



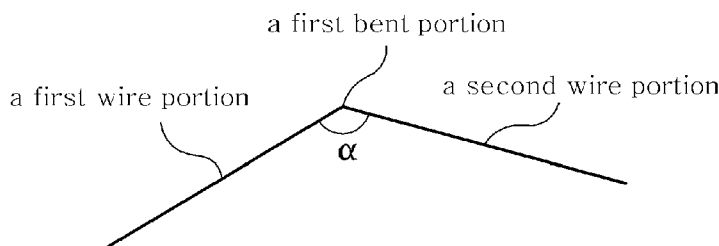
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- (54) **Title:** METAL NANOWIRE, METHOD FOR SYNTHESIZING THE METAL NANOWIRE, AND TRANSPARENT ELECTRODE AND ORGANIC LIGHT EMITTING DIODE INCLUDING THE METAL NANOWIRE MANUFACTURED BY THE METHOD



- (57) **Abstract:** A metal nanowire according to an embodiment of the invention includes at least one bent portion. An angle (a) between an n-th wire portion and an (n+1)-th wire portion connected to the n-th wire portion through an n-th bent portion satisfies an inequation of $0^\circ < a < 180^\circ$.



Description

Title of Invention: METAL NANOWIRE, METHOD FOR SYNTHESIZING THE METAL NANOWIRE, AND TRANSPARENT ELECTRODE AND ORGANIC LIGHT EMITTING DIODE INCLUDING THE METAL NANOWIRE MANUFACTURED BY THE METHOD

Technical Field

- [1] The present invention relates to a metal nanowire and a method for manufacturing the same and to a transparent electrode and an organic light emitting diode including the metal nanowire manufactured by the method.

Background Art

- [2] Recently, as technology of a display device and a solar cell progresses, demand for a transparent electrode used for the display device and the solar cell rapidly increases. An indium tin oxide (ITO) is generally to a material of the transparent electrode because the ITO is suitable for a mass production technique and for being used for the display device and the solar cell. However, a manufacturing cost of the ITO electrode is very high due to a vacuum process, and the ITO electrode is not stable to an external shock such as a thermal shock. Thus, a material replacing the ITO electrode is developing.
- [3] For materials replacing the ITO electrode, there are conductive polymers such as carbon nanotube (CNT), graphene, a zinc oxide (ZnO), poly(3,4-ethylenedioxythiophene) (PEDOT), and so on, a metal nanowire, and the like.
- [4] The metal nanowire, more particularly, a silver nanowire among them has a high chemical stability. The silver nanowire has properties of silver having high thermal conductivity and high electric conductivity and an optical property being transparent induced by the nanowire having a very small size. Thus, the metal nanowire, more particularly, the silver nanowire is in the spotlight as a metal material for manufacturing a transparent conductive film. The silver nanowire may be widely applied to electronic, magnetic, and optical elements or devices and sensors, such as, a plasma display panel (PDP), an optical filter, an electromagnetic wave shield, an organic Light emitting diode (OLED), a solar cell, a liquid crystal display (LCD), a touch screen, an EL key pad for a cellular phone, and so on for the future.
- [5] The metal nanowire may be manufactured by a synthesizing method, known as a polyol method. In the polyol method, the metal salt is reduced to a metal atom by a polyol solvent (refer to US Laid-open Patent Publication No. 2005/0056118).

Generally, the reduced metal atom initially forms seeds through a homogeneous nucleation process. And then, some of seeds grows in all direction in the solution and forms isotropic nano-structures (nanoparticles), and other seeds firstly grows according to a direction of a side surface and forms anisotropic nano-structures (nanotubes, nanowire portions, nano-belts, nanowires, and so on).

- [6] In the synthesizing method of the polyol, a diameter and a length of the metal nanowire are affected by various variables. In the conventional synthesizing method of the polyol, it is difficult to grow the nanowires to have a size of 50 μ m or more by complex factors, such as, a kinetic factor, strain, surface energy, thermal energy, and so on during the growth of nanowires. Although the metal nanowire is grown to have a large diameter, a large length, and a large aspect ratio, dispersibility is less and sheet resistance is high when the metal nanowire is used for a material of the transparent electrode.
- [7] Also, since the metal nanowire used for the transparent electrode needs a high electric conductivity, a high transmittance, and a flexibility, a surfactant (a capping agent) such as polyvinylpyrrolidone (PVP) is used. However, the surfactant increases the electric resistance at contact points between metal nanowires, and thus, electrical properties may be deteriorated.
- [8] Further, the metal nanowire has a small size and contact portions between the metal nanowires are very narrow. Thus, a current density increases and heat is generated even when a small electrical current flows. Also, the electric conductivity, which is an advantage of the metal cannot be sufficiently achieved.

