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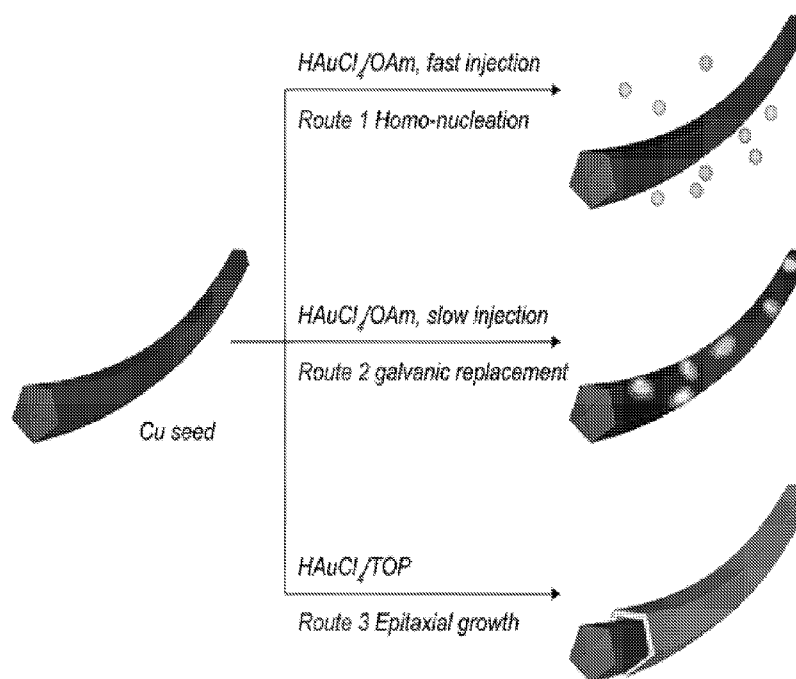


Fig. 1

(57) **Abstract:** Conductive core-shell metal nanowires that can be synthesized using a solution-based method can be used to construct transparent and flexible conductors with low cost in large scales. Noble metals, including Au, Ag, and Pt, can be formed (e.g., epitaxially) on the surface of ultra-thin metal (e.g., Cu) nanowires as a shell (e.g., a conformal shell) with tunable thickness, for example, in the range of about 1 to 3 nm. Transparent conducting films fabricated using colloidal suspensions of the core-shell nanowires exhibit excellent conductivity and comparable haze factors compared to the parent uncoated metal nanowires. The presence of conformal and epitaxial noble-metal shells has been found to significantly improve the film stability under air and humidity exposure at elevated temperature. Transparent electrodes formed from these transparent conducting films find use in numerous optoelectronic devices such as touch panels, displays, photovoltaic devices, and electrochromic windows.



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CONDUCTIVE CORE-SHELL METAL NANOWIRES FOR TRANSPARENT CONDUCTORS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application claims priority from U.S. Provisional Patent Application
62/449,963, filed January 24, 2017, titled, CONDUCTIVE CORE-SHELL METAL
NANOWIRES FOR TRANSPARENT CONDUCTORS; and from U.S. Provisional
Patent Application 62/475,102, filed March 22, 2017, titled, CONDUCTIVE CORE-
SHELL METAL NANOWIRES FOR TRANSPARENT CONDUCTORS; the
10 disclosures of which are incorporated herein by reference in their entirety.

FIELD OF THIS DISCLOSURE

[0002] This disclosure relates generally to metal nanowires, and more particularly to
the synthesis of conductive core-shell metal nanowires in solution.
15

BACKGROUND

[0003] Transparent conductors are an important component in numerous electronic
devices, such as touch panels, display devices (e.g., LCDs and OLEDs), photovoltaic
devices (e.g., solar cells), and electrochromic windows. Current technologies for
20 making transparent conductors using indium tin oxide (ITO) can provide a good
tradeoff between optical transparency and electrical sheet resistance. However, ITO
suffers from several drawbacks: (1) indium is becoming a scarce and expensive
resource; (2) sputtering and patterning (e.g., lithography) are costly; (3) ITO films are
brittle and inflexible due to poor mechanical ductility; and (4) ITO films are not
25 transparent in the infrared region, which is not ideal for solar cell and photodetector
applications.

[0004] Ongoing research and development efforts have been made to find alternative
materials that do not suffer from the drawbacks of ITO. Metal nanowires are
excellent candidates because they are solution-processable, patternable at a low cost,

highly flexible, and transparent in large wavelength ranges. Metal nanowires possess high electrical conductivity, and their optical properties can be tunable according to the size of the metal nanowires. Specifically, increasing the size of the metal nanowires can increase light scattering (haze) and reduce transparency. Ideally, the size of the metal nanowires can be very thin (e.g., less than about 30 nm in diameter), but not too thin to compromise stability and conductivity. Metal nanowires also possess high flexibility and can undergo bending hundreds or thousands of times without compromising their stability and conductivity. This can be useful in the area of flexible electronics and displays.

10 [0005] With excellent electrical properties, tunable optical properties, high flexibility, and solution-processability, there is a growing demand for cost-effective synthesis of metal nanowires.

SUMMARY

[0006] In accordance with this disclosure, conductive core-shell metal nanowires that can be synthesized using a solution-based method can be used to construct transparent and flexible conductors with low cost in large scales. Noble metals, including Au, Ag, and Pt, can be formed (e.g., epitaxially) on the surface of ultra-thin metal (e.g., Cu) nanowires as a shell (e.g., a conformal shell) with tunable thickness, for example, in the range of about 1 to 3 nm. Transparent conducting films fabricated using colloidal suspensions of the core-shell nanowires exhibit excellent conductivity and comparable haze factors compared to the parent uncoated metal nanowires. The presence of conformal and epitaxial noble-metal shells has been found to significantly improve the film stability under air exposure, particularly under air and humidity exposure at elevated temperature. Transparent electrodes formed from these transparent conducting films find use in numerous optoelectronic devices such as touch panels, displays, photovoltaic devices, and electrochromic windows.

[0007] In various embodiments, a method of making conductive core-shell metal nanowires is disclosed. The method involves forming a mixture comprising metal nanowires and a solution comprising a noble metal precursor, a noble metal reducing agent, and a ligand that strongly binds the noble metal, and allowing reaction of the mixture to form nanowires comprising a shell of the noble metal on a core of the metal.

[0008] According to various embodiments, the metal of the core may be copper. The noble metal of the shell may be gold. Where the metal noble metal of the shell is gold, the noble metal precursor may be chloroauric acid (HAuCl_4) or chloro(triphenylphosphine)gold ($\text{Au(PPh}_3\text{)Cl}$), for example.

- 5 [0009] According to various embodiments, the noble metal reducing agent can be a silane, in particular an organosilane, such as tris(trimethylsilyl)silane.

[0010] According to various embodiments, the ligand prevents galvanic replacement between the noble metal and the metal. The ligand may a phosphine, such as trioctylphosphine (TOP).

- 10 [0011] According to various embodiments, the metal nanowires of the core may be formed by a method that involves dissolving a metal precursor in a solvent comprising a surface ligand to form a solution, adding to the solution an organic reducing agent, and allowing the solution to form metal nanowires. The metal precursor may a metal salt, such as copper chloride (CuCl_2). The solvent comprising a
15 surface ligand may be oleylamine. The organic reducing agent may be an organosilane, such as tris(trimethylsilyl)silane. The solution may be heated above 100°C after addition of the organic reducing agent. The metal nanowires may be collected as a precipitate. According to various embodiments, the metal nanowires so formed and residual organic reducing agent provide the metal nanowires and noble
20 metal reducing agent of the mixture in the method of making the core-shell metal nanowires. According to this embodiment, the noble metal precursor and the ligand may be added to the formed metal nanowires in the solution comprising the residual organic reducing agent to form the mixture.

- [0012] According to various embodiments, the noble metal shell is grown on the
25 metal core. As noted above, in some embodiments, the core-shell nanowires may include copper core-gold shell nanowires, and may also be copper core-epitaxial gold shell nanowires. In some such embodiments, the copper core may be less than 25nm in diameter, for example about 15-20nm, and the gold shell maybe greater than 1nm thick, for example about 1-2nm thick. In some embodiment, the gold shell forms a
30 conformal coating on the copper core.

[0013] The methods of making nanowires may be conducted under inert atmosphere. In the method of making core-shell nanowires, the mixture maybe be

heated above 100°C but below 200°C, for example between 100 and 150°C, during the reaction of the mixture to form the nanowires.

[0014] In a specific embodiment, a method of making core-shell metal nanowires involves, under inert atmosphere, dissolving a CuCl_2 in oleylamine to form a solution, adding tris(trimethylsilyl)silane to the solution; heating the solution to a temperature below the boiling point; adding to the solution a second solution of chloroauric acid (HAuCl_4) dissolved in trioctylphosphine (TOP) at between 100 and 150°C, and cooling the solution to room temperature to form nanowires comprising a conformal epitaxial shell of gold on a copper core, wherein the copper core is about 15-20nm in diameter and the gold shell is about 1-2nm thick.

[0015] In other embodiments, a conductive core-shell metal nanowire is disclosed. The core-shell metal nanowire includes a metal core having a diameter of less than 25nm, and a noble metal shell on the metal core, the shell have a thickness of about 1-2nm. For example, the conductive core-shell metal nanowire can have a copper core having a diameter of about 15-20 nm, shell of gold have a thickness of about 1-2nm. The gold shell may be conformal and/or epitaxial.

[0016] In other embodiments the disclosure provides a transparent conductive film having a mesh of the conductive metal nanowires, such as made or described herein, the film having a sheet resistance of less than 1000 Ohms/sq, a total transmittance of at least 85% and a haze factor of less than 5%. Specific embodiments of such a the film may have a sheet resistance of less than 35 Ohms/sq, a total transmittance of at least 90% and a haze factor of less than 2%.

[0017] In other embodiments the disclosure provides a transparent electrode having a conducting film such as described herein, and an optoelectronic device including such a transparent electrode. The optoelectronic device may be a LCD display, a LED display, a photovoltaic device, a touch panel, a solar panel, a light emitting diode (LED), an organic light emitting diode (OLED), an OLED display, or a electrochromic window, for example.

[0018] In other embodiments the disclosure provides a method of making transparent conductive thin film. The method involves disposing on a planar substrate core-shell metal nanowires as made or described herein suspended in a solvent, and removing the solvent by vacuum process to form the transparent conductive thin film. The

method may involve annealing the thin film by heating to a temperature of greater than 100°C under forming gas.

[0019] These and other embodiments are described in further detail below.

5 BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Fig. 1 provides a schematic illustration of the reduction of chloroauric acid (HAuCl₄) in the presence of Cu nanowire seed under three different ligand environments and injection rates.

10 [0021] Figs. 2A-F show images and data plots of the reduction of chloroauric acid (HAuCl₄) in the presence of Cu nanowire seed with weakly bound ligand oleylamine (OAm) injected quickly or slowly.

[0022] Fig. 3 shows reduction kinetics of HAuCl₄ to gold metal in presence of (a), oleylamine and (b), trioctylphosphine ligand.

15 [0023] Fig. 4 depicts TEM images with different magnifications (a,b), SEM image (c), HAADF-STEM image (d), and the corresponding EDS mapping images (e-g) of Cu-Au core-shell nanowires.

[0024] Fig. 5 depicts the compositional line profiles of copper (dark) and gold (light) across three aligned nanowires.

20 [0025] Fig. 6 depicts HAADF-STEM images of Cu-Au core-shell nanowires synthesized with Cu:Au feedings of 5:1 (a), 10:1 (b), 20:1 (c), and corresponding atomic resolution STEM images (d-f).

[0026] Fig. 7 depicts SEM images of as-made nanowire transparent conductors, (a) with smaller loading and (b) with larger loading.

25 [0027] Fig. 8 depicts transmittance spectra of transparent conducting films made from Cu-Au core-shell nanowires.

[0028] Fig. 9 depicts plots of (a) transmittance vs sheet resistance and (b) haze factor vs total transmittance of transparent conductors made from bare copper nanowires, Cu-Au (1 nm Au) and Cu-Au (2 nm Au).

