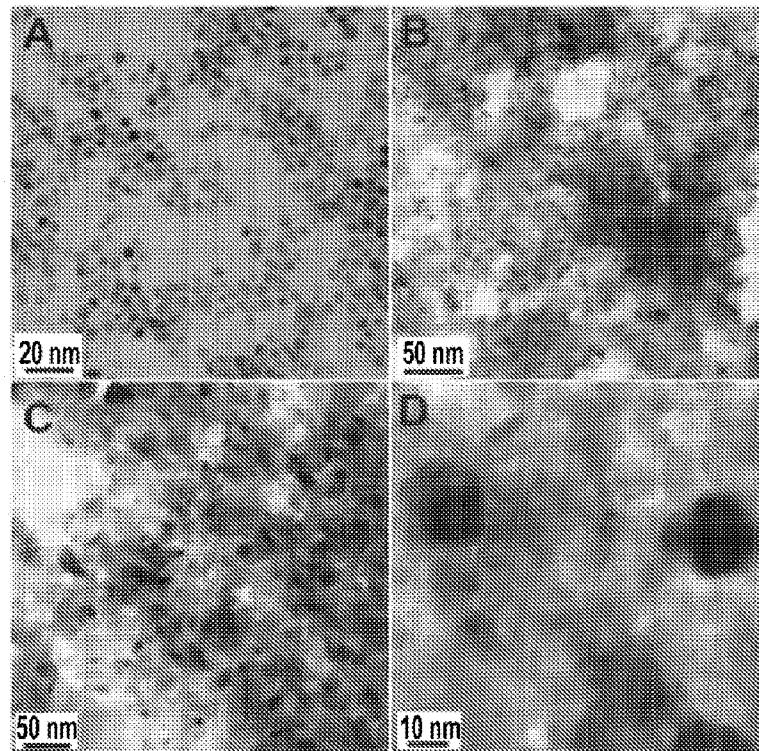
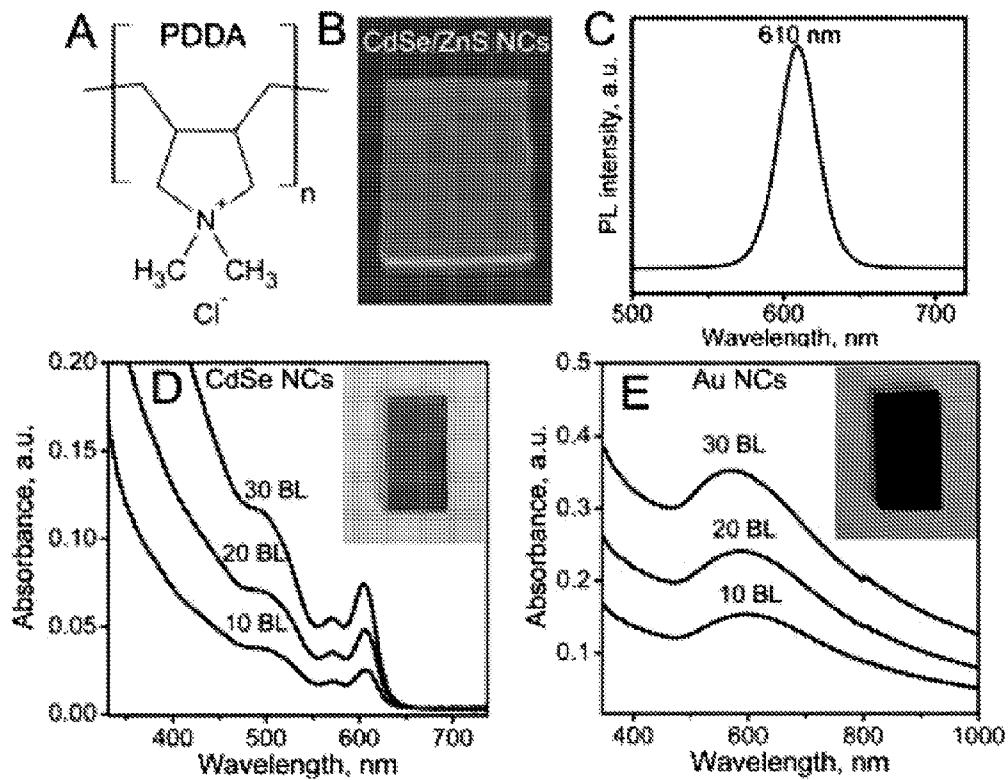