Disclosure of Invention

- [9] Terms, phrases, or expressions used in the specification are only for describing embodiments, not for limiting the scope and spirit of the invention. All of technical terms and scientific terms have meanings the same as meanings generally understood by the skilled person in the art so long as there is no special conflicting description.
- [10] In the entire specification, when an element, or a method or a step is referred to as “comprise”, “comprising”, “includes” or “including” another element or step, the element should not be understood as excluding other elements or steps so long as there is no special conflicting description, and the element may include at least one other element or step.
- [11] On the other hand, embodiments of the invention may be combined with the other embodiments so long as there is no special conflicting description. Particularly, preferable properties, structures, elements, or structures may be combined with the other properties, structure, elements, or structures. Hereinafter, embodiments of the invention and effects thereof will be described in detail with reference to the ac-

companying drawings.

[12] **Technical Problem**

[13] The invention has been made in view of the above problems, and it is an object of the invention to provide a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion. Thus, a contact probability between the metal nanowires can increase, an increase of a sheet resistance can be prevented, and an electric conductivity can be superior. Particularly, when the metal nanowire is used for a transparent electrode (particularly, for an OLED lighting, an organic solar cell, and so on), the transparent electrode has a transmittance and a haze suitable for the OLED lighting or the organic solar cell.

[14] Also, it is another object of the invention to provide a metal nanowire having a large diameter and a large aspect ratio and having different diameters. Thus, a contact probability between the metal nanowires can increase, an increase of a sheet resistance can be prevented, and an electric conductivity can be superior. Particularly, when the metal nanowire is used for a transparent electrode (particularly, for an OLED lighting, an organic solar cell, and so on), the transparent electrode has a transmittance and a haze suitable for the OLED lighting or the organic solar cell.

[15] In addition, it is yet another object of the invention to provide a core-shell nanowire having a metal coating. A sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.

[16] Further, it is still another object of the invention to provide a method for manufacturing a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion with a high yield without by-products other than the metal nanowire.

[17] Furthermore, it is yet still another object of the invention to provide a method for manufacturing a metal nanowire having a large diameter and a large aspect ratio and having different diameters with a high yield without by-products other than the metal nanowire.

[18] Also, it is yet still another object of the invention to provide a method for manufacturing a core-shell nanowire having a metal coating.

[19] Further, it is yet still another object of the invention to provide a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion as a conductor layer. Thus, an electric conductivity can be superior. Particularly, the transparent electrode has a transmittance and a haze suitable for an OLED lighting or an organic solar cell.

[20] In addition, it is yet still another object of the invention to provide a transparent

electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and having different diameters as a conductor layer. Thus, an electric conductivity can be superior. Particularly, the transparent electrode has a transmittance and a haze suitable for an OLED lighting or an organic solar cell.

- [21] Furthermore, it is yet still another object of the invention to provide a core-shell nanowire having a metal coating as a conductor layer. A sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.

[22] **Technical Solution**

- [23] A metal nanowire according to an embodiment includes at least two wire portions. An angle (α) between an n-th wire portion and an (n+1)-th wire portion connected to the n-th wire portion through an n-th bent portion satisfies an inequation of $0^\circ < \alpha < 180^\circ$.

[24] **(1) A metal nanowire**

- [25] **1) A metal nanowire including a plurality of wire portions having at least one bent portion**

- [26] A metal nanowire according to an embodiment of the invention includes at least two wire portions (or at least one bent portion). More particularly, the metal nanowire includes at least one wire portion connected to another wire portion through the bent portion. An angle (α) between an n-th wire portion and an (n+1)-th wire portion connected to the n-th wire portion through an n-th bent portion satisfies an inequation of $0^\circ < \alpha < 180^\circ$.

- [27] For example, when the metal nanowire includes two wire portions, a first wire portion and a second wire portion connected to the first wire portion through a first bent portion have an angle (α) therebetween, as shown in FIG. 1. As another example, the metal nanowire may include a plurality of wire portions, as shown in FIG. 2.

- [28] More particularly, the angle (α) between the n-th wire portion and the (n+1)-th wire portion connected to the n-th wire portion through the n-th bent portion satisfies an inequation of $130^\circ \leq \alpha \leq 170^\circ$. When the metal nanowires are synthesized by a method for manufacturing a metal nanowire including the plurality of wire portions having at least one bent portion according to the invention that will be described later, although some metal nanowires having at least one bent portion with an angle of 90° or less are formed among the metal nanowires having two wire portion(or one bent portion), almost metal nanowires have two to four wire portions (or one bent portion to three bent portions) and the angle of the bent portion is in a range of 130° to 170° .

- [29] In the metal nanowire including the wire portions having the bent portion according

to the invention, when the metal nanowire is synthesized, as crystals are grown, strain increases in order to release stress generated by a gravity applied to grown sites of the metal nanowire. Accordingly, the metal nanowire has a structure bent in a predetermined direction to have a predetermined angle. When at least one bent portion has the predetermined angle, contact points, contact areas, or a contact probability between the metal nanowires can increase. Accordingly, an electric conductivity of a transparent electrode or a conductor layer formed of the metal nanowires according to the embodiment can be superior, compared with a transparent electrode or a conductor layer formed or a metal nanowire having a shape of a straight line.

