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(54) **Title:** PARTICLES COATED BY INORGANIC LAYERED COMPOUNDS

(57) **Abstract:** This invention is related to nanoparticles coated by a single layer or by a few layers of metal chalcogenides or other inorganic layered materials. This invention is related to methods of producing the coated nanoparticles.



PARTICLES COATED BY INORGANIC LAYERED COMPOUNDS

FIELD OF THE INVENTION

[001] This invention is related to particles coated by a single layer or by a few layers of metal chalcogenides or other inorganic layered materials. This invention is related to methods of producing the coated particles.

BACKGROUND OF THE INVENTION

[002] Nanomaterials have attracted a considerable attention in the last few decades. The nanomaterials unique properties and structure arise from their confined dimensions, at least one dimension in the nanometer scale. Nanomaterials are classified by their dimension levels as follows: zero-dimensional nanostructures are limited in all three dimensions and usually form a spherical shape; one-dimensional nanostructures are limited in two dimensions and usually form nano-fibers such as nanorods and nanotubes. The length of the nanofibers can vary from nanometers to microns and even longer; two-dimensional nanomaterials are limited in one dimension and commonly form layered films (layered structures); three-dimensional nanomaterials are not limited in their dimensions and include powders, fibrous, multilayers and polycrystalline materials that comprise 0D, 1D and 2D structural elements. The various elements are in close contact with each other.

[003] In the last three decades 0D nanostructures, like gold nanoparticles (AuNPs), quantum dots and C₆₀ have been studied intensively due to their interesting optical, electronic and magnetic properties, which cannot be seen in the bulk material. Their unique properties arise from the high surface-to-volume ratio of the small nanoparticles (NPs). The small (and confined) dimensions of the NPs produce or increase the quantum effects and also the dominance of surface atoms of the NPs over those in its interior. Noble metal NPs (e.g. Au, Ag) provide good example for the unique properties of nanomaterials. Noble metal NPs and more specifically gold nanoparticles (AuNPs) have been known for centuries. The earliest use of colloidal Au is ascribed to the ancient Egyptians alchemists, who used it for the fabrication of the ruby glass. AuNPs are the most stable among metallic NPs and present unique characteristics such as magnetic, optical and catalysis properties.

[004] Those NPs exhibit a red hue and show significantly different optical properties from the bulk due to their nanosized dimensions. This phenomenon occurs due to the presence of free electrons in the Fermi level that produce resonant oscillation (known as surface plasmon resonance, SPR). In general, when the particle size is smaller than the mean free path (~50 nm in Au and Ag) there is no scattering from the bulk, and all the interactions are confined at the surface. The free electrons on a noble metal such as gold (*d* electrons), traverse the metal nanoparticle back and forth oscillating in the plasma frequency. SPR scattering occurs when the wavelength of the incident light

that is larger than the NP size, is in resonance with the frequency of the surface plasmon oscillation. The electron density is polarized establishing a standing electron density wave on the NP surface. The SPR produces an intense color, which depends on the shape, size and dielectric constants of the metal and the surrounding material.

[005] Two of the main problems of NPs is their long-term stability and toxicity (biocompatibility). Due to their large surface/volume ratio they tend to agglomerate or react with their surroundings. Furthermore, numerous materials, like gold which are not toxic in the bulk, when made smaller than 10 nm can permeate through the cell membrane and present a health risk.

[006] Accordingly, the surface of NPs is commonly protected by either amphiphilic molecules or by inorganic materials. It was shown that the coating (shell) of those NPs appears to have mild influence on their absorption characteristics. Nevertheless this shell has stronger influence on emission efficiency, spectrum, and stability of the NPs. Accordingly, coated particles are used in many applications such as biomedical and pharmaceutical applications (e.g. imaging, drug release), catalysis and electronics. For instance, Au@CdS core-shell NPs (Au core and CdS shell) have a stronger photoluminescence compared to CdS NPs. This effect is attributed to the transfer of excited (SPR) electron from the AuNP to the conduction band of CdS, where they recombine with valence band holes. Another way to enhance AuNPs stability is to coat the NP's by thiols. Such coating renders the NPs highly stable as well as preventing their agglomeration.

[007] As mentioned above, 2D nanomaterials are limited in one of their dimensions and tend to form flat films. The best-known member of the 2D materials is graphene. Analogues of graphene in other 2D materials, like layered transition metal dichalcogenides (TMD) incited a large interest in the scientific community. The lattice of the layered TMD, (e.g. MoS₂), consist of 2D X-M-X sandwich structure; wherein M is the transition metal atom which bonds with the chalcogen (S, Se or Te) atoms via strong covalent bonds. The MX₂ layers are stacked together by weak van der Waals forces. Unlike graphene which is a gapless material, MoS₂ (or WS₂) exhibit a gap making it suitable for numerous electronic as well as optical applications.

[008] The discovery of inorganic fullerene-like structures (IF) and inorganic nanotubes (INT) of TMD, led many research groups to study these new nanostructures and elucidate their properties. These structures, which are analogous of the carbon fullerenes and nanotubes, are usually synthesized from their oxide precursor under reducing conditions and at elevated temperatures. Two of the most recognized members of the layered dichalcogenide closed-cage nanostructures are MoS₂ and WS₂. These NPs exhibit excellent mechanical and tribological properties and are being used as additives to wet lubricants and also serve as dry lubricants for numerous industrial applications. Moreover, in recent years it was shown that IF-MoS₂ NPs and also INT-WS₂ are nontoxic and

biocompatible to human tissues. Owing to these unique properties MoS₂ (or WS₂), in the form of closed-cage NPs attracted a great deal of scientific interest.

[009] Recently, extensive attention was given to MoS₂ single layers (thickness of 0.62 nm). First, in contrast to graphene which is a gapless material, (bulk) MoS₂ exhibits an (indirect) bandgap in the visible range, making it suitable for exploitation in solar cells. Its structure and work function (5.1 eV) affords potential applications as cathode material in rechargeable lithium batteries and supercapacitor. Furthermore, recent studies have shown that the band-gap transforms from indirect (bulk material) into a direct transition in single-layer MoS₂. This effect was attributed to quantum confinement effect of the *d*-electrons of this system. The direct transition leads to a strong luminescence from MoS₂ monolayers. Furthermore, the large spin-orbit coupling lifts the degeneracy in the valence band. The lack of inversion symmetry in single layer MoS₂ (WS₂) enables spin polarized current (valleytronics). This makes MoS₂ monolayer a promising material for a variety of opto-electronic applications, which attracted a great deal of interest in recent years. It has been shown that (n,0) single walled INT, i.e. “zigzag” configuration should have a direct band gap (and luminescence) making them suitable for optoelectronics.

[0010] Hybrid semiconductor-nanoparticle structures have been prepared and studied in the past. One example is the attachment of NPs on the outer surface of INT-WS₂ and using the NPs as “antennas” for energy transfer to the INTs. Recent studies of catalytic and semiconductive properties of noble metal NPs (e.g. Au, Ag, Pd, Ni) and MoS₂ layers, concluded that Au NPs attach to MoS₂ layers through noncovalent bonds or chemical bonds. Moreover, these studies showed that the attachment of the AuNPs on to MoS₂ layers increase the optical absorbance of the Au-MoS₂ structure compared to the pure MoS₂.

[0011] Other studies showed that gold nanorods attached to MoS₂ single layer results in enhanced luminescence of the MoS₂ 2D monolayer. The increased luminescence occurs due to a match between the surface plasmon resonance (SPR) frequency and the direct band gap of MoS₂. Thus, this phenomenon is the outcome of the overlap between surface plasmon wave originating from the Au nanorod, and the emission of a single layered MoS₂.

SUMMARY OF THE INVENTION

[0012] In one embodiment, this invention provides a coated nanoparticle comprising:

- a nanoparticle; and
- a nanoparticle coating comprising 1-5 layers of an inorganic layered compound.

[0013] In one embodiment, the coating comprising 1 layer. In one embodiment, the nanoparticle material comprises a metal, a semiconductor, a semi-metal, an ionic compound, elemental

compound, other inorganic compounds, a metal oxide, a metal chalcogenide, a metal pnictide, a non-metal or any combination thereof. In one embodiment, the non-metal comprises inorganic material, organic material or a combination thereof. In one embodiment, the metal is selected from the group consisting of Au, Ag, Cu, Pd, Ru, Rh, Ir or a combination thereof. Each represents a separate embodiment. In one embodiment, the compound from which the nanoparticles are made is selected from the group consisting of CdS, CdSe, CdTe, GaAs, GaN, AlAs, InAs, TiO₂, SiO₂, CeO₂, ZnO, Al₂O₃ or a combination thereof. Each represents a separate embodiment. In one embodiment, the form of the nanoparticle is a sphere, a rod, an ellipsoid, or a non-symmetrical shape. In one embodiment, the size of the longest dimension of the nanoparticle ranges between 1 nm and 1000 nm. In one embodiment, the size ranges between 1 nm and 100 nm. In one embodiment, the inorganic layered compound comprises a transition metal chalcogenide. In one embodiment, transition metal chalcogenide comprises MoS₂, WS₂, MoSe₂, WSe₂, NbS₂, NbSe₂, TaS₂, TaSe₂, ZrS₂, ZrSe₂ or InS, InSe, GaS, GaSe. Each represent a separate embodiment. In one embodiment, the nanoparticle is a gold nanoparticle, the inorganic layered compound is MoS₂ and the number of coating layers is 1.

[0014] In one embodiment, this invention provides a process for preparing a coated nanoparticle, the process comprising:

- providing or forming nanoparticles;
- adding a solution comprising a coating precursor to the nanoparticles;
- mixing the solution.

[0015] In one embodiment, following the mixing step, the solution is centrifuged, thus forming a precipitate. In one embodiment, the precipitate of the centrifuge step is dried. In one embodiment, drying is conducted at an elevated temperature, under vacuum conditions or a combination thereof. In one embodiment, the elevated temperature is 50°C ±5°C. In one embodiment, following the drying, the precipitate is placed in a portion of an ampoule proximal to a first edge of the ampoule, and the precipitate is sealed in the ampoule under vacuum and is subjected to heating. In one embodiment, heating comprises a heating gradient. In one embodiment, the heating gradient comprises heating the first edge of the ampoule to a first temperature and heating a second edge of the ampoule to a second temperature, thus creating a temperature gradient along the ampoule between the edges. In one embodiment, the first temperature is 516°C ±15°C, and the second temperature is 428°C ±15°C. In one embodiment, the vacuum is 3×10⁻⁵ torr. In one embodiment, the precursor is an ionic compound. In one embodiment, the ionic compound is (NH₄)₂MoS₄. In one embodiment, the nanoparticles are made of metal. In one embodiment, the nanoparticles are gold nanoparticles. In one embodiment, the solution mixing step comprising stirring. In one embodiment,

the mixing step is conducted for a period of time ranging between 1h to 5 days. In one embodiment, the period of time ranges between 6 hours and 20 hours. In one embodiment, the process is conducted at room temperature. In one embodiment, forming of the nanoparticles comprises:

- providing a solution comprising nanoparticle precursor;
- adding a reactant to the solution;
- mixing the solution.

[0016] In one embodiment, the nanoparticle precursor comprises an ionic compound. In one embodiment, the ionic compound is or comprises a metal cation and a halogen anion. In one embodiment, the ionic compound is gold(III) chloride trihydrate. In one embodiment, the reactant is a reducing agent. In one embodiment, the reducing agent is sodium borohydride (NaBH_4). In one embodiment, mixing is conducted for a period of time ranging between 0.50 hours and 6 hours. In one embodiment, the process is conducted at room temperature. In one embodiment, the reactant is added gradually to the nanoparticle precursor solution.

[0017] In one embodiment, this invention provides a powder comprising the coated nanoparticles of the invention. In one embodiment, this invention provides a composition comprising the coated nanoparticles of this invention.

[0018] In one embodiment, this invention provides use of the nanoparticles of this invention as optical elements in an optical device, an electronic device or an opto-electronic device.

[0019] In one embodiment, this invention provides use of the nanoparticles of this invention as a lubricant. In one embodiment, this invention provides use of the nanoparticles of this invention in therapy or in catalysis.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The subject matter regarded as the invention is particularly pointed out and distinctly claimed in the concluding portion of the specification. The invention, however, both as to organization and method of operation, together with objects, features, and advantages thereof, may best be understood by reference to the following detailed description when read with the accompanying drawings in which:

[0021] **Figure 1** is a TEM image of AuNPs with $(\text{NH}_4)_2\text{MoS}_4$ precursor after evaporation of the solvent. The sample is taken before the last step (heating).

[0022] **Figures 2A-2C** are TEM images of AuNPs and $(\text{NH}_4)_2\text{MoS}_4$ which were mixed for a different periods of time and then heated. Time periods were: Figure 2A) overnight; Figure 2B) 3 days; Figure 2C) and Figure 2D) 7days.

[0023] **Figures 3A-3B** show TEM images of different steps in the synthesis; ratio of $(\text{NH}_4)_2\text{MoS}_4$ precursor to gold is 1:2. Figure 3A) Au@MoS_4^{-2} particles before heating; and Figure 3B) Au@MoS_2 after heating.

[0024] Figure 4: schematic presentation of the ampule heating, the edge containing the material (brown edge) is heated to a high temperature while the other edge (empty edge) is heated to a lower temperature.

[0025] **Figures 5A-5C** are TEM images of AuNPs with MoS_2 layers (end product) heated at different heating temperature. Only the edge containing the material was heated to Figure 5A) 400 °C, Figure 5B) 528 °C, and Figure 5C) 492 °C.

[0026] **Figures 6A-6B** are TEM images of the end product (Au coated by MoS_2), the edge containing material is heated to 516 °C and the other edge has a temperature of: Figure 6A) 428 °C and Figure 6B) 450 °C. The heating time was 15 minutes.

[0027] **Figures 7A-7B** are TEM images of Au@MoS_2 . The edge containing material was heated to 516 °C and the other edge 428 °C. The two images differ in heating time: Figure 7A) 30 minutes and Figure 7B) for 40 minutes.

[0028] **Figure 8** is HRSEM images of Au@MoS_2 particles on silicon wafer.

[0029] **Figures 9A-9C** show three images of Au@MoS_2 particles from different tilt of the tomography movie in STEM.

[0030] **Figures 10A-10F** are EELS in HRTEM, on the particles of Au@MoS_2 . Figure 10A) Graph of relative intensity vs. electron energy loss, indicates the elements in the sample. The images were taken for mapping in different elements: Figure 10B) zero loss, Figure 10C) Au, Figure 10D) Mo, Figure 10E) S and Figure 10F) C. All images are in a 20 nm scale.

[0031] **Figure 11** is Resonance Raman (RR) spectrum excited by 632.8 nm laser line at room temperature. Attached with the optical image of the particles, measurement was taken in the middle of the image.

[0032] **Figures 12A-12B:** UV-Vis spectra of the NPs at different steps of the process. Figure 12A: the arrows point to AuNPs curve; Au@MoS_4^{-2} curve immediately after adding the $(\text{NH}_4)_2\text{MoS}_4$ to the suspension of the AuNPs; Au@MoS_4^{-2} curve after $(\text{NH}_4)_2\text{MoS}_4$ was added and mixed for 3 days; Au@MoS_2 curve of the final product. Figure 12B: the AuNPs curve with the peak as shown in Figure 12A; Au@MoS_2 curve as shown in Figure 12A; two additional curves present IF- MoS_2 NPs and 2H- MoS_2 bulk; these two curves have been taken from the literature.

[0033] **Figures 13:** Suggested mechanism for the synthesis of Au@MoS₂ NP which is described by three parts: a) synthesis of AuNPs, b) adding precursor (NH₄)₂MoS₄ and formation of Au@MoS₄⁻² and c) by heating and release of H₂S, S and NH₃ creating Au@MoS₂ core-shell structure.

[0034] **Figures 14A-14B** are high resolution TEM images of Au@MoS₂. These NPs were produced by stirring the solution for two days and by subsequent annealing. At image Figure 14A) two particles sharing the same shell and Figure 14B) bonding between the shells of different particles.

[0035] **Figure 15** is a TEM image of gold nanoparticle covered by two semi-attached MoS₂ layers.

[0036] **Figures 16A-16C** are TEM images of Au@WS₂ coated nanoparticles. The samples were heated at different temperatures: Figure 16A) 529 °C for 30 minutes; Figure 16B) 516 °C for 40 minutes; and Figure 16C) 516 °C for 30 minutes.

[0037] **Figure 17** is an absorption spectrum of the gold nanoparticles.

[0038] **Figure 18** is a graph showing normalized luminescence of Au@MoS₂ nanoparticles. Excitation wavelength 438 nm.

[0039] **Figure 19** is TEM image of gold nanoparticle coated with one monolayer of WS₂. Single nanoparticle of Au@1L-WS₂. (images taken on a LaB₆ JEOL 2100 TEM at 200 kV acceleration voltage).

[0040] **Figure 20** shows the low frequency Raman lines (shear modes) of multilayered MoS₂ (top curve) and single layer (bottom curve) in which the shear mode between two MoS₂ layers (32 cm⁻¹) is completely absent.

[0041] It will be appreciated that for simplicity and clarity of illustration, elements shown in the figures have not necessarily been drawn to scale. For example, the dimensions of some of the elements may be exaggerated relative to other elements for clarity. Further, where considered appropriate, reference numerals may be repeated among the figures to indicate corresponding or analogous elements.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0042] In the following detailed description, numerous specific details are set forth in order to provide a thorough understanding of the invention. However, it will be understood by those skilled in the art that the present invention may be practiced without these specific details. In other instances, well-known methods, procedures, and components have not been described in detail so as not to obscure the present invention.

[0043] List of abbreviations: NP=Nanoparticle; AuNPs=gold nanoparticles; SPR=surface plasmon resonance; TMD=transition metal dichalcogenides; IF=inorganic fullerene-like nanostructures; INT=inorganic nanotubes; TEM=transmission electron microscope; HRTEM=high-resolution transmission electron microscope; STEM=scanning transmission electron microscope; HAADF=high-angle annular dark field; EDS=energy-dispersive X-ray spectroscopy; EELS=electron energy loss spectroscopy; SEM=scanning electron microscope; vdW=van der Waals; core@shell=a particle having a core and a shell, e.g AuNPs coated by MoS₂ in a core-shell structure is described as (Au@MoS₂) according to this notation.

[0044] Nanoparticles (NPs) and in particular AuNPs are among the most popular research topics in the last decades. Another research topic that has become popular over the last two decades is inorganic fullerenes (IF) such as MoS₂ and WS₂. This invention provides a unique combination of these two domains, AuNPs and IF-MoS₂ that paves the way for a new type of hybrid materials with novel opportunities in applications such as optics, electronics and nanomechanics.