FIG. 35



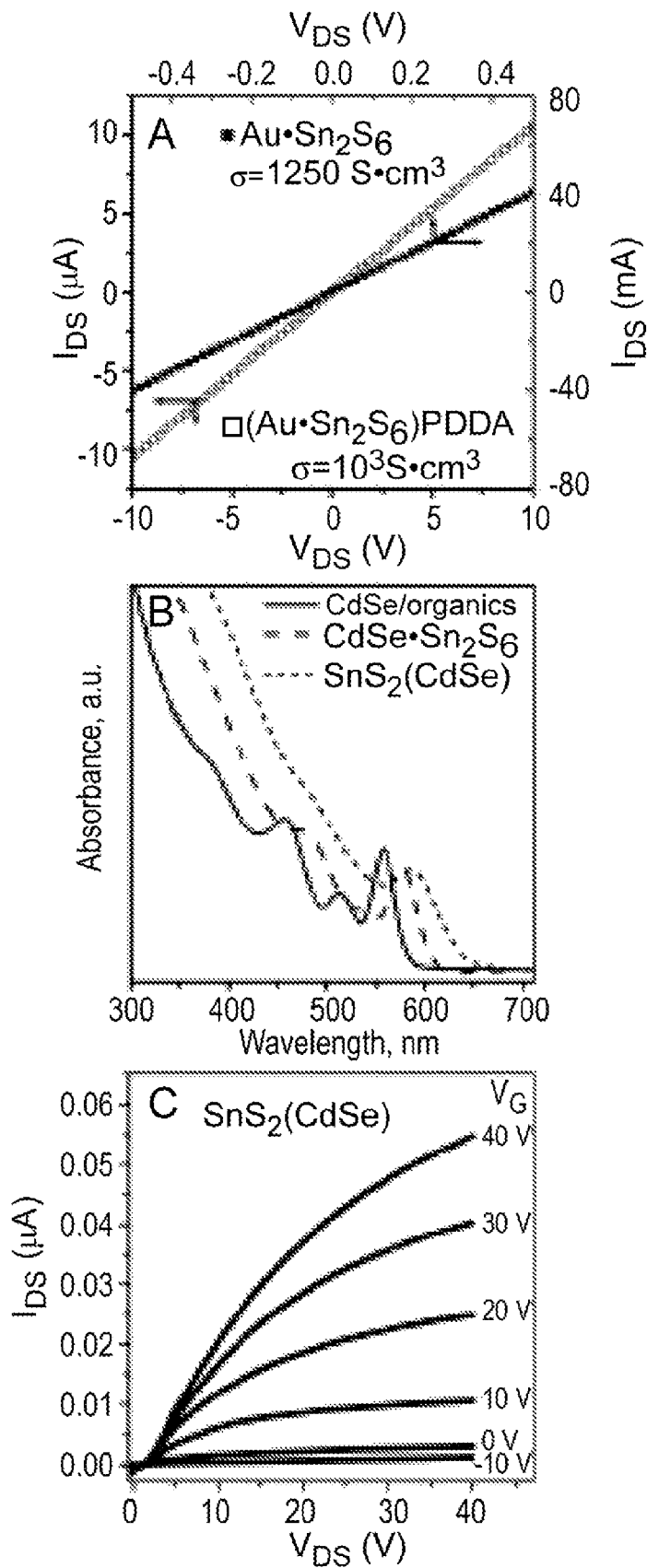


FIG. 36

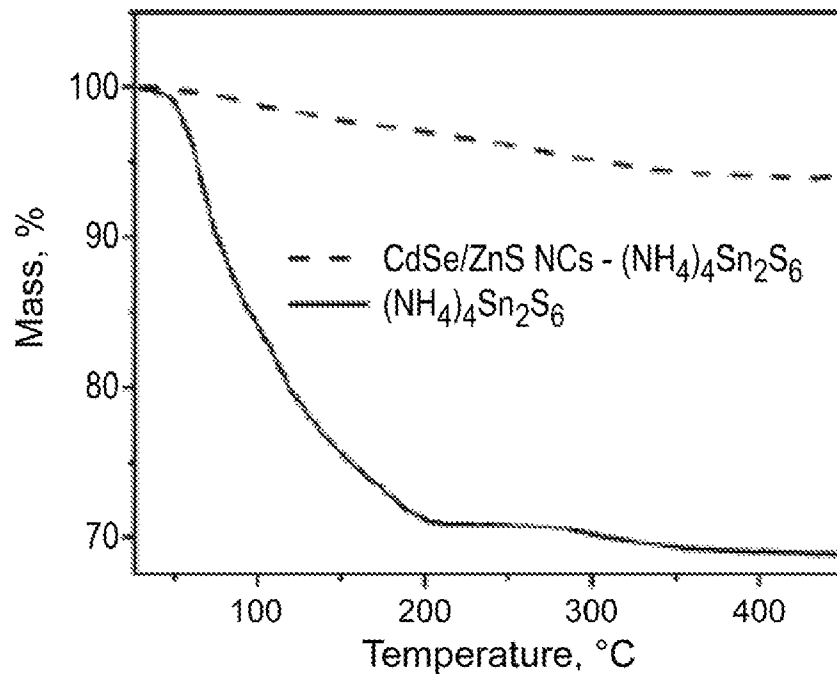


FIG. 37

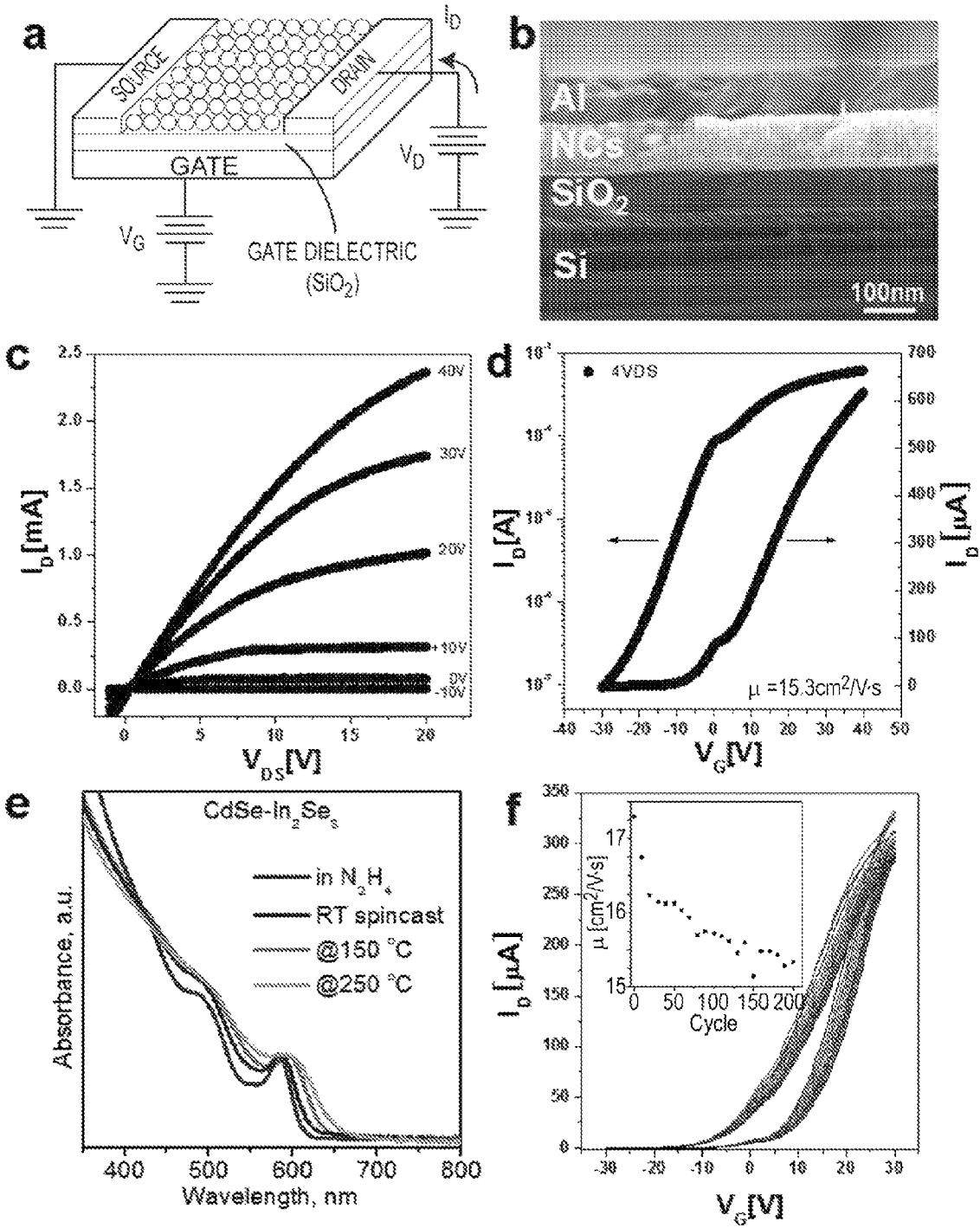


FIG. 38

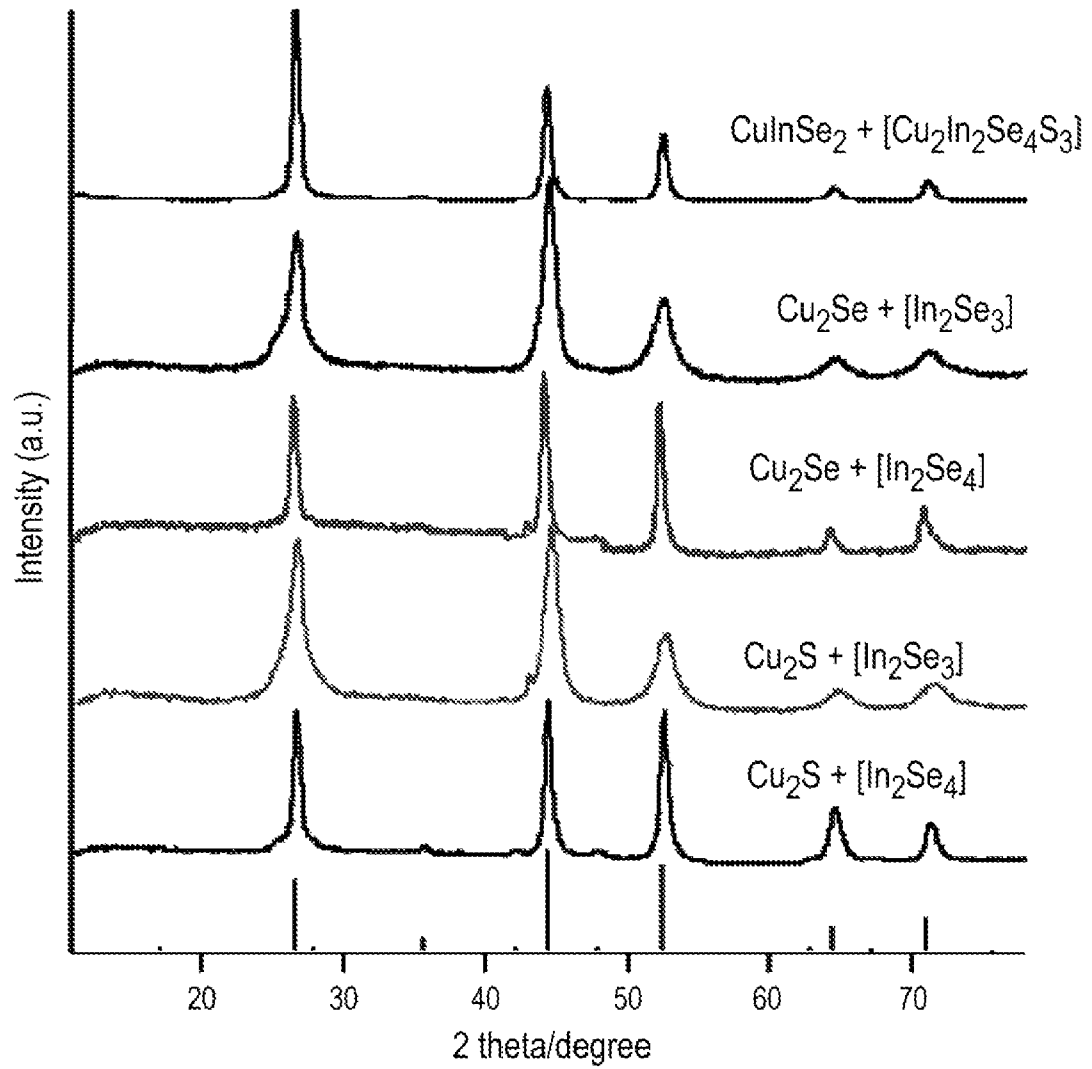


FIG. 39

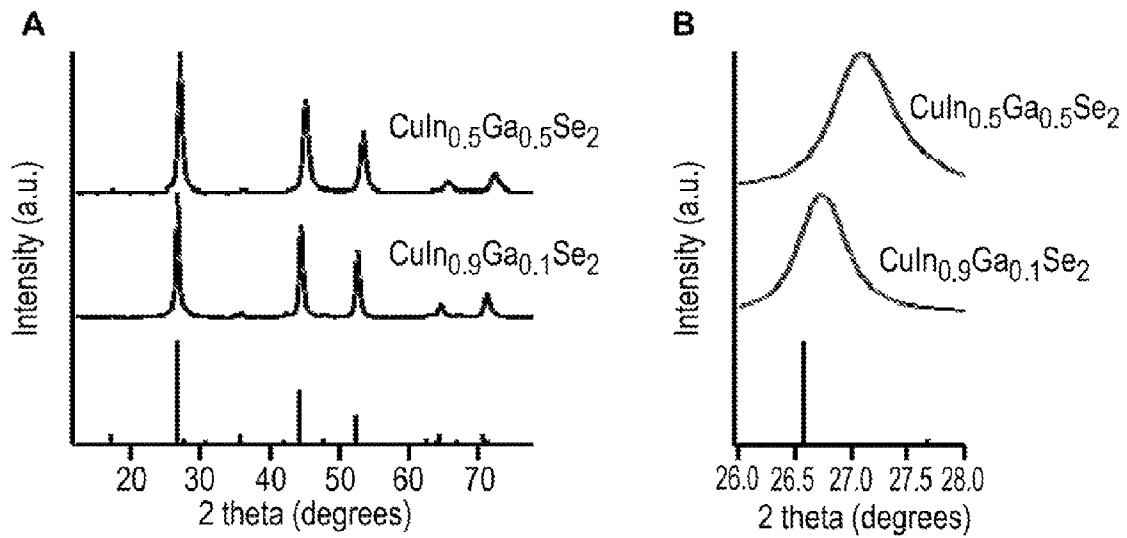


FIG. 40

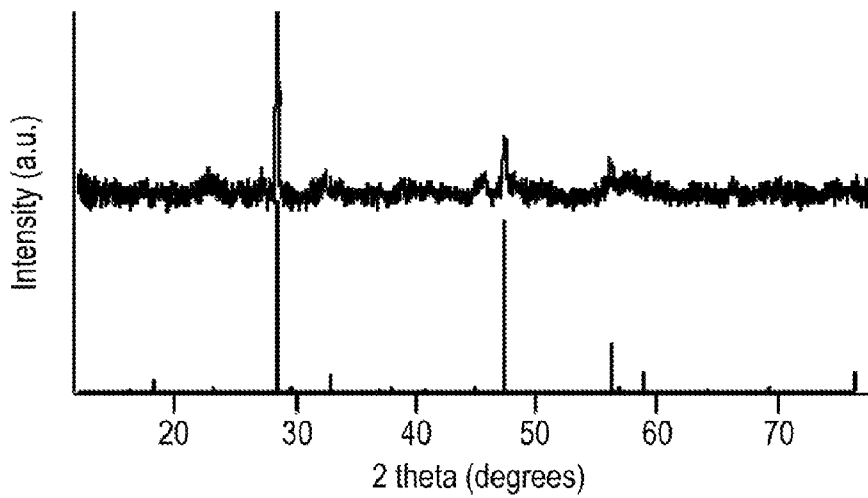


FIG. 41

MATERIALS AND METHODS FOR THE PREPARATION OF NANOCOMPOSITES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Applications 61/214,434 filed Apr. 23, 2009 and 61/264,790 filed Nov. 28, 2009, the content of which are incorporated herein in their entirety.

STATEMENT OF GOVERNMENTAL INTEREST

This invention was made with governmental support under grants from the U.S. National Science Foundation (DMR-0847535) and the U.S. Department of Energy (DE-AC02-06CH11357). The U.S. government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Disclosure

The disclosure generally relates to materials and methods for the preparation of nanocomposites. More specifically, the disclosure relates to inorganic capped colloidal materials and the methods of depositing these inorganic capped colloidal materials on a substrate to form nanocomposites. Still more specifically, the disclosure relates to the selective deposition and formation of nanocomposites on a substrate.

2. Brief Description of Related Technology

Nanoscale materials, materials with at least one dimension between about 1 and 1000 nm, have increasingly garnered attention due to their potential electronic, photophysical, chemical, and medicinal effects. The large-scale industrial application of nanoscale materials has generally focused on the formation of nanometer thick films and/or nanometer wide wires. Many of these industrially-applied nanoscale materials display extraordinary electronic and photophysical properties, but more often the materials lack the features that originally drew scientific interest toward nanocrystals, nanorods, and nanowires.

Attempts to incorporate the physical properties of nanocrystals, nanorods, and nanowires into films or bulk solids have led to the self-assembly of ordered nanoarrays. These self-assembled ordered nanoarrays have been produced from stable colloidal solutions of nanomaterials. For example, close-packed nanocrystal films have been made by spin-coating or drop casting of colloidal solutions. Often these films show short range ordering, but forces such as entropy, electrostatics, and van der Waals interactions can cause these materials to self-assemble into superlattices. These techniques have afforded binary superlattices with tunable electronic structures based on the colloidal materials employed in the synthesis.

Though some single-component and binary superlattices exhibit desirable physical and electronic properties, these materials are not robust enough for large scale advanced material applications and their synthesis is not general enough to provide easy production of idealized materials.

A larger-scale approach to the synthesis of solid state materials encompassing nanocrystals is the impregnation and forced crystallization of nanocrystals from melts of inorganic materials. This rapid quenching approach can provide nanocrystalline material in bulk inorganic phases but lacks any methodology for the formation of ordered nanoarrays in the bulk material.

While the synthesis of solid state materials with ordered arrays of nanoscale materials has progressed to the point where nanocrystals can be deposited in ordered arrays on a surface, the use of these ordered arrays are hampered by the insulating ligands generally used in the manufacture of the nanocrystal. The practical use of these nanocrystals has been discovered through the blending of these organic soluble nanocrystals with polymers. See for example U.S. Pat. No. 7,457,508. For example, nanocomposites of nanocrystals and conjugated polymers can yield tunable semiconducting photonic structures, and with unique optical, electrical, magnetic, electrochromic, and chemical properties. See for example U.S. Pat. No. 7,200,318.

The majority of applications wherein these advanced materials would be applicable employ inorganic solids as the functional material. One example of an applicable inorganic solid that incorporates nanoscale materials is the fabrication of inorganic nanocomposites described in U.S. Pat. No. 7,517,718. This methodology involves the codeposition of a nanocrystalline material with an inorganic matrix precursor from a homogeneous hydrazine solution, a technique similar to the deposition of nanocrystalline materials in polymers as described in J. W. Lee et al., *Advanced Materials* 2000, 12, 1102. This methodology fails to provide the selectivity of structure for the synthesis of tunable semiconducting materials, does not prevent the carbon contamination of the synthesized inorganic nanocomposite, and requires a highly toxic, hypergolic solvent. Hence, the industrial applicability of the methodology is limited by material requirements, and the overwhelming health and safety concerns.

Examples of materials and devices applicable to the current invention are described in the following U.S. Pat. Nos. 6,571,028; 6,611,640; 6,710,911; 7,095,959; 6,697,548; 7,110,640; 7,200,302; 6,872,450; 7,192,780; 7,482,059; 7,399,429; 7,341,734; and 7,524,746; the following U.S. patent application Ser. Nos. 11/403,090; 11/484,785; 11/679,746; 11/680,047; 11/680,344; 11/683,880; 11/687,306; 11/747,701; 11/752,748; 11/863,129; 11/866,974; 11/896,549; 11/952,783; 12/048,061; 12/052,380; and 12/350,615; and the following International Patent Applications: PCT/2005/016481; PCT/2005/024131; PCT/2005/024211; PCT/2006/003652; PCT/2006/027124; PCT/2006/027125; PCT/2007/015851; PCT/2007/025235; PCT/2007/063788; PCT/2007/063788; PCT/2007/065951; PCT/2007/065951; PCT/2007/069572; PCT/2007/069572; PCT/2007/071218; PCT/2007/071218; PCT/2007/071218; PCT/2007/072748; PCT/2007/072761; PCT/2007/079688; PCT/2007/079688; PCT/2007/080436; PCT/2007/082066; PCT/2007/085824; PCT/2007/086480; PCT/2007/086819; PCT/2007/086819; PCT/2008/052620; PCT/2008/052620; PCT/2008/053651; PCT/2008/056845; PCT/2008/057681; PCT/2007/003525; PCT/2007/003411; PCT/2007/005589; PCT/2007/007424; PCT/2007/008705; PCT/2007/008721; PCT/2007/008873; PCT/2007/009255; PCT/2007/013152; PCT/2007/013761; PCT/2007/019797; PCT/2007/024305; PCT/2007/024306; PCT/2007/024310; PCT/2007/024312; PCT/2007/024750; PCT/2007/019796; PCT/2007/014705; PCT/2007/014711; PCT/2007/014706; PCT/2007/024320; PCT/2008/007902; PCT/2008/008036; PCT/2008/008822; PCT/2008/007901; PCT/2008/008924; PCT/2008/010651; PCT/2008/013504; PCT/2009/002123; PCT/2009/002796; PCT/2009/001372; PCT/2009/002789; PCT/2009/004345; and PCT/2009/004354; each of which are incorporated by reference herein in their entirety.

SUMMARY OF THE INVENTION

Disclosed herein is a composition and a method for making that composition having a nanoparticle capped with an inor-

ganic capping agent. The method generally includes at least two immiscible solvents and the exchange of an organic capping agent on a nanoparticle with the herein described inorganic capping agent.

Another aspect of the disclosure is a composition made of the nanoparticle and the inorganic capping agent. The composition is isolable, can be purified, and importantly may display approximately the same opto-electronic characteristics as the nanoparticle with an organic capping agent.

Yet another aspect of the disclosure is the deposition of the composition on a substrate. Herein, the composition can be deposited as thin or bulk films by a variety of techniques with short or long range ordering of the nanoparticles. The deposited composition, importantly, displays approximately the same opto-electronic characteristics as the composition in solution.

Still another aspect of the disclosure is the thermal decomposition of the deposited composition to form inorganic matrices with imbedded nanoparticles. The annealed composition has an inorganic matrix that corresponds to the thermal decomposition product of the inorganic capping agent. Additionally, as the annealed composition can be produced from the deposited composition with ordered nanoparticles (arrays), the annealed composition can have ordered arrays of nanoparticles in a solid state matrix. The annealed composition can also, importantly, display approximately the same optical characteristics as the deposited composition.

Additionally, the deposited composition can be thermally treated such that the composition partially or wholly anneals. The formed alloy can have discrete regions with elemental compositions that approximate the nanoparticle and the solid state matrix as made through the above referenced thermal decomposition or the alloy can be annealed to a single phase.

The herein disclosed materials and methods provide a route to new and useful solid state materials that can exhibit for example thermoelectric, piezoelectric, ferroelectric, phase change and electroluminescent characteristics. These solid state materials can be used in devices like photovoltaic cells, piezoelectric crystals, thermoelectric layers, optoelectronic layers, light emitting diodes, ferroelectric layers, thin film transistors, floating gate memory devices, phase change layers, detectors of light, X-ray and gamma radiation, imaging devices, and sensor devices. Uses of and methods of assembling such devices are generally described in U.S. Ser. No. 12/142,454, U.S. Pat. No. 7,348,224, U.S. Ser. No. 12/328,788, U.S. Ser. No. 11/865,325, U.S. Ser. No. 11/864,877, PCT/US2007/018015, U.S. Ser. No. 12/285,158, U.S. Ser. No. 12/108,500, U.S. Ser. No. 11/942,441, PCT/US2008/002246, U.S. Ser. No. 11/584,304, U.S. Ser. No. 12/241,333, U.S. Ser. No. 12/179,807, U.S. Ser. No. 12/155,015, PCT/US2006/022250, U.S. Pat. No. 7,517,702, U.S. Ser. No. 12/050,676, U.S. Ser. No. 12/130,075, U.S. Ser. No. 11/789,344, PCT/KR2007/002885, U.S. Ser. No. 11/704,623, U.S. Ser. No. 11/856,086, U.S. Ser. No. 11/604,746, PCT/US2008/000271, U.S. Pat. No. 7,485,526, U.S. Ser. No. 12/079,088, U.S. Ser. No. 12/032,252, PCT/US2008/005430, U.S. Ser. No. 12/050,284, and U.S. Ser. No. 11/803,261 all of which are incorporated herein by reference. Solid state materials in accordance with the descriptions herein may be used in assembling any of these and similar devices.

Additional features of the invention may become apparent to those skilled in the art from a review of the following detailed description, taken in conjunction with the drawings, the examples, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

For a more complete understanding of the disclosure, reference should be made to the following detailed description and accompanying drawings wherein:

FIG. 1 is a composite of transmission electron microscope (TEM) images. The top left image (FIG. 1A) is of 8.1 nm CdSe nanocrystals capped with $\text{Sn}_2\text{S}_6^{4-}$, herein denoted 8.1 nm CdSe. Sn_2S_6 . The top right image (FIG. 1B) is of 5 nm Au. Sn_2S_6 nanocrystals. The bottom left image (FIG. 1C) is of CdSe. Sn_2S_6 nanowires, where the CdSe is 25 nm by 2-5 μm nanowires. The bottom right image (FIG. 1D) is of CdSe/CdS. Sn_2S_6 tetrapods, where the CdSe/CdS is a tetrapod.

FIG. 2 is a composite of TEM images. The top left image (FIG. 2C) is of PbS. In_2Se_4 nanocrystals. The top right image (FIG. 2D) is of Au. In_2Se_4 nanocrystals. The bottom left image (FIG. 2E) is of CdSe/CdS. In_2Se_4 nanorods. The bottom right image (FIG. 2F) is of CdS. Sn_2S_6 nanorods.

FIG. 3 is a TEM image of 5 nm Au. Sn_2S_6 nanocrystals showing the face-centered cubic superlattice formed from the deposition of the Au. Sn_2S_6 nanocrystals on a TEM substrate.

FIG. 4 is a composite of TEM images of 5 nm Au nanocrystals. The left image (FIG. 4A) is of Au.dodecanethiol, that is Au nanocrystals capped with dodecanethiol. The middle image (FIG. 4B) is of a single layer of Au. Sn_2S_6 nanocrystals in a cubic arrangement and the right image (FIG. 4C) is of a single layer of Au. Sn_2S_6 nanocrystals in a hexagonal arrangement.

FIG. 5 is energy dispersive X-ray (EDX) spectra of (Top) a sample of 4.6 nm CdSe. Sn_2S_6 nanocrystals and (bottom) a sample of 5 nm Au. Sn_2S_6 nanocrystals. The top spectrum shows an atomic composition of 46.4% Cd, 3.1% Sn, 39.0% Se and 11.5% S, which corresponds to approximately 95% CdSe and 5% Sn_2S_6 . The bottom spectrum shows an approximate molar ratio of 90.5% Au to 9.5% Sn_2S_6 .

FIG. 6 is size-histograms of 5 nm Au. Sn_2S_6 (left) and 6 nm CdSe. Sn_2S_6 (right) nanocrystals obtained by dynamic light scattering showing a single-particle population (i.e., no aggregation) in a colloidal solution.