[30] Also, the metal nanowire according to the embodiment of the invention has a two-dimensional or three-dimensional structure. When a plane including the n -th wire portion and the $(n+1)$ -th wire portion is an A plane and a plane including the $(n+1)$ -th wire portion and an $(n+2)$ -th wire portion is a B plane, an angle (β) of the B plane with respect to the A plane is in a range of -10° to 10° . FIG. 3 illustrates a metal nanowire having a three-dimensional structure according to another embodiment of the invention.

[31] The metal nanowire including the wire portions having the bent portion according to an embodiment of the invention has a diameter of 50 to 200nm and a length of 40 to 300 μ m. In the present specification, the diameter of the metal nanowire indicates a longest length of the metal nanowire in a horizontal cross section of the metal nanowire, and the length of the metal nanowire indicates a longest length of the metal nanowire in a longitudinal cross section of the metal nanowire. Also, the metal nanowire has an aspect ratio is in a range of 200 to 6000. The aspect ratio is a ratio (length/diameter) of the length to the diameter.

[32] The metal nanowire including the wire portions having the bent portion according to the embodiment of the invention has a large diameter of 50 to 200nm, and thus, the metal nanowire is grown to be bent, not to be broken, even the stress above a predetermined value is applied to the metal nanowire when the metal nanowire is synthesized. Also, since the metal nanowire has a long length of 40 to 300 μ m, the metal nanowire has the at least one bent portion. In addition, the metal nanowire is bent in a predetermined direction (that is, a gravity direction). Accordingly, when the metal nanowire has two or more bent portions, the metal nanowire has a bent curve structure, not a zigzag structure.

[33] Also, contact areas between the metal nanowires, each having the diameter, the length, and the aspect ratio of the above ranges, are larger than contact areas between metal nanowires, each has a size smaller than the above ranges. Thus, an electric conductivity of a transparent electrode or a conductor layer formed of the metal nanowires according to the embodiment can be superior. Therefore, the metal nanowire can be

suitable for a material of a transparent electrode.

[34] The metal nanowire according to the embodiment of the invention may be a nanowire of a metal material including Ni, Co, Fe, Pt, Au, Ag, Al, Cr, Cu, Mg, Mn, Mo, Rh, Si, Ta, Ti, W, U, V, Zr, Ge, and so on. The metal nanowire of silver (Ag) has a high chemical stability among various metals, has greatly superior thermal conductivity and electric conductivity, and has a transparency, which is an optical property shown by a small size of a nanowire. Thus, the metal nanowire can be suitable for a metal material for manufacturing a transparent conductive layer.

[35] In addition, the metal nanowire (particularly, the silver nanowire) according to the embodiment of the invention can be widely applied to electronic, magnetic, and optical elements or devices and sensors, such as, a plasma display panel (PDP), an optical filter, an electromagnetic wave shield, an organic Light emitting diode (OLED), a solar cell, a liquid crystal display (LCD), a touch screen, an EL key pad for a cellular phone, and so on.

[36] **2) A metal nanowire having different diameters**

[37] The metal nanowire according to another embodiment of the invention includes a plurality of wire parts having different diameters. For example, the metal nanowire includes a first wire part and a second wire part extended from the first wire part. The first wire part has a diameter (a first diameter) of 50 to 100nm and a length of 40 to 100 μ m, and the second wire part has a diameter (a second diameter) of 150 to 1100nm and a length of 5 to 15 μ m. FIG. 4 illustrates a metal nanowire including a plurality of wire parts having different diameters according to yet still another embodiment of the invention.

[38] Also, in the metal nanowire according to the embodiment of the invention, the second diameter is two times to fifteen times the first diameter. When the second diameter is below two times the first diameter, a light-scattering effect may be less. When the second diameter is above fifteen times the first diameter, the transmittance of a transparent electrode may be reduced and the dispersibility may be reduced in a case that the metal nanowire can be suitable for the transparent electrode. Preferably, the second diameter may be two times to five times the first diameter.

[39] The second wire part may be formed at one end or two ends of the first wire part. Also, two or more second wire parts may be formed at each end of the first wire part. FIG. 5 illustrates a metal nanowire including a plurality of wire parts having different diameters according to another embodiment of the invention, wherein (a) illustrates the metal nanowire having the second wire part formed at one end and (b) illustrates the metal nanowire having the second wire parts formed at both ends. Thus, the metal nanowire has an increased contact area with another metal nanowire by the second wire portion, and thus, the metal can be suitable for a metal material for manufacturing

a transparent conductive layer.