30 [0029] Fig. 10 depicts (a) stability of Cu-Au (2 nm Au) core-shell nanowire mesh films in a high humidity and high temperature environment, and (b) stability

comparison of nanowire transparent electrodes made from bare Cu, Cu-Ag (with a composition of Cu₉₀Ag₁₀), Cu-*r*-GO, Cu-Au (1 nm Au), and Cu-Au (2 nm Au).

[0030] Fig. 11 depicts a schematic of an example optoelectronic device with an active layer sandwiched between two metal nanowire films.

5

DETAILED DESCRIPTION

[0031] In accordance with this disclosure, conductive core-shell metal nanowires that can be synthesized using a solution-based method can be used to construct transparent and flexible conductors with low cost in large scales. Noble metals, including Au, Ag, and Pt, can be formed (e.g., epitaxially) on the surface of ultra-thin metal (e.g., Cu) nanowires as a shell (e.g., a conformal shell) with tunable thickness, for example, in the range of about 1 to 3 nm. Transparent conducting films fabricated using colloidal suspensions of the core-shell nanowires exhibit excellent conductivity and comparable haze factors compared to the parent uncoated metal nanowires. The presence of conformal and epitaxial noble-metal shells has been found to significantly improve the film stability under air exposure, particularly under air and humidity exposure at elevated temperature. Transparent electrodes formed from these transparent conducting films find use in numerous optoelectronic devices such as touch panels, displays, photovoltaic devices, and electrochromic windows.

[0032] In the following description, numerous specific details are set forth in order to provide a thorough understanding of the presented concepts. The presented concepts may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail so as to not unnecessarily obscure the described concepts. While some concepts will be described in conjunction with the specific embodiments, it will be understood that these embodiments are not intended to be limiting.

[0033] Nanowires can differ from their bulk counterparts in that the properties of the nanowires correlate with their size, shape, and morphology. Controlling the size, shape, and morphology of metal nanowires during synthesis can be important in tailoring their properties. For example, in making transparent conducting electrodes, it is desirable to form metal nanowires that are thin enough to minimize light

scattering, but thick enough to not compromise electrical conductivity and to ensure stability.

[0034] Metal nanowires can be synthesized based on colloidal chemistry. The resulting network of metal nanowires produced in solution can be incorporated in a variety of applications, such as optoelectronic devices. Producing the metal nanowires in solution can have the advantage of lower cost and easier mass production over the production of other materials like ITO. Different handles for tunability, such as reaction conditions and reaction chemistries, can control the size, shape, and morphology of the metal nanowires, thereby tailoring their physical and chemical properties.

[0035] Within this description, the terms “nanowires,” “nanorods,” “nanowhiskers,” and “nanopillars” and other similar terms may be used synonymously, except as otherwise indicated. Generally, these terms refer to elongate structures which have lengths and widths, where the length is defined by the longest axis of the structure and the width is defined by the axis generally normal to the longest axis of the structures, and wherein the elongate nanostructures have an aspect ratio greater than one (i.e., length > width in the ratio length: width).

[0036] In various embodiments, the diameter of, for example, a “rod” or “wire” is about 1-70 nm, about 1.2-60 nm, about 1.3-50 nm, about 1.5-40 nm, about 2-30 nm, about 2.5-25 nm, about 3-23 nm, about 10-22 nm, about 17-21 nm, about 1-10 nm, about 1-5 nm, about 1 nm, about 1.5 nm, about 2 nm, about 2.5 nm, about 3 nm, about 3.5 nm, about 4 nm, about 4.5 nm, about 5 nm, about 10 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 30 nm, about 35 nm, about 40 nm, about 50 nm, or about 60 nm. The diameter for a copper nanowire is typically about 15-25 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, or about 22 nm. The length of the “rod” or “wire” is about 50-100 nm, about 80-500 nm, about 100 nm to 1 μ m, about 200 nm to 2 μ m, about 300 nm to 3 μ m, about 400 nm to 4 μ m, about 500 nm to 5 μ m, about 600 nm to 6 μ m, about 700 nm to 7 μ m, about 800 nm to 8 μ m, about 900 nm to 9 μ m, about 1 μ m to 10 μ m, about 2 μ m to 15 μ m, about 3 μ m to 20 μ m, about 5 μ m to 50 μ m. For a metal elongated nanostructure, (e.g., a copper nanowire), the length will typically be at least 50 nm, at least 60 nm, at least

70 nm, at least 80 nm, at least 90 nm, at least 100 nm, at least 200 nm, at least 500 nm, at least 1 μ m, at least 5 μ m, at least 10 μ m, or at least 15 μ m.

[0037] The term “aspect ratio” as used herein refers to the ratio of a structure’s length to its width. Hence, the aspect ratios of the elongated structures of the disclosure will be greater than one (i.e., length > diameter). In a particular embodiment, the aspect ratio, for example, a “rod” or “wire” is greater than 1, greater than 10, greater than 100, greater than 200, greater than 300, greater than 400, greater than 500, greater than 600, greater than 700, greater than 800, greater than 900, greater than 1,000, greater than 1,500, greater than 2,000, or greater than 5,000. The aspect ratio for a copper nanowire is typically greater than 100, greater than 200, greater than 300, greater than 400, greater than 500, greater than 600, or greater than 700.

[0038] Metal nanowires can be synthesized in solution using a silane-based reducing agent. This is described in PCT Patent Application No. WO/2016/049430, titled “Methods to Produce Ultra-Thin Metal Nanowires for Transparent Conductors,” to Yang et al., filed September 25, 2015, as follows: The method includes forming a reaction mixture comprising a silane-based reducing agent, a copper metal salt and a surface ligand, wherein the surface ligand may also be a solvent; and heating and maintaining the reaction mixture at an elevated temperature between 1 to 48 hours with or without stirring. In one embodiment, the copper metal salt is selected from CuI, CuBr, CuCl, CuF, CuSCN, CuCl₂, CuBr₂, CuF₂, CuOH₂, Cu-D-gluconate, CuMoO₄, Cu(NO₃)₂, Cu(C₁₀H₄)₂, CuP₂O₇, CuSeO₃, CuSO₄, Cu-tartrate, Cu(BF₄)₂, Cu(NH₃)₄SO₄, and including any hydrates of the foregoing. In a further embodiment, the copper metal salt is CuCl₂ or a hydrate of CuCl₂. In another embodiment, the silane-based reducing agent is selected from triethylsilane, trimethylsilane, triisopropylsilane, triphenylsilane, tri-n-propylsilane, tri-n-hexylsilane, triethoxysilane, tris (trimethylsiloxy) silane, tris (trimethylsilyl) silane, di-tert-butylmethylsilane, diethylmethylsilane, diisopropylchlorosilane, dimethylchlorosilane, dimethylethoxysilane, diphenylmethylsilane, ethyldimethylsilane, ethyldichlorosilane, methyldichlorosilane, methyldiethoxysilane, octadecyldimethylsilane, phenyldimethylsilane, phenylmethylchlorosilane, 1,1,4,4-tetramethyl-1,4-disilabutane, trichlorosilane, dimethylsilane, di-tert-butylsilane, dichlorosilane, diethylsilane, diphenylsilane, phenylmethylsilane, n-hexylsilane, n-

octadecylsilane, n-octylsilane, and phenylsilane. In a further embodiment, the silane-based reducing agent is tris (trimethylsilyl) silane or triphenylsilane. In yet another embodiment, the surface ligand is selected from oleylamine, trioctylphosphine oxide, oleic acid, 1, 2-hexadecanediol, trioctylphosphine, or any combination of the foregoing. In a particular embodiment the surface ligand is oleylamine. In another embodiment, the reaction mixture is heated and maintained at a temperature between about 50°C to 250°C. In a further embodiment, the reaction mixture is heated and maintained from 160 °C to 200 °C for at least 8 hours. In another embodiment, the ultrathin copper nanowires are collected by centrifugation or filtration. In yet another embodiment, the method further comprises: washing and centrifuging the collected copper elongated nanostructure with a nonpolar organic solvent for a plurality of times. In a particular embodiment, the nonpolar organic solvent comprises hexane.

[0039] Ag and Cu have the highest intrinsic conductivity among all metals, i.e. 6.3×10^{-7} and 6.0×10^{-7} S/m, respectively. Whereas Ag nanowires are already being used in the touch panel market, the high abundance of Cu in the earth's crust evokes increasing research interest to propel the adoption of Cu nanowires in transparent conductors. Several groups have demonstrated the high transmittances of the Cu nanowire thin films at low sheet resistances. However, Cu is extremely vulnerable to species like O₂, H₂O, and sulfide in ambient atmosphere. Transmittance conductors based on Cu nanowires, therefore, suffer from rapid oxidation and steep performance decline. To this end, attempts have been made utilizing core-shell structure design to encapsulate Cu nanowires with an "inert" shell, such as Al₂O₃, Al-doped ZnO, Zn, Sn, In, Ni, Au, Ag, Pt, and graphene/graphene oxide. In despite of these efforts, it still remains a challenge to stabilize the Cu nanowires without significantly compromising their optical performance in terms of transmission and haze.

[0040] In various embodiments, a method of making conductive core-shell metal nanowires is disclosed. The method involves forming a mixture comprising metal nanowires and a solution comprising a noble metal precursor, a noble metal reducing agent, and a ligand that strongly binds the noble metal, and allowing reaction of the mixture to form nanowires comprising a shell of the noble metal on a core of the metal.

[0041] According to various embodiments, the metal of the core may be copper. The noble metal of the shell may be gold. Where the metal noble metal of the shell is

gold, the noble metal precursor may be chloroauric acid (HAuCl_4) or a hydrate thereof, such as chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), or chloro(triphenylphosphine)gold ($\text{Au}(\text{PPh}_3)\text{Cl}$), for example.

5 **[0042]** According to various embodiments, the noble metal reducing agent can be a silane, in particular an organosilane, such as tris(trimethylsilyl)silane.

According to various embodiments, the ligand prevents galvanic replacement between the noble metal and the metal. The ligand may be a phosphine, such as trioctylphosphine (TOP) or trihexylphosphine. More generally the ligand may be a soft Lewis base, for example, a long chain thiol-based ligand, such as dodecanethiol.

10 **[0043]** According to various embodiments, the metal nanowires of the core may be formed by a method that involves forming a mixture including a solution of a metal precursor in a solvent including a surface ligand, and an organic reducing agent, for example by dissolving a metal precursor in a solvent comprising a surface ligand to form a solution, adding to the solution an organic reducing agent; and allowing the
15 solution to form metal nanowires. The metal precursor may be a metal salt, such as copper chloride (CuCl_2). The solvent comprising a surface ligand may be a hydrophobic solvent with a boiling point above 100°C , such as biphenylether, octadecane, and others noted above, including oleylamine. The organic reducing agent may be an organosilane, such as tris(trimethylsilyl)silane, or others noted above.
20 The solution may be heated above 100°C after addition of the organic reducing agent. The metal nanowires may be collected as a precipitate, and stored in a nonpolar solvent such as toluene or hexane. According to various embodiments, the metal nanowires so formed and residual organic reducing agent provide the metal nanowires and noble metal reducing agent of the mixture in the method of making the core-shell
25 metal nanowires. According to this embodiment, the noble metal precursor and the ligand may be added to the formed metal nanowires in the solution comprising the residual organic reducing agent to form the mixture.

30 **[0044]** Therefore, in some embodiments, the formation of the shell may follow directly from the formation of the core metal nanowires. In a typical synthesis, a copper precursor such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ligand such as oleylamine may be combined in a reaction vessel and agitated until the dissolution of the copper precursor. A reducing agent such as tris(trimethylsilyl)silane may be added into the

solution under inert gas atmosphere. The solution may be heated above 100°C after addition of the organic reducing agent, to form the metal nanowires. Then, a TOP or other suitable long chain phosphine solution of gold shell precursor, such as $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, can be added at a temperature below the temperature at which the metals will alloy, e.g., about 130-150°C. A suitable ratio of gold to copper precursor can be 1:1 to 1:20 by weight. After the introduction of gold precursor, the solution can be cooled down to room temperature in about 30 to 120 minutes, for example 1 hour. The product can then be collected by centrifugation washed repeatedly with a nonpolar solvent such as toluene, for example using redispersion-centrifugation cycles to remove excess ligand. The gold shell-copper core nanowire product can then be dispersed in toluene for further processing, for example into transparent conductive films.