FIG. 7 is a plot of the ζ -potential measured for 5 nm Au. Sn_2S_6 showing a negative surface charge for the nanocrystal.

FIG. 8 is a plot of the ζ -potential measured for 5 nm CdSe. Sn_2S_6 showing a negative surface charge for the nanocrystal.

FIG. 9 is photographs of (top) stable colloidal solutions of 3.6 nm CdS. Sn_2Se_6 , 3.6 nm CdS. In_2Se_4 , 3.6 nm CdS. In_2Te_3 , 3.6 nm CdS. Ga_2Se_3 , 3.6 nm CdS. CuInSe_2 , 3.6 nm CdS. ZnTe , 3.6 nm CdS. HgSe_2^{2-} , and 3.6 nm CdS. Sb_2Se_3 ; and (bottom) stable colloidal solutions of 3.6 nm CdSe. Sn_2S_6 , 5.8 nm CdSe. Sn_2S_6 , 9 nm CdTe. Sn_2S_6 , 5 \times 60 nm (rods) CdS. Sn_2S_6 , 25 nm \times 2-5 μm (wires) CdS. Sn_2S_6 , 6 nm \times 25 nm (rods) Bi_2S_3 . Sn_2S_6 , 5 nm Au. Sn_2S_6 , and 3 nm Pd. Sn_2S_6 .

FIG. 10 is a plot comparing the optical absorbance spectra of 4.6 nm CdSe. Sn_2S_6 in various solvents to the optical spectrum of 4.6 nm CdSe*(organic capping agent) in hexane. The CdSe. Sn_2S_6 spectra were obtained for samples in hydrazine, dimethylsulfoxide, ethanolamine, and formamide.

FIG. 11 is a photograph of 4.6 nm CdSe. Sn_2S_6 in dimethylsulfoxide (DMSO), ethanolamine (EA), formamide (FA) and water (from left to right) under UV lamp excitation. The room temperature photoluminescence quantum yields (QY) are shown to illustrate the effect of solvent on the luminescent properties of semiconductor nanocrystals capped with inorganic capping agents.

FIG. 12 is a plot of the photoluminescence spectra of 4.6 nm CdSe.Sn₂Se₆ in dimethylsulfoxide (DMSO), ethanolamine (EA), formamide (FA), and of 4.6 nm CdSe•(organic capping agent) in hexane, and photograph of 4.6 nm CdSe.Sn₂Se₆ in dimethylsulfoxide (DMSO), ethanolamine (EA), formamide (FA) and water (from left to right) under white light.

FIG. 13 is plots of (top) drain current I_{DS} versus drain-source voltage V_{DS} for a nanocrystal FET with a channel composed of 4.5 nm CdSe.Sn₂Se₆ and annealed at 200° C. ($L=10\text{-}\mu\text{m}$, $W=3800\text{-}\mu\text{m}$, 110 nm-thick SiO₂ gate dielectric); (left) the transfer characteristics for an FET with a channel assembled of CdSe.SnS₂; plot of drain current I_{DS} vs. gate voltage V_G at a constant source-drain voltage $V_{DS}=40$ V, field-effect mobility in the saturation regime was calculated from the slope of $I_{DS}^{1/2}$ vs. V_G ; and (right) the effect of broad band light illumination (AM1.5 solar spectrum, ~ 20 mW cm⁻² light intensity) on the current flowing through a film of 5.5 nm CdSe.Sn₂Se₆ after the film was annealed at 200° C.

FIG. 14 is a comparison of I_{DS} - V_{DS} scans for thin films made from 5 nm Au.(dodecanethiol), left (FIG. 19D), and 5 nm Au.Sn₂S₆, right (FIG. 19E).

FIG. 15 is a plot of the optical absorbance spectra of thin films of CdSe•(organic capping agent), CdSe.Sn₂Se₆, and CdSe.SnSe₂ (made by annealing CdSe.Sn₂Se₆) showing insignificant changes in the absorption spectra.

FIG. 16 is a composites of SEM images at different magnifications of a product formed by the annealing Bi₂S₃.Sb₂Te₄, where the product has an approximate formula BiSbTe₃.

FIG. 17 is a (top) powder X-ray diffraction (XRD) pattern of a product formed by annealing Bi₂S₃.Sb₂Te₄, where the product has an approximate formula BiSbTe₃; and (bottom) a comparison of powder XRD patterns showing: top, the XRD pattern of a Bi_{1.3}Sb_{0.7}Te₃ nanocomposite formed by annealing Bi₂S₃.Sb₂Te₄; middle, the XRD pattern of annealed inorganic capping agent Sb₂Te₄, and bottom, the XRD patterns for the annealed Bi₂S₃•(oleic-acid) nanorods. All samples were annealed at 180° C. Note that the average grain size in the annealed Bi_{1.3}Sb_{0.7}Te₃ nanocomposite is smaller than that of the Bi₂S₃•(oleic-acid) nanorods.

FIG. 18 is a plot comparing the powder XRD patterns showing the XRD patterns of Bi_{2-x}Sb_xTe₃ nanocomposites formed by annealing Bi₂S₃.Sb₂Te₄ at different Bi:Sb ratios. All samples were annealed to 350° C. Peak marking corresponds to: “+”: rhombohedral Sb₂Te₃ (JCPDS No. 71-393, R₃m); “*”: orthorhombic Bi₂S₃ (JCPDS No. 17-0320, Pbnm); “#”: rhombohedral Bi₂Te₃ (ICDD No. 08-0021, R₃m (166))

FIG. 19 is a plot comparing EDS spectra and TEM images of two Bi_{2-x}Sb_xTe₃ nanocomposites formed by annealing Bi₂S₃.Sb₂Te₄ at high (top) and low (bottom) Bi:Sb ratios. Notably, a high Bi:Sb ratio provides very small crystalline domains while the small Bi:Sb ratio provides significantly larger crystalline domains. The EDS spectra show that the ratio of Bi:Sb persists from the colloidal particle to the colloidal material, Bi_{2-x}Sb_xTe₃ nanocomposite.

FIG. 20 is a plot comparing, top, the I-V scan of a Bi_{1.3}Sb_{0.7}Te₃ nanocomposite film (filled circles) prepared from $\sim 6 \times 25$ nm (nanorod) Bi₂S₃.Sb₂Te₄ by spin-casting and annealing (180° C.) and, bottom, the I-V scan of the film of $\sim 6 \times 25$ nm (nanorod) Bi₂S₃•(oleic-acid) (annealed at 180° C.).

FIG. 21 is a plot of the current across a Bi_{2-x}Sb_xTe₃ nanocomposite film showing ohmic behavior and high conductivity.

FIG. 22 is an illustration of the fabrication of a device by coating a sample with the described nanocomposites.

FIG. 23 illustrates plots of the absorbance versus wavelength, more specifically the absorption spectra for ~ 5 nm Au nanoparticles stabilized with (N₂H₄)₅Sn₂S₆ (A) and with dodecanethiol (B), in solutions and in thin films, where the film absorption was measured using an integrating sphere.

FIG. 24 is illustrations of a nanocrystal coated with an inorganic capping agent (Sn₂S₆⁴⁻); the linking/bridging of two nanocrystals, individually coated with an inorganic capping agent (Sn₂S₆⁴⁻), by a metal cation (Mⁿ⁺), and the linking/bridging of a plurality of coated nanocrystals, individually coated with an inorganic capping agent (Sn₂S₆⁴⁻), by metal cations (Ptⁿ⁺), thereby forming a chain or wire. The illustration additionally shows one type of regular stacking of the chain in two dimensional space.

FIG. 25 is TEM images of inorganic capped nanoparticles that are ion paired with the dimethylbis(dodecylammonium) cation (N(CH₃)₂(C₁₂H₂₅)₂⁺; DDAB).

FIG. 26 is TEM images and composite drawings of colloidal materials that comprise two different inorganic capped nanoparticles.

FIG. 27 is TGA scans for Bi₂S₃.Sb₂Te₃ dried sample showing the release of S in the course of solid-state chemical transformation toward (Bi_{0.6}Sb_{0.4})₂Te₃ phase.

FIG. 28 is a composite of (A) cross-sectional SEM image of a ~ 20 nm thick (Bi_{0.5}Sb_{0.5})₂Te₃ film prepared by spin-casting. (B) Tapping-mode AFM image of 0.3- μm thick (Bi_{0.5}Sb_{0.5})₂Te₃ films prepared by drop-casting. (C) I-V curve and (D) a plot of Seebeck voltage vs. temperature difference for a representative sample of a p-type (Bi,Sb)₂Te₃ spray-cast film. (E) Plot of Seebeck voltage vs. temperature difference for an n-type (Bi,Sb)₂(Te_{0.9}Se_{0.1})₃ drop-cast film (~ 10 molar % of Sb₂Se₃).

FIG. 29 is plots of the temperature dependence of the electrical conductivity σ (A, D), Seebeck coefficient S (B, D) and power factor $S^2\sigma$ (C, F), for p-type (Bi,Sb)₂Te₃ (A, B, C) and n-type (Bi,Sb)₂(Te_{0.9}Se_{0.1})₃ (D, E, F). Circles correspond to the forward temperature scan, whereas the triangles represent data points measured during sample cooling.

FIG. 30 is (A) low- and (B, C) high-resolution TEM images for a nanostructured [(Bi,Sb)₂Te₃](PbTe) composite prepared by combining PbTe.Sb₂Te₃ with “(Bi,Sb)₂Te₃” ink in 1:4 molar ratio followed by the annealing at 300° C. More fringes on panel (C) arise from the electron beam diffraction on vertically stacked crystallites.

FIG. 31 is (A) XRD patterns for PbTe.Sb₂Te₃, annealed at various temperatures. The absence of detectable Sb₂Te₃ peaks points to the very small content of this phase. (B) TEM images for the same sample deposited onto TEM grid and annealed at 300° C.

FIG. 32 is Electrical characterization of PbTe.Sb₂Te₃. (A) Plot of the low-field conductance (G) vs. T-1/4 in the 84-300 K temperature range, (B) Plot of Seebeck voltage vs. temperature difference, (C) Plot of drain current I_{DS} vs. source-drain voltage V_{DS} as a function of gate voltage V_G for a NC-based FET ($L=10\text{ }\mu\text{m}$, $W=3800\text{ }\mu\text{m}$, with a 100-nm thick SiO₂ gate oxide, Au drain and source electrodes, and highly doped Si as the back gate electrode).

FIG. 33 is XRD pattern for biphasic PbTe/Sb₂Te₃ composite prepared by annealing PbS.Sb₂Te₃ at 300° C.

FIG. 34 is TEM images of (A) 5-nm Au.Sb₂Te₃, (B) composite prepared by adding Au.Sb₂Te₃ to “BiSbTe ink” (dried at 80° C.), showing homogeneous distribution of particles. (C) and (D) Low- and high-resolution TEM images of the same Au/BiSbTe composite annealed at 300° C. Figure (D)

illustrated the presence of small and discrete Au inclusions in the annealed sample in addition to large Au precipitates seen from Figure (C).

FIG. 35 is (A) chemical structure of PDDA; (B) a photograph of $\{(CdSe/ZnS)_n/SnS_4/PDDA\} \times 20$ film, assembled from aqueous solutions, taken under UV irradiation. (C) PL spectrum of the film shown in (B). (D) Absorption spectra of $(CdSe/SnS_4/PDDA)_n$ films (n is number of bilayers), assembled from aqueous solutions. (E) Absorption spectra of $(Au/Sn_2S_6/PDDA)_n$ films, assembled from formamide solutions.

FIG. 36 is (A) I-V curves for thin films assembled from 5 nm Au/Sn_2S_6 (films were made from formamide solutions at $80^\circ C.$) and for LBL films composed of the same Au/Sn_2S_6 nanocrystals and PDDA. (B) Optical absorption spectra for thin films made from 4.2-nm CdSe nanocrystals capped with original organic ligands (solid line) and with $Sn_2S_6^{4-}$ before (dash) and after annealing at $200^\circ C.$ (short dash). (C) Plot of the drain current I_D versus drain-source voltage V_{DS} for a nanocrystal FET with a channel composed of 4.2-nm CdSe/ Sn_2S_6 and annealed at $200^\circ C.$ (channel length is $5 \mu m$, width $7800 \mu m$, 110-nm -thick SiO_2 gate dielectric).

FIG. 37 is TGA scans for solid $(NH_4)_4Sn_2S_6$ and for CdSe/ZnS/ Sn_2S_6 .

FIG. 38 is data corresponding to gated n-type charge transport in CdSe/ In_2Se_3 materials. (a) Schematics of a field-effect transistor with a channel assembled from CdSe/ In_2Se_3 . (b) Cross-section SEM image of selected FET devices. (c) Drain current I_D plotted versus drain-source voltage V_{DS} , as a function of gate voltage V_G for an array of 4.6 nm CdSe/ In_2Se_3 . $L=50 \mu m$, $W=460 \mu m$. (d) Plot of I_D vs. V_G at constant $V_{DS}=4V$ used to calculate transconductance and linear field-effect mobility in the array of 4.6 nm CdSe/ In_2Se_3 . (e) Absorption spectra collected using an integrating sphere for thin films assembled from CdSe/ In_2Se_4 before and after annealing at different temperature. (f) Plots of I_D vs. V_G at constant $V_{DS}=2V$ as function of operation cycles for n-channel FET assembled from 4.6 nm CdSe/ In_2Se_3 ($L=111 \mu m$, $W=1500 \mu m$). The operation of device repeated to 200 cycles.

FIG. 39 is a comparison powder XRD patterns of annealed copper indium materials, showing the synthesis of a copper indium selenide from sulfur or selenium containing starting materials.

FIG. 40 is a comparison of powder XRD patterns to the line index for $Cu(In,Ga)Se_2$, showing the product from the thermal processing of $Cu_2Se.(In_2Se_4;Ga_2Se_3)$ at two different In to Ga ratios.

FIG. 41 is a comparison of the powder XRD pattern of the product from the thermal processing of a mixture of Cu_2Se/Sn_2S_6 and ZnS/Sn_2S_6 and the diffraction pattern for CZTS (Cu_2ZnSnS_4 ; JCPDS no. 26-0575).

While the disclosed compositions and methods are susceptible of embodiments in various forms, there are illustrated in the drawings (and will hereafter be described) specific embodiments of the invention, with the understanding that the disclosure is intended to be illustrative, and is not intended to limit the invention to the specific embodiments described and illustrated herein.

DETAILED DESCRIPTION OF THE INVENTION

The compositions and methods described herein generally relate to new colloidal particles (inorganic capped nanomaterials) and materials, composites, made from these nanometer scale particles. The colloidal particles can be facilely produced from single or multi-component mixtures of nanoparticles and the materials can be produced therefrom. These

new colloidal particles, materials and the methods, described herein, may reduce the time, expense, and uncertainty in the manufacture of advanced materials.

Colloidal particles, from which the herein described materials can be produced, are discrete particles and are generally suspendable in at least one solvent. The colloidal particles are isolable, that is the colloidal particles can be isolated from reagents used in the manufacture of the colloidal particles. One characteristic of many isolable colloidal particles is that the colloidal particles can be deposited from a solution and then resuspended or redissolved in the same or a different solvent. Often colloidal particles have sizes ranging from the nanometer scale to the micron scale and can exist as mixtures with broad size ranges. Nanoparticles are those particles where at least the cross-sections of the particle in two dimensions are between about 1 and about 1000 nanometers (nm). Nanoparticles can be produced in a large variety of morphologies and sizes all of which are applicable herein. Nonlimiting examples of the morphologies of nanoparticles include, nanocrystals, nanorods, nanoplates, nanowires, dumbbell-like nanoparticles, and dendritic nanomaterials. See FIG. 1. Within each morphology there is an additional large variety of shapes available, for example nanocrystals can be produced in spheres, cubes, tetrahedra, octahedra, icosahedra, prisms, cylinders, wires, branched and hyperbranched morphologies and the like. The morphology and the size of the nanoparticles do not inhibit the general method for making colloidal materials described herein; specifically the selection of morphology and size of the nanoparticle allows for the tuning and control of the properties of the colloidal material, as will become clear.