[40] A cross section of one of each of the first wire part and the second wire part perpendicular to a longitudinal direction of the metal nanowire may have a polygonal shape, for example, a triangular shape, a quadrangular shape, a pentagonal shape, and so on. However, the embodiment is not limited thereto.

[41] When the metal nanowire having the plurality of wire parts having different diameters according to the embodiment of the invention is used for a conductor layer of a transparent electrode, a transparency is 80% or more. Thus, the metal nanowire can have properties suitable for an OLED lighting.

[42] Also, when the metal nanowire including the plurality of wire parts having different diameters according to the embodiment of the invention is used for the conductor layer of the transparent electrode, a haze is 1% or more, and a light extraction can be induced through a light-scattering effect. Accordingly, when the metal nanowire is used for the OLED lighting, efficiency of the OLED lighting can be enhanced.

[43] When the conventional metal nanowire having a uniform diameter generally has a low haze of 1% or less, there is almost never the light-scattering effect. On the other hand, the metal nanowire including the second wire part according to the embodiment has a light-scattering effect and has a large haze.

[44] In addition, the conventional metal nanowire has a large surface area even the conventional metal a small weight and volume, and thus, may be easily aggregated. Thus, when the conventional metal nanowire is generally used for the transparent electrode, the dispersibility decreases and a sheet resistance ($\Omega/\square$) increases. Meanwhile, the metal nanowire including the second wire part according to the embodiment can have a superior dispersibility and the sheet resistance of the metal nanowire can be prevented.

[45] **3) A metal nanowire including a plurality of wire portions having at least one bent portion and having different diameters**

[46] The metal nanowire including a plurality of wire portions having at least one bent portion may include wire portions having diameters different from each other, or may include at least one wire portion having multiple diameters. The wire portion may include a plurality of wire parts having different diameters. That is, the metal nanowire including the plurality of wire portions having at least one bent portion has at least two different diameters. Accordingly, the wire portions of the metal nanowire according to the embodiment of the invention may include a wire portion having a single diameter of a first diameter, a wire portion having a single diameter of a second diameter, and/or the wire portion having the multiple diameters.

[47] The wire portion having the single diameter has a first diameter of 500 to 200nm and/or a second diameter of 150 to 1100nm. The wire portion having the multiple diameters may have both of the first diameter of 50 to 200nm and the second diameter

of 150 to 1100nm. FIG. 6 illustrates the wire portions according to embodiments of the invention, and FIG. 7 illustrates the metal nanowire according to embodiments of the invention.

- [48] The second diameter is two times to fifteen times the first diameter. When the second diameter is below two times the first diameter, a light-scattering effect may be less. When the second diameter is above fifteen times the first diameter, the transmittance of a transparent electrode may be reduced and the dispersibility may be reduced in a case that the metal nanowire is used for the transparent electrode. Preferably, the second diameter may be two times to five times the first diameter.
- [49] The wire portion including the second diameter may be generally included at an end of the metal nanowire. However, the embodiment is not limited thereto. According to an amount of a capping agent when the metal nanowire is synthesized, the wire portion having the multiple diameters may be formed at an arbitrary position or a position other than the end of the metal nanowire.
- [50] As another aspect, at least one of wire portions of the metal nanowire having different diameters has a bent portion. Referring to FIG. 8, a wire portion or a wire part having a first diameter or a wire portion or a wire part having a second diameter has a shape of a straight line or has a bent portion.
- [51] When the wire portion or the wire part has the bent portion, a bent angle (α) satisfies an inequation of $130^\circ \leq \alpha \leq 170^\circ$. FIG. 8 illustrates various wire parts according to embodiments and FIG. 9 illustrates various metal nanowires according to embodiments of the invention when the nanowire includes two wire portions.
- [52] **4) A core-shell nanowire having a metal coating**
- [53] The core-shell nanowire according to an embodiment of the invention includes a nanowire core and a metal-compound shell coated on the nanowire core.
- [54] The nanowire core may be a conductive metal nanowire, for example, a silver (Ag) nanowire. Various commercialized or marketed metal nanowires may be unlimitedly used for the nanowire core. Preferably, the metal nanowire including the plurality of wire portions having the at least one bent portion, and the metal nanowire having different diameters, and the metal nanowire including the plurality of wire portions having the at least one bent portion and having different diameters may be used for the nanowire core.
- [55] For example, a cross section of the nanowire core perpendicular to a longitudinal direction of the nanowire core may have a polygonal shape, for example, one of a triangular shape, a quadrangular shape, a pentagonal shape, a hexagonal shape, and so on. However, the embodiment is not limited to the shape of the nanowire core. When the cross section of the nanowire core has the polygonal shape, the metal-compound shell can be coated so that the light-scattering property can be enhanced more.