[0045] According to various embodiments, the noble metal shell is grown on the metal core. As noted above, in some embodiments, the core-shell nanowires may include copper core-gold shell nanowires, and may also be copper core-epitaxial gold shell nanowires. In some such embodiments, the copper core may be less than 25nm in diameter, for example about 15-20nm, and the gold shell maybe greater than 1nm thick, for example about 1-2nm thick. In some embodiment, the gold shell forms a conformal coating on the copper core.

[0046] The methods of making nanowires may be conducted under inert atmosphere. In the method of making core-shell nanowires, the mixture maybe be heated above 100°C but below 200°C, for example between 100 and 150°C, during the reaction of the mixture to form the nanowires.

[0047] In a specific embodiment, a method of making core-shell metal nanowires involves, under inert atmosphere, dissolving a CuCl_2 in oleylamine to form a solution, adding tris(trimethylsilyl)silane to the solution; heating the solution to a temperature below the boiling point; adding to the solution a second solution of chloroauric acid (HAuCl_4) dissolved in trioctylphosphine (TOP) at between 100 and 150°C, and cooling the solution to room temperature to form nanowires comprising a conformal epitaxial shell of gold on a copper core, wherein the copper core is about 15-20nm in diameter and the gold shell is about 1-2nm thick.

[0048] In other embodiments, a conductive core-shell metal nanowire is disclosed. The core-shell metal nanowire includes a metal core having a diameter of less than 25nm, and a noble metal shell on the metal core, the shell have a thickness of less than 3nm, for example about 1-2nm. For example, the conductive core-shell metal nanowire can have a copper core having a diameter of about 15-20 nm, shell of gold have a thickness of about 1-2nm. The gold shell may be conformal and/or epitaxial.

[0049] In other embodiments the disclosure provides a transparent conductive film having a mesh of the conductive metal nanowires, such as made or described herein, the film having a sheet resistance of less than 1000 Ohms/sq, a total transmittance of at least 85% and a haze factor of less than 5%. Specific embodiments of such a the film may have a sheet resistance of less than 35 Ohms/sq, a total transmittance of at least 90% and a haze factor of less than 2%.

[0050] In other embodiments the disclosure provides a transparent electrode having a conducting film such as described herein, and an optoelectronic device including such a transparent electrode. The optoelectronic device may be a LCD display, a LED display, a photovoltaic device, a touch panel, a solar panel, a light emitting diode (LED), an organic light emitting diode (OLED), an OLED display, or a electrochromic window, for example. Fig. 11 shows a schematic of an example of an optoelectronic device including an active layer that is sandwiched between two metal nanowire films.

[0051] In other embodiments the disclosure provides a method of making transparent conductive thin film. The method involves disposing on a planar substrate core-shell metal nanowires as made or described herein suspended in a solvent, for example a hydrophobic solvent such as toluene, and removing the solvent by vacuum process to form the transparent conductive thin film. The method may involve annealing the thin film by heating to a temperature of greater than 100°C, for example 180 to 260°C, such as about 200°C, under forming gas, for example, 5-10% H₂ and 90-95% Ar or other inert gas, e.g., N₂ for 15 to 60 minutes, for example 30 minutes.

EXAMPLE

[0052] The following example is provided to better illustrate aspects of this disclosure. Details of various specific examples of forming conductive core-shell

metal nanowires and properties of the results core-shell metal nanowires are presented below, without limitation:

[0053] This example relates to the epitaxial growth of a conformal shell of noble metal with atomic thickness onto a less noble metal template. During the overgrowth of noble metal onto a less noble metal template, galvanic replacement usually overwhelms and results in hollow nanostructures. Yang et al. have revealed that galvanic reaction between Ag and HAuCl_4 can be blocked in the presence of strong reducing agents. Using a similar synthetic approach, Stewart et al. coated Cu nanowires with Au, Ag, and Pt shells and demonstrated their improved stability as transparent conductors.

[0054] Disclosed herein is a different synthetic strategy to epitaxially deposit a conformal, ultrathin (e.g., 1–2 nm) noble metal (e.g., Au) shell on the surface of less noble metal (e.g., Cu) nanowires by modifying the ligand environments. Transparent conducting thin films made from the ultra-thin copper-noble metal core-shell nanowires hold comparable optical and electrical properties to the parent (uncoated) ultra-thin Cu nanowires. More importantly, their high performance can be sustained in ambient atmospheric conditions, and their stability has even been demonstrated at 80% humidity at 80°C for a test duration of 700 hours.

Results and discussion

[0055] The synthesis of Cu-Au core-shell nanowires was attempted by sequential reduction of the two metals as illustrated in the seeded growth routes depicted in Fig. 1. Fig. 1 provides a schematic illustration of the reduction of gold precursor chloroauric acid (HAuCl_4) in the presence of Cu nanowire seed under three different ligand environments and injection rates. With weakly bound ligand, such as oleylamine (OAm), fast injection induced self-nucleation of gold(0) species (Route 1), while slow injection resulted in galvanic replacement between gold cations and Cu nanowires (Route 2).

[0056] The ultrathin Cu nanowires were first prepared according to Routes 1 and 2 in oleylamine (OAm) using tris(trimethylsilyl)silane as a reducing reagent. After the depletion of copper precursor, HAuCl_4 dispersed in oleylamine was injected into the growth solution.

[0057] With weakly bound ligand, such as oleylamine (OAm), fast injection induced self-nucleation of gold(0) species. The products turn out to be the mixtures of small nanoparticles and nanowires, as depicted in Fig. 2a. Energy dispersive spectroscopy (EDS) mapping (Fig. 2b) shows that the small nanoparticles are pure gold, while the
 5 nanowires are composed of copper and gold, although the atomic ratio of gold is as low as 1% according to EDS quantitative analysis. The small nanoparticles can be further separated via differential-speed centrifuge (Fig. 2c). The characteristic localized-surface-plasmon-resonance (LSPR) observed at 525 nm in the ultraviolet-visible (UV-Vis) spectrum (Fig. 2d), together with the powder x-ray diffraction (XRD)
 10 patterns (Fig. 2e) further confirm the fact that the particles are Au nanoparticles. Fig. 2f depicts TEM images of Cu-Au synthesis product with slow injection of the gold precursor, showing galvanic replacement.

[0058] Without limitation to any particular theory of operation, it is thought that this observation could be a consequence of self-nucleation during the synthesis. As
 15 HAuCl_4 is rapidly introduced into the growth solution, instantaneous reduction of the gold precursor boosts the concentration of gold atoms and triggers the crystal growth. The synthesis was then modified and HAuCl_4 was slowly fed into the growth solution via syringe pump to maintain the concentration of newly formed gold atoms at a low level. The absence of small Au nanoparticles in the products (Fig. 2f)
 20 indicates the self-nucleation is suppressed using slow injection. However, pores and voids are prevalent in the as-obtained nanowires, implying the oxidation of the copper seeds arising from the galvanic replacement with HAuCl_4 .

[0059] The occurrence of galvanic replacement is not unexpected due to the more noble nature of Au compared to Cu. A possible solution provided by this disclosure is
 25 to reduce the reduction potential of $\text{AuCl}^{4-}/\text{Au}$ pair by lowering the chemical activity of oxidizing agent (a_{ox}) based on Nernst equation:

$$E_{\text{red}} = E_{\text{red}}^{\ominus} + \frac{RT}{zF} \ln a_{\text{ox}}$$

The chemical activity of oxidizing agent can be tuned through the process of complexation with Lewis base ($\text{M} + n\text{L} \rightleftharpoons \text{ML}_n$):

$$a_{\text{ox}} = a[\text{M}] = \frac{a[\text{ML}_n]}{k \cdot a[\text{L}]^n}$$

Then, the Nernst equation can be re-written in the form of:

$$E_{\text{red}} = E_{\text{red}}^{\ominus} + \frac{RT}{zF} \ln a[\text{ML}_n] - n \frac{RT}{zF} \ln k - \frac{RT}{zF} \ln a[\text{L}]$$

This reveals that a high stability constant of complex (k) and a high concentration of the Lewis base ($a[\text{L}]$) will effectively decrease the reduction potential. The stability of metal complexes can generally be qualitatively predicted and explained by hard and soft acids and bases (HSAB) theory. Specific to this synthesis, Au cation acts as a soft Lewis acid, but the co-existing Lewis bases like chloride and alkylamine are both hard. It was determined that the introduction of a soft Lewis base such phosphine would strongly bind to Au cations and keep their chemical activities and thus the reduction potentials low.

- 10 **[0060]** Accordingly, the synthesis was enhanced/optimized by using strongly bound ligand trioctylphosphine (TOP) to replace OAm and dissolve the Au precursor (Fig. 1, Route 3). With a strongly bound ligand such as trioctylphosphine (TOP), epitaxial growth was favored, regardless of the injection rate; that is, the injection speed was of little consequence under these conditions. The reduction kinetics were studied by UV-Vis spectroscopy. When HAuCl_4 was dispersed in OAm, a strong LSPR band emerges within 3 minutes after quick injection (Fig. 3a), reflecting the fact of instant reduction of HAuCl_4 . As a sharp comparison, the adsorption spectra have little change even 30 minutes after the quick injection of $\text{HAuCl}_4/\text{TOP}$ (Fig. 3b), and the reaction solution remains colorless. This suggests that the reduction kinetics of HAuCl_4 are quite sluggish in the presence of TOP. Because the concentration of newly-reduced Au atoms always stays low with the retarded reduction rate, it is not necessary to use the time-consuming slow-injection procedure. The UV-Vis spectroscopic study indicates that TOP is capable of changing the reduction kinetics of the Au precursor, although it is initially intended to change the reaction thermodynamics and reduce the reduction potential of the Au precursor.

- 25 **[0061]** An example of a successful synthesis of Cu-Au nanowires is described below. In a typical synthesis, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (85 mg, 0.5 mmol) and oleylamine (0.5 g) were charged in a Schlenk flask. The mixture was stirred at 70°C until the dissolution of the copper precursor. Tris(trimethylsilyl)silane (0.5 g, 2 mmol) was added into the solution under inert gas atmosphere. The resulting clear blue solution was slowly heated up from 70°C to 120°C in an oil bath. When the reaction solution turned into

clear yellow at 120°C, the reaction temperature was further raised to and kept at 165°C for 18 hours under stirring. Afterwards, a TOP solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.1–0.025 M, 1 mL) was injected by syringe at 140°C. The reddish reaction solution became crimson after the introduction of gold precursor, and was cooled down to room temperature one hour later. The product was collected by centrifugation (6000 r.p.m., 5 min) and washed repeatedly with toluene using redispersion-centrifugation cycles to remove excess oleylamine. The product was dispersed in toluene for further characterization and film fabrication.

[0062] Fig. 4a depicts the transmission electron microscopic (TEM) image of the products obtained from the determined synthetic protocol. Nanowires are in high purity with an average diameter of 21 ± 4 nm. The uniform nanowires are flexible and even bend into circular shapes. In the enlarged TEM image (Fig. 4b), the nanowires are intact without any surface pores or voids. Moiré patterns spread over these nanowires were also noted, which is an indicator of superimposition of two different phases with distinct lattice constants. The lengths of nanowires are in the range of 10 to 20 micrometers as shown in the scanning electron microscope (SEM) image (Fig. 4c). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) shows a brighter contrast on the side edges of the nanowires (Fig. 4d), suggesting a local enrichment of Au atoms. The core-shell structural feature is revealed by the EDS mapping (Figs. 4e-g). Whereas Cu is distributed in the central zone of the nanowires, Au is mainly located in the outer region. The Au shell thickness is measured to be about 2 nm.

[0063] As shown in Fig. 5, the compositional line profiles of Cu and Au across three aligned nanowires present an alternating pattern (Fig. 5), also suggesting the core-shell distribution of the Cu and Au elements. The bulk composition of the core-shell nanowires is determined to be $\text{Cu}_{86}\text{Au}_{14}$ via quantitative analysis of the EDS spectra. The Au content in the products is slightly lower than the feeding ratio of the metal precursors (20% of Au/Cu). This could be attributed to the complete consumption of Au precursor due to its sluggish reduction rate in the presence of TOP. Whereas the lattice distance in the core area is measured to be 0.21 nm, it is 0.23 nm in the shell area, agreeing well with the $\text{Cu}(111)$ and $\text{Au}(111)$ lattice spacings, respectively.

