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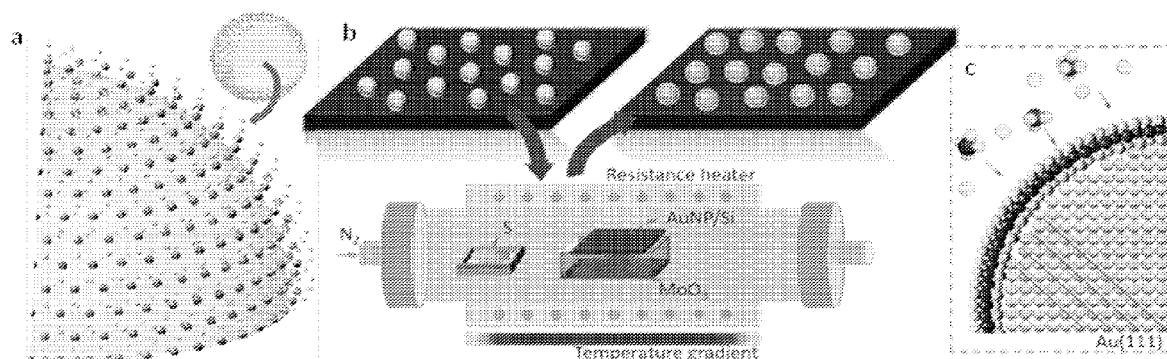
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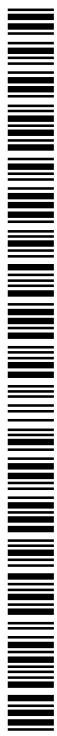
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(54) Title: CORE-SHELL HETEROSTRUCTURES COMPOSED OF METAL NANOPARTICLE CORE AND TRANSITION METAL DICHALCOGENIDE SHELL

FIG. 1



(57) **Abstract:** Provided herein are core-shell heterostructures design comprising a metal (e.g., noble metal) nanoparticle core and a transition metal dichalcogenide (TMD) shell, and methods of preparation and use thereof. In particular embodiments, the core-shell heterostructures described herein are synthesized by direct growth of a monolayer or multilayer fullerene-like TMD shell on a metal (e.g., noble metal) nanoparticle core, exhibit unique Raman scattering and photoluminescence characteristics, and are useful, for example, in plasmonic hot electron enhanced optics and optoelectronics.



CORE-SHELL HETEROSTRUCTURES COMPOSED OF METAL NANOPARTICLE CORE AND TRANSITION METAL DICHALCOGENIDE SHELL

CROSS-REFERENCE TO RELATED APPLICATION

5 The present application claims priority to U.S. Provisional Application 62/383,191, filed September 2, 2016, which is herein incorporated by reference in its entirety.

FIELD

10 Provided herein are core-shell heterostructures comprising a metal nanoparticle core and a transition metal dichalcogenide (TMD) shell, and methods of preparation and use thereof. In particular embodiments, the core-shell heterostructures described herein are synthesized by direct growth of a monolayer or multilayer fullerene-like TMD shell on a metal (e.g., noble metal) nanoparticle core, exhibit unique Raman scattering and photoluminescence characteristics, and are useful, for example, in plasmonic hot electron
15 enhanced optics and optoelectronics.

BACKGROUND

20 There exists a need to develop devices and materials for optoelectronics, optical imaging, and other energy-environmental applications.

SUMMARY

25 Provided herein are core-shell heterostructures comprising a metal (e.g., noble metal) nanoparticle core and a transition metal dichalcogenide (TMD) shell, and methods of preparation and use thereof. In particular embodiments, the core-shell heterostructures described herein are synthesized by direct growth of a monolayer or multilayer fullerene-like TMD shell on a metal (e.g., noble metal) nanoparticle core, exhibit unique Raman scattering and photoluminescence characteristics, and are useful, for example, in plasmonic hot electron enhanced optics and optoelectronics.

30 In some embodiments, provided herein are compositions comprising a metal (e.g., noble metal) core and monolayer or multilayer transition metal dichalcogenide (TMD) shell (e.g., Au@MoS₂ core-shell heterostructures comprising Au nanoparticles encapsulated within a MoS₂ shell). In some embodiments, the metal core comprises a noble metal and is a single phase or alloy of gold (Au), silver (Ag), platinum (Pt), Palladium (Pd), Ruthenium (Ru),

Rhodium (Rh), Iridium (Ir), and/or Osmium (Os). In some embodiments, the metal core comprises a transition metal such as zinc (Zn), cadmium (Cd), iron (Fe), nickel (Ni), titanium (Ti), scandium (Sc), chromium (Cr), cobalt (Co), etc. In some embodiments, a metal core comprise noble and transition metals or alloys thereof. In some embodiments, the TMD shell is a monolayer or multilayer fullerene-like shell. In some embodiments, the TMD is a single or composite semiconductor of the type MX_2 , with M a transition metal atom (Mo, W, etc.) and X a chalcogen atom (S, Se, or Te.). Typical examples of TMD include molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), rhenium disulfide (ReS_2), molybdenum diselenide ($MoSe_2$), tungsten diselenide (WSe_2), and/or Molybdenum ditelluride ($MoTe_2$). In some embodiments, the TMD shell comprises 1-50 layers (e.g., 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, or ranges therebetween). In some embodiments, the noble metal nanoparticles are 5-200 nm in diameter (e.g., 5, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 150, 200 or ranges therebetween). In some embodiments, the MoS_2 shell is 0.65-32.5 nm thick (e.g., 0.65, 1.95, 3.25, 4.55, 5.85, 7.15, 8.45, 9.75, 11.05, 12.35, 13.65, 14.95, 16.25, 17.55, 18.85, 20.15, 21.45, 22.75, 24.05, 25.35, 26.65, 27.95, 29.25, 30.55, 31.85, 32.5 or ranges therebetween).

In some embodiments, provided herein are methods for preparing the core-shell heterostructures described herein comprising directly growing a monolayer or multilayer TMD shell on a metal (e.g., noble metal) nanoparticle core. In some embodiments, the multilayer TMD shell is grown by chemical vapor deposition. In some embodiments, metal (e.g., noble metal) nanoparticles are formed by coating metal (e.g., noble metal) film onto a silicon (Si) substrate *via* galvanic deposition or physical evaporation followed by high-temperature annealing. In some embodiments, the metal (e.g., noble metal) nanoparticles are commercially available metal (e.g., noble metal) nanoparticles. In some embodiments, a metal (e.g., noble metal) nanoparticle-coated Si substrate (e.g., Au nanoparticle-coated Si substrate) is placed in a tube furnace and transition metal oxide and sulfur powder is carried over the substrate to form TMD shells on the nanoparticles.

In some embodiments, provided herein are photodetector devices comprising the metal@TMD (e.g., noble-metal@TMD (e.g., Au@ MoS_2 , etc.), etc.) core-shell heterostructures described herein.

In some embodiments, provided herein are compositions comprising the core-shell heterostructures described herein, patterned onto a substrate. In some embodiments, the noble metal (e.g., Au, etc.) nanoparticles encapsulated within a TMD (e.g., MoS_2) shell are deposited onto the substrate using a standard photolithography process.

In some embodiments, provided herein is the use of the metal@TMD (e.g., noble-metal@TMD (e.g., Au@MoS₂, etc.), etc.) core-shell heterostructures described herein in plasmonic hot electron enhanced optics and/or optoelectronics.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. CVD synthesis of Au@MoS₂ core-shell heterostructures. (a) Schematic illustrating the core-shell structure. (b,c) Schematic showing the CVD process of MoS₂ shell growth on Au nanoparticles. (d) SEM image of the Au@MoS₂ heterostructures on Si substrate. (e-g) TEM images and diffraction patterns of the Au@MoS₂ heterostructures. (h-k) STEM and corresponding EDS mapping of the Au@MoS₂ heterostructures.

Figure 2. Spectroscopic characterization of Au@MoS₂ heterostructures. (a-c) XPS peaks of Mo 3d (a), S 2p (b), and Au 4f (c). (d) Raman spectra and (e) Photoluminescence spectra of the Au@MoS₂ heterostructures and multilayer MoS₂ sheet (with comparable thickness to Au@MoS₂) on Si substrate.

Figure 3. Field enhancement on the Au@MoS₂ heterostructures. (a) Optical images of Au nanoparticles (1) and Au@MoS₂ heterostructures (2) grown on Si substrate. (b) Experimental and simulated absorbance spectra of the Au@MoS₂ heterostructures. (c) Simulated absorbance spectra of Au@MoS₂ heterostructures, Au nanoparticles and imaginary MoS₂ shell. (d-f) 3D images showing the three targets (partial) used for DDA modeling. (g-i) Normalized electric field maps on target of Au nanoparticles (g), Au@MoS₂ heterostructure (h), and the imaginary MoS₂ shell (i).

Figure 4. Fabrication of Au@MoS₂ patterns. (a,b) SEM images of “NU” Au@MoS₂ patterns. (c-f) EDS elemental mapping on one Au@MoS₂ pattern. (g-i) SEM images and corresponding EDS elemental mapping of Au@MoS₂ heterostructures in the “NU” patterns.

Figure 5. Surface plasmon-induced light-matter interaction on Au@MoS₂ patterns. (a) Raman spectra and (b) photoluminescence spectra obtained at different locations that marked in the optical image of “NU” patterns in (c). (d) Raman map and (e) photoluminescence map generated on the “NU” patterns. (f) Schematic illustrating the band structure of Au and MoS₂ before combination. (g) Realigned band structure in the Au@MoS₂ heterostructures.

Figure 6. Formation and dispersion of Au nanoparticles on Si substrate. (a) Schematic showing the galvanic deposition of Au film and its subsequent annealing to form dewetted Au nanoparticles. (b,c) SEM images of the as-deposited Au film. (d,e) SEM images of the annealed Au nanoparticles.

Figure 7. EDS line profile of Au@MoS₂. (a) TEM image of a Au@MoS₂ heterostructure. (b) EDS line profiles marked on the Au@MoS₂ heterostructure. (c) Count-position curves of different elements corresponding to various EDS lines across the yellow line in (b).

5 Figure 8. Fabrication process of Au@MoS₂ patterns. (a) Optical image and (b) SEM image of “NU” patterns after galvanic deposition. (c) “NU” patterns after annealing. (d) Optical image of circular patterns with diameter of 10 μm. (e,f) Growth of Au@MoS₂ using above patterns.

10 Figure 9. SIMS demonstration of the Au@MoS₂ patterns. (a) Optical image of various “NU” at the edge region of Si substrate. (b-e) SIMS elemental mapping (including Mo, S, and Au) on various patterns.

Figure 10. Photoluminescence mapping on various Au@MoS₂ patterns. (a,b) photoluminescence mapping with relatively low resolution on another “NU” patterns. (c,d) “NU” patterns at the center region of the substrate.

15 Figure 11. Density functional theory modeling of electronic structure. (a) Band structure of 6-layer MoS₂ flat nanosheet. (b) Atomic structure of MoS₂ nanosheet used for the DFT calculation. The x-y coordinate shows the direction for structural bending. (c) Schematic diagram of band alignment of Au and various MoS₂ systems relative to the vacuum energy level. For energy levels of MoS₂ from left to right, they are respectively pure 6-layer MoS₂ slab, a bent MoS₂ in x, y and xy directions to mimic curved shell structure on Au particles. Here the bent structure refers a curve slab with 5° center angle. All numbers are in eV. The black dashed lines are Fermi levels.

20

DEFINITIONS

25 Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments described herein, some preferred methods, compositions, devices, and materials are described herein. However, before the present materials and methods are described, it is to be understood that this invention is not limited to the particular molecules, compositions, methodologies or protocols herein

30 described, as these may vary in accordance with routine experimentation and optimization. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the embodiments described herein.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. However, in case of conflict, the present specification, including definitions, will control. Accordingly, in the context of the embodiments described herein, the following
5 definitions apply.

As used herein and in the appended claims, the singular forms “a”, “an” and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to “a nanoparticle” is a reference to one or more nanoparticles and equivalents thereof known to those skilled in the art, and so forth.

10 Many embodiments herein are described using open “comprising” language. Such embodiments encompass multiple closed “consisting of” and/or “consisting essentially of” embodiments, which may alternatively be claimed or described using such language.

As used herein, the term “plasmonic nanoparticles” refers to metal particles (e.g., gold (Au), silver (Ag), platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), osmium
15 (Os), iridium (Ir), alloys thereof, etc.) with electron density that can couple with electromagnetic radiation of wavelengths that are larger than the particle due to the nature of the dielectric-metal interface between the medium and the particle. Plasmonic nanoparticles differ from conventional surface plasmons in that their scattering, absorbance, and/or coupling properties are dependent upon their specific geometries and the
20 media in which they reside. Plasmonic nanoparticles typically exhibit very strong absorption and scattering spectra that are tunable by altering the shape, the composition, or the medium around their nanoparticle surface.