[0045] In one embodiment, this invention provides synthesis of Au@MoS₂ particles. The particles comprise a single-MoS₂ layer as the shell of the particle core-shell structure. The synthesis can be divided into three steps:

- a) AuNPs synthesis;
- b) formation of Au@MoS₄⁻² structure by adding MoS₄⁻² anions to AuNPs anions, and;
- c) formation of Au@MoS₂ NPs by heating and H₂S and S release.

[0046] In another embodiment, the first step is omitted and the (e.g. Au) nanoparticles are provided from a different source. It was found that steps b and c depend on temperature, on the ratio between Au and MoS₄⁻² precursor and on the duration of the synthesis step.

[0047] The characterization of the Au@MoS₂ structure by electron microscopy (SEM, TEM and HRTEM) confirmed that the NPs are almost spherical, with size distribution of 7-13 nm. Most importantly, the AuNPs are coated by a MoS₂ single-layer. In some cases an additional layer or two are attached to the AuNP. Additional confirmations for a complete cover of AuNPs with MoS₂ single-layer was obtained by high-angle annular dark field (HAADF) STEM-EDS electron mapping and STEM tomography measurements. Moreover, the structure and the composition of the Au@MoS₂ NPs are supported by EDS and EELS analyses, existing in STEM and HRTEM, respectively.

[0048] The electron microscopy measurements revealed an amorphous material which is observed in the interparticle space of the Au@MoS₂ NPs and contains excess MoS₂ layers and organic contamination. This amorphous material is one of the reasons for the aggregation of Au@MoS₂ NPs. The aggregation is also promoted by van der Waals forces occurring between the layers of

each two different NPs. Furthermore, occasionally, two neighboring NPs are found to share a MoS₂ layer (dimer structure). Also, in rare cases, the MoS₂ layers were found to cover the AuNP but the core and shell do not fully attach to each other. It is assumed that this state occurs due to the difference in the coefficient of thermal expansion between the gold and MoS₂ layer.

[0049] In the scientific literature there is no evidence for IF-MoS₂ made of a single-layer structure. This invention provides such novel formation of single-layer IF-MoS₂ coating AuNP. The Raman measurements showed that the spectrum of Au@MoS₂ single-layer particles resembles the spectrum of IF-MoS₂ NPs structure. This similarity is inferred from the red shift of the main Raman peaks, typical for IF-MoS₂ NPs.

[0050] One of the goals of the synthesis of Au@MoS₂ single-layer is to find new optical properties. This work presents initial UV-Vis absorption measurements of these NPs. The results show full quenching of the AuNPs SPR, and additionally yield two new peaks. The hypothesis following these results is that there is an interaction between the AuNPs SPR and the MoS₂ excitons but this should be further investigated.

[0051] Therefore, and as noted herein above, inorganic layered compounds such as MoS₂ exhibit great chemical stability and excellent mechanical and tribological properties. The present invention utilizes the properties of inorganic layered compounds and uses such compounds to uniformly coat nanoparticles in a simple and efficient manner.

[0052] Therefore, in one embodiment, this invention provides nanoparticles coated by a single layer of an inorganic layered compound. In one embodiment, this invention provides a method of preparing layered-compound coated nanoparticles. This invention further provides collections of layered-compound coated nanoparticles and uses of such coated particles.

[0053] The combination of a nanoparticle core and a layered-compound shell provides a unique and stable hybrid nanomaterial.

[0054] In one embodiment, this invention provides a new hybrid nanostructure which is a combination of AuNPs coated by a single-layer of MoS₂ in a core-shell structure (Au@MoS₂; Au forms the core and MoS₂ forms the shell). The core of the Au@MoS₂ NPs is composed of gold particles 7-13 nm in size, covered completely by at least one closed MoS₂ layer. Thus the shell can be considered to have the structure of IF-MoS₂ structure but instead of being hollow it engulfs the entire AuNP. The NPs were analyzed by transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), scanning electron microscope (SEM), Raman spectroscopy and UV-Vis absorption. A growth mechanism was proposed for the core-shell NPs. This invention provides observation for the unique properties of the

Au@IF-MoS₂ core-shell structure, including optical interaction between the SPR and the two excitons of MoS₂.

[0055] In one embodiment, gold nanoparticles (AuNPs) encapsulated by a fullerene-like MoS₂ were synthesized. In one embodiment, particles with single MoS₂ layer on NPs (Au@MoS₂) were synthesized. Electron microscopy was used for exhaustive characterization of the synthesized NPs. Study of the optical properties of the coated NP's was conducted.

[0056] The synthesis of AuNP coated by MoS₂ single-layer is disclosed herein; i.e. synthesis of a core-shell nanostructure (Au@MoS₂). Another way to describe these particles is as hybrid nanoparticles, i.e. fullerene-like MoS₂ (IF-MoS₂) with a core being stuffed by AuNPs. The characterization of the NPs was done by various tools: transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), scanning electron microscope (SEM), Raman spectroscopy and UV-Vis absorption. It was found that these AuNPs have a diameter of 7-13 nm. The AuNPs are coated by a complete single-layer of MoS₂ (or more layers) with IF-MoS₂ structure. The growth mechanism of the nanoparticles has been studied and is discussed below.

I. Nanoparticles of this invention

1. In one embodiment, this invention provides a coated nanoparticle comprising:

- a nanoparticle; and
- a nanoparticle coating comprising 1-5 layers of an inorganic layered compound.

[0057] In one embodiment, the coating comprising 1 layer. In one embodiment, the nanoparticle material comprises a metal, a semi-metal, an ionic compound, elemental compound, other inorganic compounds, a metal oxide, a metal chalcogenide, a metal pnictide, a non-metal or any combination thereof. In one embodiment, the nanoparticle comprises a conducting, semiconducting, superconducting or insulating material. In one embodiment, the nanoparticle comprises any combination of conducting, semiconducting, superconducting or insulating materials in a core-shell structure comprising more than one material. In one embodiment, the non-metal comprises inorganic material, organic material or a combination thereof. In one embodiment, the metal comprises Au, Ag, Cu, Pd, Rh, Ru, Ir, or any combination thereof. Each represents a separate embodiment. In one embodiment, the inorganic material comprises CdS, CdSe, GaAs, GaN, InAs, CdTe, TiO₂, SiO₂, ZnO, CeO₂, AlAs, Al₂O₃ or any combination thereof. Each represents a separate embodiment. In one embodiment, the nanoparticle is a sphere, a rod, an ellipsoid, or a non-symmetrical shape.

[0058] In one embodiment, the size of the longest dimension of the nanoparticle ranges between 1 nm and 1000 nm. In one embodiment, the size ranges between 1 nm and 100 nm. In one embodiment, the inorganic layered compound comprises a transition metal chalcogenide. In one embodiment, the transition metal chalcogenide comprises MoS₂, WS₂, MoSe₂, WSe₂, NbS₂, NbSe₂, TaS₂, TaSe₂, ZrS₂, ZrSe₂ or InS, InSe, GaS, GaSe. Each represents a separate embodiment. In one embodiment, the nanoparticle is a gold nanoparticle, the inorganic layered compound is MoS₂ and the number of coating layers is 1.

[0059] In one embodiment, this invention provides a coated nanoparticle comprising: a nanoparticle and a coating of the nanoparticle. In another embodiment, the coating comprises 1-5 layers of an inorganic layered compound. The coating coats the nanoparticle.

Materials:

[0060] In one embodiment, the nanoparticle is made of an inorganic material. In one embodiment, the coating is made of an inorganic material.

[0061] In one embodiment, the nanoparticle is made of one or more metals. In one embodiment, the metal is gold, platinum, palladium, or tungsten. In one embodiment, the metal is copper or silver. In one embodiment the nanoparticle contains mercury. In one embodiment, the metal is iridium, rhodium. In one embodiment, the nanoparticle comprises a metal alloy. In one embodiment, the material from which the nanoparticle is made is a gold/palladium alloy. In one embodiment, the material from which the nanoparticle is made is a salt, an oxide, a hydroxide, or any other compound containing at least two different atoms. In one embodiment the nanoparticle comprises GaN, AlAs, InAs, CdSe, CdTe, CdS, GaAs, ZnO, Al₂O₃ or SiO₂, TiO₂, CeO₂. Each represents a separate embodiment. In one embodiment the nanoparticle comprises Si, carbon or a combination thereof. In one embodiment, the nanoparticle is made of in whole or in part from an electrically conducting material. In one embodiment, the nanoparticle is made of in whole or in part from an electrically semiconducting material. In one embodiment, the nanoparticle is made of in whole or in part from an electrically insulating material. In one embodiment, the nanoparticle is made of in whole or in part from a superconducting material. In one embodiment, the nanoparticle is made of in whole or in part from YBa₂Cu₃O₇. In one embodiment, the nanoparticle comprises glass or a glassy material. In one embodiment, the nanoparticle comprises quartz, pyrex, or glass containing any metal ions. In one embodiment, the nanoparticle comprises silicon. In one embodiment, the nanoparticle comprises alumina or silica. In one embodiment, the nanoparticle comprises aluminum coated by aluminum oxide or silicon coated by silicon oxide. In one embodiment, the nanoparticle comprising an amorphous material. In one embodiment, the

nanoparticle comprising a crystalline or a semi-crystalline or polycrystalline material. In one embodiment, the nanoparticles comprising different domains with different crystal structures.

[0062] In one embodiment, nanoparticles of this invention have a layered structure. In one embodiment, nanoparticles of this invention (not including the inorganic layered-compound coating described herein above) have a core-shell structure. In one embodiment, a core-shell structure is a structure in which the core of the particle comprises one material and the shell of the particle comprises a different material.

[0063] Numerous possibilities are enabled by the coated (hybrid) particles of this invention. For example, the nanoparticles of this invention which are coated by 1 layer or by 1-5 or 1-10 layers of an inorganic layered compound can be further coated by any other material, including but not limited to Al_2O_3 . Such Al_2O_3 coating layer can be further coated by a second layer(s) of an inorganic layered compound. In such a configuration, a nanoparticle comprising three coating layers (e.g. $\text{MoS}_2/\text{Al}_2\text{O}_3/\text{WS}_2$) is formed. Also, a complex quantum dot of the form $\text{CdSe}/\text{MoS}_2/\text{CdTe}$ can be formed. For particles with multiple coating layers, many parameters can be varied in view of possible applications. Coating material, coating thickness, coating porosity, electrical and optical properties, coating mass, coating surface properties (e.g. hydrophilicity/hydrophobicity) and others are varied in order to obtain coated nanoparticles with desired characteristics. Design of such coated nanoparticles is conducted in view of their possible applications in electronics, optics, mechanics, energy, catalysis and chemical reactions.

[0064] According to this aspect and in one embodiment, the NP is a gold NP, coated by 1-10 layer(s) of inorganic layered compound, and an additional coating layer of gold covers the layer of the inorganic layered compound. According to this aspect and in one embodiment, the formed coated-NP comprises gold NP coated by inorganic layered compound, the inorganic layered compound is coated by a gold layer. Such structure is not limited by number of layers. Any number of alternating metal layers/inorganic layered compound layers can be formed on the nanoparticle. The thickness of material (of the metal and of the inorganic layered compound) can be varied in order to achieve different coated-particle properties. Such multi-layered structure is not limited by materials and may comprise different metal layers, different inorganic-layered compounds, and/or other layers of materials (metal alloys, metal oxides, non-metals, metal chalcogenide, metal sulfides, and any other material as described herein above for the nanoparticles).

[0065] In one embodiment, the nanoparticle is made of a certain element or elements and the inorganic layered compound coating the particle is made of other, different elements. In one embodiment, the nanoparticle comprises a certain metal and the inorganic layered compound coating the particle does not comprise this metal. According to this aspect and in one embodiment,

coating of the particle is performed using starting materials or precursors that are provided from an external source and not from the particle itself. Coating of the particle does not utilize the material from which the particle is made in some embodiments. In one embodiment, the particle is formed or provided first and the coating is formed on top of the particle in a subsequent step. In one embodiment, the coated nanoparticle is not Mo@MoS₂. In another embodiment, the coated particle is Mo@MoS₂.

[0066] In one embodiment, the yield of the coated nanoparticles prepared by methods of this invention is close to 100%. In one embodiment, practically all particles are coated by a monolayer of an inorganic layered compound, or by 1-5, or by 1-10 layers of the inorganic layered compound coating. In one embodiment, the yield of the coated nanoparticles is more than 70%, more than 80%, more than 90%, more than 95%, more than 97%, more than 99%, more than 99.5%, more than 99.7% or more than 99.9% of the total collection of nanoparticles used in the coating process of this invention.

[0067] In one embodiment, this invention provides nanoparticles coated by 1, 1-5 or 1-10 layers of an inorganic layered compound, wherein the nanoparticles are made according to methods of this invention. In one embodiment, this invention provides nanoparticles coated by 1, 1-5 or 1-10 layers of an inorganic layered compound, wherein the nanoparticles are made according to a process comprising:

- providing or forming nanoparticles;
- adding a solution comprising a coating precursor to said nanoparticles;
- mixing said solution.

[0068] In one embodiment, for the core-shell particles (not including the inorganic-layered-compound coating) the core of the particle is made of a combination of materials or elements, and the shell is made of a different combination of materials or elements. In one embodiment, the shell material coats the core material. In one embodiment coating is full. In one embodiment, coating is partial. In one embodiment, the shell material is the material that is present on the surface of the particle. In one embodiment the material comprising the shell of the particle is the material that may be involved in chemical reactions of the particle with other materials or molecules. In one embodiment, the surface (shell) material dictates the material or the particle reactivity. In one embodiment, the surface material dictates the particle solubility. In one embodiment, the surface material dictates the material wettability. In one embodiment the core of the particle or the inner layer of a particle is a dielectric material and the shell or the outer layer of the particle is metallic. In one embodiment, the core of the particle is metallic and the shell is a dielectric or semiconducting material. In one embodiment, the core of the particle is metallic, semi-metallic or semiconducting

and the shell or outer layer is insulating. In one embodiment, both the core and the shell are metallic. In one embodiment, both the core and the shell are semiconducting. In one embodiment, both the core and the shell are electrically insulating.

[0069] In one embodiment, in a core-shell particle, the radius of the particle is approximately the sum of: the radius of the core plus the thickness of the shell. In one embodiment, the radius of the core and the thickness of the shell are similar. In one embodiment, the radius/thickness of the core is approximately 5%, 10%, 25%, 50% or 60% of the total particle radius. In one embodiment, the radius/thickness of the core/inner layer is approximately 70%, 75%, 80%, 85%, 90%, 95%, 99% or 99.9% or more, of the total particle radius/ thickness. Thickness of the core refers to the thickness of non-spherical particles.

[0070] In one embodiment, the term shell refers to the material of which the surface (outer region) of the particle is made of before the inorganic layered-compound coating is applied. In another embodiment, the shell is the layered-compound coating. In one embodiment, the particle can have a core-shell structure as described herein above, and on top of the shell, the inorganic layered-compound coating is formed. Such coated particles comprise one core and two shells. The outermost coating shell contains the inorganic layered compound in one embodiment.

[0071] In one embodiment, the surface of the particle is rough. In one embodiment, the surface is smooth. In one embodiment, the surface possesses various degrees of roughness. In one embodiment, roughness is a measure of the topography of the surface. In one embodiment, roughness is a measure of the texture of a surface. In one embodiment, roughness is a measure of the distance between the lowest and highest points of the surface. In one embodiment, highest and lowest points refer to relative distances from the center of the particle or from a theoretical reference line or a theoretical flat surface drawn underneath the lowest point of the surface.

[0072] In one embodiment, the nanoparticle comprises metal. In one embodiment, the metal comprises gold.

Dimensions:

[0073] In one embodiment, the nanoparticle is a particle with at least one dimension in the nanoscale. In one embodiment, a nanoparticle has at least one axis, one dimension, a length, a width, a height, a thickness, a diameter or a combination thereof ranging between 1 nanometer and 1000 nanometers.

[0074] In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 1–5 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 2–6 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 4–6 nm, 7-13 nm, 5-20 nm. In one embodiment the nanoparticles

have a diameter or a long axis dimension ranging from between 1–10 nm, or between 5–10 nm, or between 1–100 nm or between 5–100 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 10–50 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 50–150 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 100–1000 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 5–15 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 100–300 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 300–500 nm. In one embodiment the nanoparticles have a diameter or a long axis dimension ranging from between 500–700 nm.

[0075] In one embodiment, the particles are monodispersed. In some embodiments, the term “monodispersed” refers to a relatively uniform particles size distribution, such that, in a given preparation, nanoparticle diameter will not vary or deviate significantly from the mean particle diameter. In some embodiments, deviation from the median size is minimal. In some embodiments, such term may be considered to be synonymous to the term “small particle size distribution”.

[0076] In one embodiment the term “monodispersed” refers to a preparation comprising nanoparticles with a percent average deviation of less than 20 % from the mean particle size in a given preparation. In one embodiment the mean size distribution is defined by the mean value obtained of particle diameters for a population of spherical particles. In one embodiment the mean diameter for a population of particles is about 7–13 nm, or in one embodiment, 7–10 nm, or in another embodiment, 9–11 nm, or in another embodiment, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 nm. In one embodiment, the average deviation from the mean for such particles will be less than 1 nm. In some embodiments, the particle diameter of a population may range from about 3 nm to about 12 nm, or in another embodiment from about 1 nm to about 15 nm or 1–20 nm. As exemplified herein, one preparation obtained ranged in size from about 7 nm to about 13 nm. In one embodiment, the size distribution of the nanoparticles collected as a product of the process ranges between 5%-20% of the mean particle size. In one embodiment, the size distribution of the nanoparticles collected as a product of the process ranges between 10%-40%, or 1%-50%, of the mean particle size. Other particle preparations yield non-monodispersed particles. Collections of particles with high variation in particle size are provided by this invention in some embodiments.

Geometry/shape:

[0077] In one embodiment, this invention is directed to coated nanoparticles. In one embodiment, the nanoparticle is spherical. In one embodiment, the particle is ball-shaped. In one embodiment, the particle has a rod-like shape. In one embodiment, the particle is oval, square, rectangular, tear-drop

shaped, cylindrical, cone-shaped, helical, or possess an hexagonal feature. In one embodiment, the particle is symmetric, and in another embodiment, asymmetric. In one embodiment, the particle has high symmetry, and in another embodiment, low symmetry. In one embodiment, the particle has no regular shape. In one embodiment, one or more regions on the surface of the particle are rounded while other one or more regions on the surface of the particle are sharp, flat, rough, pointed, cone-shaped or helix-shaped. In one embodiment, all particle characteristics described herein above may apply to curved or other non-flat regions on larger particles, and to a curved or to other non-flat region on large surfaces of large particles. In one embodiment, particles described herein may be adsorbed or bonded to surfaces that are much larger than the particles.