[0064] The thickness of the Au shell can be regulated with atomic precision by controlling the amount of Au precursor added into the reaction solution. As shown in

- Fig. 6a-c, the shell thickness could be changed from ~2 nm to ~1.5 nm and ~0.9 nm by altering the feeding ratio of the Au/Cu precursors from 20% to 10% and 5%, respectively. Atomic resolution HAADF-STEM images (Fig. 6d-f) reveal the shells containing different numbers of Au atomic layers, approximately corresponding to Cu-Au₁₂L, Cu-Au₇L, and Cu-Au₄L. From the high-resolution STEM images, it was noted that the surface of the nanowires is quite smooth without the presence of cuprous oxide layers that regularly observed in pure Cu nanostructures. The uninterrupted lattice fringes from the core to the shell manifest the epitaxial growth of Au on Cu. This affects the electrical properties of the nanowires, because the number of interface defects is reduced or minimized in this growth fashion. The distances between the adjacent lattice fringes in the cores are measured to be 0.21 nm for all the three samples, in good agreement with the lattice space of Cu(111) plane. The distances in the shell areas are 0.23 nm, which can be assigned to Au(111) plane. The lattice mismatch is about 9% and compressive strains should prevail in the shells.
- [0065]** Transparent conducting films were made on thin glass slides using a vacuum filtration method. As shown in the Fig. 7, SEM images of as-made nanowire transparent conductors (a) with smaller loading and (b) with a larger loading show that the nanowires are evenly distributed throughout the film with no obvious aggregation.
- [0066]** The UV-Vis absorption spectra of the core-shell nanowire mesh with both 1 nm and 2 nm of Au shell are given in Fig. 8. The black dashed lines are all Cu-Au (2 nm Au) with various loading amounts; the gray line is Cu-Au (1 nm Au) with a similar loading to one of the black lines. Overall, the films are highly transparent in a large wavelength window (from 350 nm to 1700 nm). Both cases of the core-shell films have the Cu signature plasma absorption dip at around 550 nm. However, a notable flattening of the Cu feature is observed for the thicker shelled conductors due to the increased content of gold. The inset of figure is the optical image of the Cu-Au nanowire film. The background pattern is seen in excellent clarity, thanks to the film's high transparency.
- [0067]** Fig. 9 summarizes the optical and electrical performance of Cu-Au core-shell nanowire electrodes, which exhibit excellent merits in transparency, conductivity and haze. Fig. 9a plots the transmittance vs sheet resistance relationship of three types of nanowire mesh films: bare Cu, Cu-Au with 1 nm shell thickness, and Cu-Au NWs

with 2nm shell thickness (transparent conductors made from bare copper nanowires (d~19nm), Cu-Au core-shell nanowires (5% of Au, d~19nm) and Cu-Au core-shell nanowires (20% of Au, d~21nm). Background substrate transmittance has been subtracted from all the data. Characteristic transmittance and haze factors are acquired at 550 nm of wavelength. Even though the electrical conductivity of bulk gold is down by 25% compare to copper, the Cu-Au core-shell nanowires exhibit almost identical transparency-resistivity performance as bare Cu nanowires. No obvious degradation of electrical conductivity is observed with thicker layer of gold depositing on the surface. This echoes with many theoretical calculations that, in the nanowire mesh geometry, the conductivity of the film is not sensitive with the bulk metal conductivity. This is especially true when the mesh is sparse. As indicated in the figure, the three data sets perfectly overlap with each other when transmittance is above 90%. However, a decrease in the conductivity in denser films is seen. This is believed to be because when more material is applied, the contribution of bulk metal's intrinsic conductivity cannot be ignored.

[0068] Another important parameter in judgement of transparent conductors is their light-scattering effect, which is quantified as haze factor. Fig. 9b presents the haze factor of the three types of films as a function of their total transmittance. In general, the haze factors of all three conductors decrease linearly with total transmittance. The overall small values of haze factors of the core-shell nanowires electrodes indicate that the light-scattering is maintained at a low level by their ultrathin dimension. When the total transmittance is at 91.5% for the 2nm Au shell NW mesh, the haze factor is only 1.85%; this value is even smaller for 1 nm Au shell nanowire, which is 1.56% at the same total transmittance. Interestingly, the core-shell nanowire mesh exhibits the same level of, or even slightly lower haze values comparing to the bare Cu electrodes. This result is counter intuitive because larger haze factor is expected with the increase in the mean diameter.

[0069] Finally, the core-shell nanowire conductors' ability to sustain their original conductivity was tested and the electrodes exhibit spectacular resistance towards degradation. The standard harsh condition (80°C, 80 ± 5% humidity in ambient atmosphere) is used to evaluate the nanowire's stability towards oxygen, moisture and heat. The results are shown in Fig. 10a. Seven individual Cu-Au (2nm shell) films with different wire loading amounts were placed under a heated, high-humidity

environment and their conductivities were traced with time. Impressively, throughout the 712 hours of testing, the conductivity of the films, no matter the initial loading amount, maintains almost the same.

[0070] Fig. 10b compares the harsh-environment aging behavior of conducting films made from nanowires with different compositions. Not surprisingly, the unprotected copper nanowire has the worst stability. After 1 hour's exposure, the sheet resistance increases more than four fold. After 3 hours, no conductivity can be detected any more. Cu-Ag core-shell nanowires appears to be more durable than bear copper, yet still show considerable decay in conductivity. After 48 hours' testing, the resistivity already increases almost 6 times. A previously reported Cu-r-GO nanowire electrodes exhibit significant enhancement in stability. 48 hours into the exposition, the sheet resistance only increases by 40 percent. Cu-Au nanowires undoubtedly have the best stability. After being exposed in high temperature, and high humidity environment for 48 hours, when most copper-based nanowire electrodes starts to lose conductivity, Au protect nanowires show no sign of degradation. The thicker the Au shell is, the more enduring the film can be. Particularly in the case of Cu-Au nanowire with 2 nm of Au shell, the sheet resistance increases no more than 25 percent throughout the 712 hours of testing. The remarkable stability of Cu-Au core-shell nanowires can be mainly accredited to the epitaxial growth of Au shell. This synthesis provides a route to a uniform and complete coverage of gold on the copper surface. Moreover, the epitaxial nucleation fertilizes a thin layer of single-crystalline gold shell, which leaves few empty sites for oxygen to attract the inner copper atoms or for copper to diffuse out.

Method Details

[0071] **Chemicals.** Tris(trimethylsilyl)silane (TTMSS, 97%), copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.999%), oleylamine (70%), trioctylphosphine (90%), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 49.0\%$) and nitrocellulose filter membranes (25 mm diameter, 220 nm pore size) were purchased from Sigma-Aldrich. Toluene ($\geq 99.9\%$) was purchased from Fisher Scientific. All chemicals were used as received without further purification.

[0072] **Characterization.** Transmission electron microscopy (TEM) was performed with a Hitachi H-7650. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy dispersive spectroscopy (EDS) mapping, and

- quantitative EDS were carried out with an FEI TitanX 60-300. Aberration-corrected high-resolution scanning transmission electron microscopy (AC-HRSTEM) was performed on a double aberration-corrected TEAM 0.5 microscope at 300 kV using a high-angle annular detector resulting in 'Z-contrast' images. Experimental AC-
- 5 HRSTEM images were deconvoluted using the maximum entropy method (ref). Scanning electron microscope (SEM) images were obtained on a JOEL JSM-6340F field emission scanning microscope. X-ray diffraction (XRD) was acquired using a Bruker D-8 General Area Detector Diffraction System (GADDS) with HI-STAR area charge-coupled device (CCD) detector, equipped with a Co-K α source ($\lambda = 1.789 \text{ \AA}$).
- 10 X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5600 X-ray photoelectron spectrometer. Sheet resistance of nanowire thin films was measured using a CDE-RESMAP-270 four-point probe resistivity mapper. The transmittance and haze measurement was carried out on a Shimadzu UV-2550 UV-Vis-NIR spectrophotometer with an integrating sphere.
- 15 **[0073] Synthesis of Cu-Au nanowires.** In a typical synthesis, CuCl₂•2H₂O (85 mg, 0.5 mmol) and oleylamine (0.5 g) were charged in a Schlenk flask. The mixture was stirred at 70 °C (suitable temperature range is room temperature to 80 °C) until the dissolution of the copper precursor. Tris(trimethylsilyl)silane (0.5 g, 2 mmol) was added into the solution under inert gas (e.g., Ar, N₂) atmosphere. The resulting clear
- 20 blue solution was slowly heated up from 70 °C to 120 °C (a range of 110 – 130 is suitable; Cu is reduced by silane in two stages, first at 120 °C, then, in the following operation, at 165 °C) in an oil bath. When the reaction solution turned into clear yellow at 120 °C, the reaction temperature was further raised to and kept at 165 °C (e.g., 160-180 °C) for 18 hours (e.g., 12-24 hours) under stirring (e.g., 20-80 rpm, or
- 25 other agitation).
- [0074]** Afterwards, a TOP solution of HAuCl₄•3H₂O (0.1–0.025 M, 1 mL) was injected by syringe at 140 °C (e.g., 130-150 °C; below the temperature at which the metals will alloy). The reddish reaction solution became crimson after the introduction of gold precursor, and was cooled down to room temperature one hour
- 30 (e.g., 30 mins to 2 hours) later. The product was collected by centrifugation (6000 r.p.m., 5 min) and washed repeatedly with toluene using redispersion-centrifugation cycles to remove excess oleylamine. The product was dispersed in toluene for further characterization and film fabrication.

[0075] Fabrication of transparent conductive film. To make a transparent conductive thin film, a dilute suspension of nanowires in toluene was made via sonication. The thin film was fabricated by filtering down the nanowire suspensions onto a nitrocellulose porous membrane (pore size 220 nm) under vacuum. The nanowire network was transferred to a transparent substrate (glass or PET) by applying pressure to the back side of the membrane and forcing an intimate contact with the substrate. The thin film was then annealed under forming gas (5-10% H₂ (to keep the Cu reduced) and 90-95% Ar (or other inert gas) at 200 °C for 30 min to improve junction contact before measurements.

[0076] Haze measurement. The haze measurement is carried out by D1003-13 standard. Four transmittance scans of a sample with different configurations were acquired for its haze calculations: T1, incident light; T2, total light transmitted by the specimen; T3, light scattered by the instrument and T4, light scattered by the instrument and specimen. The haze factor of one specimen can be calculated by the equation:

$$\text{Haze, \%} = [(T4/T2) - (T3/T1)]$$

Unless specified, all haze factors in discussion is the value measured at 550 nm of wavelength. The contribution of glass substrate is already excluded.

[0077] Harsh environment stability test. All simulations were conducted using the Lumerical FDTD Solutions 8.12 software package Stability of Cu NW and Cu r-GO NW thin films in high humidity and high temperature environment (temperature = 80 °C, humidity = 80 ± 5 %).

Conclusion

[0078] Although illustrative embodiments and applications are shown and described herein, many variations and modifications are possible which remain within the concept, scope, and spirit of the disclosure, and these variations would become clear to those of ordinary skill in the art after perusal of this application. Accordingly, the present embodiments are to be considered as illustrative and not restrictive, and the scope of the disclosure is not to be limited to the details given herein, but may be modified within the scope and equivalents of the appended claims.

CLAIMS

What is claimed is:

1. A method of making conductive core-shell metal nanowires, comprising:
forming a mixture comprising metal nanowires and a solution comprising a noble
5 metal precursor, a noble metal reducing agent, and a ligand that strongly binds the noble metal;
allowing reaction of the mixture to form nanowires comprising a shell of the noble metal on a core of the metal.
2. The method of claim 1, wherein the metal is copper.
- 10 3. The method of claim 1 or 2, wherein the noble metal is gold.
4. The method of claim 3, wherein the noble metal precursor comprises chloroauric acid (HAuCl_4) or a hydrate thereof.
5. The method of claim 4, wherein the noble metal precursor comprises chloro(triphenylphosphine)gold ($\text{Au(PPh}_3\text{)Cl}$).
- 15 6. The method of any preceding claim wherein the noble metal reducing agent is a silane.
7. The method of claim 6, wherein the silane is an organosilane.
8. The method of claim 7, wherein the organosilane comprises tris(trimethylsilyl)silane or triphenylsilane.
- 20 9. The method of any preceding claim wherein the ligand prevents galvanic replacement between the noble metal and the metal.
10. The method of any preceding claim wherein the ligand is a phosphine.
11. The method of claim 10, wherein the phosphine ligand comprises trioctylphosphine (TOP) or trihexylphosphine.