DETAILED DESCRIPTION

25 Provided herein are core-shell heterostructures design comprising a metal (e.g., noble metal) nanoparticle core and a transition metal dichalcogenide (TMD) shell, and methods of preparation and use thereof. In particular embodiments, the core-shell heterostructures described herein are synthesized by direct growth of a monolayer or multilayer fullerene-like TMD shell on a metal (e.g., noble metal) nanoparticle core, exhibit unique Raman scattering
30 and photoluminescence characteristics, and are useful, for example, in plasmonic hot electron enhanced optics and optoelectronics.

In some embodiments, the core-shell heterostructures described herein (e.g., noble-metal@TMD heterostructures described herein (e.g., Au@MoS₂ heterostructures, etc.)) exhibit interesting optical properties and behavior. The material synthesis was realized by direct growth of monolayer or multilayer fullerene-like TMD shell on metal (e.g., noble metal) nanoparticle core. As an example of the broader class of metal@TMD (e.g., noble-metal@TMD) heterostructures, the Au@MoS₂ heterostructures are found to exhibit strong light-matter interactions, for example, due to the structural curvature of MoS₂ shell and the plasmonic effect from the underlying Au nanoparticle cores; although embodiments herein are not limited to any particular mechanism of action and an understanding of the mechanism of action is not necessary to practice such embodiments. Significantly enhanced Raman scattering and photoluminescence emission were observed on Au@MoS₂ heterostructures. Such enhancement is attributed to the surface plasmon-induced electric field, which mainly accumulates within the MoS₂ shell. Experiments conducted during development of embodiments herein also indicated charge transfer-induced p-type doping of the MoS₂ shell. DFT calculation further reveals that the structural curvature of MoS₂ shell leads to a modification of its electronic structure, which facilitates the charge transfer from MoS₂ to Au core. These experiments indicate that noble-metal@TMD heterostructures generally will exhibit similar optical properties and characteristics.

The noble-metal@TMD heterostructures (e.g., Au@MoS₂ core-shell heterostructures) described herein find use, for example in optoelectronic devices, optical imaging, and other energy-environmental applications. In some embodiments, the noble-metal@TMD heterostructures (e.g., Au@MoS₂ core-shell heterostructures) are plasmonic nanostructures.

EXPERIMENTAL

Example 1

Materials and methods

Reagents

Molybdenum trioxide and Sulfur powders were purchased from Alfa Aesar (Ward Hill, MA). Galvanic deposition solution contains 1 mM KAuCl₄ and 1% HF. Buffered oxide etch (BOE) was self-prepared by mixing 40% NH₄F and 49% HF with a volume ratio of 6:1. Chemical vapor deposition was conducted in a Lindberg Blue M tube furnace. Heidelberg µPG 501 Maskless Aligner was used for the lithography preparation of Au@MoS₂ patterns on Si substrate as well as the fabrication of photodetector devices. Raman spectra and photoluminescence spectra were collected on the HORIBA LabRAM HR Evolution Confocal

Raman System. Electric test was conducted on the Signatone S-1160 Probe Station. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was used for binding energy analysis. Hitachi SU8030 SEM and JEOL JEM-2100 Fas TEM were used for morphological and structural characterizations.

5

Chemical vapor deposition of Au@MoS₂ heterostructures

Si substrate was cleaned with BOE for 15 s to remove surface oxide layer. This was followed by putting the substrate in above galvanic deposition solution for 60 s to deposit Au film, which was further annealed at 850 °C for 15 min to form Au nanoparticles. The following fullerene-like MoS₂ shell encapsulation on Au nanoparticles were conducted *via* a modified chemical vapor deposition process. The Au nanoparticle-coated substrate was put face down on an alumina boat containing 10 mg MoO₃. Another boat containing 120 mg sulfur powders was put in the upstream side. N₂ gas with a flow rate of 200 sccm was used as the carrier gas. The furnace was first heated up to 300 °C and kept for 30 min, and then ramped to the growth temperature (650 °C). The growth was continued for 15 min with a N₂ flow rate of 10 sccm. The furnace was then slowly cooled down to ambient temperature.

Fabrication of “NU” Patterns of Au@MoS₂ heterostructures

Designed patterns of Au@MoS₂ heterostructures were fabricated using a standard photolithography process. Photoresist (S1813) was first coated on Si substrate with a spin rate of 4000 rpm for 30 s. The substrate was baked at 110 °C for 1 min. UV light exposure was conducted for 26 ms with a defocus of -1. The sample was then developed in MF-319 for 30 s and further cleaned with O₂/Ar plasma for 3 min. Subsequently, an Au film of 10 nm was evaporated on the substrate and the remaining photoresist was removed in acetone. The obtained Au film patterns was annealed at 850 °C for 15 min and subjected to the same chemical vapor deposition process as above to form Au@MoS₂ patterns. The obtained patterns at various fabrication steps can be found in Figure 8.

Discrete Dipole Approximation (DDA) modeling

The computation of absorbance and surface electric field distribution of isolated targets (Au nanoparticle, Au@MoS₂ heterostructure, and imaginary MoS₂ shell, see Figure 3D-F) were performed using the Discrete Dipole Approximation algorithm implemented in the DDSCAT 7.2 code developed by Draine and Flatau. The Au nanoparticle target has a diameter of 50 nm. The Au@MoS₂ heterostructure target is composed of an Au nanoparticle

core of 50 nm and a MoS₂ shell of 6.5 nm (10 atomic layers of MoS₂). The imaginary MoS₂ shell target is same with the Au@MoS₂ heterostructure target but with no Au core. These targets were built as a lattice of polarizable cubic elements or dipoles with position r_i and possibility α_i ($i = 1, 2, \dots, N$). In the simulation, the targets were excited by a monochromatic incident wave vertical to the cross-section of the heterostructures, and the induced extinction and absorption of the targets were calculated by

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \sum_{i=1}^N \{Im[P_i(\alpha_i^{-1})^* P_i^*] - \frac{2k^3}{3} |P_i|^2\} \quad (1)$$

here * represents complex conjugate, $k = \frac{2\pi}{\lambda}$ is the wave number of the incident wave and E_0 is its amplitude, $E_{loc,i}$ is the local field calculated from the sum of the incident radiation field of dipole i and the field radiated by the other $N-1$ dipoles, and P_i is the polarization induced in dipole i , expressed as

$$P_i = \alpha_i E_{loc,i}(r_i). \quad (2)$$

The absorption efficiency (Q_{abs}) of the simulated targets (Figure 5A) were calculated from

$$Q_{abs} = C_{abs}/(\pi a_{eff}^2) \quad (3)$$

where a_{eff} is the effective radius of a sphere with volume ($\frac{4\pi a_{eff}^3}{3}$) equal to the volume of the heterostructured targets.

As mentioned, the strong light-matter interaction at the visible region leads to the generation of SPR, which further forms a constant localized electric field on/near the surface of the targets. The intensity of electric field was theoretically calculated from the sum of the incident radiation field of dipole i and the field radiated by the other $N-1$ dipoles, as shown in the following equation,

$$E_{loc,i}(r_i) = E_{inc,i} + E_{dip,i} = E_0 \exp(ikr_i) - \sum_{j \neq i} A_{ij} P_j. \quad (4)$$

The interaction matrix A can be represented as

$$A_{ij} P_j = \frac{\exp(ik|r_{ij}|)}{|r_{ij}|^3} \left\{ k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{1 - ik|r_{ij}|}{|r_{ij}|^2} \times [|r_{ij}|^2 P_i - 3r_{ij}(r_{ij} P_j)] \right\} \\ j = 1, 2, \dots, N, j \neq i \quad (5)$$

where $|r_{ij}| = |r_i - r_j|$ and P is the polarization vector.

Density functional theory calculation

Density functional theory (DFT) electronic structure calculations were performed in order to gain insights into the various band alignments in these materials. The calculations were performed using the generalized gradient approximation with PBE functional for the

exchange correlation functional and projector augmented wave potentials as implemented in VASP (Vienna Ab-initio Simulation Package). All structures are fully relaxed with respect to cell vectors and cell-internal positions. The electronic DOS (density of states) is calculated from the relaxed structures using the tetrahedron method with Blöchl corrections. To get the Fermi level relative to the vacuum level of Au, 6-layer slab of fcc Au in (111) direction with 15 Angstrom vacuum in the super cell was used to calculate work function. To assess the relative band alignments of MoS₂ system, the findings of Van de Walle and Neugebauer, who demonstrated a universal alignment of the electronic transition level of hydrogen in a wide range of materials including semiconductors, insulators and even aqueous solutions were utilized. Hence, to infer the band alignment, the energies of H defects in the rock salt compounds of interest were computed, alignment between these H energies was assumed, and the band alignment of the compounds was extracted. To align the valence band maximum position of each system, the defect formation energies of various charge states of interstitial H_q ($q = -1, 0, 1$) was considered by placing H in the host material, calculating the total energy of this structure, and subtracting the energy of the corresponding pure host material, hydrogen chemical potential, and electron chemical potential. ^{Error! Bookmark not defined.}

$$E_f(Hq) = E_{tot}(Hq) - E_{tot}(bulk) - 0.5E_{tot}(H_2) + q(E_V + \Delta E + E_F),$$

where E_V and E_F are valence band maximum and Fermi level (relative to the VBM). To select the most favorable interstitial H binding sites in host materials, multiple binding configurations are calculated. The electrostatic potential correction term ΔE is calculated by inspecting the potential in the supercell far from the impurity and aligning it with the electrostatic potential in bulk.

Example 2

Results

A modified chemical vapor deposition method was employed to realize the growth of a fullerene-like MoS₂ shell on Au nanoparticles. An Au film with a thickness of ~10 nm was first coated on fresh Si substrate *via* a galvanic deposition approach (Figure 6a). The Au film was further subjected to a high-temperature annealing process to form Au nanoparticles. The morphology of the Au film, as well as the obtained Au nanoparticles are shown in Figure 6b-e. These Au nanoparticles have an average size of 52.1 ± 9.1 nm. The subsequent chemical vapor deposition of the MoS₂ shell is similar to previous reports. Figure 1a shows a schematic of the obtained Au@MoS₂ core-shell heterostructures. The growth process and furnace setup

are further illustrated in Figure 1b. The Au nanoparticle coated Si substrate was placed face down on an alumina boat containing MoO₃. Another boat with sulfur powders were placed in the upstream region of the furnace. During the growth, volatile MoO₃ and its partially decomposed suboxides (MoO_x) react with sulfur vapor and form MoS₂ shell on Au nanoparticles (Figure 1c). Due to the high affinity of Au and S atoms, complete encapsulation of MoS₂ on the Au surface is realized.

The Au@MoS₂ core-shell heterostructures are shown in Figure 1d and e. From the TEM image it is observed that the MoS₂ shell have a multilayer structure, typically consisting of 5-10 atomic layers of S-Mo-S. The high-resolution TEM image in Figure 1f indicates a layer-to-layer spacing of 0.65 ± 0.02 nm, which is consistent with the c-axis lattice spacing of bulk MoS₂. No significant change in this spacing value was observed (e.g. due to the lattice strain induced by the shell curvature). Diffraction pattern of the heterostructures are shown in Figure 1g, indicating the presence of dominant facets Au (111), Au (310), MoS₂ (200), MoS₂ (110) and MoS₂ (100). EDS elemental mapping for the heterostructures is further demonstrated in Figure 1h-k. One can observe that the Au map region (Figure 1i) is slightly smaller than that of Mo and S (Figure 1j and k), indicating the encapsulation of MoS₂ shell on Au nanoparticles. Similar to this elemental mapping, a result of EDS line profile is also displayed in Figure 7, which demonstrates the variation of elemental distribution across a single Au@MoS₂ heterostructure.

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition and chemical states of the Au@MoS₂ heterostructures. Figure 2a displays Mo 3d peaks at 233.04 eV and 229.87 eV, corresponding to the 3d_{5/2} and 3d_{3/2} doublet. Meanwhile, the S 2p peak can be deconvoluted into two peaks at 163.88 eV and 162.70 eV (Figure 2b), attributing to the 2p_{1/2} and 2p_{3/2} orbital. These binding energy values confirm the expected charge states of Mo⁴⁺ and S²⁻ in the MoS₂ shell. Additional peaks of metallic Mo or MoO_x in higher/lower binding energy regions were not observed, which attests to the quality of MoS₂ shell obtained from the CVD growth. Moreover, Au 4f peaks were observed at 88.00 eV (4f_{5/2}) and 84.29 eV (4f_{7/2}). However, the intensity of these two peaks is relatively weaker compared with above Mo and S peaks due to the limited detection depth of X-ray photoelectrons (typically less than ~10 nm). This further indicates Au nanoparticles on the substrate are well-encapsulated by MoS₂ shell.