Clusters:

[0078] In one embodiment the coated nanoparticles of this invention form clusters. In one embodiment, "cluster" is an aggregate of particles. In one embodiment, a "cluster" is an assembly of particles. In one embodiment, a "cluster" is a structure containing a few particles. In one embodiment, the particles in a cluster are held by attractive forces between the particles. In one embodiment, forces between particles cause the surfaces of particles to be held close together. In one embodiment, attractive forces between particles in a cluster cause the merging of two particle surfaces. In one embodiment the clusters contain 2-10 nanoparticles. In one embodiment the clusters contain 2-5 nanoparticles. In one embodiment the clusters contain 5-10 nanoparticles. In one embodiment the clusters contain 10-20 nanoparticles. In one embodiment the clusters contain 20-30 nanoparticles. In one embodiment the clusters contain 30-50 nanoparticles. In one embodiment the clusters contain 10-100 nanoparticles or 10-1000 nanoparticles. In one embodiment the clusters contain 100-500 or 500-1000 nanoparticles. In one embodiment the clusters contain 1000-10,000 nanoparticles.

[0079] In one embodiment, the clusters contain particles of the same size and geometry. In one embodiment, the clusters contain particles of different size and/or of different geometry. In one embodiment, clusters contain particles with a small size distribution. In one embodiment, clusters contain particles with a large size distribution. In one embodiment, the size distribution of particles in a cluster is ± 1 nm from the particles average size. In one embodiment, the size distribution of particles in a cluster is ± 2 nm from the particles average size. In one embodiment, the size distribution of particles in a cluster is ± 3 nm from the particles average size. In one embodiment, the size distribution of particles in a cluster is ± 4 nm from the particles average size. In one embodiment, the size distribution of particles in a cluster is ± 5 nm from the particles average size. In one embodiment, the size distribution of particles in a cluster is ± 10 nm from the particles

average size. In one embodiment, the size distribution of particles in a cluster is +/- 50 nm or +/- 100 nm from the particles average size.

[0080] In one embodiment, the cluster dimensions reflect the number of particles from which the cluster is made. In one embodiment, cluster dimensions can be calculated or can be estimated from the number of particles in the cluster and from the dimensions of the particles in the cluster. For example and in one embodiment, a cluster of 13 spherical particles arranged in a closed packed cluster may have their largest dimension equal to the diameter of three particles. If for example the particle diameter is 2 nm, the cluster longest axis will be approximately $2 \text{ nm} \times 3 = 6 \text{ nm}$. Such cluster can be referred to as a "6 nm cluster". In one embodiment, the particle sizes, particle geometries, and the number of particles in a cluster given above, can be used to calculate the dimensions of clusters of the present invention.

[0081] In one embodiment, the clusters comprise an ordered array of particles. In one embodiment, clusters comprising a disordered array of particles. In one embodiment, clusters comprising particles with no order. In one embodiment, clusters comprising domains of ordered particles and domains of disordered particles. In one embodiment, particles are arranged in the cluster to give various cluster geometries. In one embodiment, cluster geometry is spherical or close to spherical. In one embodiment, cluster geometry represents a chain of particles. In one embodiment, cluster geometry can be any geometry imposed by the configuration of the particles from which the cluster is made.

[0082] In one embodiment, a cluster is an aggregate, a collection of, or an assembly of particles or molecules.

In one embodiment, this invention provides a powder comprising the coated nanoparticles of this invention. In one embodiment, this invention provides a cluster or clusters comprising the coated nanoparticles of this invention.

Particle Coating:

[0083] In one embodiment, nanoparticles of this invention comprise a coating which comprises a single layer of an inorganic layered compound. In one embodiment, nanoparticles of this invention comprise a coating which comprises 1-5 or 2-5 layers or 1-10 layers of an inorganic layered compound.

[0084] In one embodiment, the coating results in nanoparticles having a coating that coats between 60%-100% of the particle surface area. In one embodiment, the coating coats 98%-100% of the particle's surface area. In one embodiment, the nanoparticles coating coats 98%-99% of the particle surface area. In one embodiment, the coating coats 95%-99% of the particle surface area. In one embodiment, the coating coats 98%-99.9% of the particle surface area. In one embodiment, the coating coats 85%-95% of the particle surface area. In one embodiment, the coating coats 75%-90%

of the particle surface area. In one embodiment, the coating coats 40%-60% of the particle surface area. In one embodiment, the coating coats between 10%-40% of the particle surface area. In one embodiment, the coating coats more than 90%, more than 95%, more than 97%, more than 98%, more than 99%, more than 99.5%, more than 99.9% of the particle surface area. In one embodiment, the coating is of 100% of the particle surface area. In other embodiments, the coating is partial coating of the particle's surface area.

[0085] In one embodiment, the inorganic layered compound coating comprises MoS₂, WS₂, MoSe₂, WSe₂. In one embodiment any material that forms an inorganic layered compound can be used as the coating of coated nanoparticles of this invention. For example, layered metal oxides can be used for coating nanoparticles of this invention thus yielding the coated nanoparticles of this invention.

II. Processes for the preparation of coated particles and clusters of this invention

[0086] In one embodiment, this invention provides a process for preparing a coated nanoparticle, the process comprising:

- providing or forming nanoparticles;
- adding a solution comprising a coating precursor to said nanoparticles;
- mixing said solution.

[0087] In one embodiment, "providing or forming" means that the nanoparticles can be either formed (produced) or it can be provided from another source, such as being provided from a commercial supplier. A step wherein the nanoparticles are formed can be part of the process of this invention. However, in some embodiments, such step is not necessary if the nanoparticles are provided and ready for use in the following process step.

[0088] In one embodiment, following said mixing step, the solution is centrifuged, thus forming a precipitate. In one embodiment, the precipitate of said centrifuge step is dried. In one embodiment, drying is conducted at an elevated temperature, under vacuum conditions or a combination thereof. In one embodiment, the elevated temperature is 50°C ±5°C. In one embodiment, drying temperature is room temperature. In one embodiment drying temperature is lower than 50 °C. In one embodiment the drying temperature is higher than 50 °C. In one embodiment, following said drying, said precipitate is placed in a portion of an ampoule proximal to a first edge of said ampoule, and the precipitate is sealed in the ampoule under vacuum and is subjected to a heating. In one embodiment, heating comprises a heating gradient. In one embodiment, heating gradient comprises heating said first edge of said ampoule to a first temperature and heating a second edge of said ampoule to a second temperature, thus creating a temperature gradient along the ampoule between said edges.

[0089] In one embodiment, the first temperature is 516°C ±15°C, and the second temperature is 428°C ±15°C. In one embodiment, the vacuum is 3×10⁻⁵ torr. In one embodiment, the precursor is an

ionic compound. In one embodiment, the coating precursor comprises at least one of the elements that are present in the resultant coating of the coated particle. In one embodiment, the precursor comprises more than one of the elements that are comprised in the coating of the coated particle that results from the coating process of this invention. In one embodiment, the precursor comprises all the elements that are comprised in the coating of the coated particle that results from the coating process of this invention. In one embodiment, the coating precursor comprises a metal. In one embodiment, the coating precursor comprises a chalcogenide. In one embodiment, the coating precursor comprises a metal atom/ion and a chalcogenide atom/ion. In one embodiment, the coating precursor does not comprise carbon. In one embodiment, the ionic compound is $(\text{NH}_4)_2\text{MoS}_4$. In one embodiment, the nanoparticles are made of metal. In one embodiment, the nanoparticles are gold nanoparticles. In one embodiment, the solution mixing step comprising stirring. In one embodiment, the mixing step is conducted for a period of time ranging between 1 h to 5 days. In one embodiment, the period of time ranges between 6 hours and 20 hours. In one embodiment, the process is conducted at room temperature. In one embodiment, forming of the nanoparticles comprises:

- providing a solution comprising nanoparticle precursor;
- adding a reactant to said solution;
- mixing said solution.

[0090] In one embodiment, the nanoparticle precursor comprises an ionic compound. In one embodiment, the ionic compound comprises a metal cation and a halogen anion. In one embodiment, the ionic compound is gold(III) chloride trihydrate. In one embodiment, the reactant is a reducing agent. In one embodiment, the reducing agent is sodium borohydride (NaBH_4).

[0091] In one embodiment, in the process of forming the nanoparticles (the formation of the uncoated nanoparticles), mixing is conducted for a period of time ranging between 0.50 hour and 6 hours. In one embodiment, the process is conducted at room temperature. In one embodiment, the reactant is added gradually to the nanoparticle precursor solution.

[0092] In one embodiment, other processes are used to form the coated nanoparticles of this invention.

[0093] In one embodiment, atomic layer deposition (ALD) is used to form the inorganic-layered compound coating on the nanoparticle. According to this aspect and in one embodiment, the nanoparticles are exposed sequentially to vapors of precursors of an inorganic layered compound (e.g. Mo salt such as MoCl_5 and H_2S) under vacuum and at elevated temperature such that a single layer or multiple layers of an inorganic layered compound (e.g. MoS_2) is/are formed around the nanoparticle. The coated nanoparticles are annealed at high temperatures in some embodiments. In

some embodiments, the annealing temperature is higher than the elevated temperature used for preparing the coating layer as described herein above.

[0094] In one embodiment, successive ionic layer adsorption and reaction (SILAR) is used to form the inorganic-layered compound coating on the nanoparticle.

[0095] In one embodiment, a solvothermal method is used to form the inorganic-layered compound coating on the nanoparticle. According to this aspect and in one embodiment, the nanoparticles are introduced into an organic solution comprising a metal precursor (e.g. ammonium molybdate) and a non-metal precursor (e.g. elemental sulfur). The solution comprising the starting materials is heated to initiate a reaction. An inorganic layered compound is formed as a layer coating the nanoparticle. The heating temperatures used in the solvothermal methods may be less than 200 °C, thus enabling coating of organic nanoparticles as well as inorganic nanoparticles. Some processes for forming the coated nanoparticles of this invention are conducted at lower temperatures and accordingly, organic nanoparticles can be used and coated by such processes.

Possible Mechanism for Au@MoS₂ formation:

[0096] In one embodiment, for the formation of Au@MoS₂ (and possibly other coated nanoparticles), the following mechanism was proposed. However, other mechanisms may be possible for such coated nanoparticle formation. Based on experimental results, and in one embodiment, the first step in the formation of the coated nanoparticles was AuNPs synthesis via reduction of Au³⁺ by NaBH₄ in water (see Figure 13). The equation of the reaction is:



[0097] The following, second step was the addition of ammonium tetrathiomolybdate precursor [(NH₄)₂MoS₄] to the same phase (Figure 13). This precursor is a source of MoS₄²⁻ anions which cover the AuNPs (denoted as Au@MoS₄²⁻) and stabilized by cations (NH₄⁺) and the solvent itself. This coating is promoted by the affinity of gold to sulfur, i.e. similar to the thiol-Au bond which was described in the literature. Moreover, MoS₄²⁻ as a ligand, probably works like a chelate, i.e. as “passivating ligand layer”. The coating protects the AuNPs and prevents aggregation of the gold for a certain period of time. The equation of the reaction is:



[0098] The last step of the reaction was heating the precipitate and release of H₂S, S and NH₃ (Figure 13). This release resulted in producing the requested material Au@MoS₂ single-layer NPs. In order to gain control over the process, annealing time and temperature were varied and the product was examined by TEM as described herein below. The proposed equation of the reaction is:



[00099] Other reaction routes may be possible, and such reactions would be represented by other equations. The formation of Au@MoS₂ core-shell nanoparticles has not been previously reported.

Formation of Au@MoS₄⁻² (the second step):

[00100] As described herein above, the second step (in the synthesis) is the addition of (NH₄)₂MoS₄ to the AuNPs solution. The MoS₄⁻² anions bind to the AuNP forming Au@MoS₄⁻² (shown in Figure 13). An evidence for the formation of these moieties is the difficulty to precipitate the material after the addition of the (NH₄)₂MoS₄ precursor (described in Example 1). This difficulty is attributed to the negative surface charge of the NPs, which self-repel each other.

[00101] In fact the Au@MoS₄⁻² suspension is stable for ~72 h. Beyond this period the core-shell structure of the NPs starts to deform: AuNPs tend to agglomerate and seemingly the MoS₄⁻² anions start to degrade (e.g. convert to MoS₃ NP or hydrolyze). Long term mixing has profound effect on the Au@MoS₄⁻² stability leading to complete segregation of MoS₂ from the AuNPs (Figure 2A-2D).

Formation of Au@MoS₂ single-layer:

[00102] In order to form the AuNPs coated by a single-layer of MoS₂, full control over the release process of H₂S and S must be achieved. The results presented in Figure 5A-5C have shown that when the ampule-edge containing the precipitate is heated, H₂S and S are released from the Au@MoS₄⁻². At lower temperatures (400 °C), the condition for releasing H₂S and S is insufficient, probably because there is not enough energy to break the thiomolybdate bonds. Overheating of the sample (528 °C) leads to an uncontrolled formation of MoS₂ layers; these films are often observed to be detached from the AuNPs. Therefore, the optimal annealing temperature is at 516 °C according to this embodiment.

[00103] Another aspect of the control over the formation of Au@MoS₂ single-layer NPs is the establishing of a temperature gradient in the ampule. In these series of experiments the temperature of the hot edge of the ampule was fixed at 516 °C and the temperature of the cold edge was varied. When the temperature gradient was too high (> 88 °C), i.e. the cold zone was heated below 428 °C, the pressure of the H₂S and S in the cold zone was too low driving the kinetics of the reaction (in the zone) too fast. In this case the rate of growth of the MoS₂ was very fast and much of it segregated into the inter-particle space (between the nanoparticles). Therefore the monolayers of MoS₂ could not engulf the entire nanoparticle and the core-shell nanostructure diminished. Contrarily, when the temperature gradient was too low, i.e. the cold edge was heated beyond 428 °C, the MoS₂ crystallites did not grow as fast and the AuNP were not coated completely. Therefore, the release of H₂S and S needs not to be quick nor slow and the optimum conditions are achieved (for a fixed hot temperature of 516 °C) when the temperature gradient in the ampule is 88 °C.

[00104] Thus, the release of H_2S and S from the Au@MoS_4^{-2} particles is higher when the gradient is larger and causes an uncontrolled (or partially controlled) quick formation of MoS_2 layers. It can be seen that in this case the MoS_2 layers are not well attached to the AuNPs.

[00105] As for the dependence on annealing time, under the right temperature and temperature gradient (described above), more MoS_2 layers tend to grow on the AuNPs with time (Figure 7A-7B). The appropriate duration for the synthesis of MoS_2 single-layer coated by AuNPs is 30 minutes, longer period of time (>30 minutes) results with multiple layers and a shorter period of time (<30 minutes) is insufficient for complete coating according to this embodiment.

Uniformity of core-shell NPs:

[00106] During the synthesis an extensive concentration of the $(\text{NH}_4)_2\text{MoS}_4$ precursor was used in order to verify that all the AuNPs are covered. Therefore not surprisingly, excess MoS_2 layers engulfing the AuNPs were found, creating double and triple layers instead of one single layer for 30 min annealing. Moreover, some MoS_2 layers and amorphous material were found which occupied some of the inter-particle space. These excess materials can be discerned in most TEM micrographs (see for example Figures 7A-7B).

Characterization of the Au@MoS_2 :

[00107] 1. Electron microscopy:

[00108] The Au@MoS_2 core-shell structure was characterized using electron microscopy. The close-to spherical shape of the Au@MoS_2 particles was confirmed by SEM analysis and can be seen in Figure 8. In those images an agglomerated material can be observed. These aggregates are Au@MoS_2 NPs “glued” together by amorphous material (which contains: a mixture of organic contaminations and excess MoS_2 layers).

[00109] Further investigation of the particles using TEM and HRTEM confirm that the NPs are gold coated with MoS_2 layers. The size of the Au@MoS_2 NPs could be assessed by a statistical analysis (7-13nm). The gold lattice is observed in the central part of the core-shell nanoparticle, while the MoS_2 monolayer is seen only on the contour of AuNPs (Figures 14A, 14B, 15). The engulfing MoS_2 lattice is visible when the e-beam is parallel to the $(hk0)$ zone axis, which conditions are fulfilled on the contour of the core-shell nanoparticles.

[00110] The EDS elemental mapping measurement revealed that indeed the MoS_2 molecules surrounded the entire gold NPs. Thus the STEM images of the layers combined with the EDS analysis, allowed to conclude that the AuNPs were fully coated by MoS_2 layers.

[00111] A further proof for the layered coating was obtained using tomography analysis in STEM. The STEM tomography showed that two and three (2-3) MoS_2 layers can be seen on some of the AuNPs. The STEM tomography images also provide interesting information regarding the

amorphous material component in the inter-particle space of the Au@MoS₂ NPs. In some images fringes of MoS₂ appear in this amorphous material at certain tilt angles. This extra MoS₂ material is not attached to the AuNPs and it makes only a part of the amorphous material.

[00112] Another aspect of the HRTEM is the EELS analysis which enabled to confirm that Mo, S and Au are indeed the sole elements of the Au@MoS₂ NPs. However, using carbon element mapping showed that the organic contaminants are present in the NPs and also in the inter-particles space. This contamination is attributed to residuals of the solvents used for cleaning.

[00113] Aggregation of NPs is widely known. Hence the aggregation of IF-MoS₂ nanoparticles (NPs) was expected. Due to their small size, the NPs tend to have reactive surface (as mention earlier). One type of force, which contributes to the aggregation, is the van der Waals (vdW) interaction, prevalent between each two layers of MoS₂. Additional explanations to the agglomerates can be attributed to the synthesis of the Au@MoS₂ NPs: In some cases the NPs share the same MoS₂-shell (Figure 14A) hence the NPs are “glued” together. In some other cases, the outer surface of the shells possesses an extra layer, which originates from a neighboring NP. This layer adheres to the NP using vdW forces and attaching the two NPs together (Figure 14B). In addition amorphous material (excess MoS₂ layers and organic material) which is present in the inter-particle space hold the two core-shell NPs together.