- [56] The nanowire core has a diameter of 30 to 200nm and a length of 10 μm to 300 μm . When the nanowire core is the metal nanowire including the plurality of wire portions having the at least one bent portion according to the embodiment, the nanowire core has a diameter of 50 to 200nm and a length of 40 μm to 300 μm . When the nanowire core having different diameters according to the embodiment, the nanowire core has the first diameter of 50 to 100nm and the second diameter of 150nm to 1100nm, and a length of 5 μm to 15 μm .
- [57] The metal-compound shell is coated on the nanowire core to surround the nanowire core. The embodiment is not limited to a material of the metal-compound shell. However, the metal-compound shell may be preferably transparent, and may include a transparent conductive metal oxide, nitride, sulfide, or so on. For example, the transparent conductive metal-compound shell may include at least one of ZnO, SiO₂, SnO₂, TiO₂, AlN, GaN, BN, InN, ZnS, CdS, ZnSe, ZnTe, CdSe, and a compound including carbon, and may be further include a dopant for having an electric conductivity. The transparent conductive metal-compound shell may be formed of one material or be formed of an alloy or a mixture having several materials. The transparent conductive metal-compound shell may have a single-layer structure or a multiple-layer structure.
- [58] In the conventional technology, the light-scattering of the nanowire should be less with consideration of the optical property, and the haze of the conductive layer formed of the nanowire should be small. However, in the embodiment of the invention, the core-shell nanowire having an increased light-scattering effect and a high haze value is suggested, contrary to the conventional technology.
- [59] In the embodiment, the light-scattering effect can be remarkably increased since a core-shell structure is introduced in order to increase the light scattering of the nanowire and the shell has a structure having an unprecedented protruded structure having a unique shape.
- [60] As an example, the metal-compound shell includes a plurality of protruded structures in a cross section perpendicular to a longitudinal direction of the core-shell metal nanowire. The protruded structure may have a shape where an area or a width gradually decreases as the distance from the nanowire core increases. The number of the protruded structures may be 3 to 6. However, the invention is not limited thereto. The expression of "the protruded structure may have a shape where an area or a width gradually decreases as the distance from the nanowire core increases" may be interpreted in a broad sense. That is, the phrase implies may include a case that 70% or more of the protruded structure has the shape where the area or the width gradually decreases as the distance from the nanowire core increase although the protruded structure partially has a portion which area or a width gradually increase as the

distance from the nanowire core increases.

- [61] As another example, the metal-compound shell when viewed in the cross section perpendicular to the longitudinal direction of the core-shell nanowire may have a shape of a plurality of polygons. The number of the polygons may be 3 to 6. However, the invention is not limited thereto. The “polygons” may be interpreted in a broad sense. The “polygons” may include a shape similar to a polygon that is generally recognized as the polygon as well as a shape of an exact polygon in the cross section.
- [62] As yet another example, the metal-compound shell may a stripe pattern having a plurality of portions extending a longitudinal direction of the core-shell nanowire. The number of the plurality of portions constituting the stripe pattern may be three to six. However, the invention is not limited thereto.
- [63] As concrete examples, FIG. 10 to FIG. 13 illustrate core-shell nanowires according to embodiments of the invention. As shown in FIG. 10 to FIG. 13, a metal-compound shell 20 is coated on the nanowire core 10. The metal-compound shell 20 has a shape where metal-compound oxides are aggregated to each other. Metal-compound particles 21 may have diameters (e) in a range of 10 to 100nm. However, the embodiment is not limited thereto.
- [64] As shown in FIG. 10, when viewed in the cross section perpendicular to the longitudinal direction of the metal nanowire, the metal-compound shell 20 has four triangular shapes to four stripe patterns. That is, each of the four triangular shapes extends in the longitudinal direction of the core-shell nanowire.
- [65] Selectively, as shown in (a) of FIG. 11, when viewed in the cross section perpendicular to the longitudinal direction of the metal nanowire, the metal-compound shell 20 has five triangular shapes to five stripe patterns. That is, each of the five triangular shapes extends in the longitudinal direction of the core-shell nanowire. As shown in (b) of FIG. 11, when viewed in the cross section perpendicular to the longitudinal direction of the metal nanowire, the metal-compound shell 20 has six triangular shapes to six stripe patterns. That is, each of the six triangular shapes extends in the longitudinal direction of the core-shell nanowire.
- [66] Meanwhile, as shown in FIG. 12, when viewed in the cross section perpendicular to the longitudinal direction of the metal nanowire, the metal-compound shell 20 has five trapezoid shapes to five stripe patterns. That is, each of the five trapezoid shapes extends in the longitudinal direction of the core-shell nanowire. By changing conditions of a method for forming the metal-compound shell, the triangular shape or the trapezoid shape can be manufactured. For example, even the process conditions for forming the triangular shape is applied, the metal-compound shell 20 can have the trapezoid shape by insufficient process conditions, such as, short time or a small amount of precursors (refer to FIG. 13).