12. The method of any preceding claim wherein the metal nanowires are formed by a method comprising:
- forming a mixture comprising a solution of a metal precursor in a solvent comprising a surface ligand, and an organic reducing agent; and
- 5 allowing the solution to form metal nanowires.
13. The method of claim 12, wherein the metal precursor is a metal salt.
14. The method of claim 13, wherein the metal precursor comprises copper chloride (CuCl_2).
15. The method of claim 14, wherein the solvent comprising a surface ligand is
10 oleylamine.
16. The method of claim 15, wherein the organic reducing agent is an organosilane.
17. The method of claim 16, wherein the organosilane comprises tris(trimethylsilyl)silane.
- 15 18. The method of any of claims 12-17, further comprising heating the solution above 100°C after addition of the organic reducing agent.
19. The method of any of claims 12-18, further comprising collecting a precipitate of the nanowires.
20. The method of any of claims 12-19 wherein the metal nanowires and noble
20 metal reducing agent of the mixture comprise the formed metal nanowires and residual organic reducing agent.
21. The method of claim 20, wherein the noble metal precursor and the ligand are added to the formed metal nanowires in the solution comprising the residual organic reducing agent to form the mixture.
- 25 22. The method of any preceding claim wherein the noble metal shell is grown on the metal core.

23. The method of any preceding claim wherein the core-shell nanowires comprise copper core-gold shell nanowires.
24. The method of claim 23, wherein the core-shell nanowires comprises copper core-epitaxial gold shell nanowires.
- 5 25. The method of any of claims 22-24, wherein the copper core is less than 25nm in diameter and the gold shell is less than 3nm thick.
26. The method of claim 25, wherein the copper core is about 15-20nm in diameter and the gold shell is about 1-2nm thick.
27. The method of any of claims 23-26, wherein the gold shell forms a conformal
10 coating on the copper core.
28. The method of any preceding claim, wherein the method is conducted under inert atmosphere.
29. The method of any preceding claim wherein the mixture is heated above 100°C but below 200°C during the reaction of the mixture to form nanowires.
- 15 30. The method of claim 29, wherein the mixture is heated to between 100 and 150°C.
31. A method of making conductive core-shell metal nanowires, comprising:
under inert atmosphere,
dissolving a CuCl_2 in oleylamine to form a solution;
20 adding tris(trimethylsilyl)silane to the solution;
heating the solution to a temperature below the boiling point;
adding to the solution a second solution of chloroauric acid (HAuCl_4)
dissolved in trioctylphosphine (TOP) at between 100 and 150°C, and cooling the
solution to room temperature to form nanowires comprising a conformal epitaxial
25 shell of gold on a copper core, wherein the copper core is about 15-20nm in diameter
and the gold shell is about 1-2nm thick.

32. A conductive core-shell metal nanowire, comprising:
a metal core having a diameter of less than 25nm; and
a shell of noble metal on the metal core, the shell have a thickness of less than 3nm.
33. The conductive core-shell metal nanowire of claim 32, wherein the metal core
5 is a copper core having a diameter of about 15-20 nm, and the noble metal shell is a
shell of gold on the copper core that is a conformal epitaxial shell of gold have a
thickness of about 1-2nm.
34. A transparent conductive film comprising a mesh of the conductive metal
nanowires of either of claim 32 or 33, the film having a sheet resistance of less than
10 1000 Ohms/sq, a total transmittance of at least 85% and a haze factor of less than 5%.
35. The transparent conductive film of claim 34, wherein the film has a sheet
resistance of less than 35 Ohms/sq, a total transmittance of at least 90% and a haze
factor of less than 2%.
36. A transparent electrode comprising the conducting film of either of claim 34
15 or 35.
37. An optoelectronic device comprising the transparent electrode of claim 36.
38. The optoelectronic device of claim 37, wherein the optoelectronic device is
selected from the group consisting of a LCD display, a LED display, a photovoltaic
device, a touch panel, a solar panel, a light emitting diode (LED), an organic light
20 emitting diode (OLED), an OLED display, and a electrochromic window.
39. A method of making transparent conductive thin film, comprising:
disposing on a porous planar substrate a suspension of core-shell metal nanowires in
accordance with either of claims 32 or 33;
removing the solvent by vacuum process to form a thin film of the nanowires.
- 25 40. The method of claim 39, further comprising annealing the thin film by heating
to a temperature of greater than 100°C under forming gas.