[00114] In several cases, see Figure 15, the AuNP was covered by the MoS₂ layers, which nevertheless were not “glued” to the AuNP (core within hollow shell material). The detachment of the MoS₂ overlayer from the gold core could be ascribed to the difference in thermal expansion of the two materials. The Au@MoS₄⁻² particle expands during heating and shrinks during cooling, depending on the coefficient of thermal expansion. The gold has larger thermal-expansion coefficient ($\alpha=0.152/^{\circ}\text{C}$) than MoS₂ ($\alpha=1.32\cdot 10^{-5}/^{\circ}\text{C}$). This difference can be responsible for the creation of the particles presented in Figure 15. The possible explanation is that during the heating the Au@MoS₄⁻² particles expanded, at the highest point of expansion the MoS₂ starts to form a shell around the AuNP. As it cools down the AuNP shrinks back to the original size while the MoS₂ shell stays in (almost) the same size without shrinking. In addition or alternatively, it is possible that when the H₂S, S or/and NH₃ are released from the Au@MoS₄⁻², these gasses can be captured between the MoS₂ layer and the AuNP and as a result yields hollow space between the shell and its core. It can be inferred from the formation of this space that the MoS₄⁻² anions are not bound to the gold via a strong chemical bond. However, in other embodiments it may be that strong chemical bond do form between the anions and the nanoparticle.

[00115] 2. Raman:

[00116] Raman measurements can point out the difference between bulk MoS₂ structure and IF-MoS₂ structure. In the literature it can be seen consistently that for E_{2g}(Γ), A_{1g}(Γ), E_{2g}¹(M)+LA(M) and A_{1g}(M)+LA(M) modes there is a shift to lower frequency for IF-MoS₂ NPs compared to the bulk and moreover the shift is bigger as the IF-MoS₂ NPs become smaller. This phenomena is a typical observation in MoS₂ NPs. Exception is the A_{1g}(M)-LA(M) mode, where the peaks shift to higher frequency as the particle are smaller. The signal at 465 cm⁻¹, which can be observed in the bulk material, is a combination of two peaks at 456 cm⁻¹ and 466 cm⁻¹ of the 2×LA(M) mode. This split can be seen at resonance Raman measurement for IF-MoS₂ NPs. Additionally, in IF-MoS₂ NPs new modes, LA(M) and E_{1g}(Γ) at 226 cm⁻¹ and 283 cm⁻¹ respectively, can be seen, which in bulk are not observed.

[00117] Resonance Raman measurements of Au@MoS₂ single-layer NPs have been performed and are presented in Figure 11. The Raman spectrum of the core-shell NP is compared to IF-MoS₂ and bulk-MoS₂ – see Table 1. For A_{1g}(M)+LA(M), E_{2g}(Γ) and A_{1g}(Γ) modes, the peaks of the Au@MoS₂ shifted to lower frequencies compared to the bulk and IF-MoS₂ 20 nm. This observation is expected due to the typical phenomenon for MoS₂ NPs; as the particle become smaller, its spectrum shifts to lower frequency. The shift of the A_{1g}(M)-LA(M) mode to higher frequency has been also observed. The large shift for Au@MoS₂ NPs, compared to IF-MoS₂, could result from the difference in size and number of layers: the reference IF-MoS₂ NPs refers to 20 nm diameter size nanoparticles which contain 15-20 layers while the Au@MoS₂ NPs have smaller diameter (7-13 nm) and mostly contain one or at most two MoS₂ layers. Moreover, the most intensive peak refers to the A_{1g}(Γ) mode. This is not surprising for Au@MoS₂ because this mode is transversal, in which the metal (Mo) atoms rest in equilibrium position and the sulfur atoms oscillate out of phase. As mentioned above, the peak at 465 cm⁻¹ in bulk is attributed to the 2×LA(M) mode and is split into two peaks for MoS₂ NPs. Also for Au@MoS₂ NPs this peak can appear as split, but occasionally only one is observed. In addition, the same trend of shifting to lower frequency can be seen here (2×LA(M) mode). One of the peaks that pointed out the similarity between Au@MoS₂ to IF-MoS₂ is at 222.4 cm⁻¹. This peak refers to the LA(M) mode, which can be observed only in IF-MoS₂ NPs. As expected in this case, this peak also shifts to lower frequency for the core-shell NP, compared to the IF. The main conclusion from this Raman study is that the closed MoS₂ monolayer in the core-shell NP resembles better the IF-MoS₂ and not the bulk. These results are consistent with the idea that the MoS₂ single layer shell has a structure of IF, i.e. folded and closed layer. However, several peaks are missing in the Au@MoS₂ spectrum while new peaks (e.g. at 299.6 cm⁻¹) are observed. These differences emphasize the role of the gold core in the Raman spectrum of the Au@MoS₂ NP.

[00118] 3. UV-Vis absorption:

[00119] The UV-Vis absorption spectra which were taken during the synthesis provided several insights (Figure 12A and Table). First, the sharpness and clarity of AuNPs peak at 517 nm, is indicative of the narrow size distribution of the NPs. The wavelength of this peak fits the SPR wavelength, confirming that the synthesis of the AuNPs was successful. Secondly, immediately after the addition $(\text{NH}_4)_2\text{MoS}_4$, the peak got red shifted and became broader. This probably indicates that there is an interaction between the two precursors. During the 3 days of the reaction the AuNPs were gradually coated by the MoS_4^{-2} anions. This fact can be concluded from the gradual small blue shift. Third, the heating and forming the Au@MoS₂ NPs leads to notable changes in the absorption spectrum. The main observation is the full quenching of AuNPs SPR peak. Coincidentally, a clear dip in the spectrum of the Au@MoS₂ is observed in this wavelength. Moreover, the new absorption peaks appear in higher energies compared to the MoS₂ excitons (Figure 12B). Therefore, it can be conclude that there is an interaction between the SPR of AuNPs and the MoS₂ excitons which we still do not fully understand.

[00120] In one embodiment, the process of forming the uncoated particles prior to coating is done in solution. In one embodiment, a solution containing a positive metal ion is placed under conditions in which the metal ion is reduced to the metal atom. In one embodiment, the solution contains a reduction agent. In one embodiment, metal atoms join together to form a particle. In one embodiment, addition of metal atoms to the particle increases the size of the particle. In one embodiment, when growing particles get in contact with one another, they can bind to one another. In one embodiment, this process results in clusters or aggregates of particles. In one embodiment, clusters of particles grow by addition of particles to the cluster. In one embodiment clusters may grow as a result of the growth of individual particles within the cluster.

[00121] In one embodiment, nanoparticle synthesis is carried out using an aqueous solution of a gold salt. In one embodiment, the gold salt is $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. In one embodiment, a reducing agent is added to the solution. In one embodiment, the reducing agent is NaBH_4 . In one embodiment, the solution is refrigerated overnight to allow the nanoparticles to precipitate. In one embodiment, the solution is filtered and rinsed with water and/or with organic solvents.

[00122] In another embodiment, in processes of this invention, the choice of the solvent(s) in which the process is carried out may influence the surface, the particle or coating characteristics. In one embodiment, particle size, surface features, coating uniformity or coating density is affected by the choice of solvent, or by concentrations of solutes in the solvent, or concentration of particles present, or concentration of precursors used, or a combination thereof.

[00123] In one embodiment the temperature, reaction time, solution pH or additives included in the reaction mixture may influence surface characteristics, nanoparticle characteristics or coating characteristics as will be appreciated by one skilled in the art.

In one embodiment, coated or un-coated particle collection is accomplished by drying. In one embodiment, particle collection is obtained by evaporation of the solvent from the solution. In one embodiment collection of particles is done by precipitation of particles from the solution. In one embodiment particle collection is accomplished by separating the particles from the solution. In one embodiment the solution is separated from the precipitated particles by pouring, rinsing or filtering, centrifuging, decanting. In one embodiment, particles are kept in solution for further use. In one embodiment, keeping particles in solution prevents or inhibits aggregation. In one embodiment, keeping particles in solution increases the stability of the particles. In one embodiment, keeping particles in solution renders the particles ready-to-use for various applications.

III. Compositions/kits comprising the particles and clusters of the invention

[00124] In one embodiment, this invention provides a composition comprising the coated nanoparticles of this invention.

[00125] In one embodiment, such composition may be utilized in multiple applications, for example, in electronics, optical devices or electro-optic devices. In one embodiment the composition is employed for catalysis of chemical reactions. In one embodiment, the composition is employed in separation of chemicals from oil, gas, water, soil or air. In one embodiment, the composition is used as a lubricant. In one embodiment, compositions including coated particles of this invention are used as filler materials, coating materials, support materials or a combination thereof. In one embodiment, compositions including coated particles of this invention enhance the mechanical properties, the electronic properties and/or the optical properties of materials in which they are included.

[00126] In one embodiment the composition including particles of this invention are in a liquid form. In one embodiment the composition are in a solid form.

[00127] In one embodiment, nanoparticles and clusters of this invention are supported on a substrate. In one embodiment, nanoparticles of the invention are supported within the pores of a porous material. In one embodiment, nanoparticles of this invention are packed into a column. In one embodiment, nanoparticles of this invention are used in solution. In one embodiment, nanoparticles of this invention are colloids. In one embodiment, nanoparticles of this invention are used in the form of a suspension, a colloidal solution, a dispersion, a two phase system, or as a layer floating on a surface of a liquid/solution. In one embodiment, the nanoparticles precipitate to the bottom of a solution, and are used in this way. In one embodiment, this invention comprises a kit comprising coated nanoparticles of this invention. In one embodiment, the kit further comprises

solutions, liquids, solids, apparatuses for mixing/stirring, heating/cooling systems, filters, measurement tools, measurement systems, containers/vessels and any other component/element that enables the use of a kit of this invention.

IV. Methods of use of nanoparticles and clusters of this invention

[00128] In some embodiments, nanoparticles or clusters of this invention may be used for enforcing a material. In one embodiment, nanoparticles or clusters of this invention may be used for coating or filling a material. In one embodiment, nano particles or clusters of this invention may be used in mixtures containing other materials. In one embodiment, particles/clusters of this invention may be used in products such as metal, wood, paper, polymers, ink and paint. In one embodiment, particles/clusters of this invention may be used with compositions containing herbicides or insecticides or precursors thereof. In one embodiment, particles/clusters of this invention may be used with compositions containing explosives or precursors thereof.

[00129] In one embodiment, this invention provides coated nanoparticles that are attached to organic moieties. In one embodiment the organic-nanoparticle structures of this invention may find application as a filler or coating for paper, plastics, inorganic or metallic materials or substrates. In one embodiment mixing the complex nanoparticles-organic structure with paper, polymeric or a metal substrate enhances the mechanical properties of the material/substrate.

[00130] In one embodiment, this invention provides use of the nanoparticles of this invention as optical or electrical elements in an optical device, in an electronic device or in an opto-electronic device. In one embodiment, this invention provides use of the nanoparticles of this invention as a lubricant. In one embodiment, this invention provides use of the nanoparticles of this invention in pharmaceuticals, in medical devices, in therapy. In one embodiment, this invention provides use of the nanoparticles of this invention in catalysis.

[00131] In one embodiment, in processes of this invention, control over the synthesis is achieved with respect to the number of layered-compound layers coating the nanoparticle. In one embodiment, in processes of this invention, control over the synthesis is achieved with respect to the size and shape of the nanoparticle. In one embodiment, in processes of this invention, the optical properties of the coated nanoparticles are controlled and can be modified using different particle material, different layered-compound coatings, number of coating layers, size and shape of the particle etc. Absorption and luminescence characteristics of multiple layer and of single layer coated Au@MoS₂ core-shell NPs of this invention are some of the interesting optical properties associated with particles of this invention in one embodiment. In one embodiment, enhancement due to surface plasmon resonance is exhibited by particles of this invention.

[00132] In one embodiment, other layered-compound coated nanoparticles are prepared by processes of this invention. For example, nanoparticles comprising or consisting of Ag or Se are coated by TMD such as VS₂ or WS₂. In one embodiment, coated nanoparticles of this invention comprise other combinations of materials.

[00133] In one embodiment, processes of this invention further comprise elimination of the metal (e.g. gold) core. Such process step allows the formation of a single-layer hollow MoS₂ fullerene structure, or the formation of a hollow structure comprising a few layers of a layered compound.

Definitions:

[00134] An inorganic layered compound is a term known in the art for inorganic compounds capable of being arranged in layers, forming two-dimensional sheets. The atoms within each layer are held together by strong chemical bonds (e.g. covalent bonds), while the forces holding two layers together are weak van der Waals forces. Inorganic Layered compounds include the metal chalcogenides, a group of materials comprising at least one metal and an element from the chalcogenide group, e.g. S, Se, Te.

[00135] The sign “@” in the context of this invention is used to describe the core/shell particles of this invention such that C@S means that C is the core and S is the shell of the nanoparticle, i.e. the term preceding the sign “@” describes the core of the nanoparticle and the term that follows the “@” sign is the term that describes the shell of the particle.

[00136] In some embodiments, metal dichalcogenide is referred to as metal chalcogenide in short. In some embodiments, dichalcogenide is referred to as chalcogenide in short.

[00137] In one embodiment, “fullerene-like” structure means a structure that resembles the structure of a carbon fullerene. The “fullerene-like” structure is meant to describe the structure of a material that is made of other elements (not carbon), but is similar in the structure to fullerene. The term fullerene-like” structure is used as no specific name is available in the scientific literature to describe such structures. The name “fullerene-like” structure is understood in the context of layered materials by any person of ordinary skill in the art. The term fullerene-like refers to a folded and closed-layer form of the structure described. The term “fullerene-like” is commonly used in the literature of inorganic layered compounds.

[00138] In one embodiment, the nanoparticles of this invention that are coated by 1 or more layers of an inorganic layered compound are referred to as “hybrid nanoparticles”. “Hybrid nanoparticles” is a term used for nanoparticles consisting of more than one material.

[00139] In one embodiment, in coated particles of this invention, the coated nanoparticle comprises a nanoparticle and a coating of this nanoparticle, the coating comprising 1-5 layers of an

inorganic layered compound. Coating of the nanoparticle means in some embodiments that the particle is covered, contained, engulfed, surrounded, enclosed within/by the coating.

[00140] In one embodiment, precursor is one material that is used to prepare another material. In one embodiment, a precursor is a material that is consumed in the synthesis of another material. In one embodiment, a precursor comprises one or more of the elements that are present in the material that results from a process utilizing the precursor. A precursor is a reactant in a process that yields a certain product in some embodiments. The term precursor in the context of this invention is known to the skilled artisan.

[00141] In one embodiment, the term “a” or “one” or “an” refers to at least one. In one embodiment the phrase “two or more” may be of any denomination, which will suit a particular purpose. In one embodiment, “about” or “approximately” may comprise a deviance from the indicated term of + 1 %, or in some embodiments, - 1 %, or in some embodiments, ± 2.5 %, or in some embodiments, ± 5 %, or in some embodiments, ± 7.5 %, or in some embodiments, ± 10 %, or in some embodiments, ± 15 %, or in some embodiments, ± 20 %.

EXAMPLES

EXAMPLE 1

Synthesis of gold-molybdenum disulfide (Au@MoS₂) core-shell nanoparticle

[00142] 1. *Synthesis of Au nanoparticles:*

[00143] Gold NPs were synthesized using a known method. The gold NPs were synthesized using a 20 mM solution of Gold(III) chloride trihydrate (SIGMA-ALDRICH). In a 100 ml flask, 56.5 ml double distilled water (DDW) and 1 ml gold(III) chloride trihydrate solution (2×10^{-5} mol, made 3.478×10^{-4} M) were mixed. To this mixture, 5.5 ml of sodium borohydride (NaBH₄, Fluka Analytical) (0.014 M, 8×10^{-5} mol, 3.026 mg dissolved in water) was gradually added dropwise (1 drop every 3 seconds) and vigorously stirred for 1.5 hours. Following the addition of NaBH₄, the gold yellow solution turned red.

[00144] 2. *Coating of Au nanoparticles by MoS₂:*

[00145] To the gold nanoparticles (AuNPs) an aqua solution of ammonium tetrathiomolybdate ((NH₄)₂MoS₄, SIGMA-ALDRICH) was added (6×10^{-5} mol, 15.6 mg, 1.844 mM). The solution was stirred overnight and the color turned to purple-brown color.

[00146] Following this procedure the solution was centrifuged at 6000 RPM for 60 minutes. The precipitates were placed in a quartz ampoule (12 mm o.d.). The ampoule was then dried at 50 °C under vacuum conditions until complete dryness and sealed under a vacuum of 3×10^{-5} Torr. The

lower edge (with the precipitates) of the sealed ampoule was heated at 516 °C while the other edge was kept at 428 °C producing a gradient of 88 °C.

[00147] Results: Occasionally, the precipitation of the material was difficult; therefore an evaporation of the solvent on a stirring hot-plate was necessary. Due to the evaporation, the color of the solvent changes from purple to blue. Figure 1 demonstrates the material before the heating step. The AuNPs are aggregated and a layer of MoS₂ is being formed on its surface. The size of the AuNPs was 7-13 nm (Figure 3A). This synthesis results with almost identical spherical nanoparticle in size.

Stability of the coated NPs-time dependence:

[00148] It was found that duration of the mixing of solution of the AuNPs suspension with (NH₄)₂MoS₄ has an important consequence on the end product. The AuNPs and (NH₄)₂MoS₄ solution was mixed for a week during which samples were taken frequently. During the first ~72 hours, no drastic effect was observed (Figure 2A, 2B). After 7 days of mixing, the solution of the NPs started to show signs of degradation; the AuNPs were no longer covered with MoS₂ and large chunks of isolated MoS₂ crystallites were observed (Figure 2C, 2D).

Dependence on the ratio of Au(III) and MoS₄⁻² precursors:

[00149] In order to assure that all the AuNPs will be coated with MoS₂, the ratio of HAuCl₄ and (NH₄)₂MoS₄ precursors remained 1:3 (respectively) during most of the syntheses. In an attempt to reduce the excess MoS₂ layers on the AuNPs and the surrounding, the concentration ratio of Au(III) and MoS₄⁻² anions were changed to 1:2. Using the new ratio (1:2) in the synthesis made the precipitation of the NPs quite difficult. Thus in order to retrieve the NP's the solvent was evaporated in order to continue the process. The result show that the formation Au@MoS₂ NPs is not homogeneous in size, the AuNPs are qualitatively covered with MoS₂ single-layer but excess layers of MoS₂ still exist (Figure 3A-3B).

Temperature dependence

[00150] Synthesis of Au@MoS₂ core-shell single-layer requires full control over the ampule's temperature during the heating. Such control is obtained by heating the edges of the ampule in two different temperatures, shown schematically in Figure 4. The ampule contains the precipitate on one edge while the other edge is empty.