- [67] When a side of the polygon adjacent to the nanowire core is a bottom side (d) of the polygon, the bottom side (d) of the polygon may have a length of 40nm to 200nm and the polygon has a height of 10nm to 200nm. When the height of the bottom side is below the range, the light-scattering effect may be less. When the length of the bottom side and/or the height is above the range, light loss due to the light absorption may increase.
- [68] The length (a) of the core-shell nanowire is not limited. For example, the length (a) may be in a range of 10 μ m to 200 μ m, and a ratio (c/a) of the height (c) of the polygon to the length (a) of the core-shell nanowire may be in a range of 0.00006 to 0.02. In addition, when viewed in the cross section of the core-shell nanowire perpendicular to a longitudinal direction of the core-shell nanowire, a ratio (longest diameter/length) of the longest diameter of the core-shell nanowire to the length (a) of core-shell nanowire may be in a range of 0.0001 to 0.06. By the above structure, light of various wavelengths can be scattered.
- [69] The core-shell nanowire having the above structure has a superior light-scattering property. The haze detected when the core-shell nanowire is coated on a transparent substrate may be 3% or more at a wavelength of 550nm, and, preferably, 20% or more at the wavelength of 550nm. The haze may be 60% or more, as in following Embodiments.
- [70] Also, the sheet resistance of the coated layer including the core-shell nanowire is superior, for example, 60 ($\Omega/\square$) or less. The sheet resistance of the coated layer including the core-shell nanowire according to the embodiment is not largely worse than the sheet resistance of the coated layer including the metal nanowire that is not coated. Also, the sheet resistance of the coated layer including the core-shell nanowire according to the embodiment may be lower than the sheet resistance of the coated layer including the metal nanowire that is not coated. In addition, the light transmittance at the wavelength of 550nm (excepting for a substrate absorption) can be high, for example, 70 to 98%.
- [71] When the core-shell nanowire according to the embodiment of the invention is used for a conductor layer of a transparent electrode, a transmittance of the conductor layer of the transparent electrode is 80% or more. Thus, the core-shell nanowire can have properties suitable for an OLED lighting.
- [72] Also, when the core-shell nanowire according to the embodiment of the invention is used for the conductor layer of the transparent electrode, a haze is 1% or more, and a light extraction can be induced through a light-scattering effect. Accordingly, when the conductor layer of the transparent electrode including the metal nanowire is used for the OLED lighting, efficiency of the OLED lighting can be enhanced.
- [73] In addition, the conventional metal nanowire has a large surface area even the metal

nanowire has a small weight and volume, and thus, the conventional metal nanowire may be easily aggregated. Thus, when the conventional metal nanowire is generally used for the transparent electrode, the dispersibility decreases and a sheet resistance ($\Omega/\square$) increases. Meanwhile, the core-shell nanowire according to the embodiment can have a superior dispersibility and the increase of a sheet resistance can be prevented.

[74] **(2) A method for manufacturing a metal nanowire**

[75] **1) A method for manufacturing a metal nanowire including a plurality of wire portions having at least one bent portion**

[76] In a method for manufacturing a metal nanowire including a plurality of wire portions having at least one bent portion according to an embodiment of the invention, all materials of a reaction mixture are added to a reaction container and a synthesized reaction is performed at a pressure of an atmospheric pressure or a pressure higher than the atmospheric pressure (for example, 1 to 5 atm) to manufacture the metal nanowire including the plurality of wire portions having the at least one bent portion.

[77] The manufacturing method according to the embodiment of the invention can synthesize a metal nanowire having a diameter of 50 to 200nm and a length of 40 to 300 μ m. The metal nanowire is grown to be bent, not to be broken, even the stress above a predetermined value is applied to the metal nanowire when the metal nanowire is synthesized. And thus, the metal nanowire including at least two wire portions connected through the at least one bent portion can be manufactured.

[78] In addition, the method is an one-pot synthesis. In the one-pot synthesis, a purification of intermediate products is not necessary, and the metal nanowire including at least two wire portions having the at least one bent portion can be manufactured with a high yield without by-products other than the metal nanowire.

[79] More particularly, the method for manufacturing the metal nanowire may include a step S10 of preparing a reaction mixture and a step S20 of synthesizing a metal nanowire. In the step S10 of preparing the reaction mixture, the reaction mixture including a metal salt, a capping agent, a reducing solvent, and a catalyst are prepared. In the step S20 of synthesizing the metal nanowire, the metal nanowire is grown by adding the reaction mixture to a reaction container and reacting with the reaction mixture in the reaction container. By controlling a composition and an amount of the reaction mixture, a reaction temperature, a reaction pressure, a reaction time, and so on, the metal nanowire including the plurality of wire portion having at least one bent portion with a large diameter and a large aspect ratio can be synthesized.

[80] In the step S10 of preparing the reaction mixture, the reaction mixture is prepared by adding the metal salt, the capping agent, the reducing solvent, and the catalyst to the reaction container with a predetermined ratio and mixing them in the reaction container at a room temperature. The reducing solvent reduces the metal salt to a metal. The

capping agent grows the reduced metal to have a wire shape.