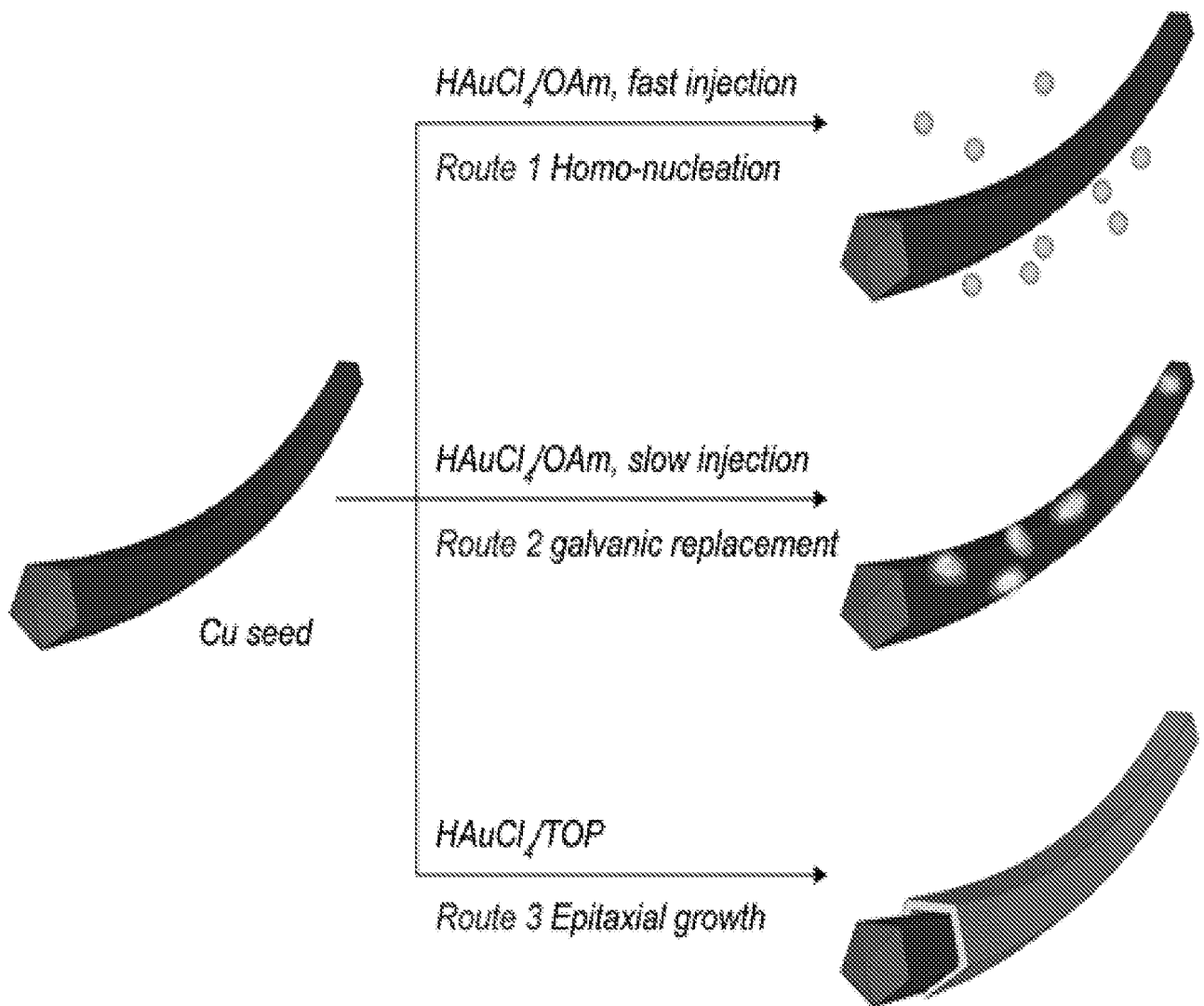


Fig. 1

Fig. 2A

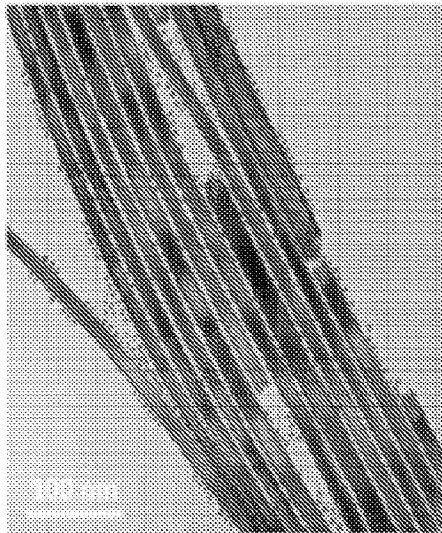


Fig. 2B

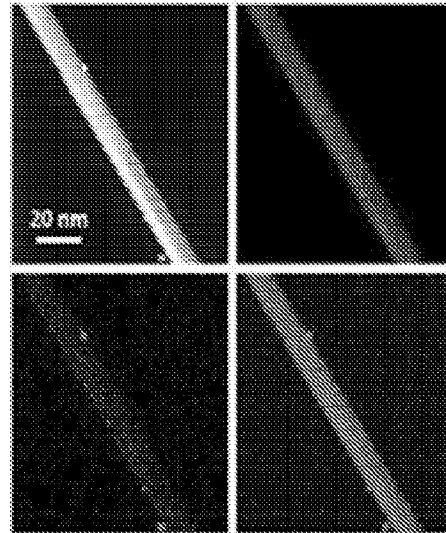


Fig. 2C

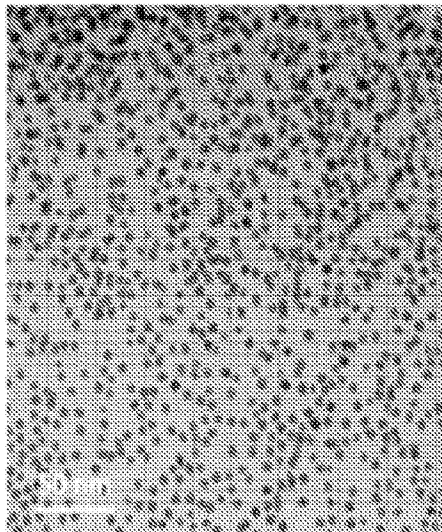


Fig. 2D

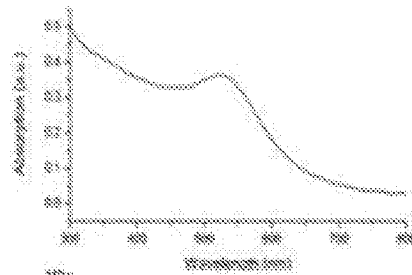


Fig. 2E

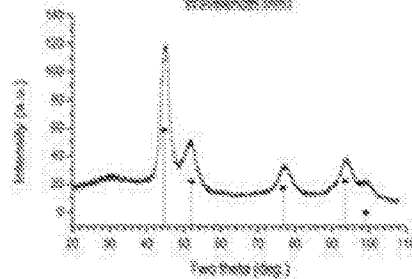


Fig. 2F

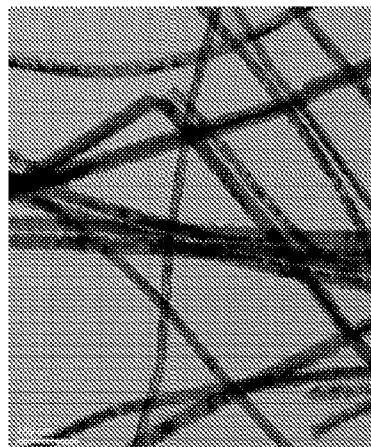
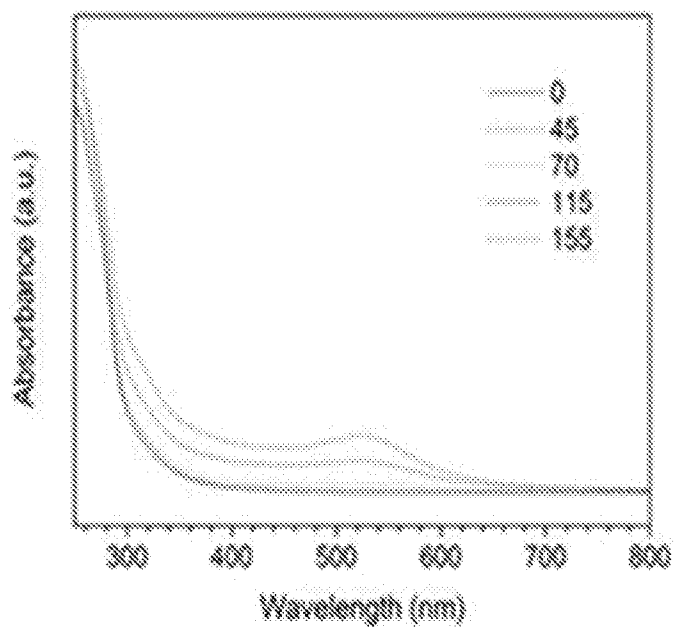
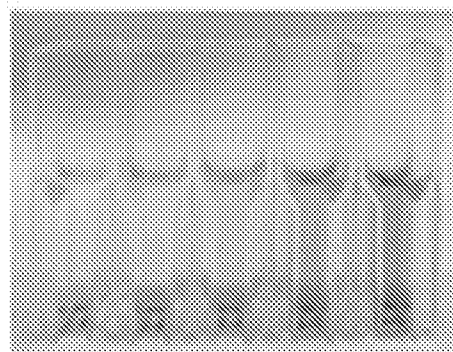
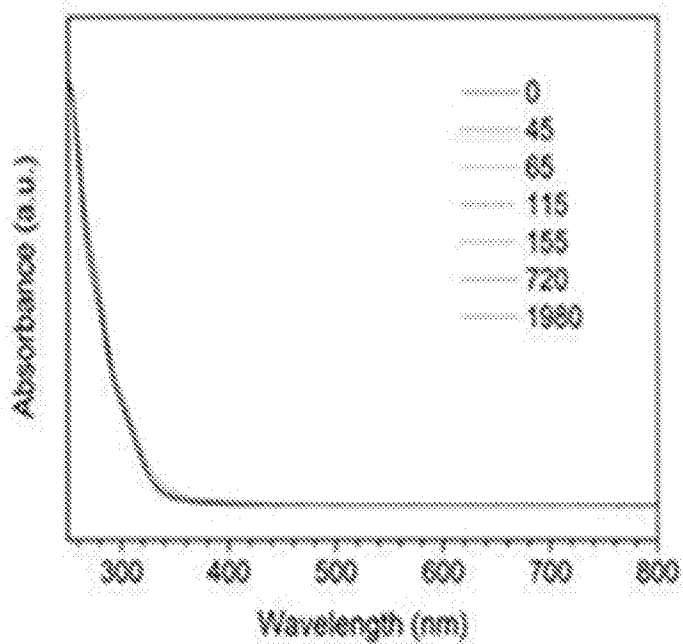
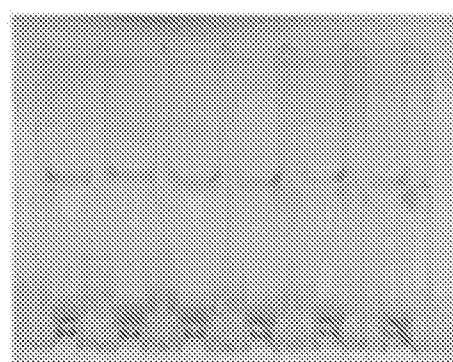


Fig. 3A

HAuCl₄/OAm @140 °C

0 45 70 115 155 (sec.)

Fig. 3B

HAuCl₄/TOP @140 °C

45 65 115 155 720 1980 (sec.)

Fig. 4A

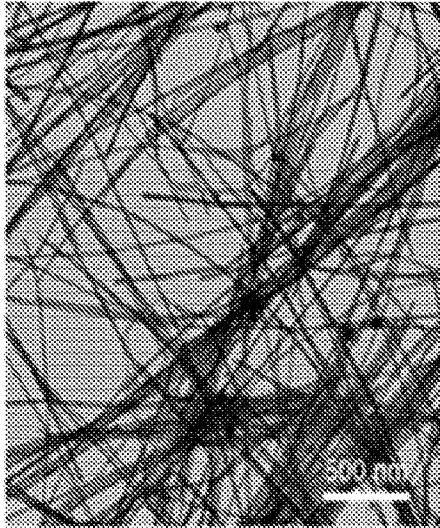


Fig. 4D

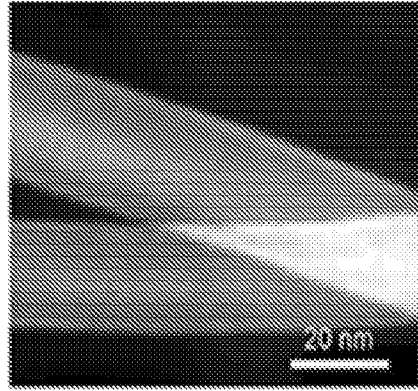


Fig. 4E

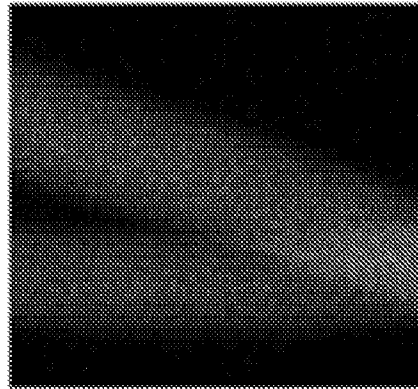


Fig. 4B

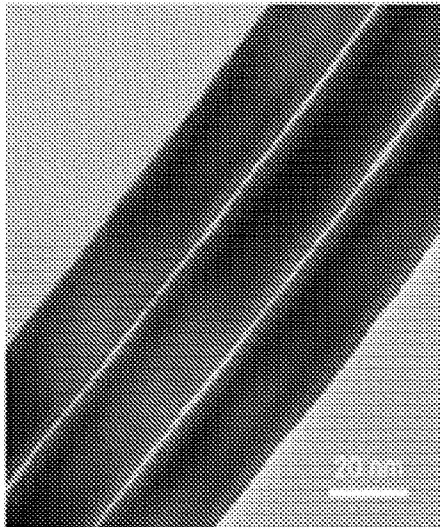


Fig. 4F

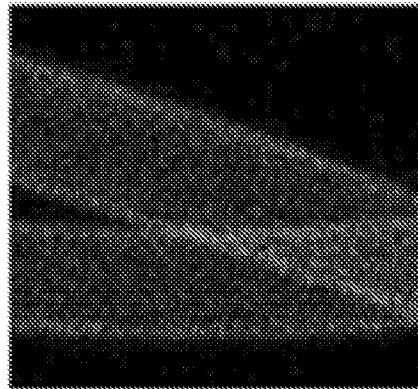


Fig. 4C

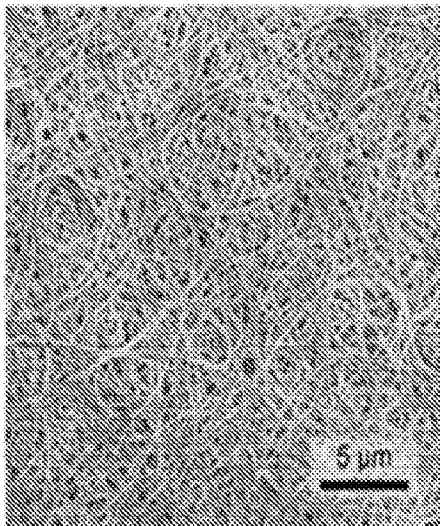
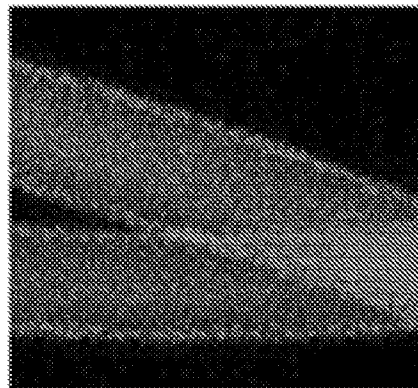


Fig. 4G



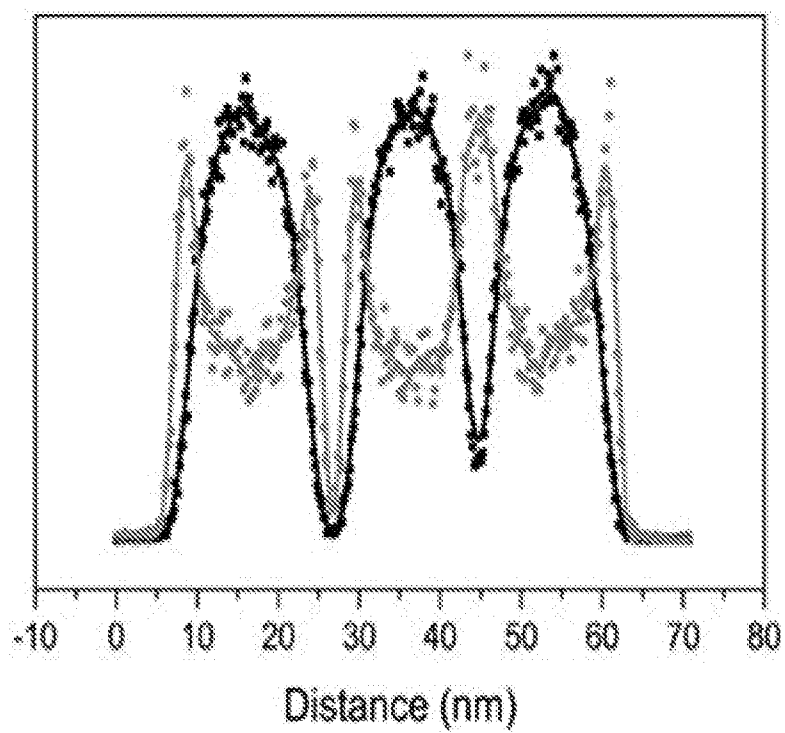
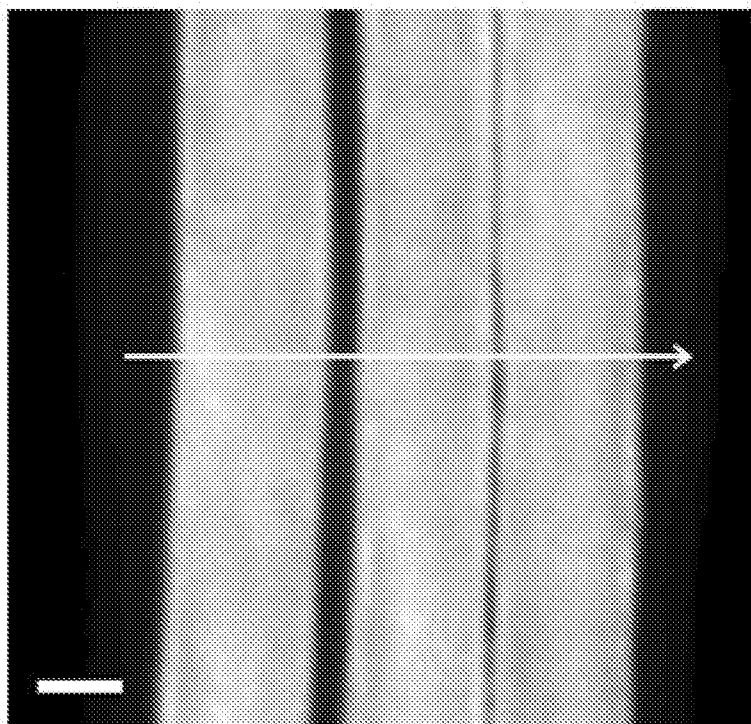
*Fig. 5*