[00151] Before understanding that full control over the ampule's temperature must be obtained, attempts were made to synthesize the Au@MoS₂ single-layer by heating the edge containing the material alone. As demonstrated in Figure 5A, heating the edge which contains the precipitate at a low temperature of 400 °C does not support the synthesis of the MoS₂ coating layer. The MoS₂

layer starts to appear at higher heating temperatures; in a temperature of 528 °C the MoS₂ layers are poorly attached to the AuNPs and most of the monolayers are separated from the AuNPs (instead of coating them) (Figure 5B). i.e. the synthesis of MoS₂ single-layer on AuNPs at high temperature (528 °C) is un-controlled. However, heating the edge of the ampoule which contains the precipitation to an intermediate temperature (between 400-528 °C) results in the formation of MoS₂ single-layer that attach to the AuNPs (Figure 5C).

[00152] Heating the ampule at the precipitate edge is not sufficient to maintain good control of the synthesis. In order to form the MoS₂ single-layer structure, a gradient temperature should be formed between the two sides of the ampule. Hence the opposite edge of the ampule (which does not contain the precipitate- the “empty edge”) is also heated to create a fine control over the temperature gradient.

[00153] Two different end products, synthesized under different temperature profiles (between the two edges of ampoule) are presented in Figure 6A-6B. The edge with the precipitate was heated to 516 °C while the empty edge was heated to a different temperature (428 °C and 450 °C). Synthesis under larger gradient (the empty edge was not heated at all), resulted, as mentioned before, with not full covering of the AuNPs. Decreasing the gradient temperature of 88 °C, resulted with a MoS₂ covering the entire AuNPs outer surface. Further decrease in the gradient, again showed a poor coverage of the MoS₂ on the AuNPs.

Time dependence:

[00154] In order to have a better control over the synthesis, heating durations were extended a few times until proper results were obtained. Heating the ampule (at optimal temperature) for 30 minutes resulted with the desirable condition for MoS₂ single-layer coating of the AuNPs (Figure 7A). It can be clearly seen that when the heating time is extended to 40 minutes, a larger number of MoS₂ layers appear around the AuNPs (Figure 7B).

EXAMPLE 2

Au@MoS₂ nanoparticle characterization

[00155] 1. *Electron microscopy:*

[00156] Characterization of the nanoparticles was done using JOEL JEM-2100 transmission electron microscope (TEM) operating at 200kV equipped with an energy-dispersive X-ray spectroscopy (EDS) detector for chemical analysis and Thermo Scientific UltraDry EDS Detector.

[00157] High-resolution transmission electron microscopy (HRTEM) imaging was achieved with an FEI Tecnai F30-UT with a field-emission gun operating at 300 kV. The microscope is

equipped with a parallel electron energy loss spectroscopy (EELS) detector (Gatan imaging filter, GIF; Gatan).

[00158] ChemiSTEM 60-200 kV (ER-C Juelich) was used for high-angle annular dark field (HAADF) analysis and elemental mapping with Super-X large solid angle EDS detector. This instrument has double hexapole probe aberration corrector, which made it high beam current density. This TEM is equipped with 4 detectors of EDS detectors which are placed symmetrically around the sample with small take up angle, allowing high throughput analysis.

[00159] For atomic resolution analysis, a probe aberration-corrected FEI Titan 50-300 PICO TEM operating at 80 kV was used.

[00160] Using an FEI Tecnai F20 scanning transmission electron microscope (STEM), operating at 200 kV with variable tilt angle from -60 degrees to 60 degrees, tomography of nanoparticle was accomplished.

[00161] Additionally, Carl Zeiss ULTRA 55 high-resolution scanning electron microscope (HR-SEM) has been used. The sample was sitting on silicon wafer and detect by InLens detector.

[00162] *1.1 Scanning Electron microscopy (SEM):*

[00163] Figure 8 shows that the Au@MoS₂ NPs are spherical and of relatively uniform size (7-13 nm). The NPs seems to adhere to amorphous material. This amorphous material can be residual MoS₂ and organic contamination.

[00164] Acquiring high magnification images was not possible due to beam damage which resulted in destruction of the particles under the electron current.

[00165] *1.2 TEM and HRTEM:*

[00166] Further investigation of the materials was done using TEM and HRTEM. Those microscopes enabled us to monitor the accurate syntheses conditions and to determine the structure of the layer, the size distribution of NPs and detailed structural analysis of the Au@MoS₂ single-layer core-shell NPs.

[00167] *1.3 Tomography analysis:*

[00168] In TEM measurements, due to limitations in seeing the MoS₂ on the AuNP area, it is difficult to prove that the AuNPs is fully coated with MoS₂. Therefore, using STEM-tomography method which provides a 360° degrees (3D) image of Au@MoS₂ NPs is preferable. In order to get a 3D image, 60 STEM images of the same particle were made while the sample was tilted from -60 degrees to 60 degrees with interval of 2°. This observation of the 3D image clearly demonstrated that the AuNPs is fully covered by at least one layer of MoS₂. In some angles it can be seen that there is more than one layer of MoS₂ on the same particle (although the particle is mostly covered by a single-layer). Additionally, there is an amorphous material which occupies some of the inter-

particle space. In some tilt angles the zone-axis of the material in the inter-particle space in parallel to the e-beam (see Figure 2B). The image in this situation clearly shows that the inter-particle material is in fact MoS₂, which is not surprising given the chemical reaction.

[00169] 1.4. EELS:

[00170] A graph of electron energy loss spectroscopic (EELS) which analyzes the Au@MoS₂ NPs can be seen in Figure 10A. The sample is exposed to the electron beam, in the electron microscopy, at a known and narrow range of kinetic energy. The electrons undergo inelastic scattering therefore they lose energy; this interaction can lead to inner-shell ionization (K, L, M). The energy loss provides the specific elemental composition of the NP. This analysis indicates that the elements comprising the NPs are gold, molybdenum and sulfur. However, this analysis is not fully quantitative and suggests a tentative composition, only.

[00171] Mapping of the same area was done repeatedly for different element (shown in Figure 10B-10F). This elemental mapping shows that gold, molybdenum and sulfur are present in the NPs. On top of that carbon can be seen both in places with and without the NPs. Additionally, this mapping provides us an explanation for the amorphous material which surrounds the NPs, most of it is made from an organic material.

[00172] 2. Raman

[00173] Raman spectroscopy was carried-out using a Horiba-Jobin Yvon (Lille, France) LabRAM HR Evolution using HeNe laser with a wavelength of 632.8 nm. The instrument was equipped with Olympus objectives: MPlan N 100 × NA 0.9 and MPlan N 50 × NA 0.75. The measurements were conducted using a 300 gr/mm grating with spectrograph with focal length of 80 cm. Each spectrum was acquired for 20 seconds and averaged 100 times, which enabled the use of low excitation power to preserve the sample integrity. The spectral range collected was from 100 cm⁻¹ to 1000 cm⁻¹.

[00174] Results, Raman analysis:

Table 1: Resonance Raman peaks of Au@MoS₂ NPs compared to literature values. Light source-He-Ne laser (632.8 nm)

Au@MoS ₂ [cm ⁻¹]	Lit. IF-MoS ₂ nm [cm ⁻¹]	20	Lit. bulk MoS ₂	Symmetry assignment
183.7	179		177	A _{1g} (M)-LA(M)
222.4	226			LA(M)
	248			
	283			E _{1g} (Γ)

299.6			
375.3	378	382	$E_{2g}(\Gamma)$
401.6	406	407	$A_{1g}(\Gamma)$
431.8	week	421	
447.4	452	465	$2xLA(M)$
		526	$E_{1g}(M)+LA(M)$
	543		
	563	572	$2xE_{1g}(\Gamma)$
	593	599	$E_{2g}^1(M)+LA(M)$
626.5	633	641	$A_{1g}(M)+LA(M)$
669.1			

[00175] Resonance Raman measurement on bulk-MoS₂ and IF-MoS₂ structures was reported in the literature. The main differences between the Raman spectra of the two structures are the frequency shift, broadening of the peaks and observation of a new mode in IF-MoS₂ NPs. The low frequency mode at $\sim 178\text{ cm}^{-1}$ can be assigned to the $A_{1g}(M)$ -LA(M) mode. For IF-MoS₂ 20 nm NPs this mode is red-shifted. Moreover, a two new modes for IF-MoS₂ are observed, LA(M) in 226 cm^{-1} and $E_{1g}(\Gamma)$ in 283 cm^{-1} . The LA(M) (second order) mode is blue shifted for the smaller NPs compared to the bulk crystal. The main peaks are 382 cm^{-1} , 407 cm^{-1} which are assigned to the $E_{2g}(\Gamma)$ and $A_{1g}(\Gamma)$ modes, respectively; these modes are shifted to lower energies for IF-MoS₂ NPs. Additionally to those peaks, another intensity peak appears at 465 cm^{-1} . This mode is attributed to the combination of the second order $2xLA(M)$ mode which is split into two peaks, at 456 cm^{-1} and 466 cm^{-1} . This split can be seen (abundantly) in the Raman spectra of IF-MoS₂ NPs. In the higher frequency region, one finds the $E_{1g}(M)+LA(M)$ mode which can be seen only in bulk-MoS₂ at 526 cm^{-1} ; and $E_{2g}^1(M)+LA(M)$ and $A_{1g}(M)+LA(M)$ modes at 599 cm^{-1} and 641 cm^{-1} (respectively) which again are blue shifted for the IF-MoS₂ NPs.

[00176] Table 1 summarizes the results of the Raman spectroscopy. The Au@MoS₂ spectrum is compared to that of (20 nm) IF-MoS₂ and bulk MoS₂ as a reference. It can be clearly seen that the spectrum of the Au@MoS₂ particles are closer to that of IF-MoS₂ than to the bulk. Au@MoS₂ particles' signals is shifted to lower energy by $4\text{--}5\text{ cm}^{-1}$, compared to the 20 nm IF-MoS₂ particles, except for two situations: 1. $A_{1g}(M)+LA(M)$ state which shifts by 10 cm^{-1} compared to IF-MoS₂ and; 2. $A_{1g}(M)$ -LA(M) state which shifts to higher energy. The most intensive peak was observed at 407 cm^{-1} which correspond to the $A_{1g}(\Gamma)$ mode. Moreover, a peak at 222.4 cm^{-1} can be attributed to LA(M) mode which can be observed only in IF-MoS₂ NPs. Additionally, at 299.6 cm^{-1} , a strong

peak was observed which does not appear in the literature, as well as the peak at 669.1 cm^{-1} . The peak at 520 cm^{-1} comes from the Si substrate.

[00177] Figure 20 represents Normalized low frequency Raman (stokes) spectrum of the shear mode measured on bulk 2H-MoS₂ (top curve) and Au@1L-MoS₂ core-shell NP (bottom curve);

[00178] 3. Absorption

[00179] UV-Vis absorption measurements were carried out on a Cary-5000 spectrometer. The sample was added to the water and sonicated for ~1 min using ultrasonic bath. All the measurements used quartz cuvettes.

Table 2: Main UV-Vis peaks of the NPs at different stages of the synthesis

Material	Main peaks [nm]
AuNPs	517
Au@MoS ₄ ⁻² , immediately after adding (NH ₄) ₂ MoS ₄ (t=0)	562
Au@MoS ₄ ⁻² , after 3 days of mixing with (NH ₄) ₂ MoS ₄ (t=3 days)	543
Au@MoS ₂	403, 625

[00180] Figure 12A and Table 2 provide initial results of Au@MoS₂ optical absorption during the synthesis. The AuNPs plasmon peak at 517 nm (Figure 12A) is sharp and clear. Adding (NH₄)₂MoS₄ precursor to the AuNPs leads the peak to red shift. Immediately after adding (NH₄)₂MoS₄ the peak shifts to 562 nm (Figure 12A), but after 3 days of mixing the peak shifts to 543 nm (Figure 12A). According to the synthesis, the last step is heating and attainment of the end material Au@MoS₂. This material presents two main peaks, at 403 nm and 625 nm (Figure 12A) and a dip at 520 nm coinciding with the main scattering peak of the AuNPs.

[00181] The AuNPs and Au@MoS₂ curves are compared to the 2H-MoS₂ (bulk) and 1T-MoS₂ from Yadgarov, L. *et al.* ACS nano 2014, 8, 3575. This comparison is presented in Figure 12B. The A and B excitons of MoS₂ (~580 nm and ~650 nm) are accentuated in the spectra of 2H-MoS₂ and 1T-MoS₂. It can be clearly seen that the Au@MoS₂ presents a very different spectrum with a dip where the AuNPs shows a maximum due to plasmon scattering (absorption). Another absorption spectrum is shown in Figure 17.

[00182] 4. Luminescence

[00183] Figure 18 shows luminescence spectrum for the Au@MoS₂ coated particles. The luminescence provides an evidence for the formation of a single MoS₂ monolayer around the gold

particles. This is because uncoated gold nanoparticles do not luminesce, and MoS₂ does not luminesce unless it is a monolayer.

EXAMPLE 3

Synthesis and characterization of gold tungsten disulfide (Au@WS₂) core-shell nanoparticles

[00184] 1. *Synthesis of Au nanoparticles:*

[00185] Gold NPs were synthesized using a known method. The gold NPs were synthesized using a 20 mM solution of Gold(III) chloride trihydrate (SIGMA-ALDRICH). In a 20 ml flask, 14.75 ml double distilled water (DDW) and 250 μ l gold(III) chloride trihydrate solution (5.2×10^{-6} mol) were mixed. To this mixture, 693.35 μ l of sodium borohydride (NaBH₄, Fluka Analytical) (0.030 M, 2.087×10^{-5} mol) was gradually added dropwise (1 drop every 3 seconds) and vigorously stirred for 1.5 hours. Following the addition of NaBH₄, the gold yellow solution turned red. This reduction process is known for a long time in the literature.

[00186] 2. *Coating Au nanoparticles by WS₂:*

[00187] An aqua solution of ammonium tetrathiotungstate ((NH₄)₂WS₄, SIGMA-ALDRICH) was added (1.56×10^{-5} mol, 5.45 mg) to the gold nanoparticles (AuNPs). The solution was stirred overnight and the color turned to purple-brown color.

[00188] Following this procedure the solution was centrifuged at 6000 RPM for 60 minutes. The precipitates were placed in a quartz ampoule (12 mm o.d.). The ampoule was then dried at 50 °C under vacuum conditions until complete dryness and sealed under a vacuum of 3×10^{-5} Torr. The lower edge (with the precipitates) of the sealed ampoule was heated at 516 °C or at 529 °C while the other edge was kept at 428 °C producing a gradient of 88 °C.

[00189] Figures 16A-16C shows TEM images of Au@WS₂ coated nanoparticles. The samples were heated at different temperatures: Figure 16A) 529 °C for 30 minutes; Figure 16B) 516 °C for 40 minutes; and Figure 16C) 516 °C for 30 minutes.

[00190] It is important to note that although Au@1L-WS₂ NP were also obtained (19), their synthesis was not yet optimized and consequently the yield is rather low (5%). In the figures, WS₂ monolayer is seen as a dark fringe on the contour of the NPs and the gold lattice is clearly observed in the center.

[00191] While certain features of the invention have been illustrated and described herein, many modifications, substitutions, changes, and equivalents will now occur to those of ordinary skill in

the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

CLAIMS

What is claimed is:

1. A coated nanoparticle comprising:
 - a nanoparticle; and
 - a nanoparticle coating comprising 1-5 layers of an inorganic layered compound.
2. The coated nanoparticle of claim 1, wherein said coating comprising 1 layer.
3. The coated nanoparticle of claim 1, wherein said nanoparticle comprises an inorganic material, an organic material or a combination thereof.
4. The coated nanoparticle of claim 3, wherein said inorganic material comprises a metal, a semi-metal, a non-metal, a compound comprising a metal and a non-metal, or a combination thereof.
5. The coated nanoparticle of claim 4, wherein said metal is selected from the group consisting of Au, Ag, Cu, Pd, Ru, Rh, Ir or a combination thereof.
6. The coated nanoparticle of claim 4, wherein said compound comprising a metal and a non-metal elements, is selected from the group consisting of CdS, CdSe, CdTe, GaAs, GaN, AlAs, InAs, TiO₂, CeO₂, ZnO, SiO₂, Al₂O₃ or a combination thereof.
7. The coated nanoparticle of claim 1, wherein the form of said nanoparticle is a sphere, a rod, an ellipsoid, or a non-symmetrical shape.
8. The coated nanoparticle of claim 1, wherein the size of the longest dimension of said nanoparticle ranges between 1 nm and 1000 nm.
9. The coated nanoparticle of claim 8, wherein said size ranges between 1 nm and 100 nm.
10. The coated nanoparticle of claim 1, wherein said inorganic layered compound comprises a transition metal chalcogenide.
11. The coated nanoparticle of claim 10, wherein said transition metal chalcogenide comprises MoS₂, WS₂, MoSe₂, WSe₂, NbS₂, NbSe₂, TaS₂, TaSe₂, ZrS₂, ZrSe₂ or InS, InSe, GaS, GaSe.
12. The coated nanoparticle of claim 1, wherein said nanoparticle is a gold nanoparticle, said inorganic layered compound is MoS₂ and the number of coating layers is 1.
13. A process for preparing a coated nanoparticle, said process comprising:
 - providing or forming nanoparticles;
 - adding a solution comprising a coating precursor to said nanoparticles;
 - mixing said solution.

14. The process of claim 13, wherein following said mixing step, said solution is centrifuged, thus forming a precipitate.
15. The process of claim 14, wherein said precipitate of said centrifuge step is dried.
16. The process of claim 15, wherein said drying is conducted at an elevated temperature, under vacuum conditions or a combination thereof.
17. The process of claim 16, wherein said elevated temperature is $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$.
18. The process of claim 16, wherein following said drying, said precipitate is placed in a portion of an ampoule proximal to a first edge of said ampoule, and wherein said precipitate is sealed in said ampoule under vacuum and is subjected to heating.
19. The process of claim 18, wherein said heating comprises a heating gradient.
20. The process of claim 19, wherein said heating gradient comprises heating said first edge of said ampoule to a first temperature and heating a second edge of said ampoule to a second temperature, thus creating a temperature gradient along the ampoule between said edges.
21. The process of claim 20, wherein said first temperature is $516^{\circ}\text{C} \pm 15^{\circ}\text{C}$, and wherein said second temperature is $428^{\circ}\text{C} \pm 15^{\circ}\text{C}$.
22. The process of claim 18, wherein said vacuum is 3×10^{-5} torr.
23. The process of claim 13, wherein said precursor is an ionic compound.
24. The process of claim 23, wherein said ionic compound is $(\text{NH}_4)_2\text{MoS}_4$.
25. The process of claim 13, wherein said nanoparticles are made of metal.
26. The process of claim 25, wherein said nanoparticles are gold nanoparticles.
27. The process of claim 13, wherein said solution mixing step comprising stirring.
28. The process of claim 13, wherein said mixing step is conducted for a period of time ranging between 1h to 5 days.
29. The process of claim 28, wherein said period of time ranges between 6 hours and 20 hours.
30. The process of claim 13, wherein said process is conducted at room temperature.
31. The process of claim 13, wherein said forming of said nanoparticles comprises:
 - providing a solution comprising a nanoparticle precursor;
 - adding a reactant to said solution;
 - mixing said solution.
32. The process of claim 31, wherein said nanoparticle precursor comprises an ionic compound.
33. The process of claim 32, wherein said ionic compound comprises a metal cation and a halogen anion.
34. The process of claim 32, wherein said ionic compound is gold(III) chloride trihydrate.
35. The process of claim 31, wherein said reactant is a reducing agent.