Raman spectroscopy allows for determination of the crystallinity and layer thickness of two-dimensional MoS₂ by measuring the position and frequency difference of two characteristic vibration modes, E_{2g} and A_{1g}. The E_{2g} mode is attributed to the in-plane

vibration of Mo and S atoms, while the A_{1g} mode is related to the out-of-plane vibration of S atoms. Figure 2d shows the Raman spectra of the Au@MoS₂ heterostructures as well as a flat multilayer MoS₂ sheet grown on Si substrate. The measurements were conducted using a Neon laser (532 nm) with power of 8.8 μ W to eliminate the effect of optical heating. The Au@MoS₂ heterostructures show the two vibration modes centered at 380.7 cm^{-1} and 405.6 cm^{-1} while the multilayer MoS₂ sheet exhibits modes at 383.8 cm^{-1} and 408.6 cm^{-1} . Both spectra give similar E_{2g} -to- A_{1g} frequency difference of ~ 24.8 - 24.9 cm^{-1} . This value is slightly smaller than that of bulk MoS₂, indicating their multilayered crystal structure. Raman spectroscopy is also utilized to investigate the effect of lattice strain, doping levels, and the van der Waals interaction at the interface of 2D crystals. The in-plane Raman mode, E_{2g} , is sensitive to the built-in strain of 2D MoS₂ while the out-of-plane mode, A_{1g} , is a reflection of interlayer van der Waals interactions. Thus, it is reasonable to conclude that the red-shift of E_{2g} and A_{1g} modes of the Au@MoS₂ heterostructures in Figure 2d is attributed to the effect of lattice strain due to the curvature of MoS₂ shell. Besides the variation of Raman frequency, we also observed a significant enhancement of the peak intensity in our Au@MoS₂ heterostructures (Figure 2d). This is attributable to the effect of localized surface plasmon resonance (LSPR) of Au nanoparticle cores, typically called surface-enhanced Raman scattering (SERS). Interactions of incident light with Au nanoparticles excites localized surface plasmons. When the frequency of plasmon oscillation is in resonance with the irradiation, a strongly enhanced electromagnetic field forms on the surface, leading to a significant increase in the intensity of Raman models as indicated in Figure 2d.

Similar plasmonic enhancement was also observed in the photoluminescence emission. As shown in Figure 2e, the multilayer MoS₂ sheet reveals an A peak at 673.1 nm and another B peak at 628.0 nm. The A peak is due to neutral exciton emission from the interband transition at the Brillouin zone K point while the B peak arises from exciton emission from another direct transition between the conduction band and a lower-lying valence band. However, this B peak is not observed in the Au@MoS₂ heterostructures. Its photoluminescence spectrum shows an intensity of ~ 13.6 times higher than that of the flat multilayer MoS₂ sheet, and exhibits the A peak at 666.2 nm and another A⁻ peak centered at 689.1 nm. The evolution of A⁻ peak is associated with the recombination of negatively charged excitons through the A transition (A⁻, a free electron bound to a neutral exciton *via* Coulomb interaction). This A⁻ is attributable to the Au nanoparticle cores, which provide a high level of trapped donors on the surface. In addition, the lattice strain in MoS₂ nanosheets may lead to a red-shift of A exciton peak. However, such red-shift was not observed on the

Au@MoS₂ heterostructures. Instead, a slight blue-shift with significantly increased intensity was observed as compared to the A peak of flat multilayer MoS₂ sheet (Figure 2e).

Experimental and simulation investigations were conducted to study light-induced absorption and surface electric field distribution. Figure 3a shows an optical microscopic image of Au nanoparticles decorated on Si substrates before (1) and after (2) growth of MoS₂ shell. UV-vis Reflectance spectrum was collected on the Au@MoS₂ sample (2) and further converted into Absorbance (Figure 3b). A broad absorption peak was observed from 500 nm to 750 nm. The deconvoluted subcomponents clearly show the A and A' peaks at ~660 nm and ~685 nm, which is well-consistent with the photoluminescence spectrum of Au@MoS₂ heterostructures in Figure 2E. The absorption peak located at ~580 nm corresponds to surface plasmon resonance from Au nanoparticle cores. Another absorption shoulder appeared at ~425 nm is attributed to the C excitonic transitions of MoS₂, which further confirms its band structure in 2H crystal polytype.

Simulated absorbance spectrum of a single Au@MoS₂ heterostructure (Au core of 50 nm with a MoS₂ shell of 10 atomic layers, see Figure 3e) is displayed in Figure 3b. The simulation was conducted using Discrete Dipole Approximation (DDA) method. The simulated spectrum is consistent with the experimental data. However, since the plasmon hot electron induced charge transfer (doping effect) is not considered in our DDA simulation (which mainly considers the surface plasmon induced light-matter interactions), the A' transition peak was not observed in the simulated spectrum. Moreover, the C transition was blue-shifted by ~75 nm, which is attributable to quantum size effect from the reduction in the lateral size of MoS₂ nanostructures to less than 50 nm. The simulation was also conducted on a bare Au nanoparticle of 50 nm (Figure 3d) and an imaginary 10-layer MoS₂ shell with inner diameter equals to 50 nm (Figure 3f). The obtained Absorbance spectra are shown in Figure 3c. A significant red-shift was observed of the LSRP peak from bare Au nanoparticle to the Au@MoS₂ heterostructure. This has been attributed to strong plasmon-exciton coupling between Au and MoS₂. The imaginary MoS₂ shell exhibits pronounced C and D excitonic peaks, however the A peak is very weak due to the low optical cross sections of few-layer MoS₂. This further indicates the importance of the inner Au nanoparticle core.

The distribution of surface electric field on various targets in Figure 3d-f was also calculated to demonstrate above field enhancement on Raman scattering and photoluminescence emission. Figure 3g shows a typical electric field map on the surface of Au nanoparticles with a maximum normalized electric field strength ($|E/E_0|^2_{\max}$) of 6.40. However, on the Au@MoS₂ heterostructure, it was found that the electric field was mainly

confined within the MoS₂ shell (Figure 3h), with a slightly increased $|E/E_0|_{\max}^2$. The strongest electric field “hot spots” mostly accumulate at the interface of Au and MoS₂ due to the plasmon-exciton coupling. The electric field on the imaginary MoS₂ shell is also confined inside its shell, however, the intensity is much lower. This well-explains the significant field enhancement of Raman and photoluminescence emission in Figure 2d and e and indicates useful applications of the Au@MoS₂ heterostructures, for instance, in future plasmonic transistors and emitters.

Example 3

Au@MoS₂ patterns

In some embodiments, the Au@MoS₂ heterostructures are fabricated on Si substrate with specific patterns, giving an additional level of control over the architecture and geometry. This this allows for the use of the heterostructures in light-driven applications such as SERS, imaging, and phototransistors. The fabrication steps were demonstrated in Figure 8 “NU” patterns of Au film were fabricated on a Si substrate (Figure 8a and b) using a photolithography method. This was followed by the same air-annealing process (850 °C for 15 min) to form Au nanoparticles (Figure 8c). Chemical vapor deposition was further carried out on the patterned substrate, resulting in the formation of Au@MoS₂ patterns in “NU” shape (Figure 8d). It was observed that isolated triangle islands of MoS₂ were formed in the blank regions (with no Au nanoparticles) of the Si substrate. On the region near the solid-state precursors, the islands merged into continuous films. Enlarged images of individual “NU” patterns are shown in Figure 4a and b. It was found that the presence of Au nanoparticles has a heterogeneous seeding effect, which induces the extended lateral growth of triangle MoS₂ films from NU patterns. To further support these findings, disk-like patterns (20 μm, Figure 8e) of Au nanoparticles were also fabricated using the same lithography process. Au@MoS₂ patterns with similar laterally-grown MoS₂ flakes were obtained after the chemical vapor deposition (Figure 8f). Elemental composition characterization of the Au@MoS₂ patterns was conducted by EDS mapping (Figure 4c-f), which indicates the presence of Au (only within the patterns), Mo, and S. SEM image of a local region inside the Au@MoS₂ pattern is further demonstrated in Figure 4g, in which a single Au@MoS₂ heterostructure is also shown in Figure 4h, indicating its core-shell geometry as described above. EDS mapping was conducted on three individual Au@MoS₂ heterostructures. The obtained elemental maps in Figure 4i confirm the chemical composition of Au@MoS₂ core-shell inside the patterns.

SIMS elemental mapping was also conducted on a large region of the substrate, and the results are displayed in Figure 9.

Raman spectra (Figure 5a) were collected on various spots of the Au@MoS₂ patterns (as marked in Figure 5b). Raman peaks obtained on the extended MoS₂ flakes show relatively weak intensity with a frequency difference of 20.7 cm⁻¹, which indicates their few-layer structure. The Raman signals on Au@MoS₂ heterostructures are similar to those shown in Figure 2d, with a frequency of 24.2 cm⁻¹ for multilayered MoS₂ structure. The significantly enhanced Raman intensity is attributed to the presence of LSPR as demonstrated above. Raman mapping was further conducted on the Au@MoS₂ pattern (Figure 5c). Consistently enhanced Raman signals were observed on the Au@MoS₂ patterned regions, indicating the Au@MoS₂ heterostructures are a substrate material for SERS and other plasmonic imaging systems.

Photoluminescence emission spectra were also collected from the same spots. The blue spot on Au@MoS₂ heterostructures shows increased intensity as compared to these few-layer MoS₂ flakes (the black and red spots) due to the field enhancement. It is also worth noting that the photoluminescence on the red spot is much weaker than that on the black spot, showing an obvious photoluminescence quenching effect. This phenomenon was further confirmed by the photoluminescence map shown in Figure 5e, as the regions surrounding the “NU” pattern consistently show suppressed photoluminescence emission. The suppression of photoluminescence signal is attributable to charge transfer induced by the p-type doping effect of Au cores, which is similar to that observed in Figure 2e (the emergence of A⁻ excitations). Thus, incorporating Au in MoS₂ shell leads to both field enhancement effect and p-type doping effect. The final photoluminescence emission is a comprehensive result of both process. Since the electric field was mainly confined in the MoS₂ shell (Figure 3h), a significant photoluminescence enhancement was observed on the Au@MoS₂ pattern. However, in the lateral MoS₂ flake surrounding the pattern, field enhancement is weak, and thus a quenched photoluminescence signal was observed.

To better understand such charge-transfer induced p-type doping, density functional theory (DFT) electronic structure calculations were conducted to reveal the band alignments due to the direct combination of Au and MoS₂. A 6-layer MoS₂ sheet with and without curvature were considered. The obtained band structure of the flat MoS₂ is shown in Figure 11a, suggesting an indirect band gap of 1.35 eV. The MoS₂ sheet was further bent in *x*, *y*, and *xy* direction as illustrated in Figure 11b to introduce curvature into the system. The obtained band alignment for Au and several bent/unbent MoS₂ structures were shown in Figure 11c.

The Fermi level of flat MoS₂ (~4.7 eV) is slightly higher than that of Au nanoparticles (~5.1 eV). The introduction of structural curvature leads to decrease of Fermi levels of MoS₂, suggesting electron transfer from the conduction band of MoS₂ to Au would be facilitated. Schematic in Figure 5f illustrates the band structure of individual Au and MoS₂. Their direct
5 combination results in a realigned Fermi level with significant band bending effect (Figure 5g). Under illumination, the excited electrons on the conduction band, instead of decaying back to the ground state, are prone to transfer to the Au core. This leaves numerous holes in the valence band (p-doping effect) and explains the photoluminescence quenching effect observed in Figure 5d.