Fig. 6A

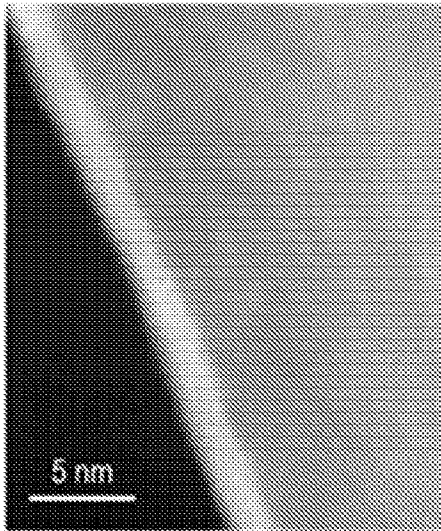


Fig. 6D

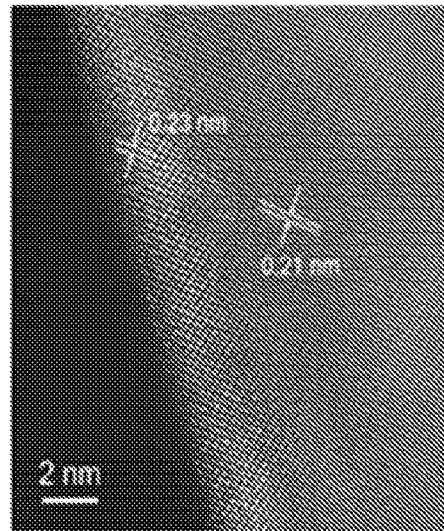


Fig. 6B

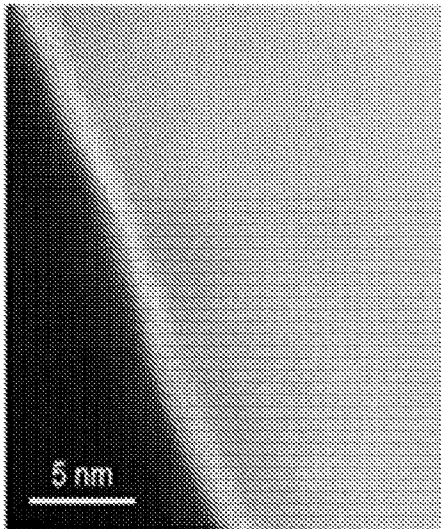


Fig. 6E

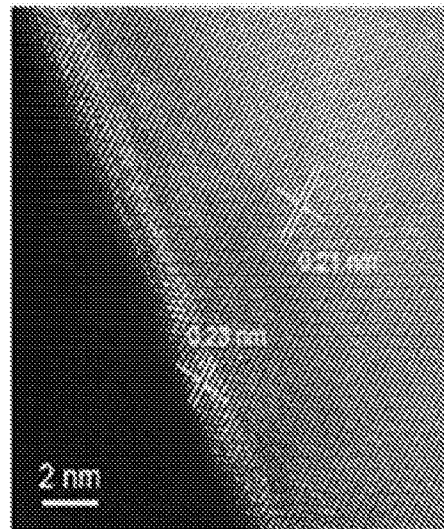


Fig. 6C

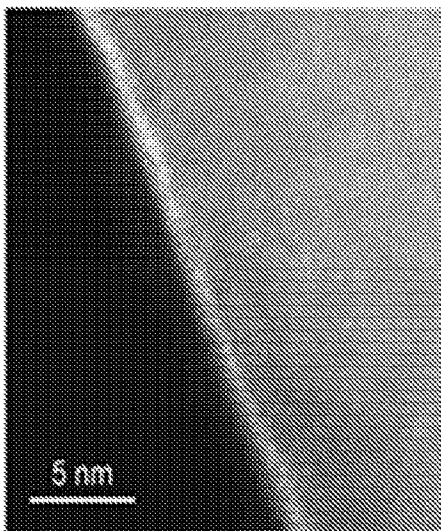
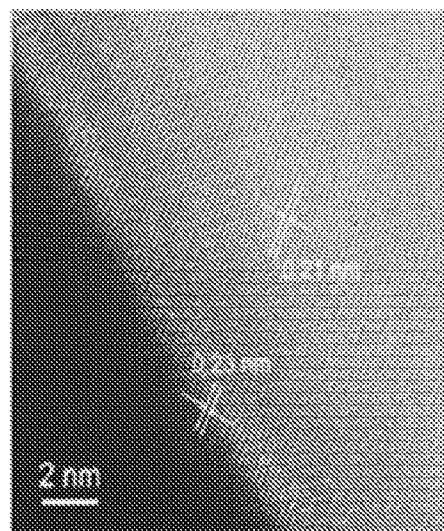