36. The process of claim 35, wherein said reducing agent is sodium borohydride (NaBH_4).
37. The process of claim 22, wherein said mixing is conducted for a period of time ranging between 0.50 hours and 6 hours.
38. The process of claim 31, wherein said process is conducted at room temperature.
39. The process of claim 31, wherein said reactant is added gradually to said nanoparticle precursor solution.
40. A process for preparing the coated nanoparticle of claim 1, said process comprising: atomic layer deposition (ALD), successive ionic layer adsorption and reaction (SILAR) or solvothermal methods.
41. A powder comprising the coated nanoparticles of claim 1.
42. A composition comprising the coated nanoparticles of claim 1.
43. An optical device, an electronic device or an opto-electronic device comprising the coated nanoparticles of claim 1.
44. A lubricant comprising the coated nanoparticles of claim 1.
45. Use of the coated nanoparticles of claim 1 in therapy.
46. A catalyst comprising the nanoparticles of claim 1.

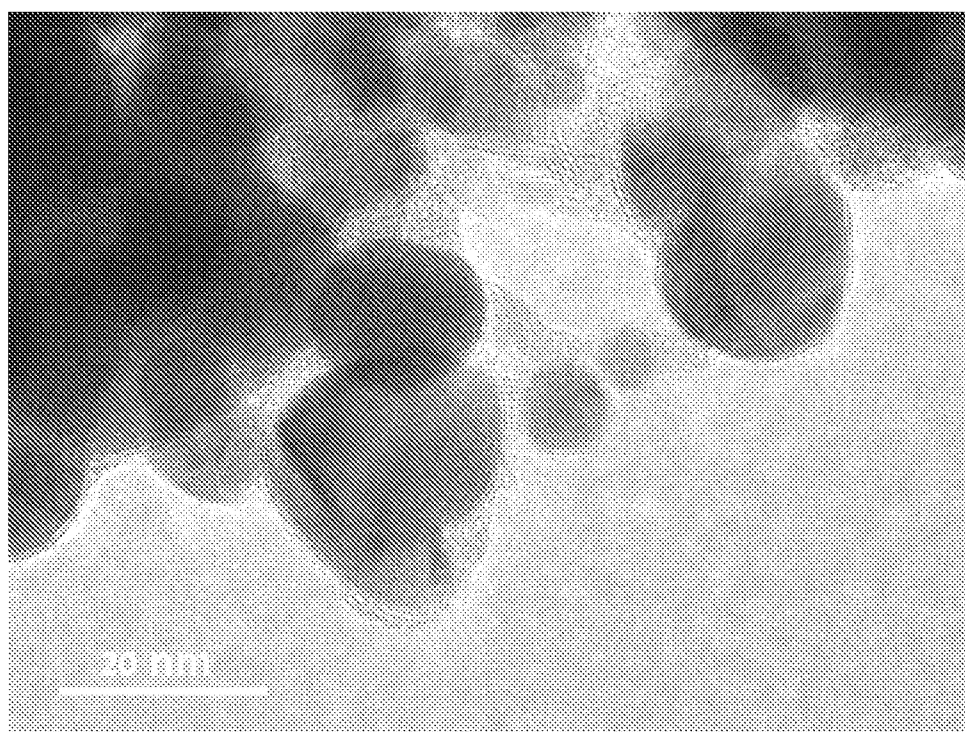
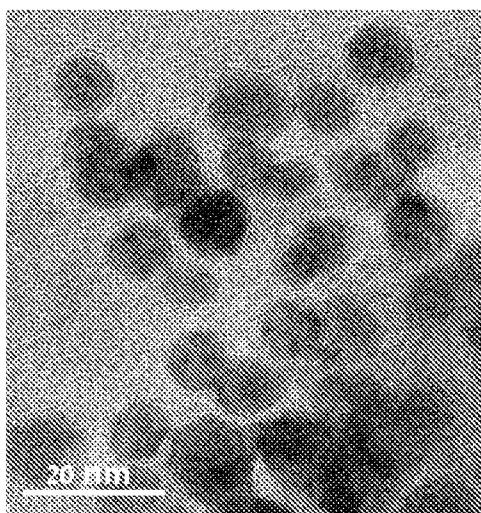
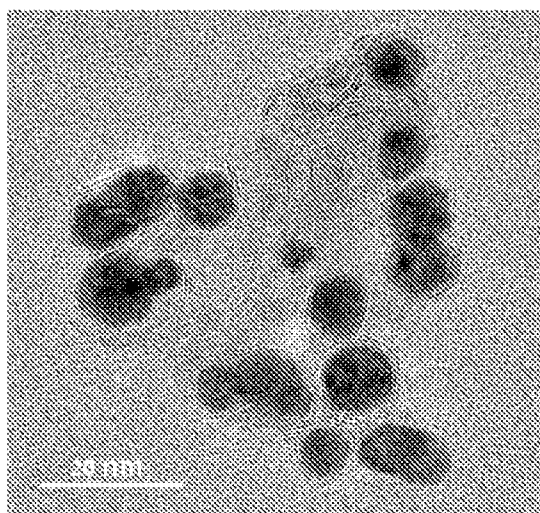
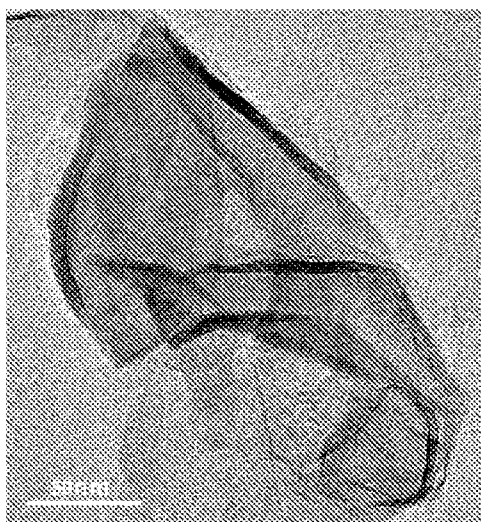
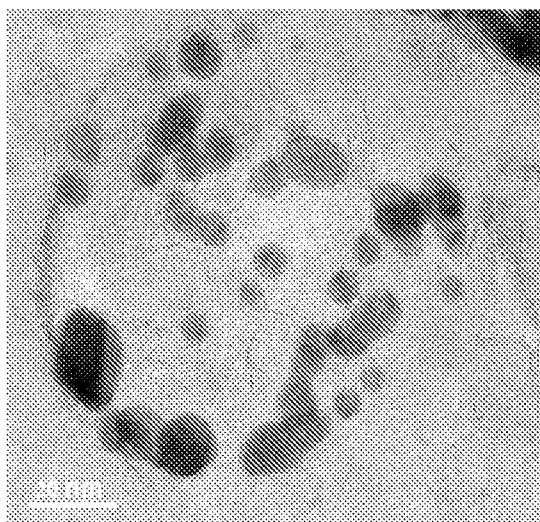


FIGURE 1

**FIGURE 2A****FIGURE 2B****FIGURE 2C****FIGURE 2D**

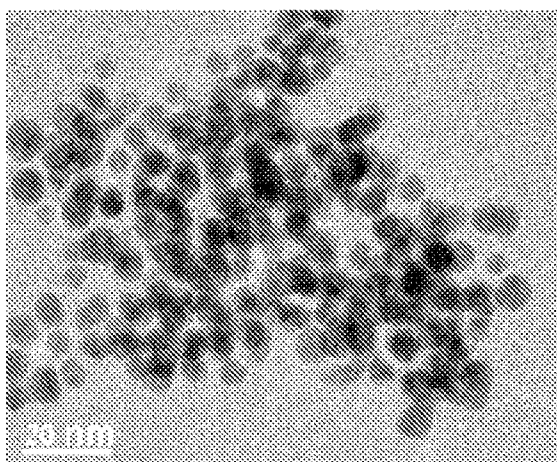


FIGURE 3A

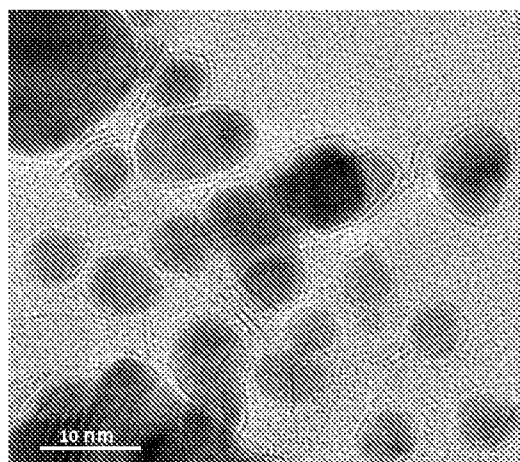


FIGURE 3B

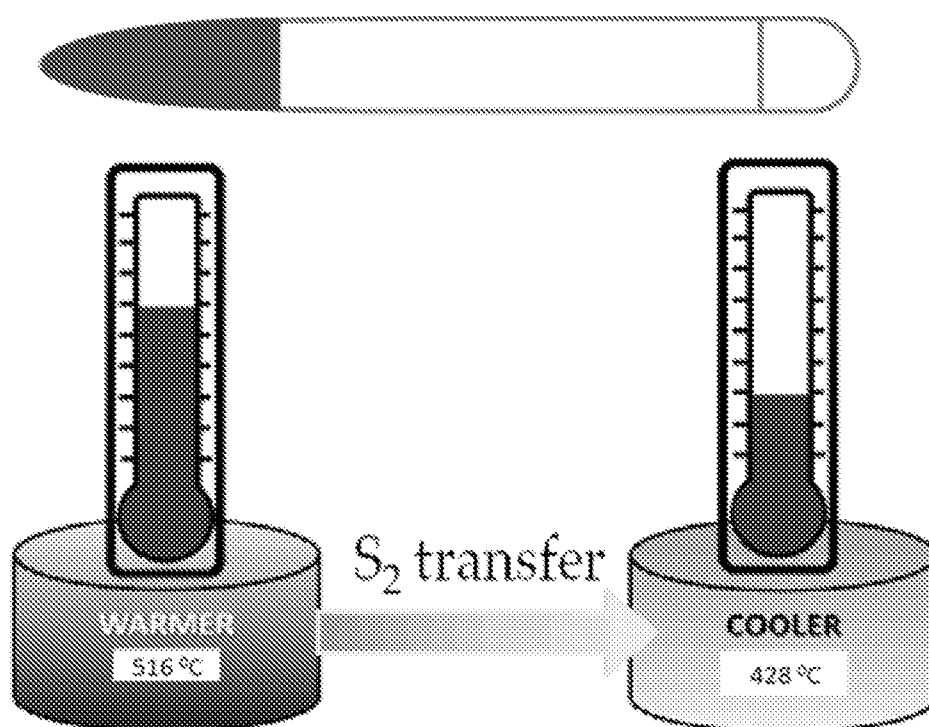


FIGURE 4

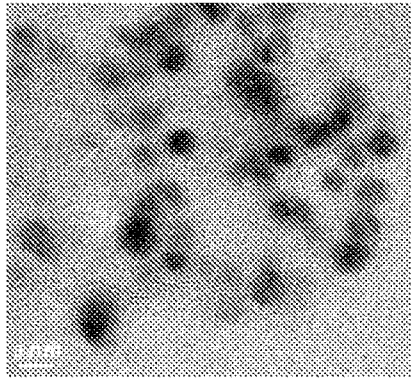


FIGURE 5A

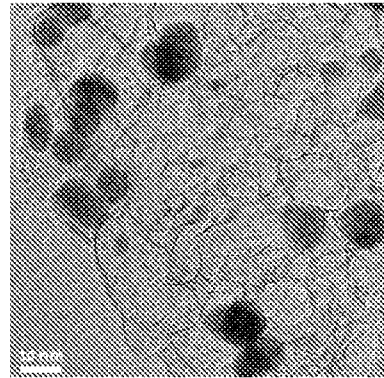


FIGURE 5B

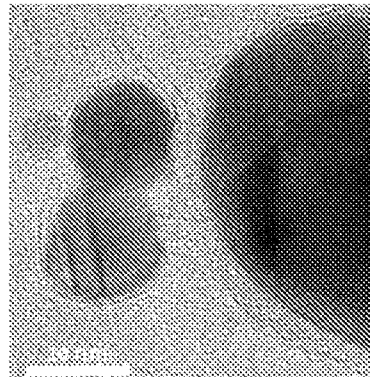


FIGURE 5C

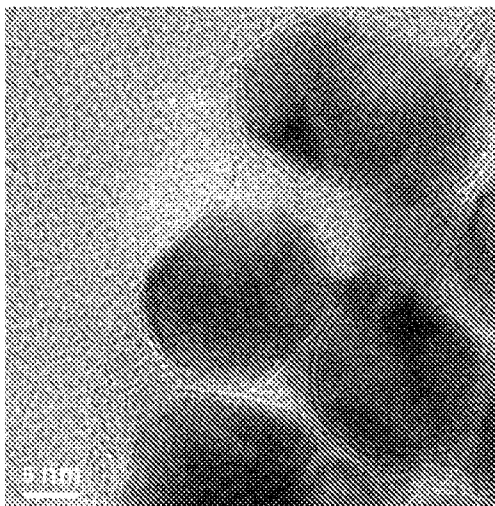


FIGURE 6A

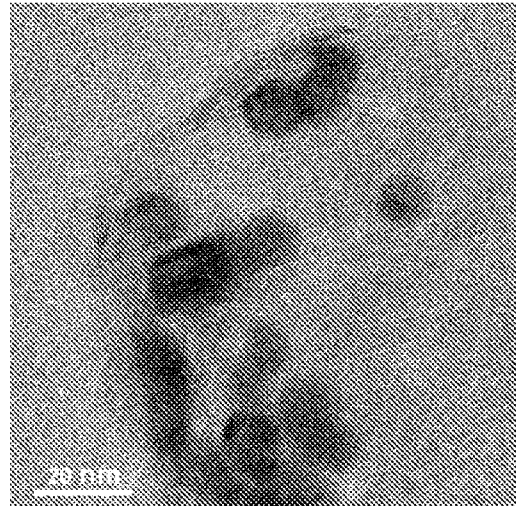
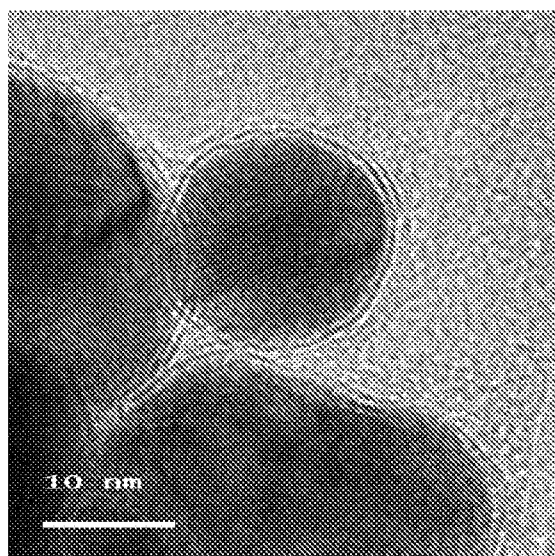
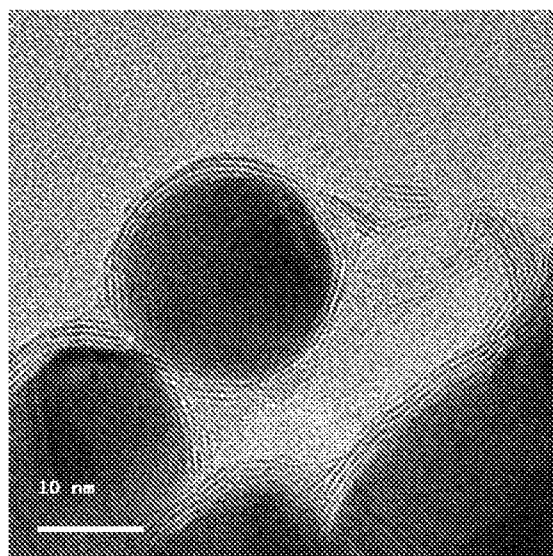
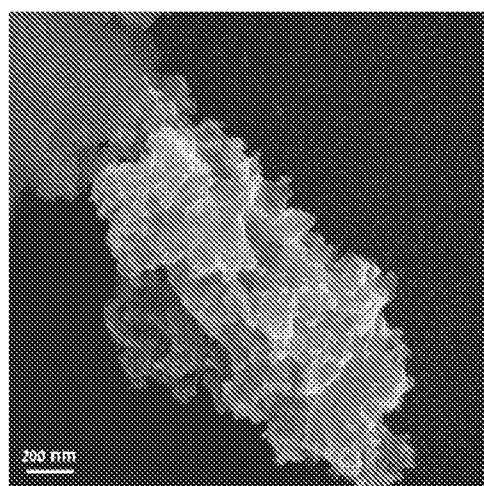
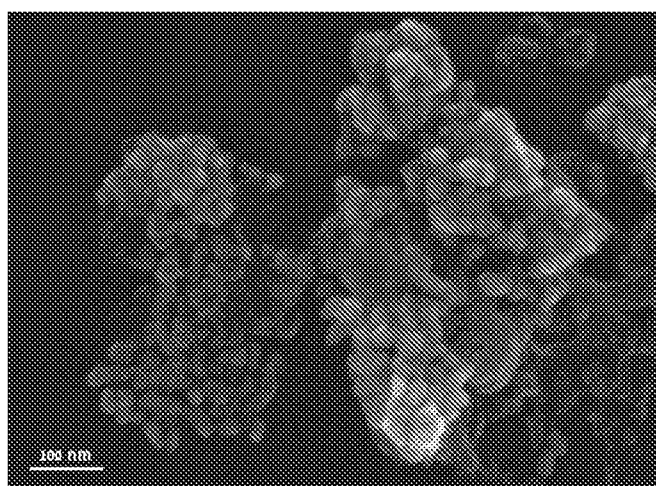