Non-limiting examples of nanoparticles applicable herein include: AlN, AlP, AlAs, Ag, Au, Bi, Bi_2S_3 , Bi_2Se_3 , Bi_2Te_3 , CdS, CdSe, CdTe, Co, CoPt, CoPt₃, Cu, Cu_2S , Cu_2Se , $CuInSe_2$, $CuIn_{(1-x)}Ga_x(S,Se)_2$, $Cu_2ZnSn(S,Se)_4$, Fe, FeO, Fe_2O_3 , Fe_3O_4 , FePt, GaN, GaP, GaAs, GaSb, GaSe, Ge, HgS, HgSe, HgTe, InN, InP, InSb, InAs, Ni, PbS, PbSe, PbTe, Pd, Pt, Ru, Rh, Si, Sn, ZnS, ZnSe, ZnTe, and mixtures thereof. Examples of applicable nanoparticles include core/shell nanoparticles like Au/PbS, Au/PbSe, Au/PbTe, Ag/PbS, Ag/PbSe, Ag/PbTe, Pt/PbS, Pt/PbSe, Pt/PbTe, Au/CdS, Au/CdSe, Au/CdTe, Ag/CdS, Ag/CdSe, Ag/CdTe, Pt/CdS, Pt/CdSe, Pt/CdTe, Au/FeO, Au/ Fe_2O_3 , Au/ Fe_3O_4 , Pt/FeO, Pt/ Fe_2O_3 , Pt/ Fe_3O_4 , FePt/PbS, FePt/PbSe, FePt/PbTe, FePt/CdS, FePt/CdSe, FePt/CdTe, CdSe/CdS, CdSe/ZnS, InP/CdSe, InP/ZnS, InP/ZnSe, InAs/CdSe, and InAs/ZnSe; nanorods like CdSe, core/shell nanorods like CdSe/CdS; nanotetrapods like CdTe, and core/shell nano-tetrapods like CdSe/CdS.

Often nanoparticles are synthesized in such a manner that the resulting nanoparticle is capped, or coated, in a stabilizing organic material, an organic capping agent. One typical example of an organic capping agent is trioctylphosphine oxide (TOPO), used in the manufacture of CdSe. The TOPO capping agent prevents the agglomeration of the nanoparticle during and after the synthesis of the particle, additionally the long organic chains radiating from the capping agent on the surface of the nanoparticle assist in the suspension and/or solubility of the nanoparticle in a solvent. A second type of organic capping agent is an organic thiol, often used in the manufacture of silver or gold nanoparticles. These organic thiols range from simple long chain alkane thiols, like dodecane thiol, to complex monothiols. The long organic chain of the organic thiol capping agent, as with the TOPO capping agent, assists in the suspension and/or solubility of the capped nanoparticle. Other known capping agents include long-chain aliphatic amines, long-chain aliphatic phosphines,

long-chain aliphatic carboxylic acids, long-chain aliphatic phosphonic acids and mixtures thereof.

The present disclosure provides techniques for replacement of the organic capping agents with inorganic capping agents. As used herein, inorganic capping agents are those soluble reagents free of organic functionality that displace organic capping agents from nanoparticles and, preferably, wherein the inorganic capped nanoparticle is dispersible, that is suspendable and/or soluble. Inorganic capping agents comprises metals selected from transition metals, lanthanides, actinides, main group metals, metalloids, and mixtures thereof. Inorganic capping agents further comprise soluble metal chalcogenides and/or metal carbonyl chalcogenides. One aspect of the technique of replacing the organic capping agents with inorganic capping agents is the complete, or substantially complete, displacement of the organic capping agents from the nanoparticle and replacement with the inorganic capping agent. See FIG. 2.

Inorganic capping agents can be neutral or ionic, can be discrete species, linear or branched chains, or two-dimensional sheets. Ionic inorganic capping agents are commonly referred to as salts, a pairing of a cation and an anion, and the portion of the salt specifically referred to as an inorganic capping agent is the ion that displaces the organic capping agent and caps the nanoparticle. Often an inorganic ion is paired with an ion that has organic functionality; the paired ion that does not displace organic capping agents is referred to herein as a counter ion. The counter ion can affect the solubility and reactivity of the inorganic capping agent as well as the inorganic capped nanomaterial but the great variability of counter ions allows for their facile replacement and a balance of desired properties.

The inorganic capping agents described herein are often designated by formulations derived from a variety of analytical techniques, including elemental analysis, mass spectroscopy, and NMR. These designations may or may not accurately describe the molecular compositions of these inorganic capping agents in a solution and further do not prescribe to them a specific structure. It is believed that at least some of the herein described inorganic capping agents exhibit variable solution structure equilibria, possibly dependent on temperature, concentration, purity, and other factors.

In one embodiment the inorganic capping agents are Zintl ions. As used herein, Zintl ions refers to homopolyatomic anions and heteropolyatomic anions that have intermetallic bonds between the same or different metals of the main group, transition metals, lanthanides, and/or actinides. Non-limiting examples of Zintl ions include: As_3^{3-} , As_4^{2-} , As_5^{3-} , As_7^{3-} , Ae_{11}^{3-} , AsS_3^{3-} , $As_2Se_6^{3-}$, $As_2Te_6^{3-}$, $As_{10}Te_3^{2-}$, $Au_2Te_4^{2-}$, $Au_3Te_4^{3-}$, Bi_3^{3-} , Bi_4^{2-} , Bi_5^{3-} , $GaTe^{2-}$, Ge_9^{2-} , Ge_9^{4-} , $Ge_2S_6^{4-}$, $HgSe_2^{2-}$, $Hg_3Se_4^{2-}$, $In_2Se_4^{2-}$, $In_2Te_4^{2-}$, $Ni_5Sb_{17}^{4-}$, Pb_5^{2-} , Pb_7^{4-} , Pb_9^{4-} , $Pb_2Sb_2^{2-}$, Sb_3^{3-} , Sb_4^{2-} , Sb_7^{3-} , $SbSe_4^{3-}$, $SbSe_5^{5-}$, $SbTe_4^{5-}$, $Sb_2Se_3^{-}$, $Sb_2Te_5^{4-}$, $Sb_2Te_7^{4-}$, $Sb_4Te_4^{4-}$, $Sb_9Te_6^{3-}$, Se_2^{2-} , Se_3^{2-} , Se_4^{2-} , $Se_{5,6}^{2-}$, Se_6^{2-} , Sn_5^{2-} , Sn_9^{3-} , Sn_2^{4-} , SnS_4^{4-} , $SnSe_4^{4-}$, $SnTe_4^{4-}$, $SnS_4Mn_2^{5-}$, $SnS_2S_4^{4-}$, $Sn_2Se_6^{4-}$, $Sn_2Te_6^{4-}$, $Sn_2Bi_2^{2-}$, Sn_8Sb^{3-} , Te_2^{2-} , Te_3^{2-} , Te_4^{2-} , $Tl_2Te_2^{2-}$, $TlSn_8^{3-}$, $TlSn_8^{5-}$, $TlSn_9^{3-}$, $TlTe_2^{2-}$, mixed metal $SnS_4Mn_2^{5-}$, and the like. The positively charged counter ions can be alkali metal ions, ammonium, hydrazinium, tetraalkylammonium, and the like.

Another embodiment of applicable inorganic capping agents include, for example, molecular compounds derived from $CuInSe_2$, $CuIn_xGa_{1-x}Se_2$, Ga_2Se_3 , In_2Se_3 , In_2Te_3 , Sb_2S_3 , Sb_2Se_3 , Sb_2Te_3 , and $ZnTe$, the inorganic complexes disclosed in Roof, L. C., Kolis, J. W. *Chem. Rev.* 1993, 93, 1037-80 and incorporated herein by reference, and the inorganic complexes disclosed in Corbett, J. D. *Chem. Rev.* 1985,

85, 383-97 and incorporated herein by reference. For many of these molecular compounds the exact stoichiometry in a solution has not yet been adequately established, this does not preclude the use herein.

Further embodiments include non-stoichiometric Zintl ions and inorganic capping agents derived from molecular compounds. These include, for example, inorganic capping agents derived from molecular compounds wherein excess chalcogenide is added. One example is an inorganic capping agent derived from Sb_2Te_3 with excess tellurium, $[Sb_2Te_3:Te]$. Analysis of $Sb_2Te_3:Te$ indicates a solution composition that contains $SbTe_3^{3-}$, $Sb_2Te_5^{4-}$, and $Sb_2Te_7^{4-}$ by ESI-MS and a stoichiometry of $Sb_2Te_7^{4-}$ by elemental analysis.

Still further, these inorganic capping agents include mixtures of Zintl ions and molecular compounds.

These inorganic capping agents further include transition metal chalcogenides. Examples of transition metal chalcogenides include the tetrasulfides and tetraselenides of vanadium, niobium, tantalum, molybdenum, tungsten, and rhenium, and the tetratellurides of niobium, tantalum, and tungsten. These transition metal chalcogenides further include the monometallic and polymetallic polysulfides, polyselenides, and mixtures thereof, e.g., $MoS(Se_4)_2^{2-}$, $Mo_2S_6^{2-}$, and the like.

Inorganic capped nanoparticles differ from core/shell nanoparticles. Core/shell nanoparticles are those particles where one nanocrystal has an outer crystalline layer with a different chemical formula. Core/shell nanoparticle compositions are commonly designated through the simple notation of (core composition)/(shell composition), for example $CdSe/CdS$ has a $CdSe$ core and a CdS shell. The crystalline layer, the shell, generally forms over the entire nanocrystal but as used herein core/shell nanoparticles refers to those nanoparticles where at least one surface of the nanocrystal is coated with a crystalline layer. While the inorganic capping agents may form ordered arrays on the surface of a nanocrystal these arrays differ from a core/shell crystalline layer, in part because the thickness of the array is dependent on the size of the inorganic capping agent not the concentration of reagent provided or the growth time of the layer.

The disclosed colloidal particles (inorganic capped nanoparticles) are soluble and/or suspendable in a solvent. Typically, the purification of chemicals requires some isolation procedure and for inorganic materials this procedure is often the precipitation of the inorganic product. The precipitation of inorganic products permits one of ordinary skill to wash the inorganic product of impurities and/or unreacted materials. The isolation of the precipitated inorganic products then allows for the selective application of those materials.

Moreover, the disclosed colloidal particles are isolable and dispersible, soluble or suspendable, in a variety of solvents. Manufacturing techniques, environmental and/or work-place rules often require the application of certain solvents. Colloidal materials dispersible in a variety of solvents are applicable for a broader use than those colloidal materials that require specific, toxic, environmentally hazardous, or costly solvents.

Solvents applicable herein include but are not limited to: 1,3-butanediol, acetonitrile, ammonia, benzonitrile, butanol, dimethylacetamide, dimethylamine, dimethylethylenediamine, dimethylformamide, dimethylsulfoxide, dioxane, ethanol, ethanohalmine, ethylenediamine, ethyleneglycol, formamide, glycerol, methanol, methoxyethanol, methylamine, methylformamide, methylpyrrolidinone, pyridine, tetramethylethylenediamine, triethylamine, trimethylamine, trimethylethylenediamine, water, and mixtures thereof.

The above-described colloidal particles can be made by mixing the nanoparticle in form of powder, suspension or a colloidal solution with the inorganic capping agent in accordance with the techniques described herein. The mixing of the nanoparticle with the inorganic capping agent causes a reaction of the nanoparticle with the inorganic capping agent and rapidly produces insoluble and intractable materials. Herein a mixture of immiscible solvents is used to control the reaction of the nanoparticle with the inorganic capping agent. Immiscible solvents facilitate a rapid and complete exchange of the organic capping agents with the inorganic capping agents.

Generally, the inorganic capping agent is dissolved in a polar solvent, a first solvent, while the nanoparticle is dissolved in an immiscible, generally non-polar, solvent, a second solvent. These two solutions are then combined in a single vessel. Non-limiting examples of polar solvents include 1,3-butanediol, acetonitrile, ammonia, benzonitrile, butanol, dimethylacetamide, dimethylamine, dimethylethylenediamine, dimethylformamide, dimethylsulfoxide, dioxane, ethanol, ethanolamine, ethylenediamine, ethyleneglycol, formamide, glycerol, methanol, methoxyethanol, methylamine, methylformamide, methylpyrrolidinone, pyridine, tetramethylethylenediamine, triethylamine, trimethylamine, trimethylethylenediamine, water, and mixtures thereof. Non-limiting examples of non-polar solvents include pentane, pentanes, cyclopentane, hexane, hexanes, cyclohexane, heptane, octane, isooctane, nonane, decane, dodecane, hexadecane, benzene, 2,2,4-trimethylpentane, toluene, petroleum ether, ethyl acetate, diisopropyl ether, diethyl ether, carbon tetrachloride, carbon disulfide, and mixtures thereof; provided that the non-polar solvent is immiscible with the polar solvent. Other immiscible solvent systems that are applicable include aqueous-fluorous, organic-fluorous, and those using ionic liquids.

Without wishing to be bound by theory, it is thought that the nanoparticle reacts with the inorganic capping agent at or near the solvent boundary, the region where the two solvents meet, and a portion of the organic capping agent is exchanged/replaced with the inorganic capping agent. That is, the inorganic capping agent displaces an organic capping agent from a surface of the nanoparticle and the inorganic capping agent binds to the surface of the nanoparticle. Without wishing to be bound by theory, it is thought that this process continues until an equilibrium is established between the inorganic capping agent on a nanoparticle and the free inorganic capping agent. Preferably, the equilibrium favors the inorganic capping agent on a nanoparticle, although other equilibria are applicable for making mixed colloidal particles. The herein described immiscible solvent method of forming nanoparticles capped with inorganic capping agents has the added benefit of providing for the extraction of the organic capping agents from the inorganic capped nanocrystals.

The extraction of the organic capping agent can provide a solution of an inorganic capped nanocrystal that is substantially free of the organic capping agent. Herein, substantially free means the relative concentration of the organic capping agent to the nanoparticle in the solution of the inorganic capped nanocrystal is less than 10%, 5%, 4%, 3%, 2%, 1%, 0.5%, and/or 0.1% of the concentration in a solution of the organic capped nanocrystal. One means for determining if a solution is substantially free of the organic capping agent is IR spectroscopy and the observation of the absence of C—H stretching frequencies.

The benefit of this method can be easily understood through a non-limiting example of a CdSe nanoparticle and a $\text{Sn}_2\text{Se}_6^{2-}$ inorganic capping agent—a more detailed example is presented below. Typically, as-made CdSe is coated by a

layer of organic capping agents and is soluble in non-polar solvents like hexane. The inorganic capping agent, $\text{Sn}_2\text{Se}_6^{2-}$, is soluble in polar solvents like dimethylsulfoxide (DMSO). DMSO and hexane are appreciably immiscible. Therefore, a hexane solution of CdSe rests above a DMSO solution of $\text{Sn}_2\text{Se}_6^{2-}$. Within a short time after combining the two solutions, the color of the hexane solution, due to the CdSe, will fade and the DMSO layer will become colored. Without wishing to be bound by theory, it is thought that this occurs because the organic capping agents are displaced by the inorganic capping agents and the resulting surface charged nanoparticle is then soluble in the polar DMSO solution. See, for example, FIGS. 7 and 8 which show a negative ζ -potential for $\text{Sn}_2\text{Se}_6^{4-}$ capped Au and for $\text{Sn}_2\text{Se}_6^{4-}$ capped CdSe nanocrystals indicative of a negative surface charge on the nanocrystals. Commonly, the uncharged organic capping agent is preferably soluble in the non-polar solvent and is thereby physically separated from the nanocrystals, affording the opportunity to remove all of the organic capping agent from the inorganic capped nanocrystal. This facile method of making inorganic capped nanoparticles allows for the selective precipitation of these colloidal particles, the selective precipitation of excess inorganic capping agent, or the direct use of the colloidal particle solution in the manufacture of films, crystals, or devices.