Fig. 6F



Thin film

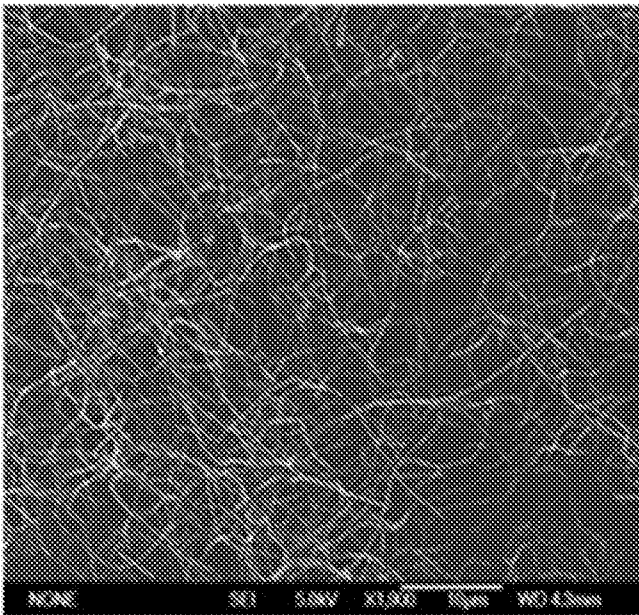


Fig. 7A

Thick film

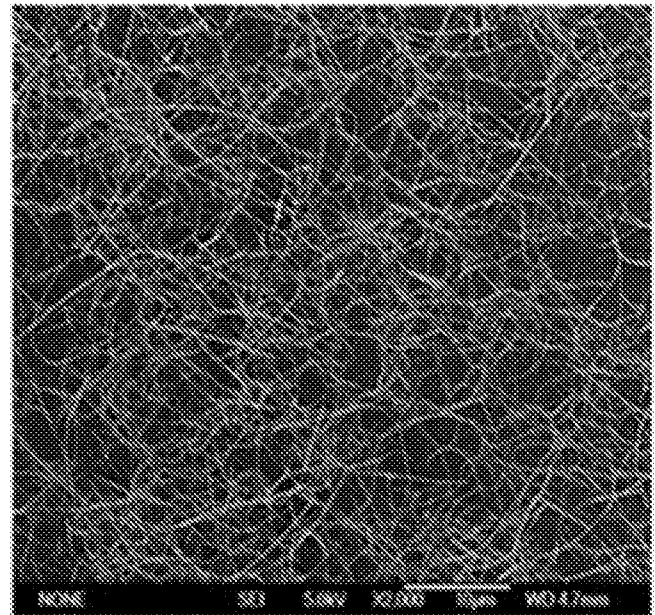


Fig. 7B

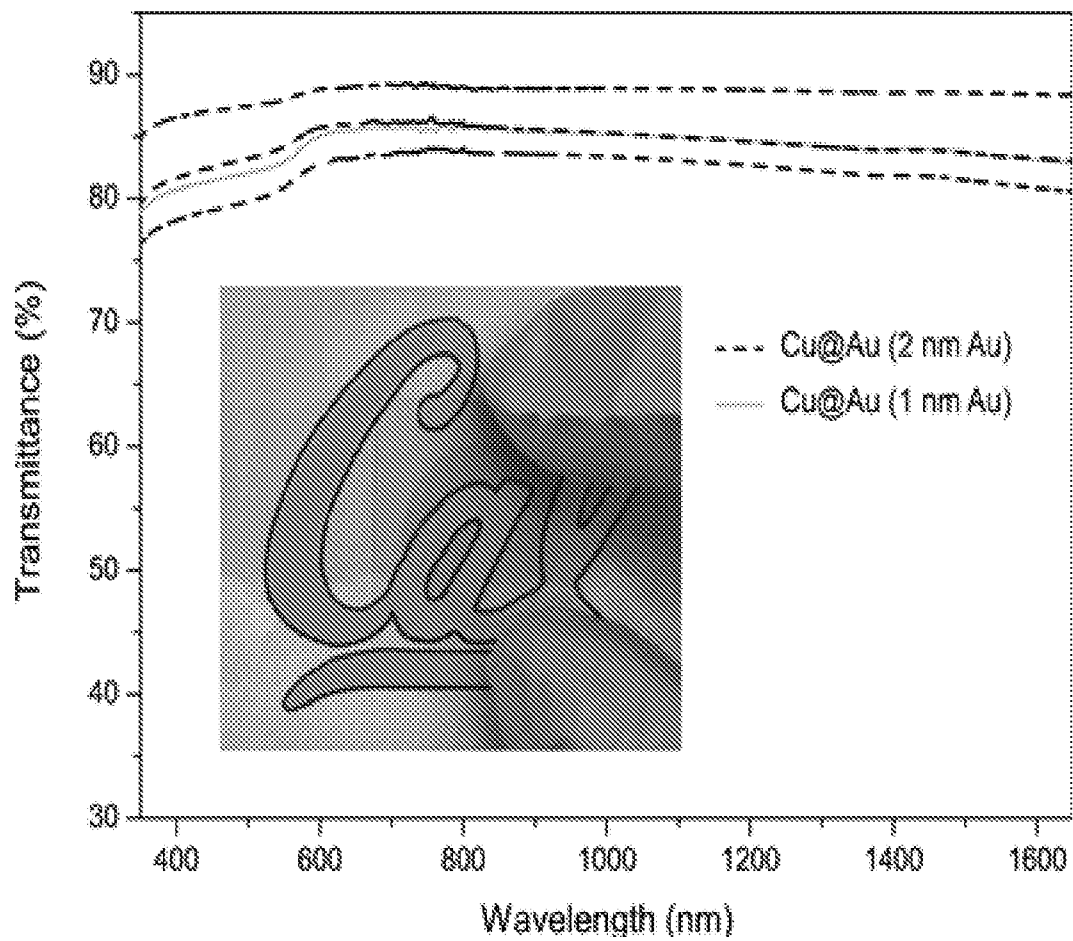


Fig. 8

Fig. 9A

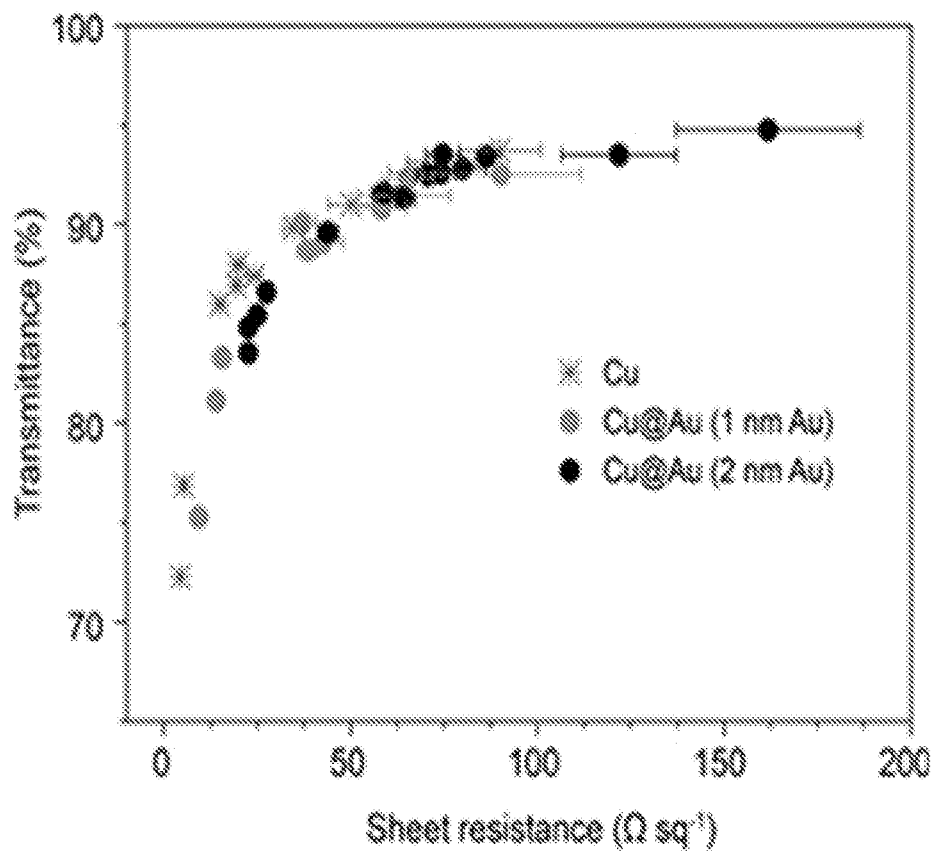


Fig. 9B

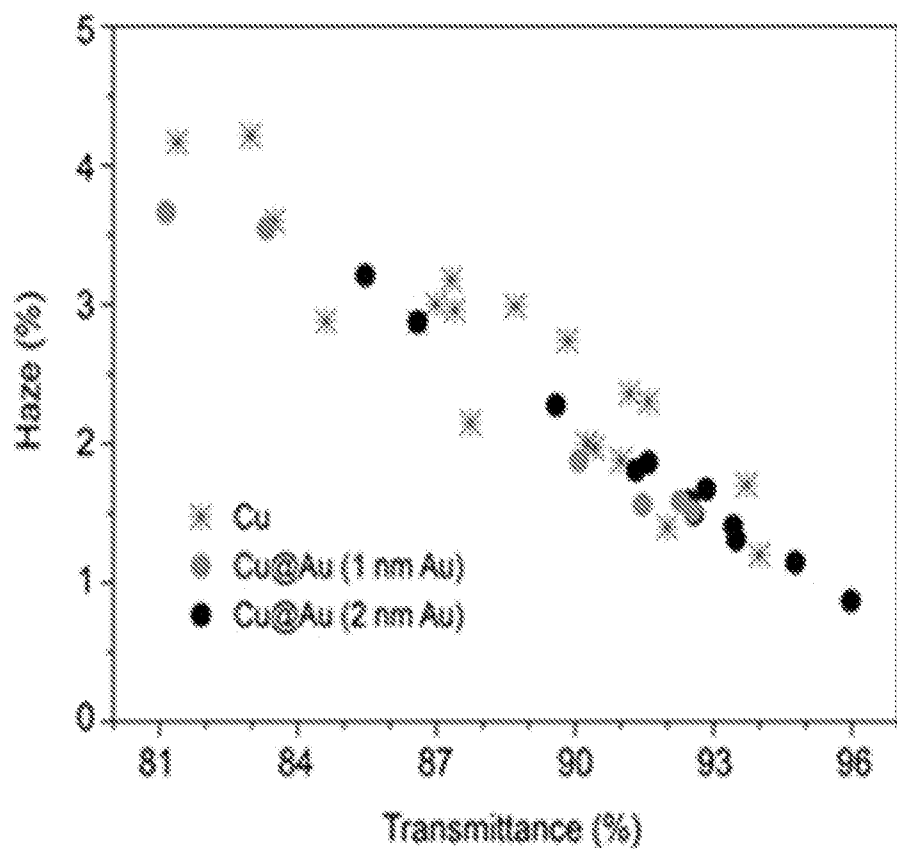


Fig. 10A

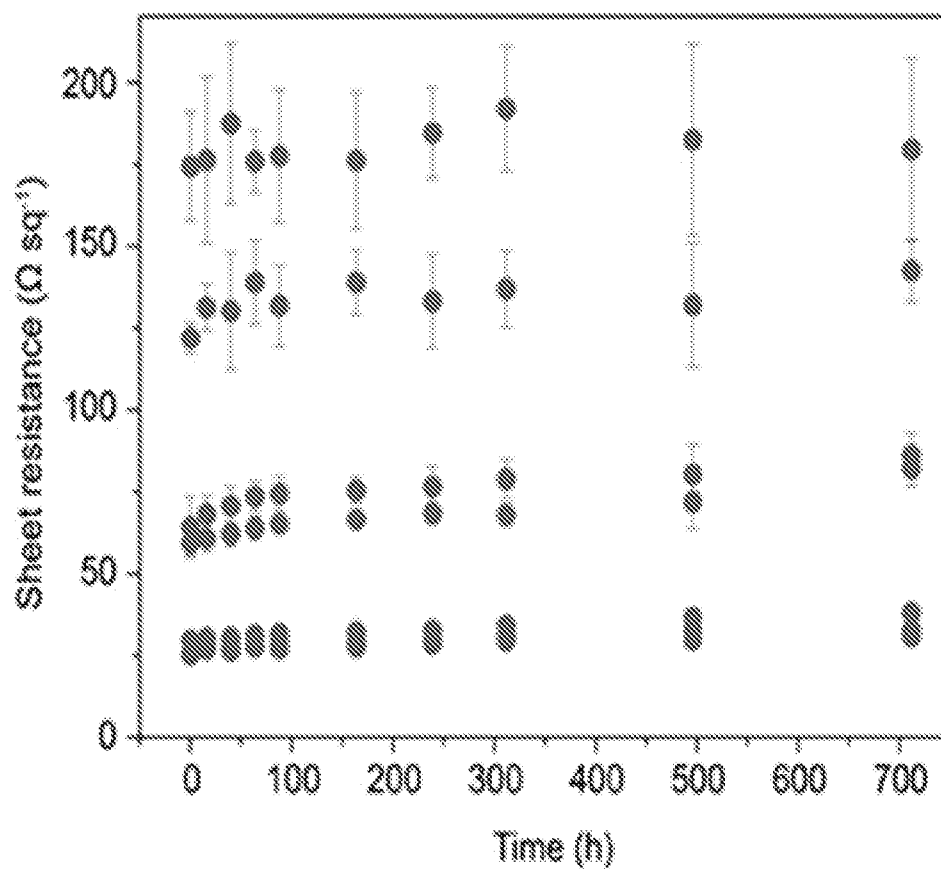
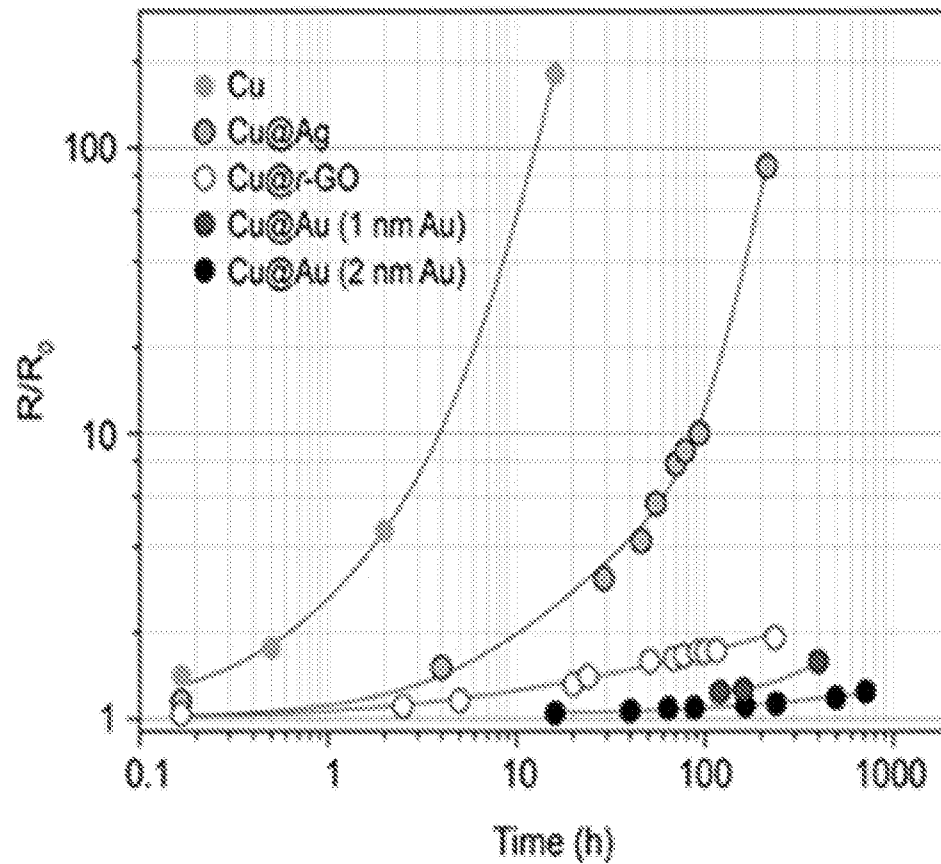


Fig. 10B



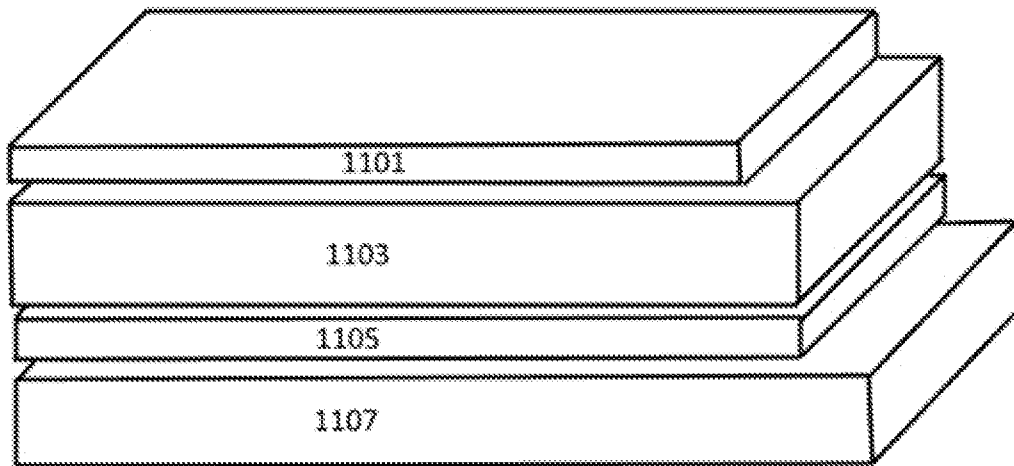


Fig. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/013006**A. CLASSIFICATION OF SUBJECT MATTER****H01B 5/00(2006.01)i, H01B 1/02(2006.01)i, H01L 25/16(2006.01)i**

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)

H01B 5/00; B05D 5/12; H01B 1/22; H01B 1/08; B32B 5/12; H01B 1/02; H01L 43/02; H01B 5/14; H01L 25/16

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: nanowire, core, shell, metal, transparent, conductive, film

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013-0285008 A1 (BEN-GURION UNIVERSITY OF THE NEGEV RESEARCH AND DEVELOPMENT AUTHORITY) 31 October 2013 See paragraphs [8],[85],[89],[225] and claim 9.	1-5,31-40
Y	WO 2013-086139 A1 (DUKE UNIVERSITY) 13 June 2013 See paragraphs [2]-[55] and claims 1-12.	1-5,34-40
Y	US 2012-0094192 A1 (QU et al.) 19 April 2012 See paragraphs [41]-[87], claim 9 and figures 1-3.	31-40
A	US 2015-0364227 A1 (NATIONAL TSING HUA UNIVERSITY) 17 December 2015 See the whole document.	1-5,31-40
A	WO 2013-192437 A2 (C3NANO INC.) 27 December 2013 See the whole document.	1-5,31-40

☐ 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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

08 May 2018 (08.05.2018)

Date of mailing of the international search report

08 May 2018 (08.05.2018)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

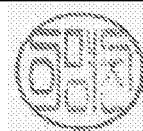


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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/013006**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.: 7,8,11,13-17,21,24,26,30
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:
Claims 7,8,11,13-17,21,24,26,30 are unclear, because they refer to multiple dependent claims which do not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 6,9,10,12,18-20,22,23,25,27-29
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 any 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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/013006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013-0285008 A1	31/10/2013	US 2010-0272993 A1 US 8470409 B2 US 8772756 B2	28/10/2010 25/06/2013 08/07/2014
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