CLAIMS

1. A heterostructure composition composing a metal core encapsulated within a transition metal dichalcogenide (TMD) shell.
2. The composition of claim 1, wherein the metal core is a noble metal core.
3. The composition of claim 2, wherein the noble metal core comprises a single phase or alloy of gold (Au), silver (Ag), platinum (Pt), Palladium (Pd), Ruthenium (Ru), Rhodium (Rh), Iridium (Ir), and/or Osmium (Os).
4. The composition of claim 3, wherein the noble metal core comprises gold (Au).
5. The composition of claim 1, wherein the TMD shell is a monolayer or multilayer fullerene-like shell.
6. The composition of claim 1, wherein the TMD shell is a single or composite semiconductor of the type MX_2 , wherein M is a transition metal and X is a chalcogen.
7. The composition of claim 6, wherein the transition metal is selected from Mo and W.
8. The composition of claim 6, wherein the chalcogen is selected from S, Se, and Te.
9. The composition of claim 6, wherein TMD shell comprises molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), rhenium disulfide (ReS_2), molybdenum diselenide ($MoSe_2$), tungsten diselenide (WSe_2), and/or Molybdenum ditelluride ($MoTe_2$).
10. The composition of claim 6, wherein the TMD shell comprises 1-50 layers.
11. The composition of claim 1, wherein the noble metal nanoparticles are 5-200 nm in diameter.
12. The composition of claim 1, wherein the TMD shell is 0.65-32.5 nm thick.

13. A method for preparing the composition of claim 1 comprising directly growing a monolayer or multilayer of the TMD shell on the metal nanoparticle core.
14. The method of claim 13, wherein the monolayer or multilayer TMD shell is grown by chemical vapor deposition.
15. The method of claim 13, wherein the metal nanoparticle is formed by coating metal film onto a Si substrate via galvanic deposition or physical evaporation followed by high-temperature annealing.
16. The method of claim 13, wherein the metal nanoparticle-coated Si substrate is placed in a tube furnace and transition metal oxide and sulfur powder is carried over the substrate to form TMD shells on the nanoparticles.
17. A photodetector device comprising the composition of claim 1.
18. A composition comprising the composition of claim 1 patterned onto a substrate.
19. The composition of claim 17, wherein metal nanoparticles encapsulated within a TMD shell are deposited onto the substrate using standard photolithography process.
20. The composition of claim 19, wherein Au nanoparticles encapsulated within a MoS₂ shell are deposited onto the substrate using standard photolithography process.
21. The use of the composition of claim 1 in plasmonic hot electron enhanced optics and/or optoelectronics.

FIG. 1

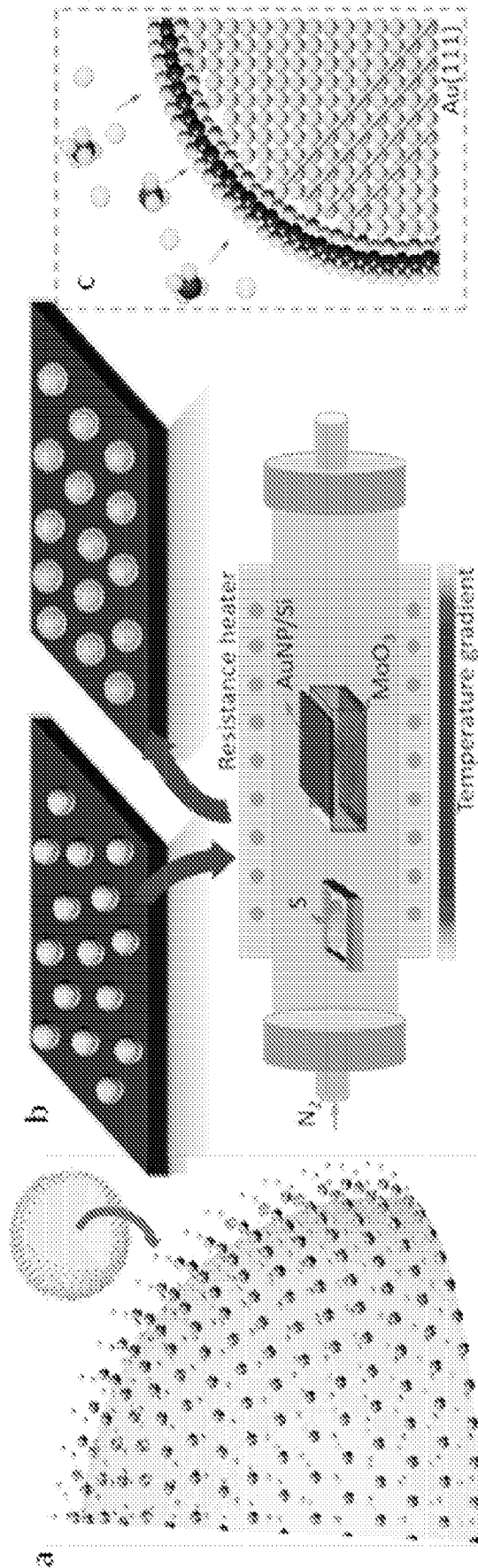


FIG. 1 (cont.)

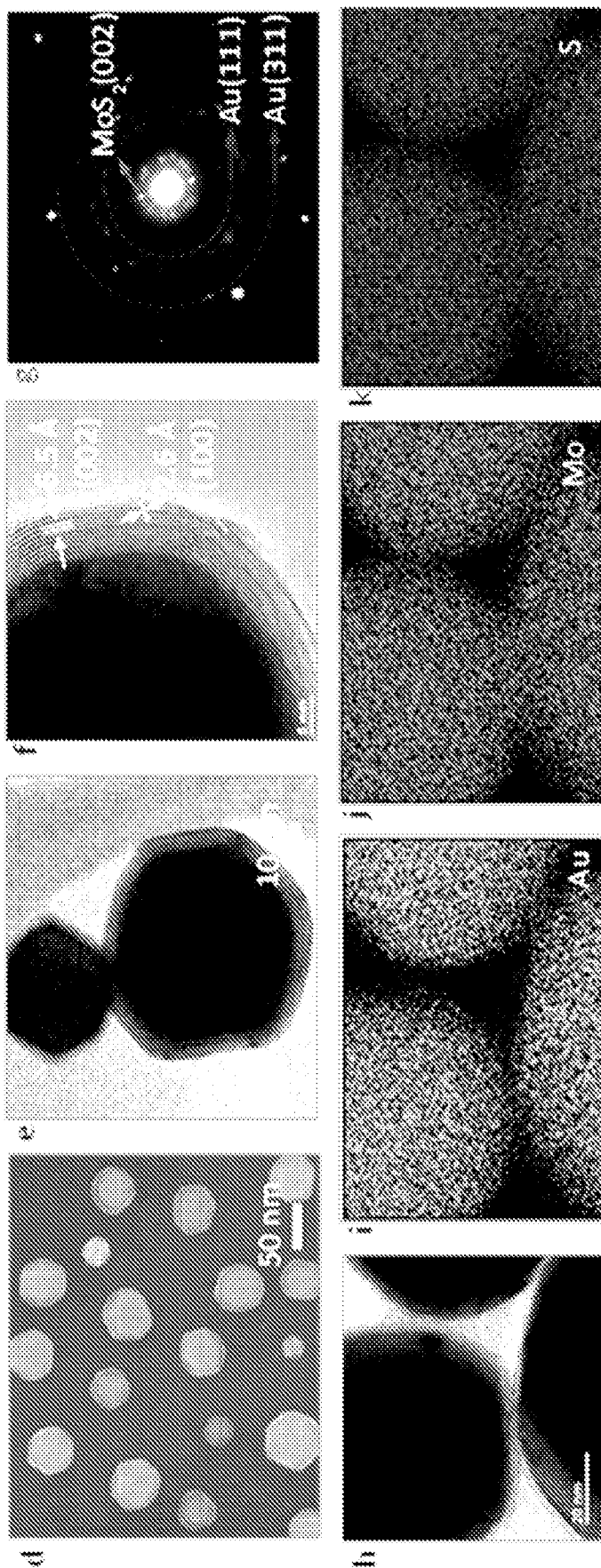


FIG. 2

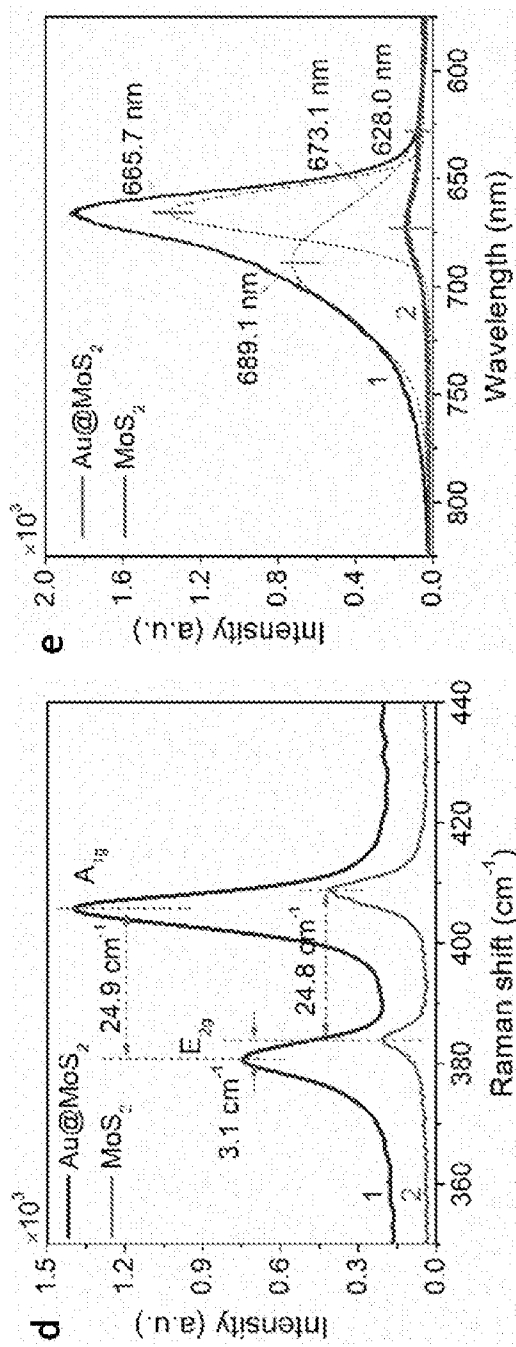
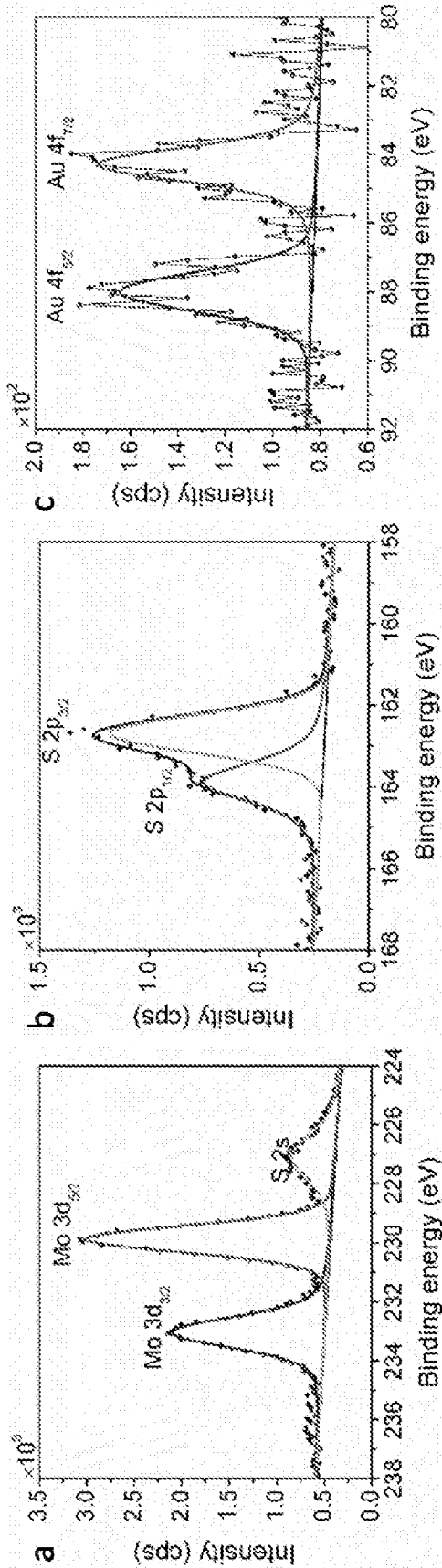