Examples of colloidal particles include Au.AsS₃, Au.Sn₂S₆, Au.SnS₄, Au.Sn₂Se₆, Au.In₂Se₄, Bi₂S₃.Sb₂Te₅, Bi₂S₃.Sb₂Te₇, Bi₂Se₃.Sb₂Te₅, Bi₂Se₃.Sb₂Te₇, CdSe.Sn₂S₆, CdSe.Sn₂Te₆, CdSe.In₂Se₄, CdSe.Ge₂S₆, CdSe.Ge₂Se₃, CdSe.HgSe₂, CdSe.ZnTe, CdSe.Sb₂S₃, CdSe.SbSe₄, CdSe.Sb₂Te₇, CdSe.In₂Te₃, CdTe.Sn₂S₆, CdTe.Sn₂Te₆, CdTe.In₂Se₄, Au/PbS.Sn₂S₆, Au/PbSe.Sn₂S₆, Au/PbTe.Sn₂S₆, Au/CdS.Sn₂S₆, Au/CdTe.Sn₂S₆, FePt/PbS.Sn₂S₆, FePt/PbSe.Sn₂S₆, FePt/PbTe.Sn₂S₆, FePt/CdS.Sn₂S₆, FePt/CdSe.Sn₂S₆, FePt/CdTe.Sn₂S₆, Au/PbS.SnS₄, Au/PbSe.SnS₄, Au/PbTe.SnS₄, Au/CdS.SnS₄, Au/CdSe.SnS₄, Au/CdTe.SnS₄, FePt/PbS.SnS₄, FePt/PbSe.SnS₄, FePt/PbTe.SnS₄, FePt/CdS.SnS₄, FePt/CdSe.SnS₄, FePt/CdTe.SnS₄, Au/PbS.In₂Se₄, Au/PbSe.In₂Se₄, Au/PbTe.In₂Se₄, Au/CdS.In₂Se₄, Au/CdSe.In₂Se₄, Au/CdTe.In₂Se₄, FePt/PbS.In₂Se₄, FePt/PbSe.In₂Se₄, FePt/PbTe.In₂Se₄, FePt/CdS.In₂Se₄, FePt/CdSe.In₂Se₄, FePt/CdTe.In₂Se₄, CdSe/CdS.Sn₂S₆, CdSe/CdS.SnS₄, CdSe/ZnS.SnS₄, CdSe/CdS.Ge₂S₆, CdSe/CdS.In₂Se₄, CdSe/ZnS.In₂Se₄, Cu.In₂Se₄, Cu₂Se.Sn₂S₆, Pd.AsS₃, PbS.SnS₄, PbS.Sn₂S₆, PbS.Sn₂Se₆, PbS.In₂Se₄, PbS.Sn₂Te₆, PbS.AsS₃, ZnSe.Sn₂S₆, ZnSe.SnS₄, ZnS.Sn₂S₆, and ZnS.SnS₄. See for example, FIGS. 1-4. As used herein the denotation Au.Sn₂S₆ refers to a Au nanocrystal capped with a Sn_2S_6 inorganic capping agent. Charges on the inorganic capping agent are omitted for clarity. This nomenclature [nanocrystal].[inorganic capping agent] is used throughout this description. The specific percentages of nanoparticle and inorganic capping agent vary between the colloidal particles. For example, in one implementation, the energy dispersive X-ray (EDX) spectrum of a sample of CdSe.Sn₂Se₆ shows a composition that corresponds to approximately 95% CdSe nanocrystals and about 5% Sn_2Se_6 . See FIG. 5. In another implementation, the EDX spectrum of Au.Sn₂Se₆ shows a composition that corresponds to approximately 90% Au nanocrystals and 10% Sn_2Se_6 . See FIG. 5. Without being bound to theory, the different percentages of Sn_2Se_6 observed in the samples in FIG. 5 are believed to correlate with the thio-affinity of the nanocrystal surface and surface area.

The described method does not affect the extent of aggregation of the colloidal particles. For example, dynamic light scattering shows that a sample of 5 nm Au nanoparticles

coated with the inorganic capping agent Sn_2S_6 ($\text{Au.Sn}_2\text{S}_6$) can have an average hydrodynamic colloidal particle size of about 8 nm and show no aggregation. See FIG. 6. Similarly, a sample of 6 nm CdSe nanoparticles coated with the inorganic capping agent Sn_2S_6 ($\text{CdSe.Sn}_2\text{S}_6$) has an average colloidal particle size of about 8 nm and shows no aggregation. See FIG. 6.

Likewise, the described method does not affect the optical absorbance of the capped nanoparticles. FIG. 9 shows a white light photograph of colloidal particles prepared from 3.6 nm CdSe nanocrystals. The color of the samples (indicative of the electronic characteristics of the nanocrystal) did not significantly change when the CdSe is capped with different inorganic capping agents. Similarly, a single inorganic capping agent, here $\text{Sn}_2\text{S}_6^{4-}$, can cap a wide variety of nanoparticles, see e.g., FIG. 9. FIG. 10 shows that the herein described colloidal particles are stable and soluble in a variety of solvents and that the electronic characteristics of the underlying nanoparticle are neither changed by the presence of the inorganic capping agent nor the solvent. Had the electronic characteristics of the nanoparticle been affected by the solvent then the optical absorption of the nanoparticle would have changed. See also FIG. 12.

Furthermore, the photoluminescence of the nanoparticle is preserved when capped with an inorganic capping agent. FIG. 11 shows photoluminescence under UV excitation and lists quantum yields from a sample of $\text{CdSe.Sn}_2\text{S}_6$ in different solvents. See FIG. 12 for a white light photograph of the same samples. Similarly, FIG. 12 includes a series of plots of the photoluminescence of a sample of $\text{CdSe.Sn}_2\text{S}_6$ in different solvents showing that the emission maximum does not significantly change between solvents.

Moreover, the above described method can be adapted to make a wide variety of colloidal particles. Adaptations of the method include adding two different inorganic capping agents to a single nanoparticle (e.g., $\text{Au.}(\text{Sn}_2\text{S}_6;\text{In}_2\text{Se}_4)$; $\text{Cu}_2\text{Se.}(\text{In}_2\text{Se}_4;\text{Ga}_2\text{Se}_3)$), adding two different nanoparticles to a single inorganic capping agent (e.g., $(\text{Au};\text{CdSe}).\text{Sn}_2\text{S}_6$; $(\text{Cu}_2\text{Se};\text{ZnS}).\text{Sn}_2\text{S}_6$), adding two different nanoparticles to two different inorganic capping agents (e.g., $(\text{Au};\text{CdSe}).(\text{Sn}_2\text{S}_6;\text{In}_2\text{Se}_4)$), and/or additional multiplicities.

The sequential addition of inorganic capping agents to a nanoparticle is available under the disclosed method. Depending, for example, upon concentration, nucleophilicity, capping agent to nanoparticle bond strength, and crystal face dependent capping agent to nanoparticle bond strength, the inorganic capping of the nanoparticle can be manipulated to yield other combinations. For example, assume that a nanoparticle has two faces, face A and face B, and that the bond strength of the organic capping agent to face A is twice that of the bond strength to face B. The organic capping agents on face B would be preferentially exchanged when employing the herein described methodology. Isolation and reaction of this intermediate species, having organic and inorganic capping agents, with a second inorganic capping agent would produce a colloidal particle with a first inorganic capping agent on face B and a second inorganic capping agent on face A. Alternatively, the preferential binding of inorganic capping agents to specific nanoparticle faces can yield the same result from a single mixture of multiple inorganic capping agents.

Another aspect of the disclosed method is the possibility of a chemical reactivity between inorganic capping agents. For example, a first inorganic capping agent bound to the surface of a nanocrystal and reactive with a second inorganic capping agent can directionally react with the second inorganic capping agent. This methodology provides for the synthesis of

colloidal particles that could not be selectively made from a solution of nanoparticle and inorganic capping agents. The interaction of the first inorganic capping agent with the nanoparticle controls both the direction and scope of the reactivity of the first inorganic capping agent with the second inorganic capping agent. Furthermore, this methodology controls what part of the new inorganic capping agent binds to the nanocrystal. Presumably, the result of the addition of a combined-inorganic capping agent capping to a nanocrystal by other methods would produce a random arrangement of the combined-inorganic capping agent on the nanocrystal.

Yet another method of making colloidal particles involves the mixing of a nanoparticle in a non-polar organic solvent with a purified colloidal particle in a polar organic solvent. In this example, the colloidal particle in the polar solvent is the inorganic capping agent. These methodologies can form colloidal particle capped nanoparticles and other variations on the herein described capping architecture.

Still another aspect of the current disclosure is the bridging of colloidal particles with metal ion complexing agents. See FIG. 24. Herein bridging means that one or more metal ions individually bind, ionically or covalently, binding sites on the exterior of a plurality of colloidal particles. Preferably, binding sites are parts of the inorganic capping agent that is disposed perpendicular to a surface on the nanoparticle. Understanding that the bridging between two colloidal particles can involve a plurality of metal ions, for descriptive purposes the binding of a single metal ion between two colloidal particles is exemplified herein. As described above, inorganic capping agents include anionic and neutral capping agents. When, for example, anionic inorganic capping agents are bound to the surface of a nanoparticle, the anionic charge associated with the inorganic capping agent remains (providing a theoretical basis for electrostatic repulsion between colloidal particles having anionic inorganic capping agents). The addition of a cationic ion, preferably a cationic metal ion, still more preferably a polycationic (wherein the charge on the metal ion is greater than 1) metal ion to the colloidal particle can produce a colloidal particle with the cationic ion bound to a surface of the colloidal particle, specifically to the inorganic capping agent. Additionally, the cationic ion can bind to the surface of a second colloidal particle thereby bridging between the two colloidal particles. Preferably, the cationic ion is a transition metal ion, a main group ion, a lanthanide ion, or an actinide ion. More preferably, the cationic ion is selected from those ions that can impart advanced electronic, magnetic (e.g., Mn^{2+} , Co^{2+}), or photophysical properties on the bridged colloidal particles. Still more preferably the cationic ion is Pt^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} , Mn^{3+} , Eu^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ge^{4+} , Cu^{2+} , Cu^+ , Pb^{2+} , Bi^{3+} , Sb^{3+} , In^{3+} , Ga^{3+} , Au^+ , Au^{3+} , Ag^+ , Sn^{2+} , Sn^{4+} , or Hg^{2+} . A descriptive drawing of the bridging of a colloidal particle with a cationic ion is shown in FIG. 24. When the addition of the cationic ion to the colloidal particle is conducted on a scale wherein there is a multiplicity of colloidal particles, the binding and bridging of the colloidal particles is termed a polycondensation reaction. Herein, a controlled polycondensation reaction yields colloidal materials. Moreover, the selection of cationic ion and polycondensation reaction conditions allows for control of the three-dimensional structure of the colloidal material. Without being bound by theory, these polycondensation reactions are envisioned as behaving analogously to molecular self-assembled three-dimensional arrays.

Another aspect of the current disclosure is the isolation of the colloidal particles as colloidal materials. As used herein, colloidal materials are samples of the herein described colloidal particle in a solid form. The form can be ordered or

disordered. The nanoparticle may have a crystalline, that is, ordered internal structure but the precipitation of the colloidal particles may produce a random (disordered) arrangement of particles. Alternatively, the controlled dissolution or spontaneous self-assembly of the colloidal particles can yield ordered arrays of particles.

The careful deposition of thin layers of colloidal arrays can yield ordered arrays dependent on the packing of the colloidal particle in three dimensional space. As non-limiting examples, the deposition of colloidal particles of nanocrystals that are roughly spherical has yielded hexagonal close-packed arrays of colloidal particles or cubic close-packed arrays of colloidal particles. See FIGS. 3, 4, 25, and 26. Such selective deposition of colloidal particles has advanced materials applications for which the selection of the nanoparticle and the ordering of the three dimensional array can change, for example, the physical, magnetic, optical and/or electronic characteristics of the material.

Nanocrystals of different size and functionality (e.g. noble metals, semiconductors, oxides, magnetic alloys) can be induced to self-assemble into ordered binary superlattices retaining the size tunable properties of their constituents. A variety of binary superlattices can be built from monodisperse PbS, PbSe, CoPt₃, Fe₂O₃, Au, Ag, Pd and the like nanocrystals, mixing and matching these nanoscale building blocks to yield multifunctional nanocomposites. See, for example, FIG. 26. Superlattices with AB, AB₂, AB₃, AB₄, AB₅, AB₆ and AB₁₃ stoichiometry with cubic, hexagonal, tetragonal and orthorhombic symmetries can be formed. Assemblies with the same stoichiometry can be produced in several polymorphous forms by tailoring the particle size and deposition conditions. Binary superlattices can be isostructural with NaCl, CuAu, CsCl, AlB₂, MgZn₂, MgNi₂, Cu₃Au, Fe₃C, CaCu₅, CaB₆, NaZn₁₃ and cub-AB₁₃ and other compounds emphasizing the parallels between nanoparticle assembly and atomic scale crystal growth.

The deposition of layers of the colloidal particles to make colloidal material thin films is another aspect of the current disclosure. See FIG. 35. Depending on the desired application or the available resources, multiple film deposition methodologies are available. One method that is applicable to form colloidal material thin films is a reverse Langmuir-Blodgett technique. Herein the insolubility of the colloidal particle in nonpolar solvents permits the monolayer deposition of films of the colloidal particle on a substrate. Multiple application of the Langmuir-Blodgett technique can be employed to grow multilayer films of the colloidal particle or mixed layer films of colloidal particles.

A second applicable technique for the deposition of layers of the colloidal particles to make colloidal material thin films is spin coating. Here a solution of the colloidal particle is applied to a substrate and the substrate and solution are rapidly rotated to leave a thin layer of the solution on the substrate, this solution is then dried leaving the colloidal material thin film. Herein, the use of multiple solvents described above provide control in the manufacture of these films. The wetting of the substrate by the colloidal particle solution is an important factor in achieving uniform thin films and the ability to apply the colloidal particle in a variety of different solvents enhances the commercial applicability of this technique. One method to achieve uniform wetting of the substrate surface is to match the surface free energy of the substrate with the surface tension of the liquid (colloidal particle solution). Theoretically, the perfect wetting of a substrate by a colloidal particle solution would yield a uniform colloidal material thin film on the substrate.

Additional techniques for the deposition of layers of the colloidal particles to make colloidal material thin films include doctor blading, spin coating, spray coating, spray pyrolysis, dipping/dip-coating, sputtering, printing, inkjet printing, stamping and the like and combinations of spray coating, spray pyrolysis dipping, sputtering, printing and the like with spin coating.

In another embodiment, colloidal material can be produced through the bridging of the colloidal particles with complexing agents thereby forming complexed colloidal particles and/or complexed colloidal materials; a distinction that is dependent, in part, on the amount of complexing agent employed. By way of an illustrative example, in one embodiment, complexed colloidal particles can be formed by the addition of a complexing agent to a colloidal particle. Examples of complexed colloidal particles include but are not limited to combinations of a cationic ion-complexing agent and an anionic colloidal particle. The herein described colloidal particle can complex with, for example, transition metal cations, transition metal cation complexes, main group cations, and the like. Examples of complexing agents include chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, palladium, silver, cadmium, osmium, iridium, platinum, gold, and mercury cations, e.g., Pt²⁺, Zn²⁺, Cd²⁺, Mn²⁺, Mn³⁺, Eu²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ge⁴⁺, Cu²⁺, Cu⁺, Pb²⁺, Bi³⁺, Sb³⁺, In³⁺, Ga³⁺, Au⁺, Au³⁺, Ag⁺, Sn²⁺, Sn⁴⁺, and Hg²⁺. With sufficient complexing agent the resultant material, complexed colloidal material, can be insoluble and described as a polymeric material. See FIG. 24.

In another embodiment, the complexed colloidal material is formed by the alternating addition of a substrate to a solution of colloidal particles and to a solution of complexing agent. In this embodiment, the substrate, preferably, has a sufficient affinity for the first material, whether colloidal particles or complexing agents, such that a layer of the first material uniformly deposits on the surface of the substrate. Examples of substrates wherein the colloidal particle could be the first material include but are not limited to mono or multilayers of copper, silver, gold, nickel, palladium, platinum, alloys, and amalgams thereof. Generally for complexed colloidal materials, when a colloidal particle has sulfur, selenium, and or tellurium atoms on the exposed surface (the outermost surface of the colloidal particle) thiophilic substrates can be employed. Herein, thiophilic means having a thermodynamic preference for binding to sulfur, selenium, and/or tellurium. Examples of thiophilic substrates include monolayers, multilayers, or bulk amounts of silver, gold, and other known thiophilic substrates.