FIGURE 6B

**FIGURE 7A****FIGURE 7B****FIGURE 8**

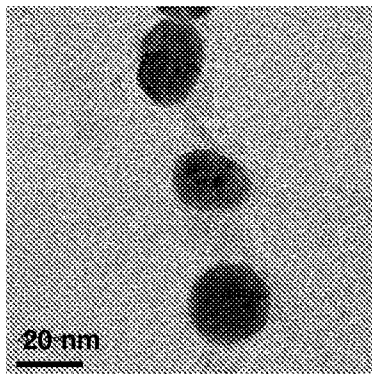


FIGURE 9A

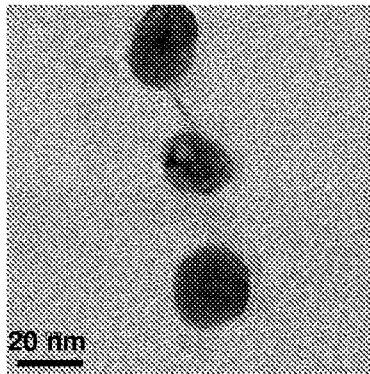


FIGURE 9B

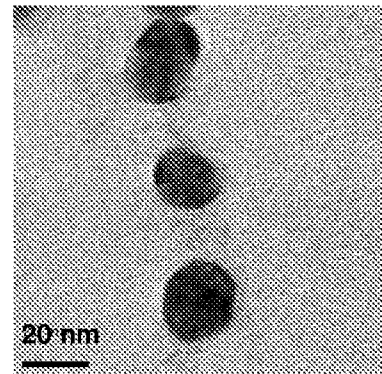


FIGURE 9C

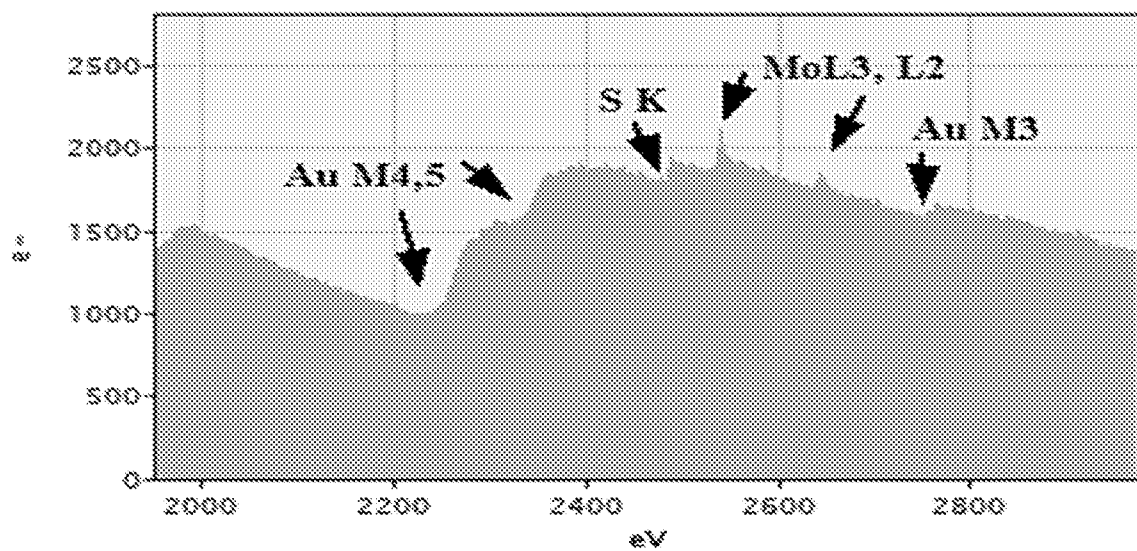
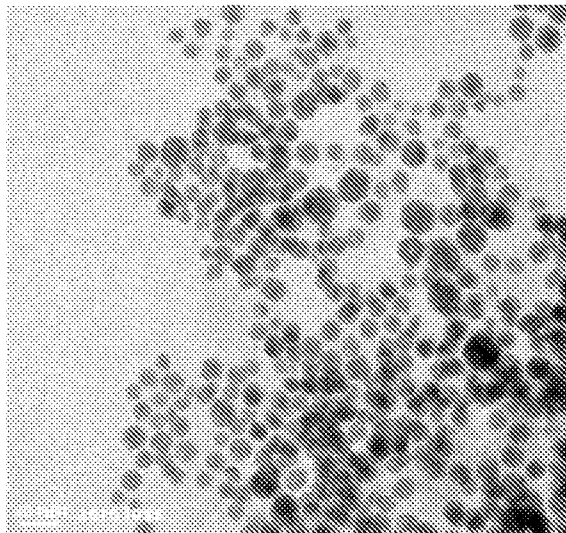
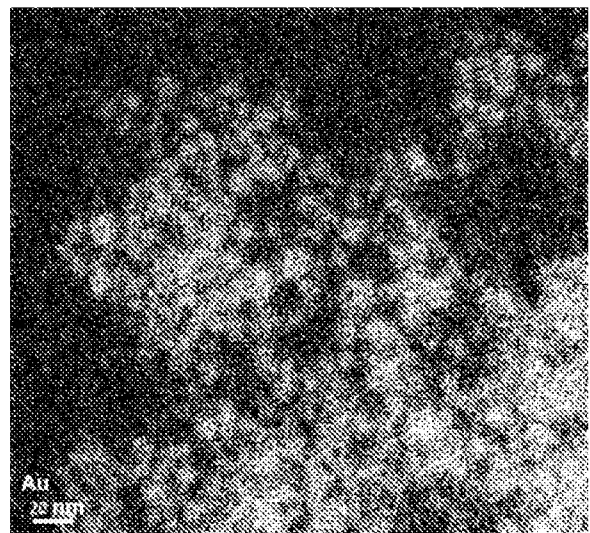


FIGURE 10A



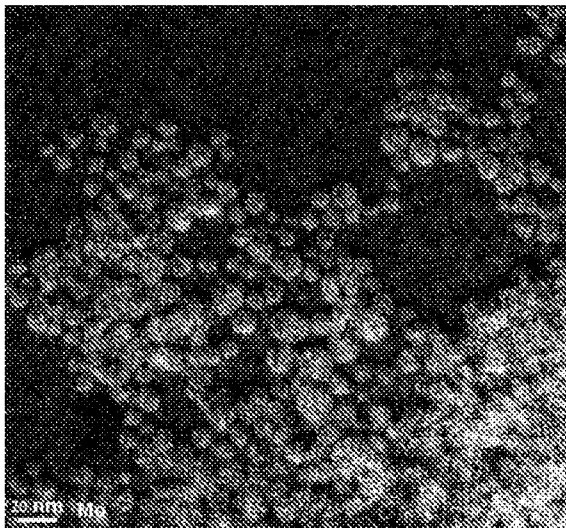
20 nm zero loss

FIGURE 10B



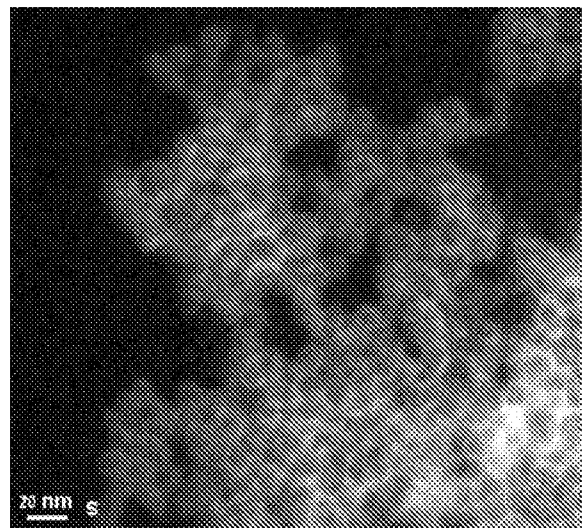
Au
20 nm

FIGURE 10C



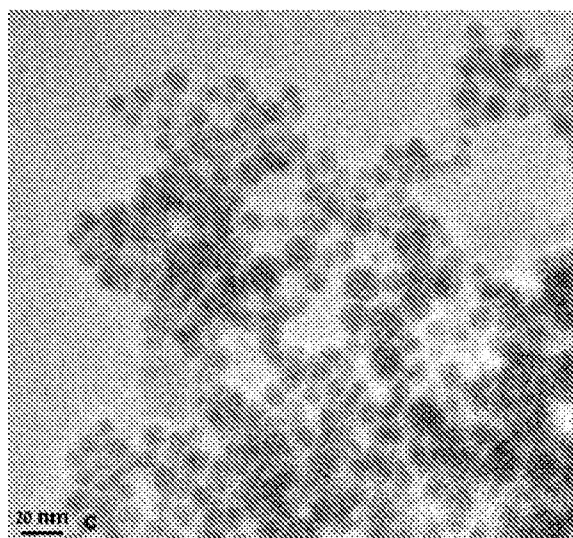
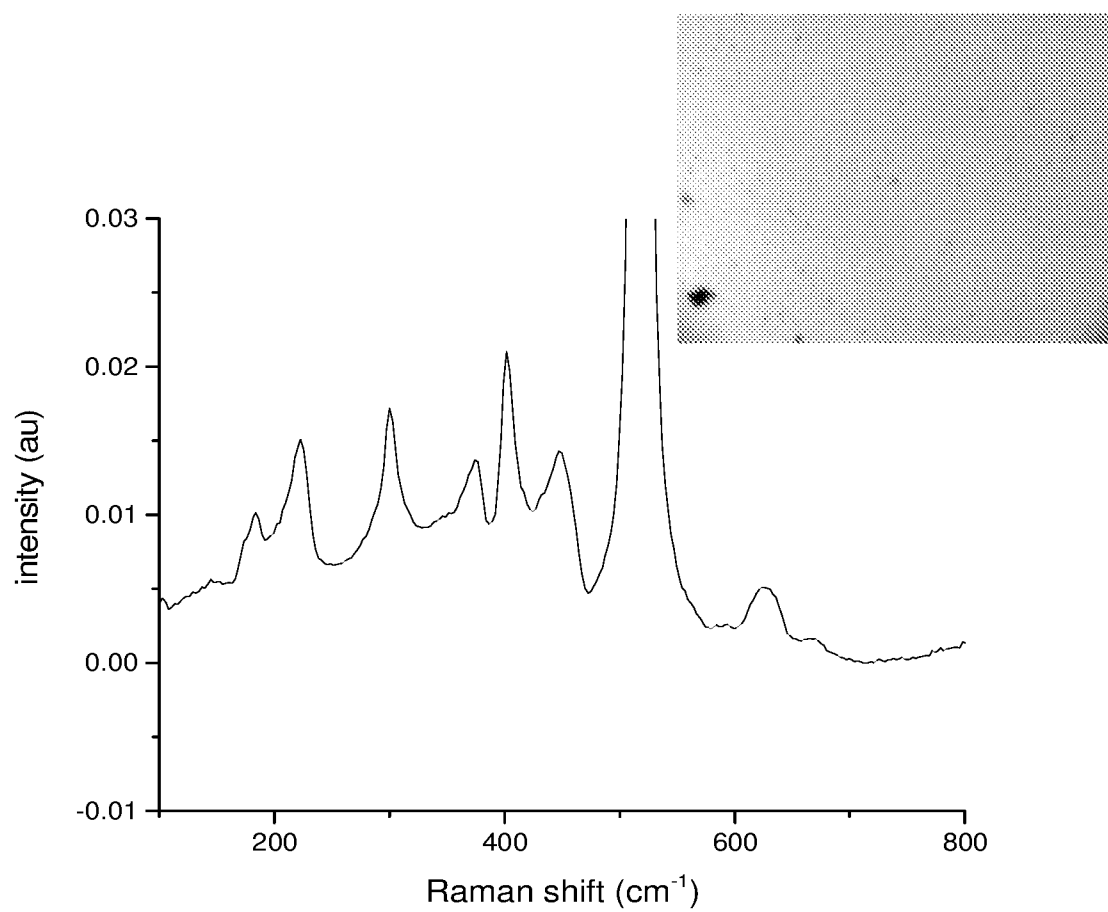
20 nm Mo