FIG. 3

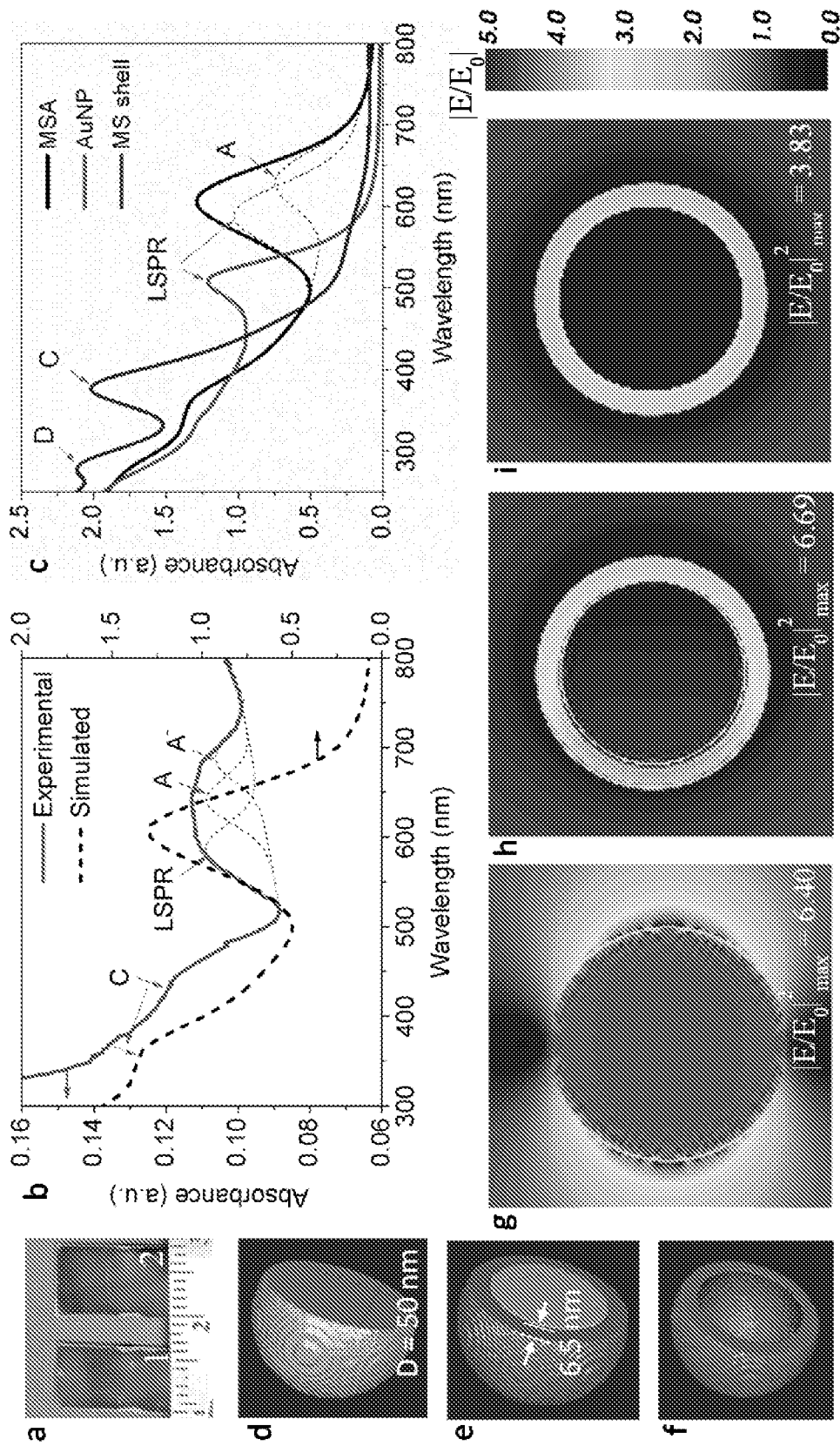


FIG. 4

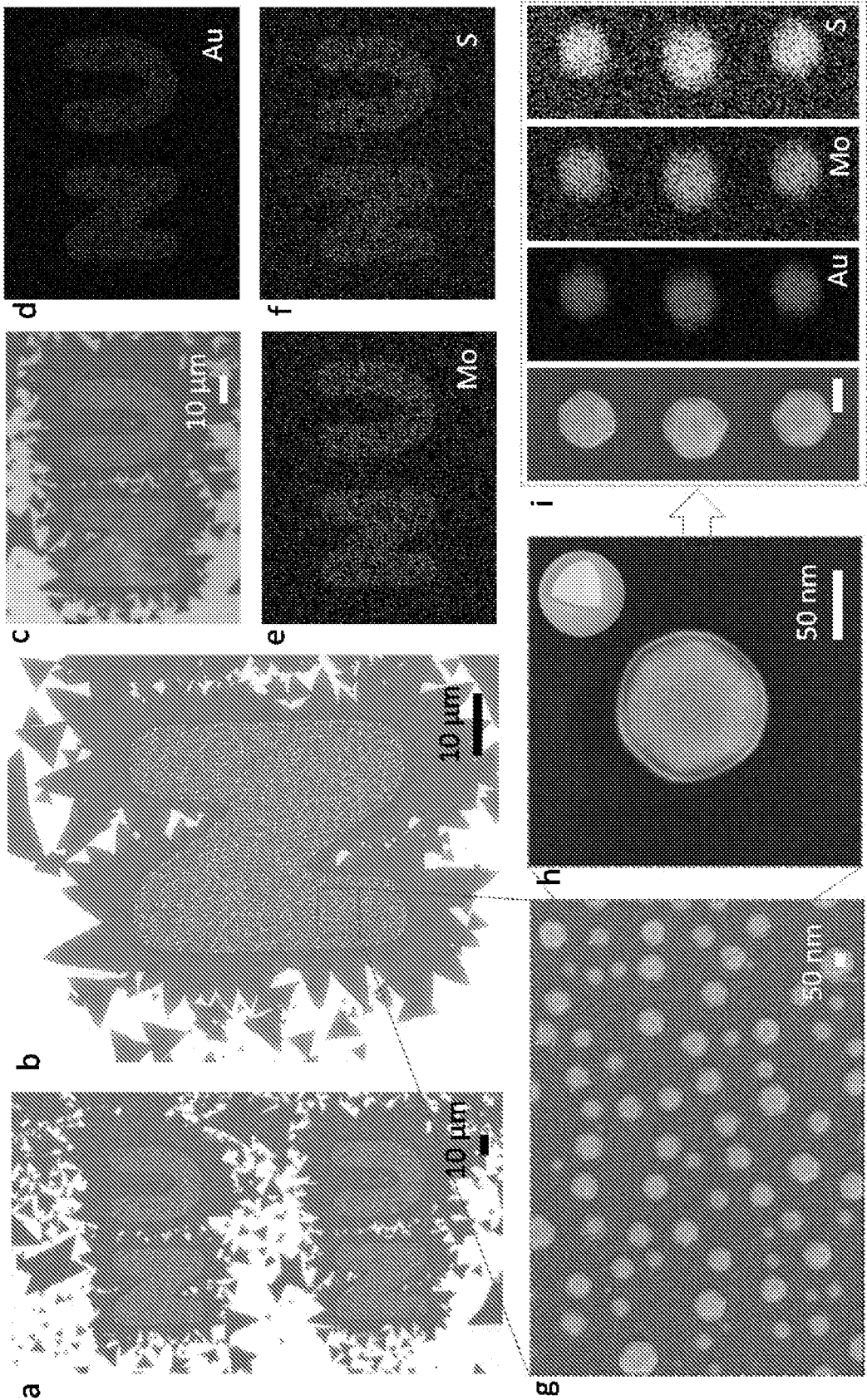


FIG. 5

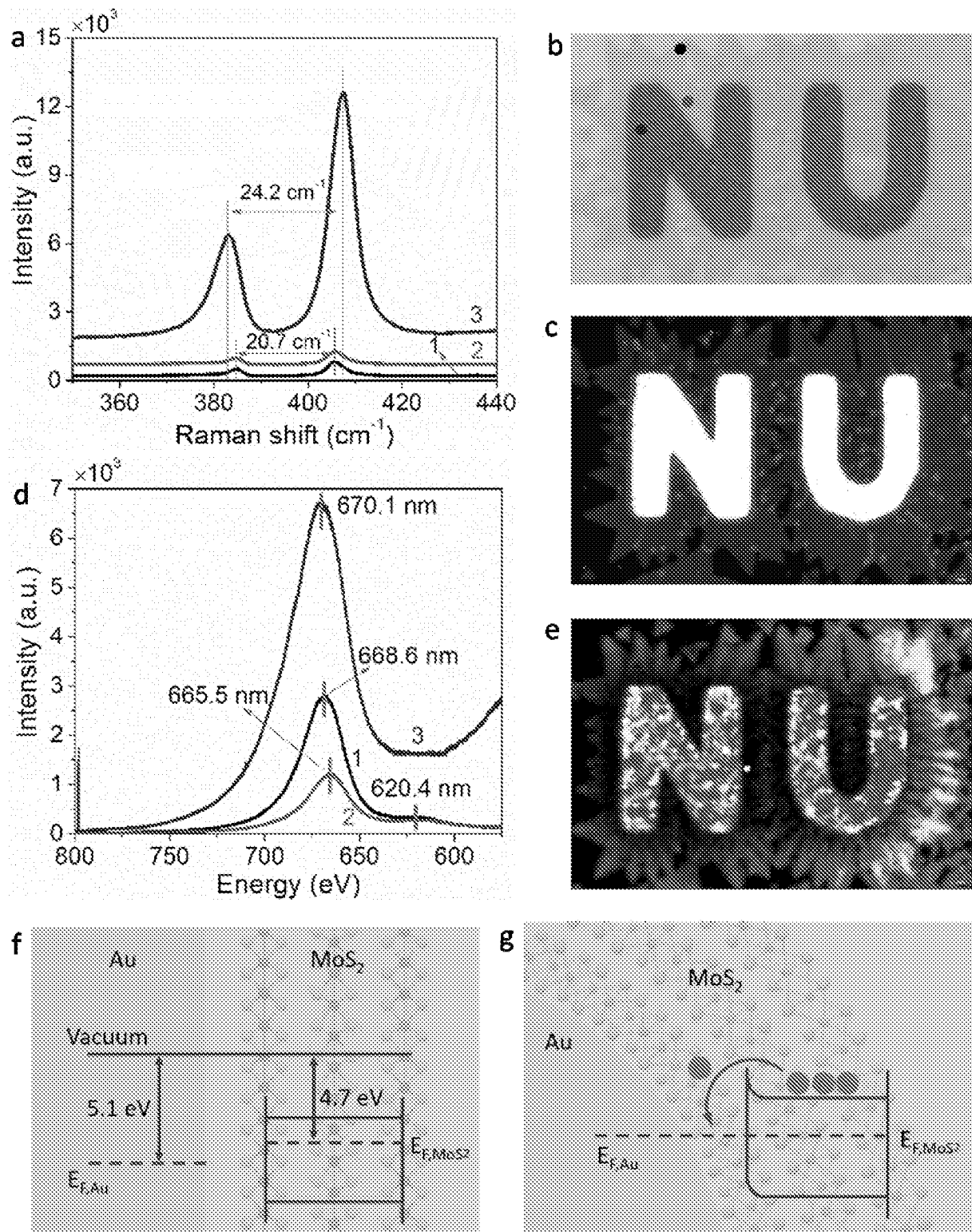


FIG. 6

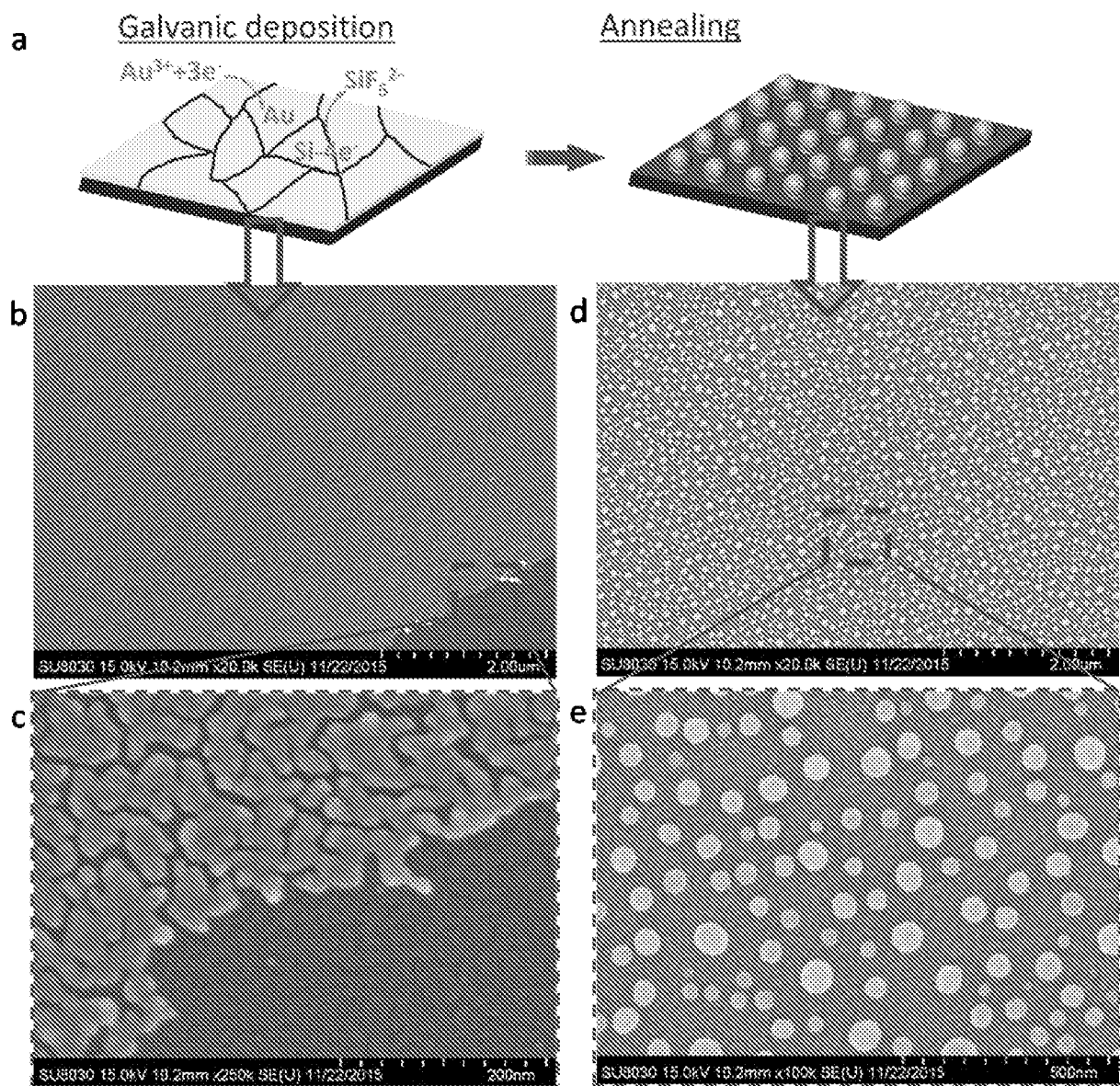


FIG. 3

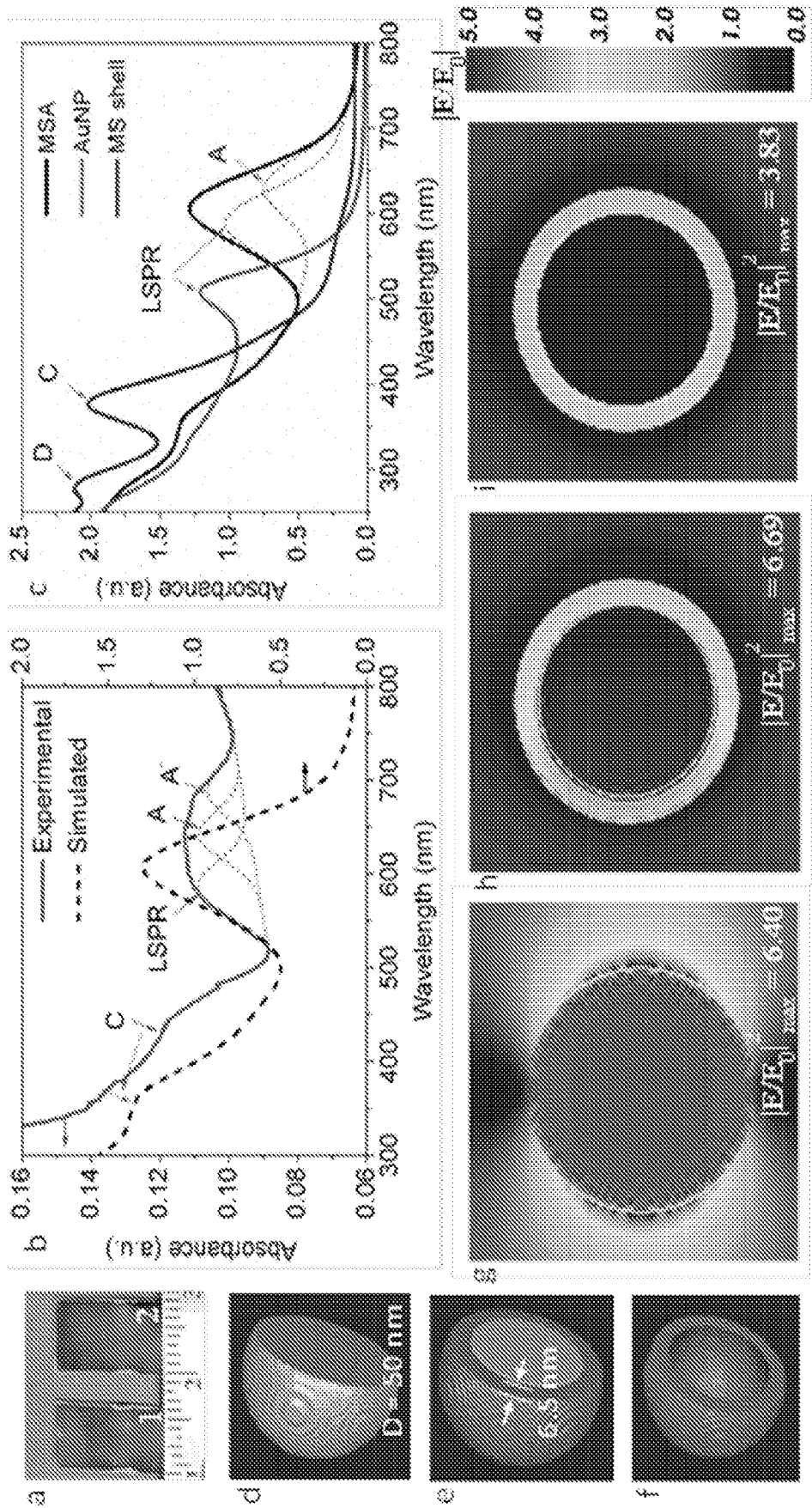


FIG. 4

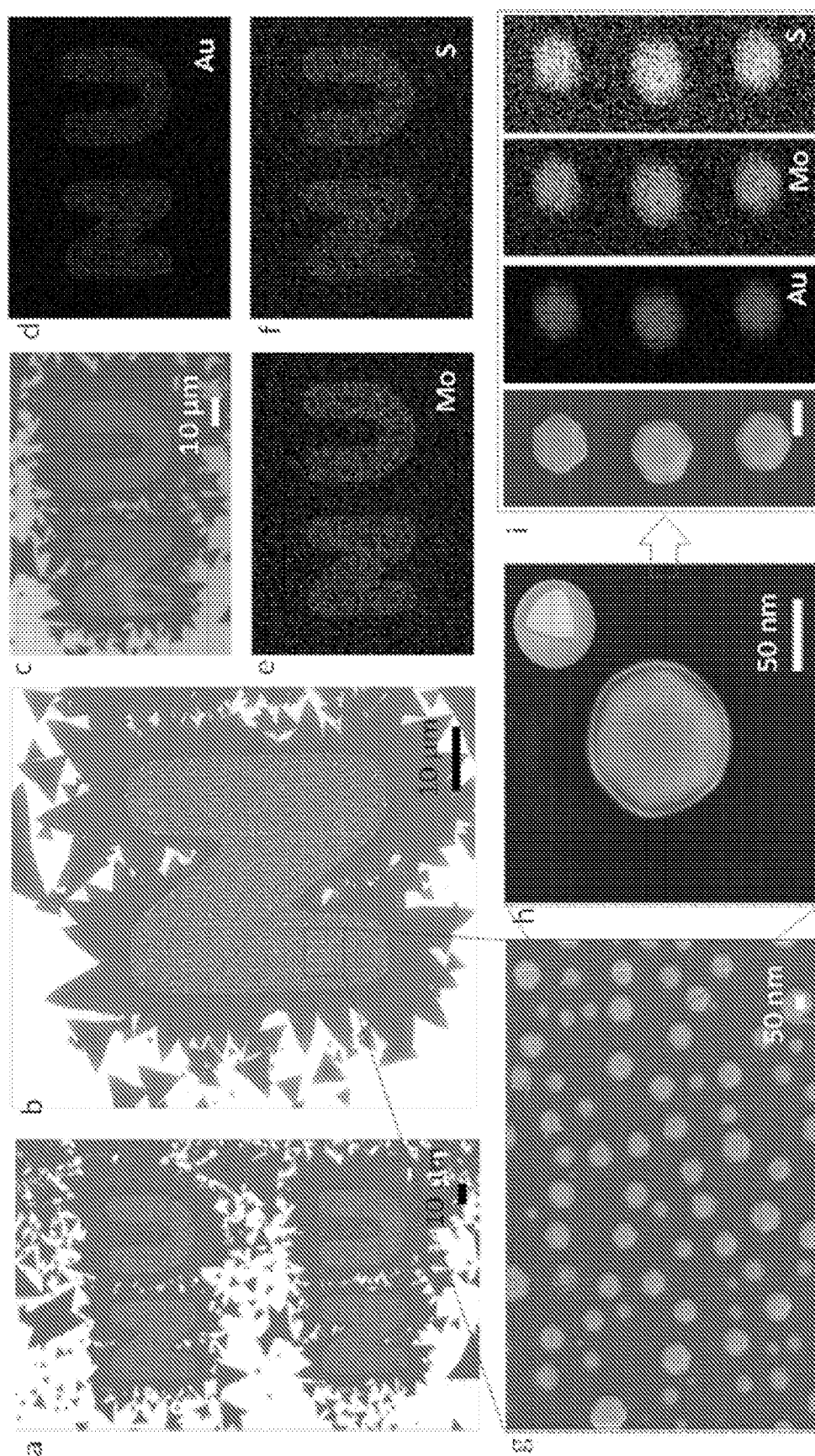


FIG. 5

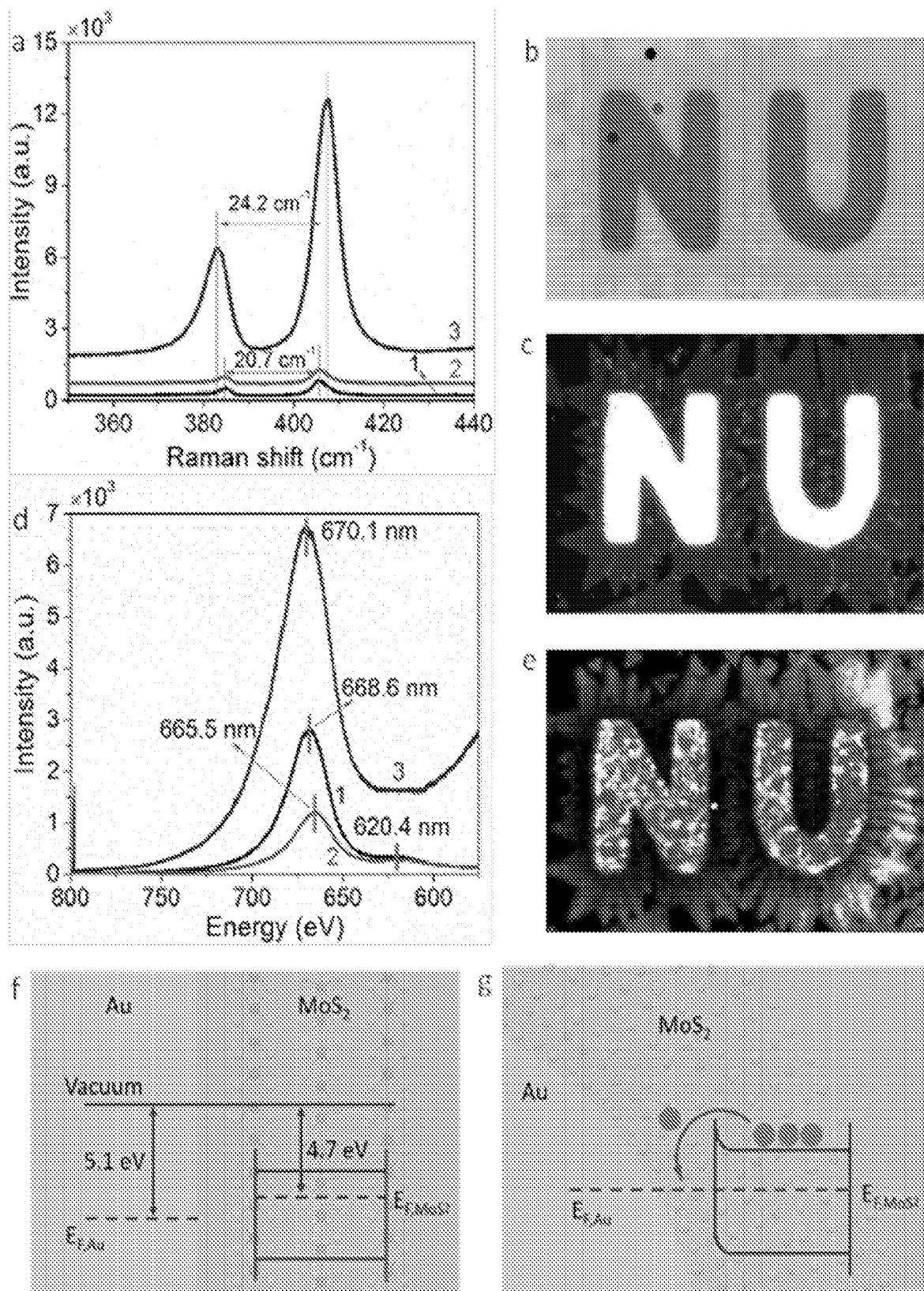


FIG. 6

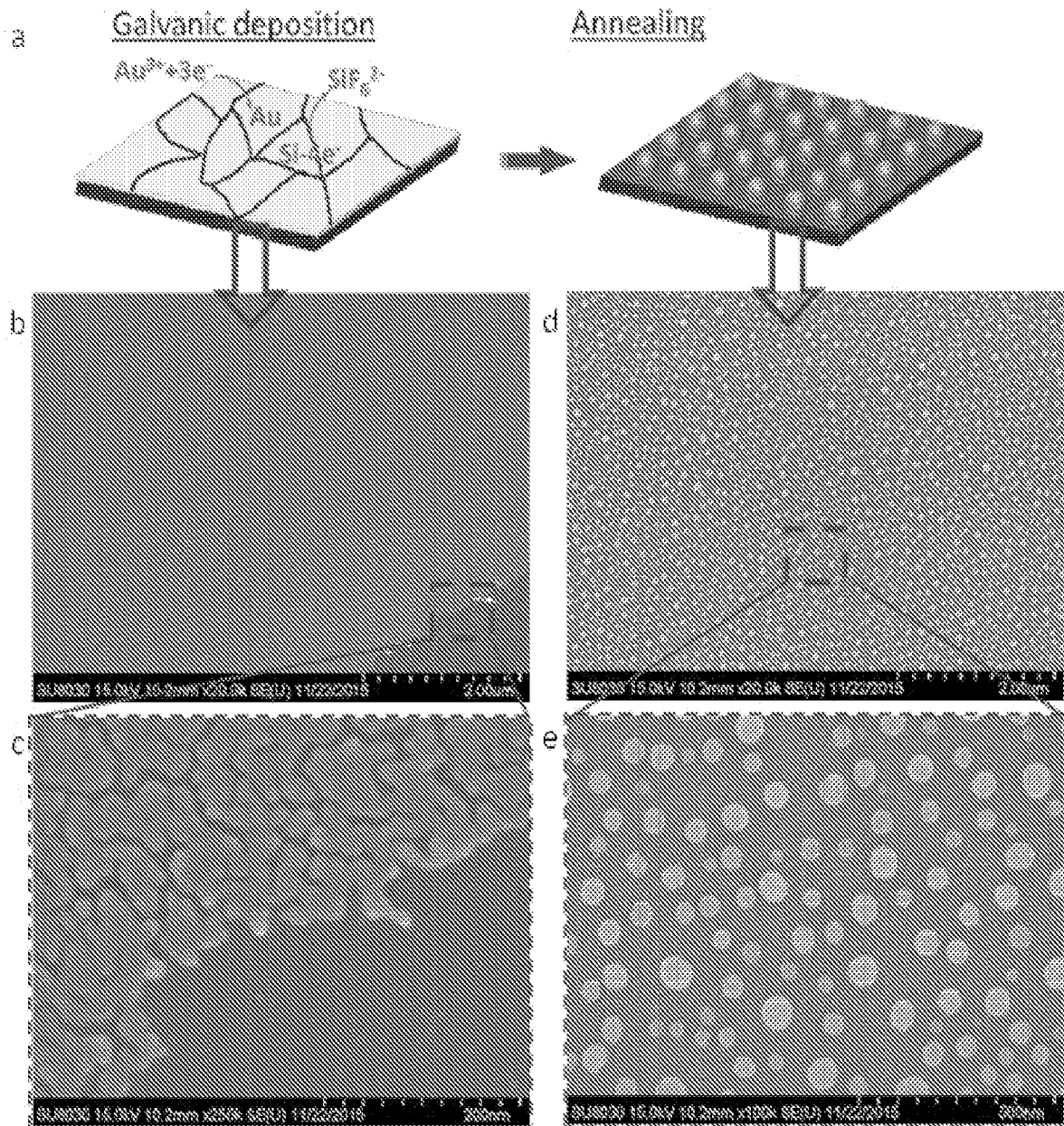


FIG. 7

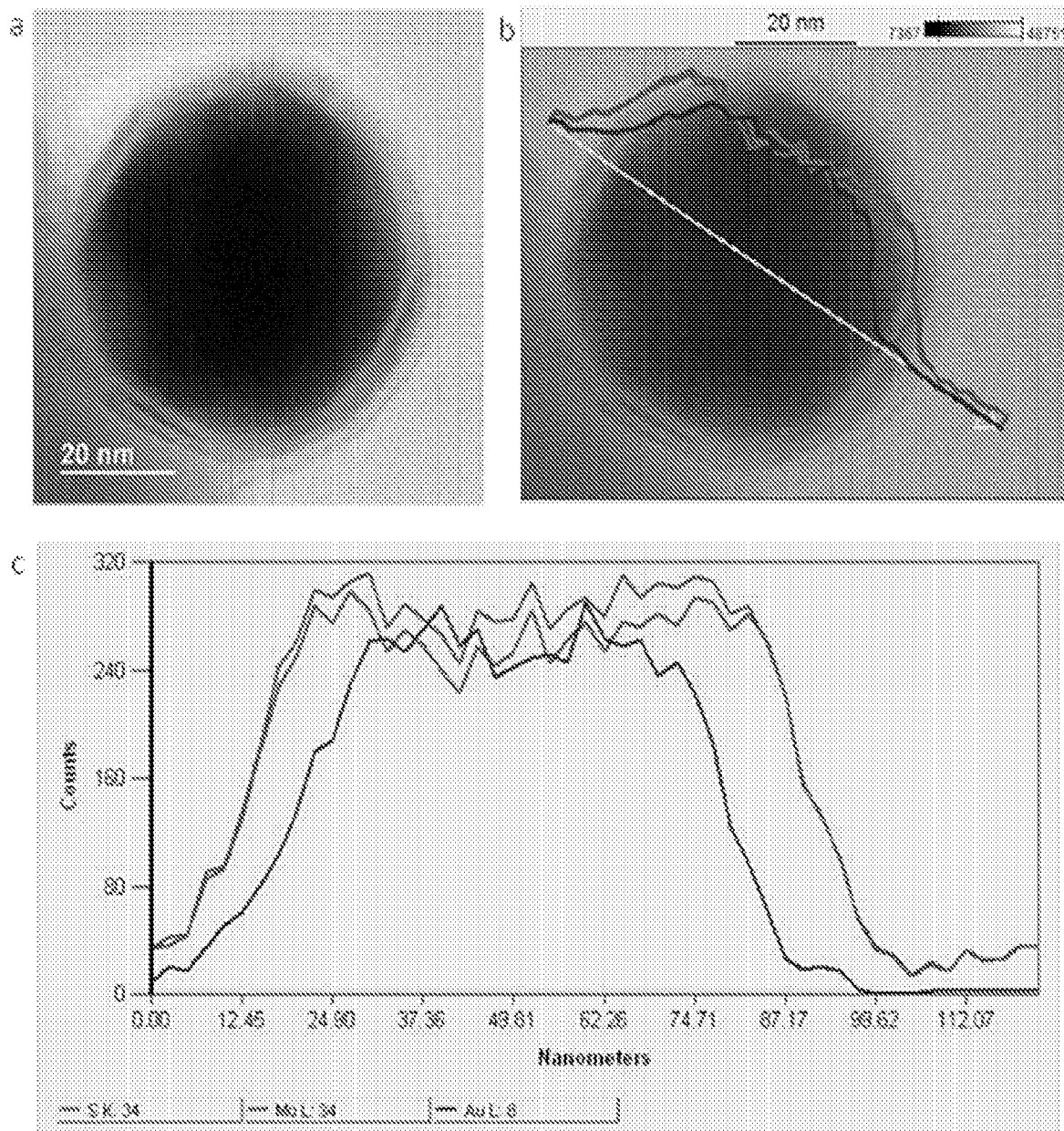


FIG. 8

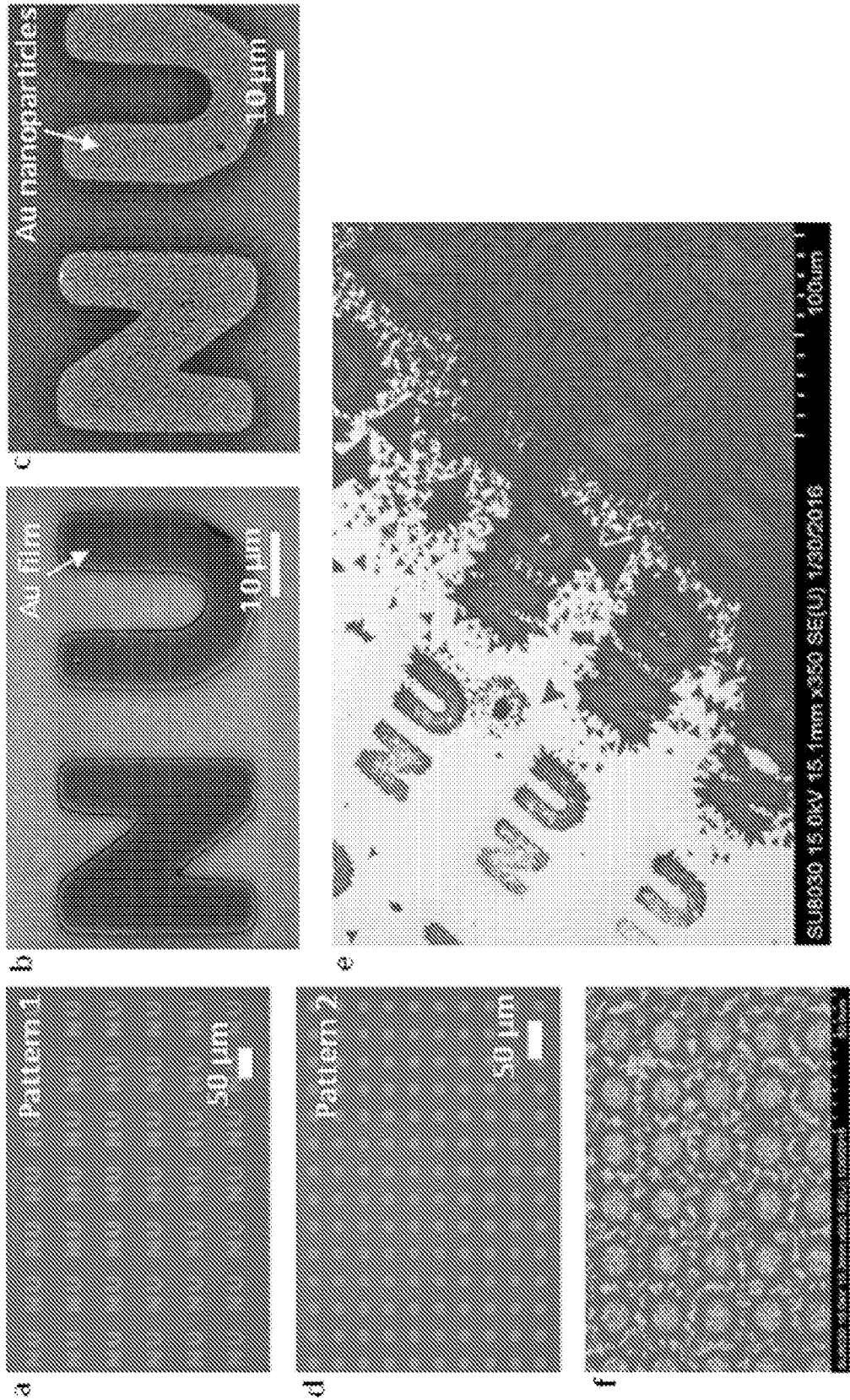