Another substrate applicable when the first material is a neutral or anionic colloidal particle is a positively charged substrate. Substrates made from glass, sapphire, quartz, silicon, or other solid materials can be manipulated to have a positive charge through many known methods. For example, the chemical treatment of a substrate with an amine functionalized siloxane can produce a positively charged surface on the substrate.

Still another embodiment of complexed colloidal materials includes the combination of cationic polymers with the colloidal particle. For example, an alternating dip coating process can be employed to build layers of a cationic polymer and a colloidal particle. See FIG. 35. As with the embodiments described above, the first material added to a substrate can be either a cationic polymer or a colloidal particle. Known methods to form films of polymers on substrates are applicable herein and often a substrate is first coated with the polymer. Examples of polymers include the polyquaternium polymers, e.g., poly(diallyldimethylammonium) chloride (polyquater-

nium-6 (CAS#: 26062-79-3); PDDA) and polyethyleneimine (PEI). The alternating dip coating can include repetitively, dipping a substrate in a first solution, rinsing the substrate, dipping the substrate in a second solution, and rinsing the substrate. Non-limiting examples of Layer-by-Layer assemblies made by this method include 10, 20, and 30 layer films of CdSe/ZnS.SnS₄ and PDDA, and 10, 20, and 30 layer films of Au.SnS₄ and PDDA. A substrate prior to any dipping can preferentially bind the colloidal particle thereby the first solution is a solution having the colloidal particle dispersed therein. Additional combination procedures are available, for example first spin coating a substrate with a solution of a colloidal particle then dipping the substrate in a solution of a cationic ion and then repeating.

Complexed colloidal materials can further yield ordered arrays. See FIGS. 25-26. For example the complexing agent can be a non-polymeric material. One applicable type is cationic amines (NR¹R²R³R⁴⁺) and phosphines (PR¹R²R³R⁴⁺) with aliphatic substituents, for example, where at least one R group has a C₆, C₇, C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈, C₃₀, or C₄₀ alkyl chain. One operative example is the dimethylbisdodecylammonium cation (N(CH₃)₂(C₁₂H₂₅)₂⁺). The addition of the cationic amine or phosphine can be by a biphasic transfer of the colloidal particle form a polar solvent into a non-polar solvent. One operative example includes the dissolution of a dodecylammonium Sn₂S₆ salt in a non-polar solvent and the dissolution of CdSe.Sn₂S₆ in a polar solvent. The cation exchange can transfer the colloidal particle into the non-polar solvent.

Another technique wherein the ability to select the solvent in which the colloidal material is dissolved and from which it is deposited is ink-jet deposition. Ink-jet deposition often requires the ability to adjust liquid surface tensions to applicable ranges. One easy method for adjusting the surface tension of a liquid containing colloidal particles is the blending or mixing of a multiplicity of solvents.

Yet another application of the present disclosure is the deposition of colloidal particles to make non-thin film solids. Herein, the described colloidal particles are deposited by bulk techniques to yield three dimensional solids. Known bulk deposition techniques include pressing of powders, growth of three-dimensional ordered arrays, painting, printing, and the like, e.g., the hot pressing of colloidal materials to yield colloidal matrices and/or alloys.

Examples of colloidal materials that have been formed through the present techniques include Au.Sn₂S₆, Au.Sn₂Se₆, Au.In₂Se₄, Au.AsS₃, Pd.AsS₃, CdSe.Sn₂S₆, CdSe.SnS₄, CdSe.SnTe₄, CdSe.Sn₂Te₆, CdSe.In₂Se₄, CdSe.Ge₂S₆, CdSe.Ge₂Se₃, CdSe.HgSe₂, CdSe.ZnTe, CdSe.Sb₂S₃, CdSe.SbSe₄, CdSe.Sb₂Te₇, CdSe.In₂Te₃, CdSe/CdS.Sn₂S₆, CdSe/CdS.Ge₂S₆, CdSe/CdS.In₂Se₄, CdSe/CdS.Sn₂S₆, CdSe/ZnS.Sn₂S₆, Bi₂Se₃.Sb₂Te₄, PbS.AsS₃, PbS.SnS₄, PbS.Sn₂S₆, PbS.Sn₂Se₆, PbS.In₂Se₄, PbS.Sn₂Te₆, PbS.AsS₃, PbTe.SnTe₄, FePt.Sn₂S₆, and the like. As used herein the notation for the colloidal materials is the same as the notation described herein are solid state samples including the herein described colloidal particles.

Still another aspect of the techniques described above for the production or deposition of colloidal materials is the production or deposition of mixed, colloidal particle, solids. These hetero-colloidal materials comprise a plurality of colloidal particles in the resulting solid material. Similar to the disclosure above, multiple techniques can be used to produce hetero-colloidal materials. Non-limiting examples include, mixing of colloidal particles in a solvent followed by deposition of a hetero-colloidal material, alternating deposition of

colloidal material films to produce a layered hetero-colloidal material, multispray coating of a substrate, and blending of colloidal material solids followed by pressing into a cohesive material.

One example of the hetero-colloidal materials described herein is a binary superlattice. Binary superlattices are those organized structures wherein the three-dimensional packing of two different nanoparticles produces an ordered structure. Multiple physical and chemical characteristics can facilitate the production of binary superlattices, for example, nanoparticle size, nanoparticle shape, and nanoparticle Coulombic potential. This assembly of two different colloidal particles into a binary superlattice is a general and inexpensive method to produce multiple hetero-colloidal materials with precise control of the chemical composition and physical properties. See FIG. 26.

Yet another aspect of the current disclosure is the thermal treatment of the herein described colloidal materials. As discussed above, many of the inorganic capping agents are precursors to inorganic materials (matrices) and low-temperature thermal treatment of these inorganic capping agents provides a gentle method to produce crystalline films from these materials. The thermal treatment of colloidal materials yields, for example, ordered arrays of nanoparticles within an inorganic matrix, hetero-alloys, or alloys. In at least one embodiment herein, the thermal treatment of the colloidal material includes heating to a temperature less than about 350, 300, 250, 200, and/or 180° C.

Still another aspect of the current disclosure is a low mass/volume loss on thermal treatment. The herein described colloidal materials lose less than about 20%, 15%, 10%, and/or 5% of their mass, as determined by thermogravimetric analysis (TGA), upon a thermal treatment up to about 400 and/or 450° C. For example, CdSe/ZnS.Sn₂S₆ loses about 5% of its mass upon heating to about 450° C., whereas the (NH₄)₄Sn₂S₆ used as the inorganic capping agent for the colloidal particle loses about 30% of its mass over the same temperature range. See FIG. 37.

As used herein, colloidal matrices are arrays of nanoparticles within an inorganic matrix. Generally, the inorganic matrix separates the nanoparticles. The inorganic matrix can be a glass, a solid, or a crystalline material. Additionally, in ordered arrays, the order of the array of nanoparticles can be short range or long range. Very dilute samples of nanoparticles in the inorganic matrix are expected to have lower relative ordering than concentrated samples wherein the nanoparticles may be ordered prior to and preferably after the formation of the inorganic matrix.

Colloidal matrices can be homo-colloidal matrices or hetero-colloidal matrices and can be produced as thin films, films, coatings, and/or solids. A homo-colloidal matrix is a colloidal matrix having one species of nanoparticle and an inorganic matrix derived from a single inorganic capping agent. Non-limiting examples of homo-colloidal matrices include SnS₂(Au), SnS₂(CdSe), SnS₂(CdSe/CdS), and SnS₂(PbS). See FIGS. 13-15. As used herein the denotation SnS₂(Au) refers to Au nanocrystals in a matrix having the approximate formula SnS₂. A hetero-colloidal matrix is a colloidal matrix having, for example, a multiplicity of nanoparticle species in an inorganic matrix derived from a single inorganic capping agent, or one species of nanoparticle in an inorganic matrix derived from a multiplicity of inorganic capping agents. One example of the latter hetero-colloidal matrix is the matrix produced by thermally treating a mixture of CdSe.Sn₂S₆ and CdSe/CdS.Sn₂S₆, denoted SnS₂(CdSe; CdSe/CdS).

Additional embodiments of hetero-colloidal matrices include those formed by selective deposition of colloidal materials in confined spatial arrangements followed by thermal treatment to form the inorganic matrix. The layered, structured, or patterned deposition of a plurality of colloidal materials followed by thermal treatment to form an inorganic matrix can create solid-state architectures that are not available by other known methodologies. One illustrative example of the present embodiment is the patterned deposition of CdSe.Sn₂S₆ nanoparticles followed by the patterned deposition of Au.Sn₂S₆. The thermal treatment of this illustrative example can produce three distinct material regions within a single inorganic matrix derived from Sn₂S₆⁴⁻, that is, this patterned colloidal matrix will include regions of matrix encapsulated CdSe nanoparticles, regions containing a matrix encapsulated mixture of CdSe and Au nanoparticles, and regions of matrix encapsulated Au nanoparticles.

The colloidal matrices can be produced in thin films, films, coatings, solids and/or mixed solids. Moreover, the colloidal matrices can be produced in bulk, layered, structured, or patterned arrangements on a substrate. Additionally, the procedure described herein can yield colloidal matrices that effectively preserve the electronic characteristics of the nanoparticle after thermal treatment. FIG. 15 shows the optical absorbance spectrum of thin films of an organic capped CdSe (CdSe*(organic capping agent(s))), an inorganic capped CdSe (CdSe.Sn₂S₆), and a CdSe colloidal matrix (Sn₂(CdSe)). The absorption at approximately 600 nm is apparent in all samples and is characteristic of the presence of the CdSe nanocrystal.

Another embodiment of the materials and methods disclosed herein is an alloy made from a nanoparticle and an inorganic capping agent. Alloys are continuous homogeneous phases of a composition and herein alloys are produced by the thermal treatment of the disclosed colloidal particles. Similar to the colloidal matrices, the formulation of the alloy is dependent on the nanoparticle and inorganic capping agent. Unlike the colloidal matrices, the formation of the alloy involves the destructive reaction of the inorganic capping agent, and/or optionally additional reagent(s), with the nanoparticle, herein a destructive reaction means the nanoparticle loses at least one aspect of its defining physical characteristic, examples include size, shape, photoactivity, formulation, and the like. Non-limiting examples include the formation of a Cd_xSn_ySe_z alloy from CdSe.Sn₂S₆ colloidal particles; the formation of a CuInSe₂ alloy from any one of the following colloidal particles: Cu₂Se.In₂Se₃, Cu₂Se.In₂Se₄, Cu₂S.In₂Se₃, and/or Cu₂S.In₂Se₄; the formation of a CuZnSnS₄ alloy from a mixture of Cu₂S.Sn₂S₆ and ZnS.Sn₂S₆; and the formation of Cu₂In_{1-x}Ga_xSe₂ (e.g., Cu₂In_{0.15}Ga_{0.15}Se₂ and Cu₂In_{0.9}Ga_{0.11}Se₂) alloy from Cu₂Se.(In₂Se₄;Ga₂Se₃). See FIG. 40A&B.

Generally, the formation of an alloy requires some atom mobility during the thermal treatment phase and processing conditions can and often do affect the formation of an alloy. The incomplete alloying of the disclosed materials, whether purposefully or serendipitously, yields a hetero-alloy. As used herein, hetero-alloys are solid state materials formed from the thermal treatment of a colloidal material that is characterized by a multiplicity of domains, wherein the domains may have different formulations and/or crystal structures and/or crystallinity. Whether a thermal treatment of a colloidal material forms an alloy or a hetero-alloy is often difficult to determine, but, without being bound by theory, it is believed that a lower temperature thermal treatment limits atom mobility and therefore prohibits the formation of a homogeneous phase (alloy).

Representative, non-limiting, examples of the formation of what are believed to be hetero-alloys are the thermal treatment of Bi₂S₃.Sb₂Te₃ nanorods to form a Bi_{1.3}Sb_{0.7}Te₃ hetero-alloy, see FIGS. 16-21 and 27-29.

The structure of the resulting alloy or hetero-alloy is dependent on the formulation of the colloidal particle. For example, a Bi_{2-x}Sb_xTe₃ alloy or hetero-alloy made from a colloidal material that has a high Bi:Sb ratio has a significantly smaller crystal domain than a Bi_{2-x}Sb_xTe₃ alloy or hetero-alloy made from a colloidal material that has a low Bi:Sb ratio. See FIG. 19. Not only do the two materials have different crystal domain sizes, EDS spectra indicate that the relative concentration of Bi in the latter sample is indeed lower than in the former. See FIG. 19. This comparative example indicates that multiple hetero-alloys can be produced from identical starting materials and that the relative composition of the alloy can be controlled by selective synthesis of the precursor colloidal material. See FIG. 18.

Often the differences between the materials herein described as colloidal matrices and as hetero-alloys are difficult to determine experimentally. Furthermore, the process for forming these materials may affect the nature of the resultant materials. While time and temperature are well known to affect the formation of alloys herein phase solubility can further affect the formation of a homogeneous phase. For example, PbTe is largely insoluble in Sb₂Te₃. See FIGS. 31-33. The resultant material from the thermal processing of PbTe.Sb₂Te₃ can be described as either a hetero-alloy or a colloidal matrix depending on the structure of the PbTe in the final material, still further the resultant material can be comprised of both a hetero-alloy and a colloidal matrix.

One reaction condition that may affect the characteristics of the resultant materials is the relative concentration of the nanoparticle. The dilution in the solid phase of the nanoparticle in an excess of the inorganic capping agent can lead to smaller nanoparticles in the resultant material. As the relative concentration of the nanoparticle increases, the inter-particle interactions can increase and the size and nature of the nanoparticle can change. See FIG. 34. At an extreme, the concentration of the nanoparticle can be sufficiently high that the resultant materials can be a phase corresponding to the composition (or reaction product) of the nanoparticle and optionally include phase corresponding to the composition of the inorganic capping agent. Without being bound to theory, it is believed that Ostwald ripening can affect the phases in the materials.

The reactive loss of a chalcogenide can further facilitate the formation of colloidal matrices, alloys, and/or hetero-alloys. When, for example, thermodynamics favor the formation of selenides or tellurides over sulfides the reactive loss of sulfur can facilitate the formation of selenium and/or tellurium based materials. This reactive loss of chalcogenide can be facilitated by the addition of an excess of a selenium or tellurium containing inorganic capping agent and/or through the addition of an excess of selenium or tellurium. Non-limiting examples include the thermal processing of Cu₂S.In₂Se₃ and/or Cu₂S.In₂Se₄ where selenium reacts to displace sulfur, see FIG. 39; and Bi₂S₃.Sb₂Te₃, Bi₂S₃.(Sb₂Te₃;Te), Bi₂S₃.Sb_xTe_y, and/or PbS.Sb_xTe_y, wherein X is a value of either 1 or 2 and Y is a value from 3 to 10, where tellurium reacts to displace sulfur and yield telluride materials. This technique is remarkably facile and especially useful when the selenium or tellurium nanocrystals are inaccessible due to thermal, stability, or other limitations.

Similar to the disclosure above where multiple inorganic capping agents can be employed, selenides or tellurides can be doped into the formation of colloidal matrices, alloys or

heteroalloys by reactive loss of a chalcogenide. In one embodiment, selenium can be doped into a reaction that provides a telluride colloidal matrix, alloy or heteroalloy by reactive loss of sulfur by the addition of an amount of selenide-containing inorganic capping agent to the colloidal material. In a similar embodiment, tellurium can be doped into a selenide colloidal matrix, alloy or heteroalloy by reactive loss of sulfur by the addition of an amount of telluride-containing inorganic capping agent to the colloidal material. By way of a non-limiting example, selenium can be doped into a tellurium containing alloy by the addition of an amount of the selenium-containing inorganic capping agent Sb_2Se_3 to the colloidal particle $Bi_{2-x}S_3$, Sb_2Te_3 , or Bi_2S_3 , $(Sb_2Te_3; Sb_2Se_3)$, the admixture can then be thermally processed to form an n-doped $Bi_{2-x}Sb_xTe_{3-y}Se_y$. See FIGS. 28-29.

The balancing of thermal stability against reactivity can yield materials where some nanocrystals react and others alloy. For example, mixing the processes of alloying and hetero-alloying ion capped Bi_2S_3 , Sb_2Te_3 and $PbTe$, Sb_2Te_3 yields a $(PbTe)(Bi_2S_3, Sb_2Te_3)$ hetero-alloy. See FIG. 30. Similarly, the thermal processing of a colloidal material that comprises a mixture of Au , Sb_2Te_3 and Bi_2S_3 , Sb_2Te_3 yields a $(Au)(Bi_{2-x}Sb_xTe_3)$ heteroalloy where discrete Au nanocrystals can be observed in the TEM images. See FIG. 34.