FIGURE 10D



20 nm S

FIGURE 10E

**FIGURE 10F****FIGURE 11**

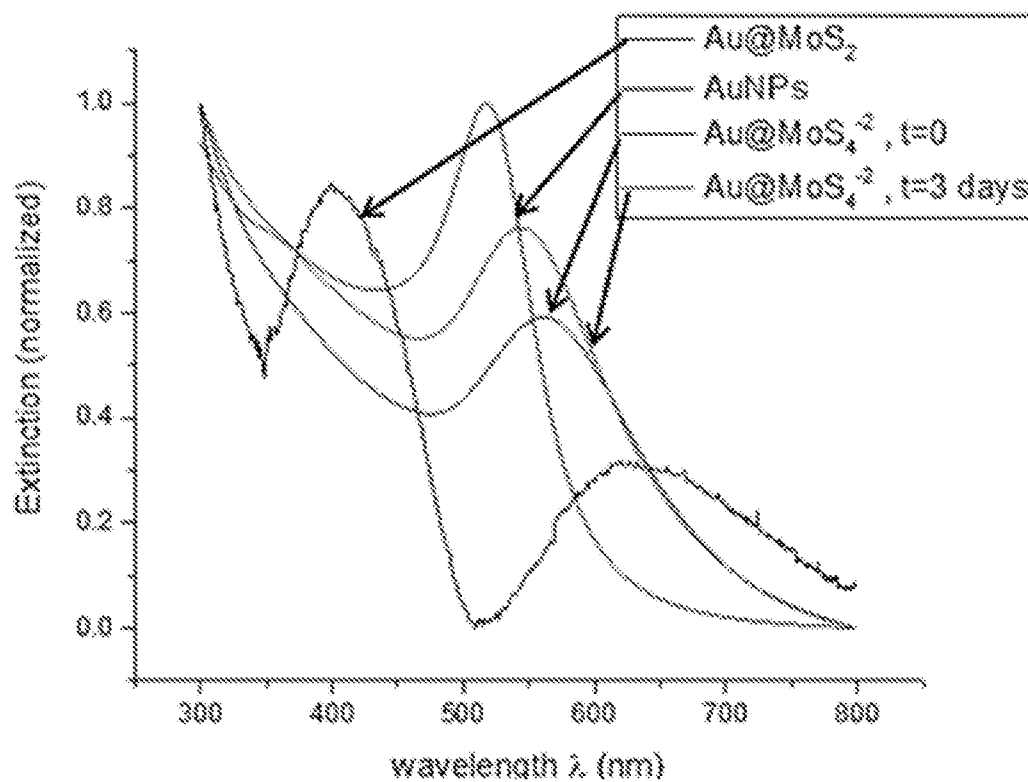


FIGURE 12A

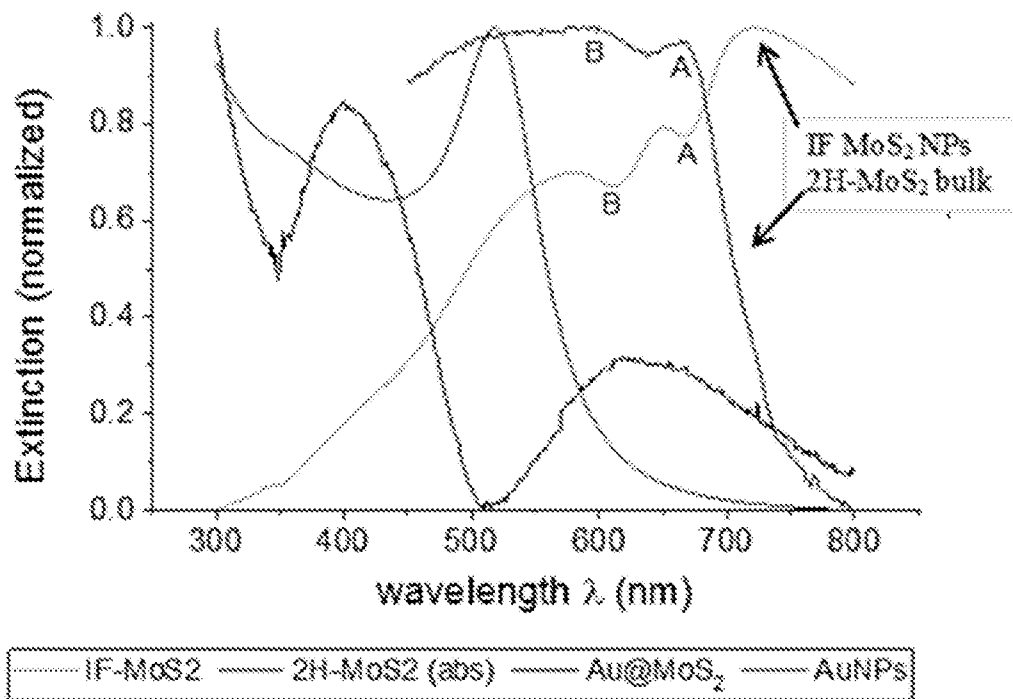


FIGURE 12B

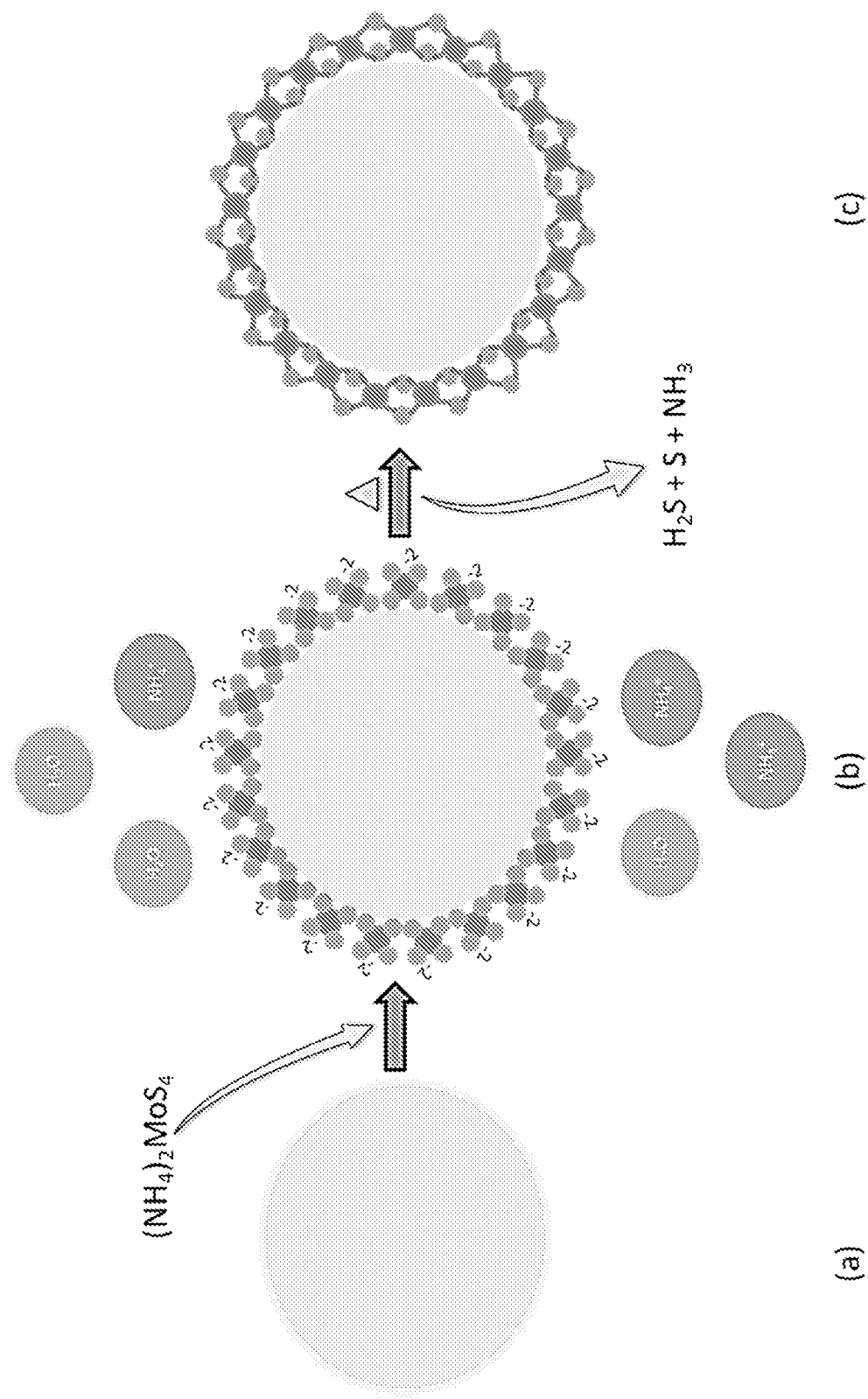
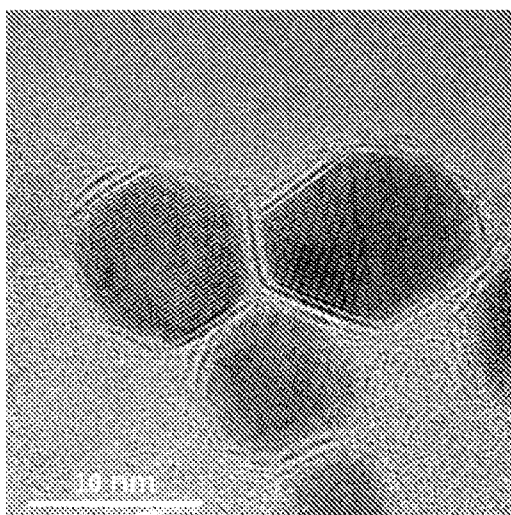
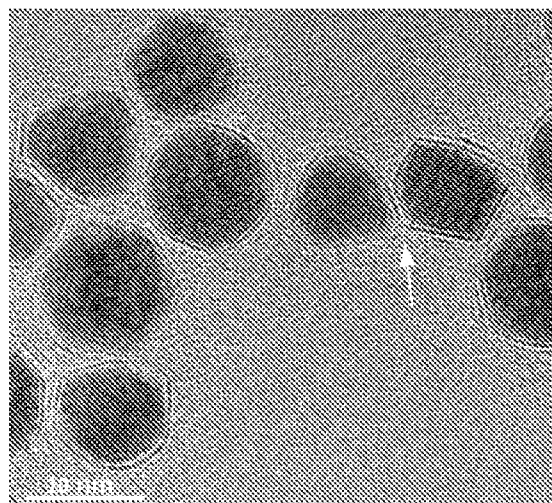
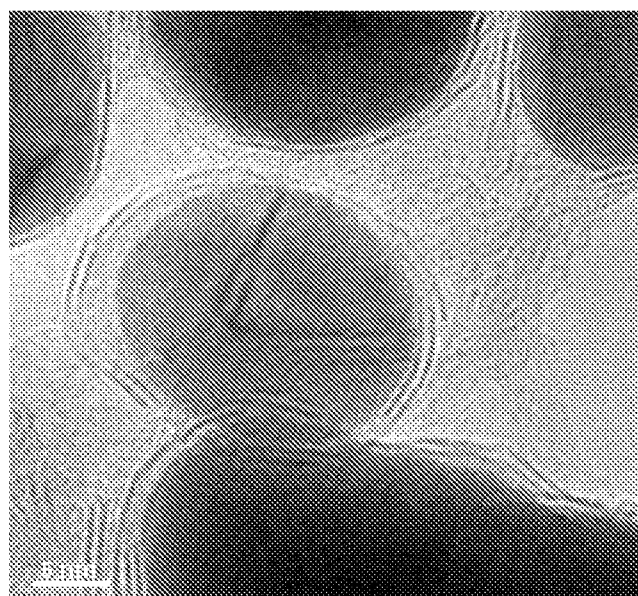


FIGURE 13

**FIGURE 14A****FIGURE 14B****FIGURE 15**

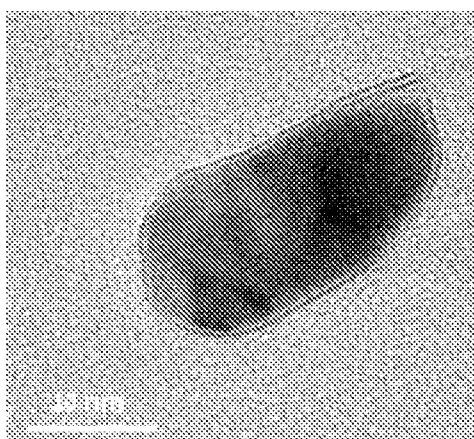


FIGURE 16A

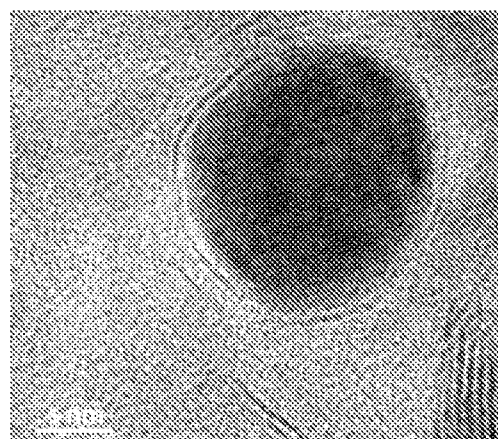


FIGURE 16B

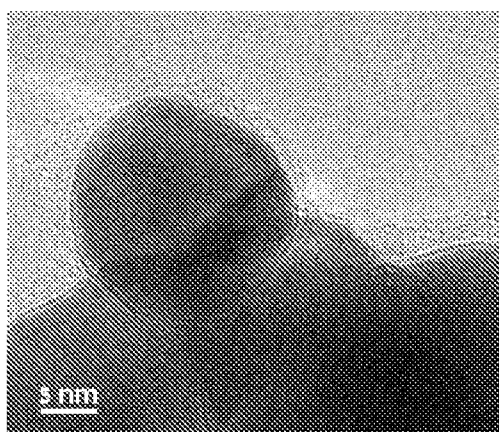


FIGURE 16C

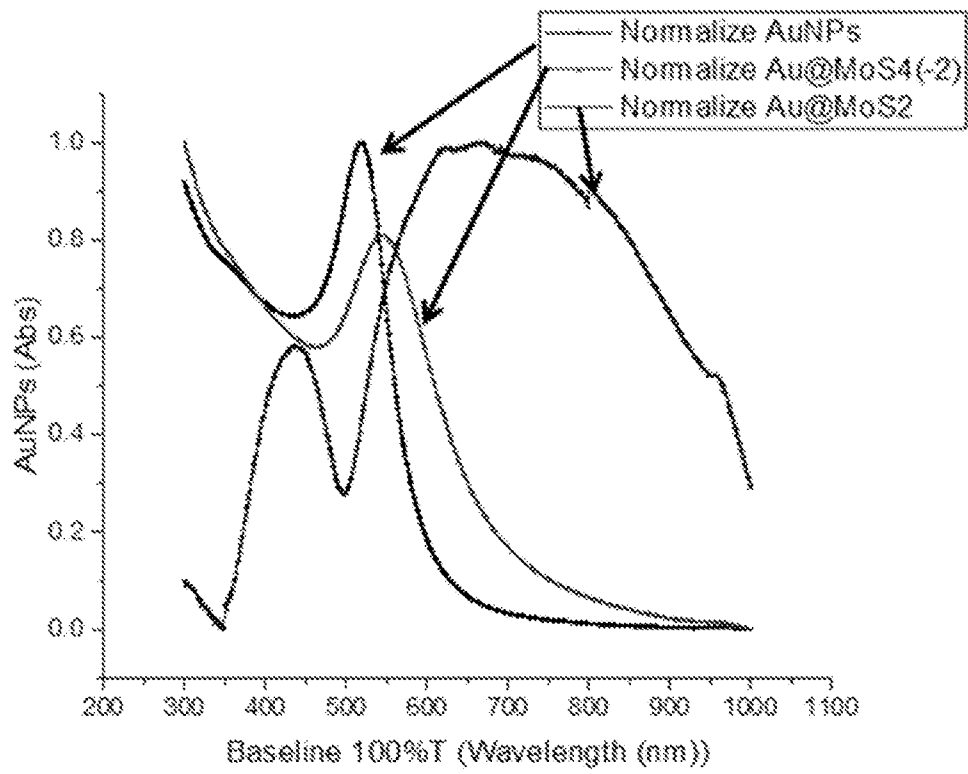


FIGURE 17

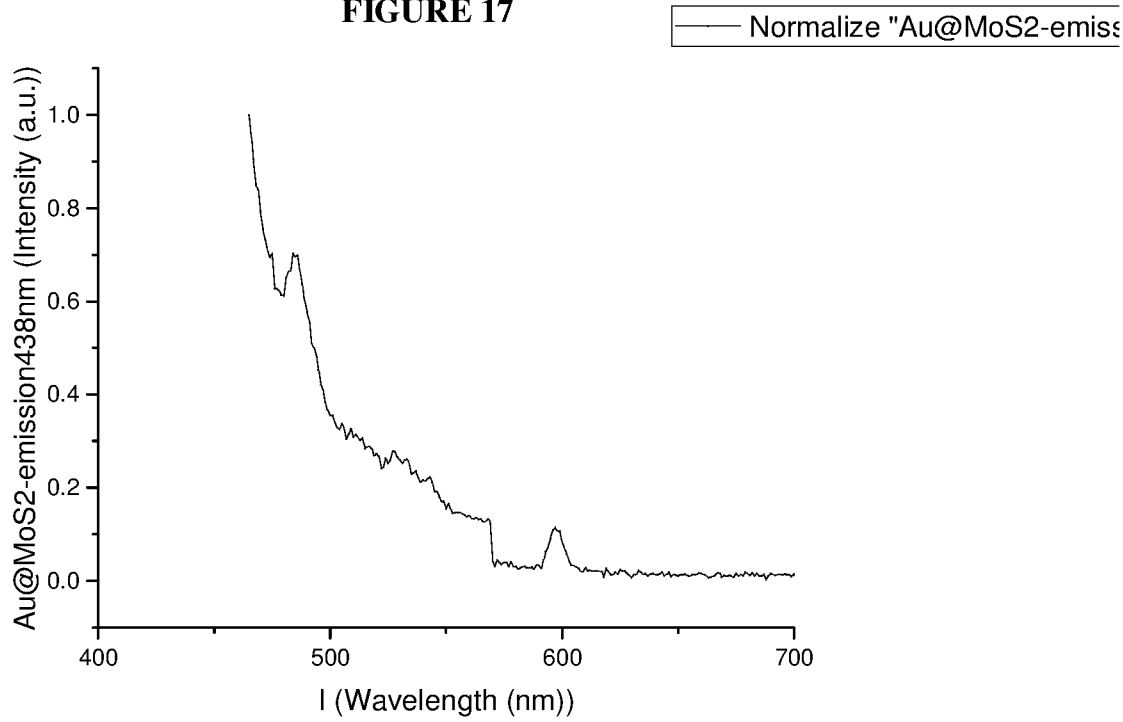
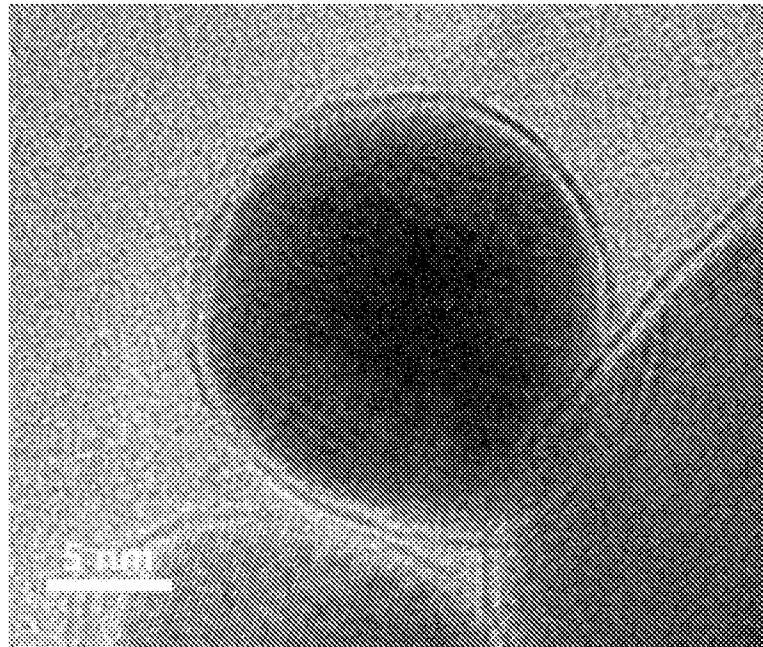
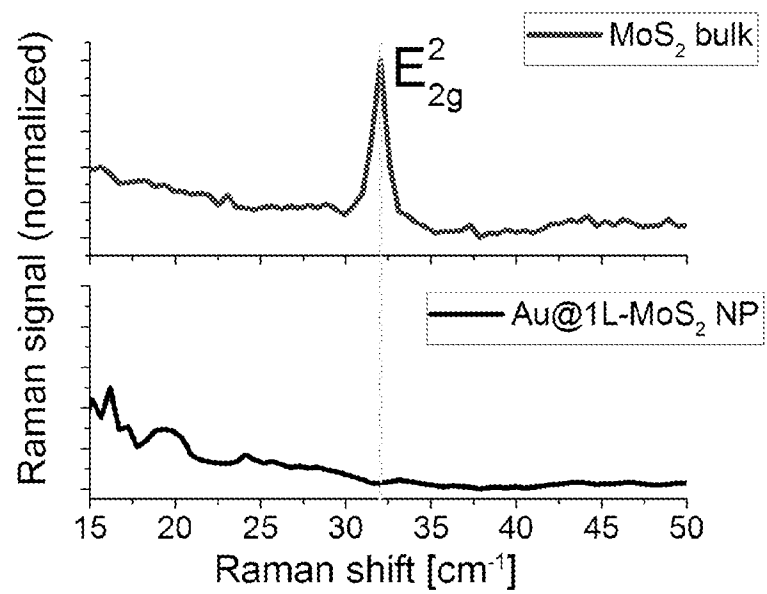


FIGURE 18

**FIGURE 19****FIGURE 20**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2017/050366

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F1/00 B22F9/24
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEN P X ET AL: "A novel surface-enhanced Raman spectroscopy substrate based on a large area of MoS ₂ and Ag nanoparticles hybrid system", APPLIED SURFACE SCIENCE, ELSEVIER, AMSTERDAM, NL, vol. 375, 9 March 2016 (2016-03-09), pages 207-214, XP029530577, ISSN: 0169-4332, DOI: 10.1016/J.APSUSC.2016.03.053	1-5, 7-12, 14-30, 40-46
A	2.1 The preparation of MoS ₂ /AgNP hybrid system; pages 208-9 3. Results and Discussion; page 210 ----- -/-	31-39



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 July 2017

Date of mailing of the international search report

31/07/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Helgadóttir, Inga

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2017/050366

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 6(completely); 1-5, 7-11, 13-46(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 6(completely); 1-5, 7-11, 13-46(partially)

Present claims 1-46 relate to an extremely large number of possible products, as the combination of any type of nanoparticle with any type of inorganic layer coating yields a near infinite number of possible combinations. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the products claimed. In fact, there are only three experimental examples given; two for gold coated with molybdenum disulfide, the third with tungsten disulfide (examples 1-3).

The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-46 (PCT Guidelines 9.19 and 9.23).

The search of claims 1-46 was restricted to those claimed products which appear to be supported along with a reasonable generalisation, that is that the nanoparticle is a metal, selected from the group consisting of Au, Ag, Cu, Pd, Ru, Rh, Ir or a combination thereof, and the coating comprises a transition metal chalcogenide; the support for which can be found in claims 6 and 10, respectively. As a result, claim 6, which lies outside this scope, was not searched, while claim 12, which lies firmly within it, was searched in full. For all remaining claims, they were searched only to the extent to which they overlap with the generalisation mentioned above.

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

INTERNATIONAL SEARCH REPORT

International application No

PCT/IL2017/050366

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI ZHEN ET AL: "Few-layer MoS ₂ -encapsulated Cu nanoparticle hybrids fabricated by two-step annealing process for surface enhanced Raman scattering", SENSORS AND ACTUATORS B: CHEMICAL: INTERNATIONAL JOURNAL DEVOTED TO RESEARCH AND DEVELOPMENT OF PHYSICAL AND CHEMICAL TRANSDUCERS, ELSEVIER BV, NL, vol. 230, 3 March 2016 (2016-03-03), pages 645-652, XP029506820, ISSN: 0925-4005, DOI: 10.1016/J.SNB.2016.02.120	1-5, 7-30, 40-46
A	2.1 Preparation of MoS ₂ @CuNP substrates; pages 646-7	31-39
X	----- YEMING XU ET AL: "Heterostructured CIGS-Au nanoparticles: from Au-CIGS side-by-side structure to Au-core/CIGS-shell configuration", NANOSCALE, vol. 3, no. 8, 1 January 2011 (2011-01-01), page 3238, XP055392976, United Kingdom	1-5, 7-11, 13-46
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