- [81] The metal salt is a compound consisting of metal cation and organic or inorganic anion. For example, the metal cation may be a cation of a metal of Ni, Co, Fe, Pt, Au, Ag, Al, Cr, Cu, Mg, Mn, Mo, Rh, Si, Ta, Ti, W, U, V, Zr, Ge, and so on. The organic or inorganic anion may be $[\text{NO}_3]^-$, $[\text{ClO}_4]^-$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{CH}_3\text{COO}]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{SO}_4]^{2-}$, $[\text{CH}_3\text{COCH}=\text{COCH}_3]^-$, and so on. Two or more metal salts having similar ionization degrees may be mixed and the mixed metal salts may be used. Preferably, a silver salt consisting of cation of silver (Ag^+) and the organic or inorganic anion may be used.
- [82] The metal salt is dissolved by the reducing solvent, and is decomposed to the metal cation and the organic or inorganic anion. The decomposed metal cation is reduced, and then, is crystallized or grown to the metal nanowire.
- [83] A molar concentration of the metal salt is 0.03 mol/l to 0.4 mol/l. When the molar concentration is below 0.03 mol/l, an output of generated metal nanowire rapidly decreases. When the molar concentration is above 0.4 mol/l, the wires may be aggregated by an overproduction. More preferably, the molar concentration of the metal salt may be 0.05 mol/l to 0.10 mol/l.
- [84] The reducing solvent may be a polar solvent being able to dissolve the metal salt, the catalyst, and the capping agent. The reducing solvent has at least two hydroxyl groups in molecule. For example, a solvent such as a diol, a polyol, a glycol, or so on may be used. The reducing solvent acts as a reducing agent, and reduces the metal salt and forms a metal. As an example, at least one of ethyleneglycol, propyleneglycol, and glycerol may be used. More particularly, at least one of ethyleneglycol, 1, 2-propyleneglycol, 1, 3-propyleneglycol, glycerin, glycerol and diethylglycol may be used.
- [85] The capping agent is a chemical agent firstly interacting with side surfaces of the grown nanowire and being attached to the side surfaces of the grown nanowire so that a surface of a horizontal cross section of the nanowire can be crystallized. That is, the capping agent interacts with the side surface stronger than the surface of the horizontal cross section. Thus, the side surfaces are passivated, while the surface of the horizontal cross section is additionally crystallized to produce the nanowire.
- [86] For the capping agent, a surface-attached polymer such as polyvinylpyrrolidone (PVP), polyvinylalcohol (PVA), polyacrylamide (PAM), polyacrylicacid (PAA), and so on may be used.
- [87] The capping agent is included in an amount of 0.5 to 3.0 parts by weight with respect to 28 parts by weight of the reducing solvent. When the capping agent is included below 0.5 parts by weight, the diameter of the metal nanowire may increase. When the capping agent is included above 3.0 parts by weight, the length of the metal nanowire

may largely decrease. The capping agent may be included by 2.0 to 3.0 parts by weight with respect to 28 parts by weight of the reducing solvent.

- [88] The catalyst is a salt additive including a cation and an anion bonded to each other through an ionic bond. The catalyst is separated to ions in the polar solvent such as water, an alcohol, a diol, and a polyol. In this instance, a cation may be an organic material or an inorganic material, and an anion may be generally an inorganic material and has a halogen ion (Cl, Br, F, or so on). Anisotropy nano structures are firstly grown by the catalyst, thereby obtaining the nanowire with a relatively high yield.
- [89] The catalyst may include at least one of a compound where a cation and an anion bonded to each other through an ionic bond and a hydrate thereof. The cation may be a cation of Al, NH₄, Sb, As, Ba, Bi, Cd, Ca, Cr, Co, Cu, Fe, H, Pb, Mg, Hg, Ni, K, Ag, Na, Sr, and/or Zn. The anion may be an anion of C₂H₃O₂, Br, CO₃, Cl, CrO₄, OH, I, NO₃, O, C₂O₄, PO₄, SiO₃, SO₄, S, and/or SO₃.
- [90] A molar concentration of the catalyst may be in a range of 10⁻⁵ mol/l to 10⁻² mol/l. When the molar concentration is below 10⁻⁵ mol/l, the generation of the metal nanowire may be declined by a reduction of an initial nucleation. When the molar concentration is above 10⁻² mol/l, a macro-aggregation may be induced or the surplus catalyst prevents an anisotropic growth of the metal nanowire, the diameter increases, and a generation of spherical particles may increase.
- [91] In the step S20 of synthesizing the metal nanowire, the prepared reaction mixture is reacted in the reaction container. Then, the crystal grows to the metal nanowire through reducing the metal cation and growing crystals from metal nucleation sites through the metal cation. By controlling the reaction temperature and the reaction time as well as the composition of the reaction mixture, the metal nanowire having a large diameter and a large aspect ratio and including the wire portion having the at least one bent portion is synthesized. According to reaction conditions, the diameter, the length, and properties related the bent portion of the synthesized metal nanowire can be controlled.
- [92] The reaction temperature of the step of synthesizing the metal nanowire may in a range of 110 to 150°C. When the reaction temperature is below 110°C, the time for synthesizing the metal nanowire may increase, an output may decrease. When the reaction temperature is above 150°C, the metal nanowire may be aggregated by an increase of the rapid reaction velocity.
- [93] The reaction time of the step of synthesizing the metal nanowire may be in a range of 3 to 12 hours. When the reaction time is below 3, the grown time of the nanowire may be not sufficient and the length may be small. When the reaction time is above 12, the nanowires may be aggregated by an overproduction.
- [94] In the step of synthesizing the metal nanowire, all materials of a reaction mixture are