Typically, the colloidal materials, colloidal matrices, and alloys are fabricated by a deposition on a substrate. Suitable examples of substrates include but are not limited to silicon, amorphous hydrogenated silicon, silicon carbide, silicon dioxide, silicon nitride, aluminum oxide, aluminum nitride, carbon, hydrogenated carbon, gallium nitride, gallium arsenide, germanium, silicon-germanium, indium tin oxide, boron carbide, boron nitride, borosilicate, cerium oxide, tin oxide, zinc titanate, a glass, a metal, an organic semiconductor, a polymeric material or a combination thereof. Examples of organic semiconductors and/or polymeric materials include polycarbonates, poly(3-hexylthiophene), poly(p-phenylene vinylene), poly(9,9'-dioctylfluorene-co-benzothiadiazole) ("F8BT"), poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine), poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)diphenylamine) ("TFB"), poly(4,4'-oxydiphenylene-pyromellitimide) ("Kapton"), polyethylene terephthalate (e.g., "Mylar"), poly(paraphenylene terephthalamide) (e.g., "Kevlar"), polyacetylenes, and the like. Furthermore, substrates can be planar or nonplanar.

Yet another embodiment of the materials and methods disclosed herein is the deposition of colloidal matrices, alloys, or hetero-alloys on a surface to form an advanced material, a printed circuit, a photovoltaic cell, a piezoelectric crystal, a thermoelectric layer, an optoelectronic layer, a light emitting diode, a ferroelectric layer, a thin film transistor, a floating gate memory device, a phase change layer, a sensor device, detectors of light, X-ray and gamma-radiation, an imaging device, and the like. See FIG. 22. The colloidal materials disclosed herein are applicable for the printing or deposition of colloidal matrices, alloys, or hetero-alloys through the application and, optionally, heating of the colloidal material on a substrate. Representative examples of the application of the disclosed colloidal materials include sputter deposition, electrostatic deposition, spray deposition, spin coating, inkjet deposition, laser printing (matrices), and the like. An alternative method of deposition is the electrochemical deposition of a colloidal matrix from a solution of a colloidal material.

The low temperature formation of the colloidal matrix, alloy, or hetero-alloy makes the disclosed methodology compatible with photolithographic patterning, for example,

wherein a photolithographic applied substrate mask is removed after the thermal treatment of the colloidal material.

Another aspect of the disclosed materials and methods is the formation of materials that exhibit enhanced thermoelectric properties; that is the direct conversion of a thermal gradient to electrical energy. Thermoelectric energy conversion is an all-solid-state effect that converts thermal gradients directly to electrical energy without an electromechanical generator. The derived voltage and power, work, drains the heat from the location of the thermal gradient. Materials that display thermoelectric energy conversion are useful in heat pumps, power generators, and thermoelectric coolers. Thermoelectric devices have no moving parts and therefore have advantages in reliability, silent operation, high power density, and high efficiency for moderate power applications. In addition, thermoelectric materials can be used for cooling by driving current through the material.

The efficiency of thermoelectric generators is limited to a fraction of the generators' Carnot efficiency determined by the thermoelectric figure of merit, zT :

$$zT = T(S^2\sigma)/\kappa$$

where S is the thermoelectric power, the Seebeck coefficient of the material, σ is the electrical conductivity of the material, κ is the thermal conductivity of the material, and T is the absolute temperature. The higher zT , the more efficient the material is at converting heat to electricity. All current commercial thermoelectric materials have figures of merit of approximately 1.

The materials and methods described herein are applicable for the manufacture of high zT thermoelectric materials and devices. $Bi_{2-x}Sb_xTe_3$ is a thermoelectric material easily manufactured by the disclosed methods. Moreover, as theoretical studies suggest that an increase in the phonon scattering at the domain boundaries increases the thermoelectric figure of merit and the domain boundaries in the disclosed $Bi_{2-x}Sb_xTe_3$ material are dependent on the annealing process and the size of the nanoparticle, the thermoelectric figure of merit in the disclosed materials is tunable. Preferably, the thermoelectric figure of merit, zT , for the $Bi_{2-x}Sb_xTe_3$ material is greater than 0.7, 1, 1.5, 2, and/or 3.

EXAMPLES

The following examples are provided to illustrate the invention, but are not intended to limit the scope thereof.

Example 1

Aqueous NH_4OH solution (8 mL, 28-30% of NH_3) was mixed with aqueous $(NH_4)_4Sn_2S_6$ (0.5 mL, ~0.1 M) or Na_4SnS_4 (0.3 mL, ~0.1 M). Hexane (6 mL) and toluene solution of 3-10 nm CdSe or 6.5-nm CdSe/ZnS NCs (1 mL, ~25 mg/mL) were added to the same vial and the mixture was vigorously stirred until the phase transfer of NCs from the organic phase into aqueous phase was completed. The aqueous phase was rinsed 3 times with hexane and filtered through a 0.45- μm PTFE filter. In order to separate the excess amount of inorganic capping agents, a minimal amount of acetonitrile was added to precipitate the colloidal particles. The colloidal particles were collected by centrifuging, redispersed in water and centrifuged/filtered to remove traces of insoluble materials, if any.

Example 2

5 mL formamide were mixed with 0.4 mL $Na_4Sn_2S_6$ in FA (0.05 M), hexane (5 mL) and 8-nm CdSe NCs in toluene (0.4

mL, 40 mg/mL) and stirred until the phase-transfer of CdSe NCs was completed. formamide phase was washed with hexane 3 times, filtered and mixed with acetonitrile (1:1 v/v) to precipitate colloidal particles. After centrifuging, colloidal particles were redissolved in 5 mL formamide. Similar procedure was also applied for 3-10 nm PbS, 5-nm Au and 4-nm FePt NCs. The reaction can be facilitated by heating solutions to 70° C.

Example 3

In a glovebox, 5 mL formamide (vacuum dried at 100° C.) was mixed with 0.5-1 mL K_4SnTe_4 in formamide (0.1 M), 6 mL anhydrous hexane, and the toluene solution of either CdSe, CdTe or PbTe NCs (1 mL, ~25 mg/mL) and stirred until the completion of transfer of NCs into the formamide phase. After the organic phase was discarded, the colloidal particle solution was rinsed 3 times with hexane, filtered, mixed with acetonitrile (1:5 v/v) to precipitate the colloidal particles and to remove excessive K_4SnTe_4 . NCs were isolated by centrifuging and redispersed in formamide, DMSO, DMF or methanol.

Example 4

A solution of $(N_2H_5)_4Sn_2S_6$ in ethanolamine was diluted with DMSO. This DMSO solution was added to a hexane solution of CdSe nanocrystals. The mixture was vigorously stirred, while NH_3 was purged through the solution. The completion of the reaction, as determined by the transfer of color from the hexane to the DMSO, was complete within about 20 minutes. Then the hexane phase was removed, the DMSO solution was washed with hexane, and the product (CdSe. Sn_2S_6) isolated from the DMSO or used in situ.

Representative examples of Colloidal Particles that have been made by the methodology of Example 1 and illustrated in the following table:

Nanoparticle	Inorganic Capping Agent	Comments
Au nanocrystals	$Sn_2S_6^{4-}$, $Sn_2Se_6^{4-}$, AsS_3^{3-} , $In_2Se_4^{2-}$	Form fcc superlattices, highly conductive.
CdSe quantum dots	$Sn_2S_6^{4-}$, $Sn_2Te_6^{4-}$, AsS_3^{3-} , $In_2Se_4^{2-}$, $Ge_2S_6^{4-}$	Form short-range ordered assemblies, conductive, n-type transport, materials with distributed donor-acceptor junctions
CdSe/CdS core-shell nanocrystals	AsS_3^{3-} , $Sn_2S_6^{4-}$, $Ge_2S_6^{4-}$	Strong excitonic photoluminescence in solution and films
CdSe/CdS nanorods	AsS_3^{3-} , $Sn_2S_6^{4-}$, $In_2Se_4^{2-}$	Strong photoluminescence, Liquid crystalline nematic ordering
CdSe/CdS nanotetrapods	$Sn_2S_6^{4-}$, $In_2Se_4^{2-}$	Strong photoluminescence
CdSe nanowires	AsS_3^{3-} , $Sn_2S_6^{4-}$, $In_2Se_4^{2-}$	N-conductive nematic phases
Bi_2S_3 nanorods	$Sb_2Te_4^{2-}$	Highly conductive Bi_2Te_3/Sb_2Te_3 nanocomposites
PbS quantum dots	AsS_3^{3-} , $Sn_2S_6^{4-}$, $Sn_2Se_6^{4-}$, $In_2Se_4^{2-}$, $Sn_2Te_6^{4-}$, $Sn_2Te_7^{4-}$	Conductive, p- and n-type transport
PbTe quantum dots	AsS_3 , $Sb_2Te_7^{4-}$, $Sn_2S_6^{4-}$, $Sn_2Se_6^{4-}$, $In_2Se_4^{2-}$	Conductive, p- and n-type transport
Pd nanocrystals	$Sn_2S_6^{4-}$, AsS_3	
ZnS nanocrystals	$Sn_2S_6^{4-}$	
Cu_2S nanocrystals	$Sn_2S_6^{4-}$, $In_2Se_4^{2-}$	

-continued

Nanoparticle	Inorganic Capping Agent	Comments
Cu_2Se nanocrystals	$Sn_2S_6^{4-}$, $In_2Se_4^{2-}$	

Example 5

Under an inert atmosphere, a solution of $(N_2H_5)_4Sb_2Te$, in hydrazine was combined with a hexane solution of Bi_2S_3 nanorods. The mixture was stirred for approximately 3 hours and then the hexane layer was decanted from the mixture. The product solution, generally black in color, was washed four times with hexane, filtered, and then stored under an inert atmosphere.

Example 6

Employing the procedure in Example 5 a series of $Bi_2S_3.Sb_2Te$, samples can be prepared where the Bi to Sb ratio is changed. First a stock solution of $Sb_2Te_7^{4-}$ in hydrazine was prepared. The amount of the stock solution used depended on the desired ratio but for all samples the stock solution was combined with excess hydrazine to produce an approximately constant volume of the inorganic capping agent solution. Varying amounts of Bi_2S_3 nanorods were dissolved in a constant volume of hexane and then added to the inorganic capping agent solution according to Example 5. The following ratios of Bi to Sb were prepared: 5% Bi/95% Sb; 20% Bi/80% Sb; 40% Bi/60% Sb; 60% Bi/40% Sb; 95% Bi/5% Sb.

After washing and filtration, the samples were dried by evaporation of hydrazine under a stream of N_2 . The silver-black solids were annealed at 350° C. under N_2 and the metallic powder analyzed. See FIGS. 16-20 and 27-29.

Example 7

A highly-doped silicon wafer with a 100 nm thick thermal silicon oxide gate dielectric was patterned with bottom Ti/Au electrodes on the silicon oxide by photolithography. This wafer was washed with acetone, isopropanol, and ethanol, then plasma cleaned in air for 30 min. Under inert atmosphere, the wafer was covered with several drops of the solution prepared in Example 5. The sample was allowed to stand for 20 min and then was spun according to the following series of steps: 1) spun at 450 rpm for 20 s; 2) spun at 900 rpm for 20 s; 3) spun up to 4000 rpm within 20 s; and then 4) spun at 4000 rpm for 20 s. The wafer, coated with a mirror-like film, was heated to 350° C. for 90 min to anneal the composite.

Substrates were freshly hydrophilized by 15-min treatment with oxygen plasma. The colloidal particle was then deposited by drop-casting at 80° C. or by spray-coating. The homogeneity and thickness of the drop-cast films were adjusted by controlling the volume and the concentration of colloidal particle in a solution. 1-10% v/v DMSO were usually added to N_2H_4 solutions to improve homogeneity of drop-cast films. For spray coating, glass substrates were placed on a hot plate at 100-200° C., while a $(Bi,Sb)_2Te_3$ NC-ink solution was applied at a sprayer pressure of 15-20 psi using N_2 as a carrier gas. The film thickness was adjusted by the number of applied spraying cycles, typically 5 to 80. As-deposited $(Bi,Sb)_2Te_3$ films were heated at 300° C./hour and annealed at 300° C. for 15 min, followed by slow cooling to room temperature.

Colloidal particles and more particularly colloidal matrices formed using techniques as described herein may be formed into various semiconductor materials and structures.

When two or more metallic or semiconducting nanoparticles are in close proximity to each other, their wave-functions can couple together forming states delocalized over several nanocrystals or propagating throughout the entire nanocrystalline solid. The quantum mechanical coupling energy can be approximated as

$$\beta \sim h\Gamma \sim \exp\{-2(m^* \Delta E / \hbar^2)^{1/2} \Delta x\},$$

where h is Planck's constant, Γ is the tunneling rate between two nanocrystal neighbors, m^* is the carrier effective mass, ΔE and Δx are the height of the tunneling barrier and the shortest edge-to-edge distance between the nanocrystals, respectively. As a result, it was explored whether the present techniques could replace the bulky insulating hydrocarbon chains between nanocrystals with much smaller and more conductive inorganic capped nanoparticles to significantly facilitate electron sharing between colloidal particles. Specifically, the coupling between colloidal particles formed herein was analyzed by optical absorption and charge transport measurements. Thus, for 4.6 nm CdSe nanoparticles capped with conventional hydrocarbon ligands the absorption spectra of colloidal solutions and close-packed films are very similar to each other, indicative of strong localization of electron and hole wave functions on individual nanoparticles as shown in FIG. 13. In contrast, the excitonic features in close-packed films of CdSe nanoparticles capped with $\text{Sn}_2\text{S}_6^{4-}$ showed a pronounced 46 meV red shift compared to individual nanoparticles in solution, as shown in FIG. 15. Such a shift implies partial leakage of the wave functions into neighboring nanoparticles that relaxes the quantum confinement. Conversion of the $\text{Sn}_2\text{S}_6^{4-}$ ligands to SnS_2 at 180° C. lowers the barrier heights, ΔE , leading to an additional 34 meV red shift of the optical transitions in the nanoparticle solid, while maintaining excitonic features and quantum confinement, as shown in FIG. 13. Similarly, Au nanoparticles capped with $\text{Sn}_2\text{S}_6^{4-}$ showed a pronounced plasmonic absorption peak around 535 nm in solution which completely disappeared in nanocrystal films (FIG. 23A), indicating strong delocalization of the electronic states. Note that all observed spectral changes were reversible—the plasmonic peak appeared again after redissolution of the nanoparticles film. The reference samples of dodecanethiol capped Au nanoparticles showed strong plasmonic absorption in solutions and in close-packed films (FIG. 23B).

To examine charge transport, highly doped Si wafers with a 110 nm thick layer of thermal oxide and lithographically patterned Ti/Au electrode structures were used. The Si substrate was used as the back gate electrode for field-effect transistor (FET) measurements. Close packed nanoparticle films were deposited on these substrates by spin-coating or dropcasting. The film thickness was measured using AFM profiles and cross-sectional SEM studies. The amount of the inorganic capping agent was kept below 10 wt %, sufficient to provide colloidal stabilization but insufficient to form any continuous conductive channels of phase-separated metal chalcogenide, as evidenced by XRD studies.

The original organic ligands rendered nanoparticle films highly insulating with conductivities (a) on the order of $\sim 10^{-9}$ S cm^{-1} for 5 nm Au nanocrystals (NCs) (FIG. 14) and less than 10^{-12} S cm^{-1} for 5.5 nm CdSe nanoparticles. Replacing dodecanethiol ligands with $\text{Sn}_2\text{S}_6^{4-}$ increased the conductivity of Au NC solids by ~ 11 orders of magnitude approaching $\sigma \sim 200$ S cm^{-1} (FIG. 14). After electrical measurements the film could be easily dissolved in hydrazine or H_2O . Compari-

son of TEM images before and after electrical measurements revealed no changes in nanoparticle size and shape, ruling out sintering as a possible reason for the observed very high conductivity. The TEM analysis revealed a strong decrease in the mean interparticle distance from ~ 1.6 nm for dodecanethiol-capped Au nanoparticles to less than 0.5 nm for $\text{Sn}_2\text{S}_6^{4-}$ -capped Au particles (FIGS. 4A, 4B, and 4C).