FIG. 9

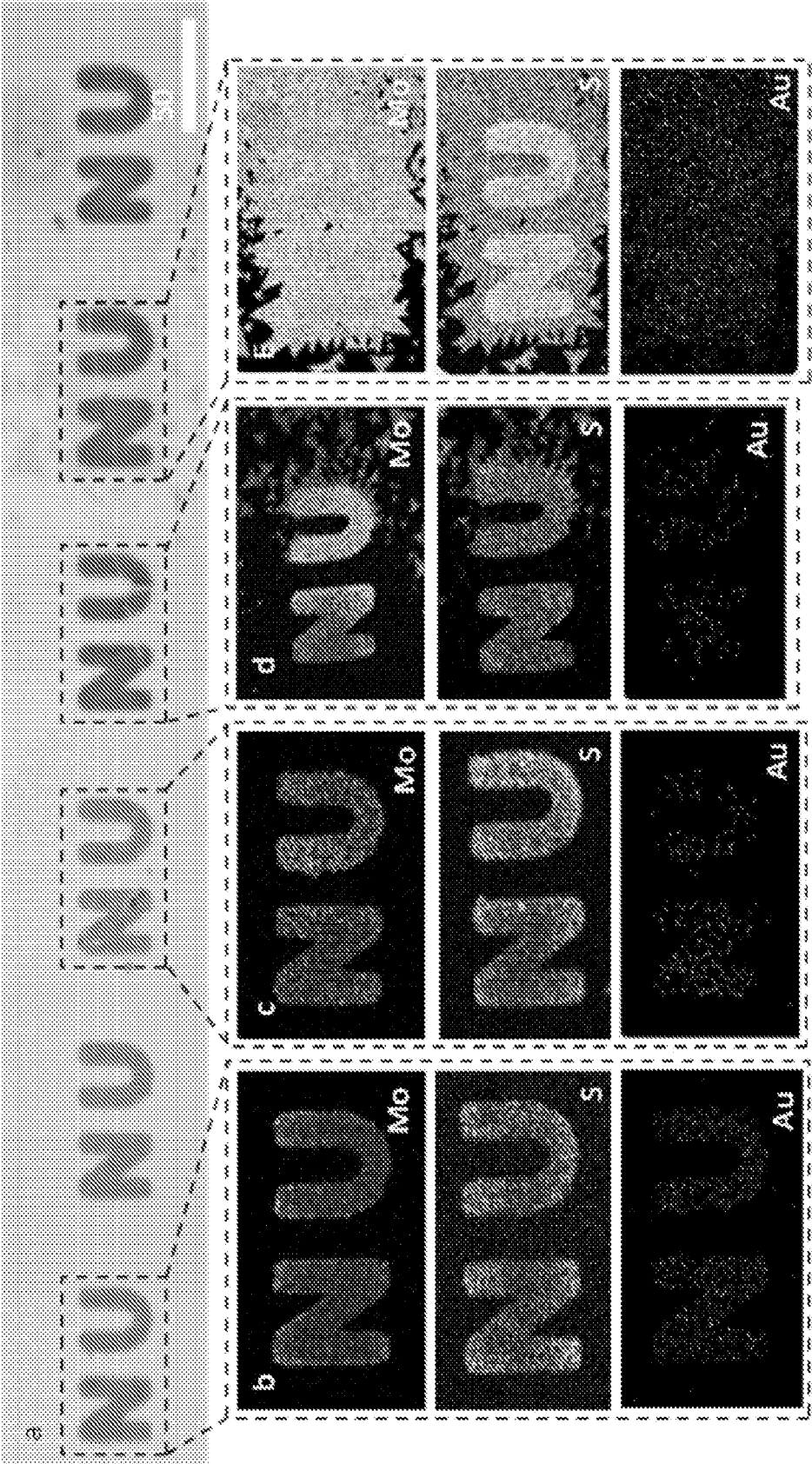


FIG. 10

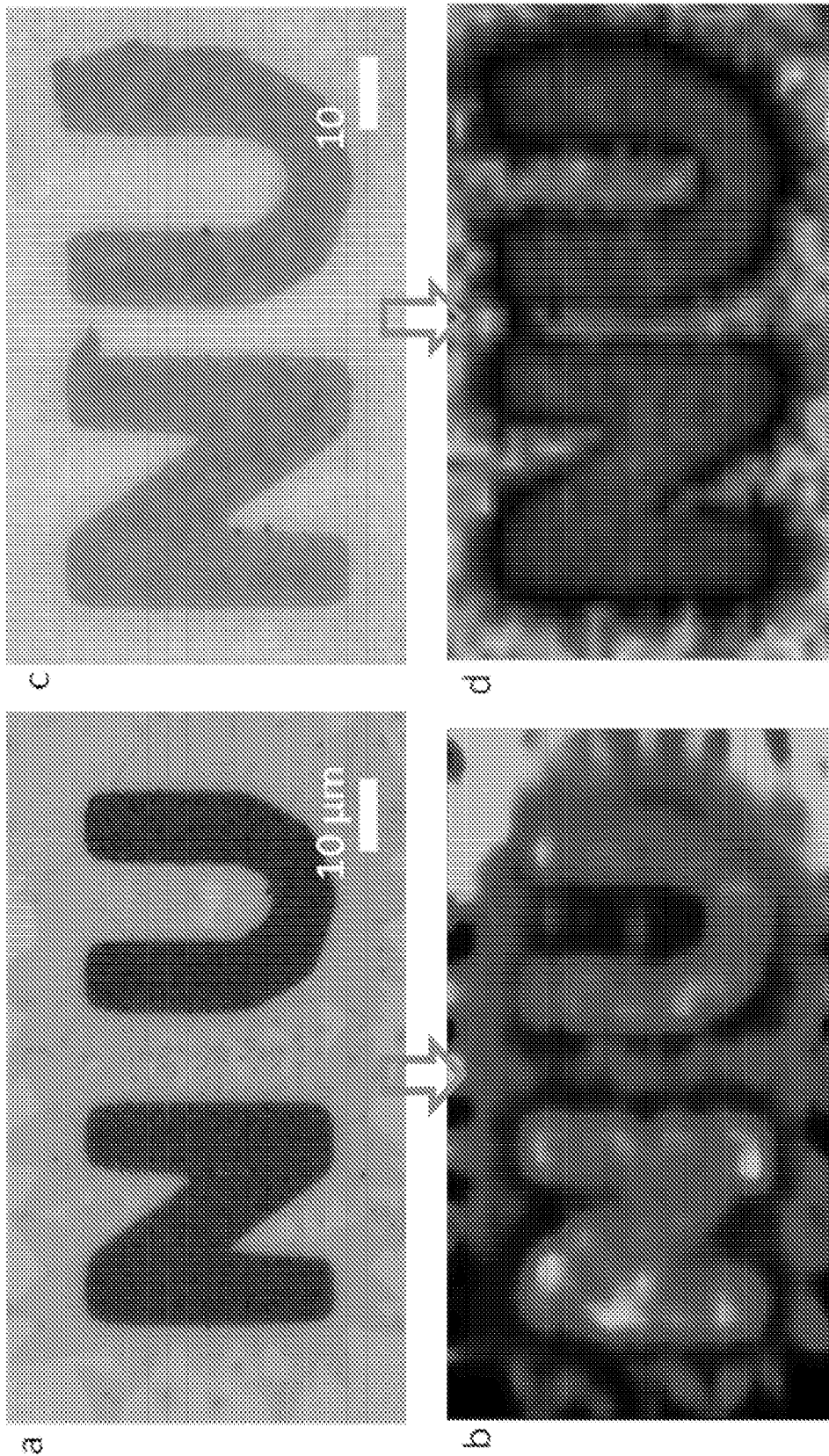
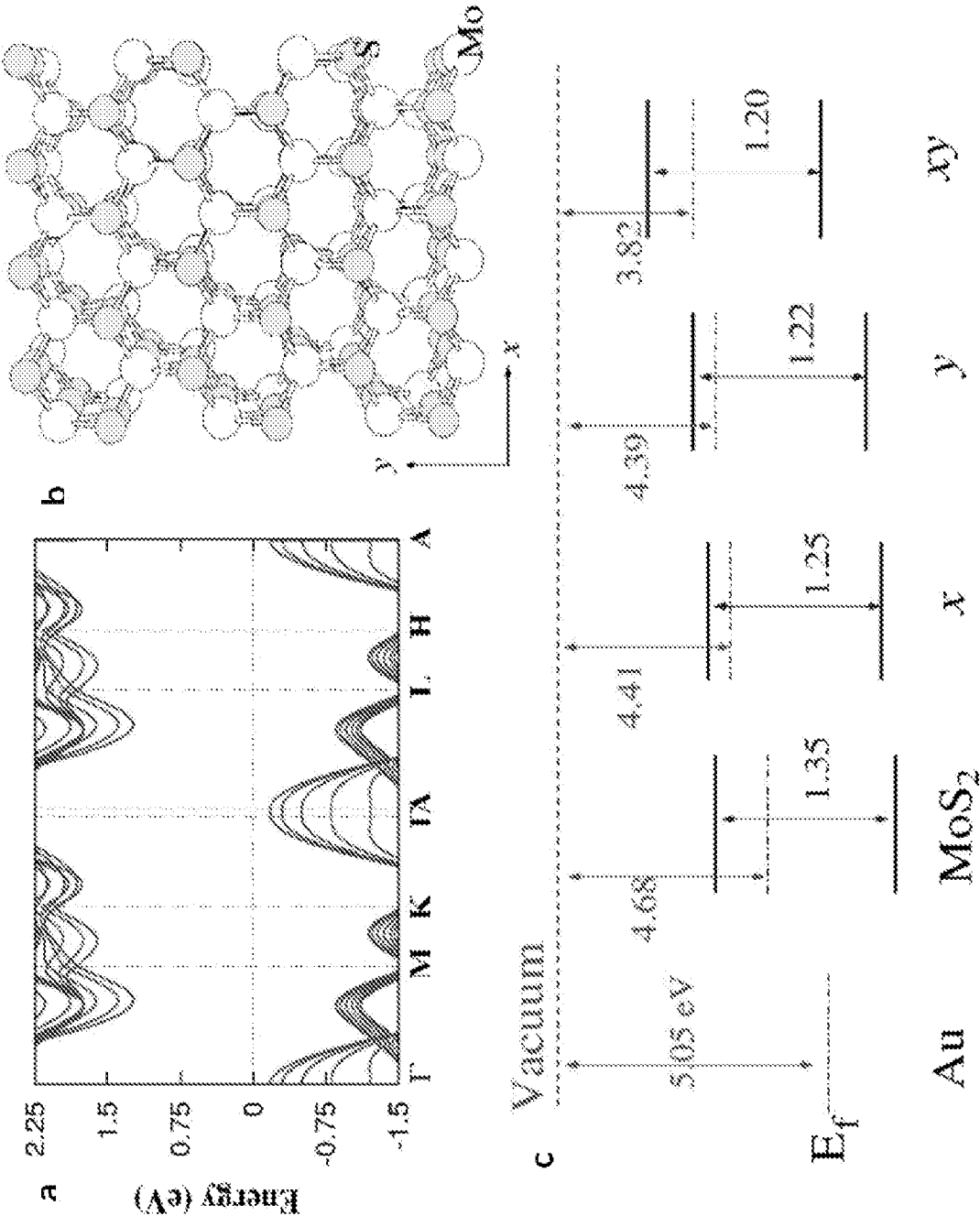


FIG. 11



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/049826

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/58; C01G 39/00; C01G 39/06; H01M 4/00; H01M 4/02; H01M 4/36 (2017.01)

CPC - H01M 4/5815; C01G 39/00; C01G 39/06; H01M 4/00; H01M 4/02; H01M 4/36; H01M 4/58; H01M 4/581 (2017.08)

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)

See Search History document

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)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104971744 A (ZHEJIANG UNIVERSITY OF SCIENCE AND TECHNOLOGY) 14 October 2015 (14.10.2015) see machine translation	1, 6-10, 12
X	CN 104492460 A (ZHEJIANG UNIVERSITY) 08 April 2015 (08.04.2015) see machine translation	1, 13
P, X	LI et al., Au@MoS ₂ Core-Shell Heterostructures with Strong Light-Matter Interactions, Nano Letters, Vol. 16, No. 12, 14 December 2016 [retrieved on 20 October 2017]. Retrieved from the Internet. <URL: https://www.ncbi.nlm.nih.gov/pubmed/27782405 >. see abstract	1-21

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"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

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Date of the actual completion of the international search

20 October 2017

Date of mailing of the international search report

07 NOV 2017

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