In particular, inorganic capping agent-capping of colloidal particles is a promising approach to designing solution-processed inorganic semiconductors. FIGS. 13 and 36 show characteristics of a field-effect transistor with a channel assembled of 4.5 nm CdSe nanoparticles capped with $\text{Sn}_2\text{S}_6^{4-}$ and annealed for a short time at 200° C. An n-type gate effect with current modulation $I_{on}/I_{off} \sim 10^5$ was observed along with an electron mobility $\mu \sim 3 \times 10^{-2}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the saturation regime. Compared to other CdSe nanoparticles, inorganic capping agent-capped CdSe NCs enabled appreciable performance of solid state FETs while retaining optical and electronic tunability provided by the quantum confinement. Furthermore, illumination of the inorganic capping agent-capped CdSe nanoparticles increased their conductivity by several orders of magnitude, as shown for $\text{Sn}_2\text{S}_6^{4-}$ -capped CdSe NCs (FIG. 13).

Close-packed films (colloidal materials) of colloidal particles can be deposited on highly doped Si wafers with 110 nm thick layer of thermal oxide and back-gate geometry by spin-coating and then aluminum electrodes are deposited on the film using a shadow mask. The total amount of inorganic capping agent in the colloidal materials was less than about 10 wt % of the colloidal materials; at this weight percentage the inorganic capping agent can provide colloidal stabilization but does not form a continuous conductive matrix of phase-separated metal chalcogenide (FIG. 38b). The deposited close-packed films can be annealed at 200° C. for about 0.5–1 hr. After annealing, the conductivity of films made from CdSe. In_2Se_3 dramatically increased. The current between source and drain electrodes (I_D) could be modulated by applying voltage to the gate terminal (V_G). I_D increased with increasing V_G , typical for n-type conductivity through FET channel (FIGS. 38c,d). The field effect mobility (μ_{fe}) estimated from the slope of I_D vs V_G plot (FIG. 38d) was significantly improved as 11.32–15.3 cm^2/Vs and the I_{ON}/I_{OFF} ratio was 1×10^3 . Without being bound to theory, it is believed that the wave functions of the colloidal materials with physically-smaller inorganic capping agents can strongly couple and form short-range and/or long-range delocalized electronic structure. The quantum mechanical coupling energy can be approximated as $\beta \sim h\Gamma \sim \exp\{-2(2m^* \Delta E / \hbar^2)^{1/2} \Delta x\}$, where h is Planck's constant, Γ is the tunneling rate between two nanocrystal neighbors, m^* is the carrier effective mass, ΔE and Δx are the height of tunneling barrier and the shortest edge-to-edge distance between the nanoparticles, respectively. Replacement of bulky insulating hydrocarbon chains with much smaller and more conductive inorganic capping agents theoretically reduces both the tunneling barrier and edge-to-edge distances and promotes favorable electronic communication between nanoparticles. Furthermore, conversion of the $\text{In}_2\text{Se}_3^{2-}$ inorganic capping agent to In_2Se_3 at 200° C. lowers the barrier heights, ΔE , leading to an additional red shift of the optical transitions in the annealed material, while maintaining the excitonic features and quantum confinement (FIG. 38e).

In the previous examples, inorganic capping agents behaved as electronically transparent “glue” for nanoparticles. However, inorganic capping agents can also be used for creating composite materials where the properties of the inorganic capping agent and nanoparticle components comple-

ment each other. Thermal decomposition of the hydrazinium-based inorganic capping agents, for example, was shown to generate various chalcogenide phases with n- and p-type conductivity, and phase-change properties. For example, combining electron-conducting nanowires (e.g., CdS) with hole-conducting hosts (e.g., $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$) can form materials with distributed networks of p-n junctions. It is also possible to create new phases through solid-state reactions between nanoparticles and inorganic capping agents. As an example, a highly conductive $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ film was fabricated using Bi_2S_3 nanorods and a soluble $\text{Sb}_2\text{Te}_3\text{—N}_2\text{H}_4$ complex containing an excess of Te. Upon heating to 180°C ., the inorganic capping agent decomposed into Sb_2Te_3 releasing free tellurium which immediately reacted with the Bi_2S_3 phase ($\text{Bi}_2\text{S}_3+3\text{Te}\rightarrow\text{Bi}_2\text{Te}_3+3\text{S}$), leading to the formation of a nanocrystalline $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ composite phase (see, e.g., FIG. 22), presumably with Bi— and Sb-rich nanometer scale regions. The original Bi_2S_3 nanorods capped with oleic acid were highly insulating ($\sigma\sim 5\times 10^{-10}\text{ S cm}^{-1}$). However, spin-coated films of inorganic capping agent-capped Bi_2S_3 nanorods dried at 60°C . showed conductivity of 0.074 S cm^{-1} , which increased to 22 S cm^{-1} upon formation of a $\text{Bi}_{1.3}\text{Sb}_{0.7}\text{Te}_3$ nanocomposite at 180°C . (FIG. 28). A film of oleic-acid capped Bi_2S_3 nanorods annealed at 180°C . showed a much lower conductivity of $\sigma\sim 4\times 10^{-5}\text{ S cm}^{-1}$. Solid solutions and quantum well superlattices of Bi_2Te_3 and Sb_2Te_3 are known as superior materials for thermoelectrics. Therefore, such materials can be formed into various thermoelectric materials.

Fresh solution of $\text{Bi}_2\text{S}_3\text{.Sb}_2\text{Te}_7$ nanorods in hydrazine (NC-inks) were used for solution deposition of uniform TE films. Spin-casting can generate smooth and continuous thin films (10-50 nm thick, FIG. 28A); however, thicker films are required for practical TE applications. Therefore, further comparative studies were conducted on either drop-cast and spray-coated samples fabricated on glass substrates. Both techniques readily produce 0.1-0.4 km thick films, with low surface roughness of 10-50 nm (FIG. 28B). Sample compositions were adjusted to $\text{Bi}_{1.2}\text{Sb}_{0.8}\text{Te}_3$ with $\pm 10\%$ batch-to-batch variations. All samples were annealed at 300°C . I-V curves for each sample with gold electrodes showed high conductivity and excellent linearity over the entire range of applied voltages. The measured conductivities for drop-cast films spread in a broad range from 30 to 200 S cm^{-1} , depending upon the concentration of cracks and other structural defects. In contrast, spray-coated samples on average showed higher conductivities of 200-450 S cm^{-1} at room temperature (FIG. 28C). Thermopower measurements revealed p-type conductivity and Seebeck coefficients of $\sim 170\text{--}250\text{ }\mu\text{V/K}$ (FIG. 28D). Unlike electrical conductivity which is very sensitive to homogeneity of the sample, thermopower is an inherent material property and is reproducible within $\pm 10\%$ for the series of same-formulated samples. Our values of S are similar to the previously reported value ($\sim 210\text{ }\mu\text{V/K}$) for the bulk $(\text{Bi,Sb})_2\text{Te}_3$ generated by hot-pressing ball-milled nanopowders, and this is currently the best bismuth-telluride material with conductivity in excess of 1000 S cm^{-1} and $\text{ZT}=1.2$ at room temperature. Our solution-processed samples compare quite favourably with the vacuum-deposited thin film Bi—Te materials, which are naturally less conductive than bulk materials. Representative literature examples include flash-evaporated n-type Bi—Te-based thin films ($\sigma\sim 540\text{ S cm}^{-1}$), flash-evaporated $\text{Bi}_{0.16}\text{Sb}_{1.5}\text{Te}_3$ thin films ($\sigma\sim 550\text{ S cm}^{-1}$), co-evaporated Bi_2Te_3 thin films ($\sigma\sim 166\text{ S cm}^{-1}$, 770 S cm^{-1}), and sputtered Bi—Sb—Te thin films ($\sigma\sim 70\text{--}200\text{ S cm}^{-1}$).

Example 8

Using the procedure in Example 4, formamide solutions of $\text{Cu}_2\text{Se.Sn}_2\text{S}_6$ and $\text{ZnS.Sn}_2\text{S}_6$ were prepared. These solutions

were admixed at an approximate 2:1 atomic ratio for Cu to Zn and the amount of Sn_2S_6 was adjusted to an approximate 1:1 atomic ratio for Zn to Sn. The deposition solution was drop-cast onto a hydrophilized glass substrate. The cast colloidal material was then thermally processed at 600°C . for 2 h. The powder X-ray diffraction pattern of the as-made alloy matches the diffraction pattern for CZTS (JCPDS no. 26-0575), $\text{Cu}_2\text{ZnSnS}_4$. See FIG. 41. The composition of the as-made alloy is believed to contain selenium and have the approximate formula $\text{Cu}_2\text{ZnSn(S,Se)}_4$.

Example 9

Samples of platinum bridged $\text{CdSe.Sn}_2\text{Se}_6$ and platinum bridged $\text{CdSe.Sn}_2\text{S}_6$ were prepared by warming solutions of the respective colloidal particles in formamide to 80°C . To these solutions, solutions of K_2PtCl_4 in formamide were added. From these solutions the colloidal materials $\text{Pt}[\text{CdSe.Sn}_2\text{Se}_6]$ and $\text{Pt}[\text{CdSe.Sn}_2\text{S}_6]$ precipitated. The colloidal materials were then isolated and washed with a solvent, e.g., formamide and/or water, capable of removing any free ionic species.

Example 10

A hydrazine solution of $\text{In}_2\text{Se}_3\text{—Se}$ (49 μL ; 0.25M) was diluted with 1.5 mL N_2H_4 in a 6 mL vial. Then 1 mL of 5 mg/mL Cu_2Se in toluene and 1 mL extra toluene were added to the vial. The two-phase mixture was vigorously stirred at room temperature for 4 hours. The upper (toluene) phase was discarded and the bottom (hydrazine) phase was washed 3 times with 2 mL toluene. Afterwards, 21 μL of a Ga_2Se_3 solution (0.25M in hydrazine) was added to the washed colloidal particle solution (here the In/Ga ratio is approximately 7/3). The deposition of the colloidal particles $\{\text{Cu}_2\text{Se}[(\text{In}_2\text{Se}_4)_{0.7};(\text{Ga}_2\text{Se}_3)_{0.3}]\}$, evaporation of the solvent, and thermal annealing yielded pure copper indium-gallium selenide, as confirmed by XRD studies. See FIG. 40.

Example 11

Using the procedure of Example 10, a solution of $\text{CuInSe}_2\text{.In}_2\text{Se}_4$ is made from CuInSe_2 and $\text{In}_2\text{Se}_4^{2-}$. Deposition and thermal processing of the colloidal particles yields copper indium diselenide films where mass lost during thermal processing is less than about 5%, as determined by TGA.

The foregoing description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the invention may be apparent to those having ordinary skill in the art.

What is claimed is:

1. An isolable colloidal particle comprising an inorganic capping agent comprising a Zintl ion, said inorganic capping agent bound to a surface of a nanoparticle and substantially free of an organic capping agent.

2. The particle of claim 1, wherein the inorganic capping agent is selected from a group consisting of a polyatomic anion, a soluble metal chalcogenide, a soluble polyatomic metal chalcogenide anion, and a mixture thereof.

3. The particle of claim 1, wherein the inorganic capping agent further comprises an ion selected from the group consisting of As_3^{3-} , As_4^{2-} , As_5^{3-} , As_7^{3-} , As_{11}^{3-} , AsS_3^{3-} , $\text{As}_2\text{Se}_6^{3-}$, $\text{As}_2\text{Te}_6^{3-}$, $\text{As}_{10}\text{Te}_3^{2-}$, $\text{Au}_2\text{Te}_4^{2-}$, $\text{Au}_3\text{Te}_4^{3-}$, Bi_3^{3-} , Bi_4^{2-} , Bi_5^{3-} , Bi_7^{3-} , GaTe_2^{2-} , Ge_9^{2-} , Ge_9^{4-} , $\text{Ge}_2\text{S}_6^{4-}$, HgSe_2^{2-} , $\text{Hg}_3\text{Se}_4^{2-}$, $\text{In}_2\text{Se}_4^{2-}$, $\text{In}_2\text{Te}_4^{2-}$, $\text{Ni}_5\text{Sb}_{17}^{4-}$, Pb_5^{2-} , Pb_7^{4-} , Pb_9^{4-} , $\text{Pb}_2\text{Sb}_2^{2-}$, Sb_3^{3-} , Sb_4^{2-} , Sb_7^{3-} , SbSe_4^{3-} , SbSe_4^{5-} ,

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SbTe₄⁵⁻, Sb₂Se₃⁻, Sb₂Te₅⁴⁻, Sb₂Te₇⁴⁻, Sb₄Te₄⁴⁻, Sb₉Te₆³⁻, Se₂²⁻, Se₃²⁻, Se₄²⁻, Se_{5,6}²⁻, Se₆²⁻, Sn₄²⁻, Sn₅²⁻, Sn₉³⁻, Sn₉⁴⁻, SnS₄⁴⁻, SnSe₄⁴⁻, SnTe₄⁴⁻, SnS₄Mn₂⁵⁻, Sn₂S₆⁴⁻, Sn₂Se₆⁴⁻, Sn₂Te₆⁴⁻, Sn₂Bi₂²⁻, Sn₈Sb³⁻, Te₂²⁻, Te₃²⁻, Te₄²⁻, Tl₂Te₂²⁻, TlSn₈³⁻, TlSn₈⁵⁻, TlSn₉³⁻, TlTe₂²⁻, and a mixture thereof.

4. The particle of claim 1, wherein the inorganic capping agent further comprises a metal selected from the group consisting of a transition metal, a lanthanide, an actinide, a main group metal, a metalloid, and a mixture thereof.

5. The particle of claim 1, wherein the inorganic capping agent further comprises a soluble metal chalcogenide selected from the group consisting of molecular compounds derived from CuInSe₂, CuIn_xGa_{1-x}Se₂, Ga₂Se₃, In₂Se₃, In₂Te₃, Sb₂S₃, Sb₂Se₃, Sb₂Te₃, ZnTe, and a mixture thereof.

6. The particle of claim 1, wherein the nanoparticle is selected from the group consisting of a nanocrystal, a nanorod, a nanowire, and a mixture thereof.

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7. The particle of claim 1, wherein the nanoparticle is selected from a group consisting of AN, AlP, AlAs, Ag, Au, Bi, Bi₂S₃, Bi₂Se₃, Bi₂Te₃, CdS, CdSe, CdTe, Co, CoPt, CoPt₃, Cu, Cu₂S, Cu₂Se, CuInSe₂, CuIn_(1-x)Ga_x(S,Se)₂, Cu₂ZnSn(S,Se)₄, Fe, FeO, Fe₂O₃, Fe₃O₄, FePt, GaN, GaP, GaAs, GaSb, GaSe, Ge, HgS, HgSe, HgTe, InN, InP, InSb, InAs, Ni, PbS, PbSe, PbTe, Pd, Pt, Ru, Rh, Si, Sn, ZnS, ZnSe, ZnTe, Au/PbS, Au/PbSe, Au/PbTe, Ag/PbS, Ag/PbSe, Ag/PbTe, Pt/PbS, Pt/PbSe, Pt/PbTe, Au/CdS, Au/CdSe, Au/CdTe, Ag/CdS, Ag/CdSe, Ag/CdTe, Pt/CdS, Pt/CdSe, Pt/CdTe, Au/FeO, Au/Fe₂O₃, Au/Fe₃O₄, Pt/FeO, Pt/Fe₂O₃, Pt/Fe₃O₄, FePt/PbS, FePt/PbSe, FePt/PbTe, FePt/CdS, FePt/CdSe, FePt/CdTe, CdSe/CdS, CdSe/ZnS, InP/CdSe, InP/ZnS, InP/ZnSe, InAs/CdSe, InAs/ZnSe, and a mixture thereof.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

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INVENTOR(S) : Dmitri V. Talapin et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims:

At column 30, line 2, "AN," should be -- AIN, --.

Signed and Sealed this
Twenty-ninth Day of November, 2016



Michelle K. Lee
Director of the United States Patent and Trademark Office