added to a reaction container and a synthesized reaction is performed at a pressure of an atmospheric pressure or a pressure high than the atmospheric pressure to synthesize the metal nanowire. By using an increased pressure, an evaporation point increases, and thus, the volatilization of the reaction solution can be minimized and a composition of the reaction solution can be maintained. Accordingly, the length of the metal nanowire according to the embodiment is 1.5 times or more the conventional metal nanowire. For increasing the pressure, the reaction container may be sealed, or an inert gas may be injected in the reaction container.

- [95] If the composition of the reaction mixture is changed when the metal nanowire is synthesized, the length of the synthesized metal nanowire may be varied. When the reaction is generated in the state that the reaction container is sealed, inflow and outflow of substances can be prevented during the reaction, and the constant composition can be maintained. Accordingly, the metal nanowires having uniform lengths can be obtained.
- [96] Additives may be added to synthesize the metal nanowire as necessary. For example, a stabilizer such as an antioxidant and so on, a dispersant, a viscosity increasing agent or a thickener, and so on may be further added, however, the embodiment is not limited. For example, so the length of the metal nanowire can be large, HCl or HNO₃ may be included in an amount of 0.1 to 1 parts by weight with respect to all catalysts contained.
- [97] The metal nanowire is cooled to a room temperature after the step of synthesizing the metal nanowire, and is cleaned by acetone, ethanol, so on, and then, is purified. Accordingly, the metal nanowire having a large diameter and a large aspect ratio and including wire portions having at least one bent portion can be obtained.
- [98] When the metal nanowire is manufactured by a manufacturing method according to an embodiment of the invention, the metal nanowire having different diameters, as well as, the metal nanowire including wire portions having at least one bent portion, can be synthesized.
- [99] **2) A method for manufacturing a metal nanowire having different diameters**
- [100] In a method for manufacturing a metal nanowire having different diameters according to an embodiment of the invention, all materials of a reaction mixture are added to a reaction container and a synthesized reaction is performed at a pressure of an atmospheric pressure or a pressure higher than the atmospheric pressure (for example, 1 to 5 atm) to manufacture the metal nanowire having different diameters by controlling an amount of a capping agent in the reaction compound and a reaction time.
- [101] The manufacturing method according to an embodiment of the invention is for manufacturing the metal nanowire having at least two wire portions or wire parts. The metal

nanowire includes an n-th wire portion or part and an (n+1) wire portion or part connected to the n-th wire portion or part. According to the manufacturing method, the metal nanowire having the n-th wire portion or part of the n-th diameter and the (n+1)-th wire portion or part of the (n+1)-th diameter of can be synthesized. By controlling elements preventing the surface growth of the metal nanowire, the metal nanowire having different diameters can be synthesized.

[102] The manufacturing method according to the embodiment of the invention can synthesize a metal nanowire having a diameter of 50 to 200nm and a length of 40 to 300 μ m. The metal nanowire is grown to be bent, not to be broken, even the stress above a predetermined value is applied to the metal nanowire when the metal nanowire is synthesized. And thus, the metal nanowire having different diameters can be manufactured.

[103] In addition, the method is an one-pot synthesis. In the one-pot synthesis, a purification of intermediate products is not necessary, and the metal nanowire having different diameters can be manufactured with a high yield without by-products other than the metal nanowire.

[104] More particularly, the method for manufacturing the metal nanowire may include a step S11 of preparing a reaction mixture and a step S21 of synthesizing a metal nanowire. In the step S11 of preparing the reaction mixture, the reaction mixture including a metal salt, a capping agent, a reducing solvent, and a catalyst are prepared. In the step S21 of synthesizing the metal nanowire, the metal nanowire is grown by adding the reaction mixture to a reaction container and reacting with the reaction mixture in the reaction container. By controlling a composition and an amount of the reaction mixture, a reaction temperature, a reaction pressure, a reaction time, and so on, the metal nanowire having different diameters with a large diameter and a large aspect ratio can be synthesized.

[105] In the step S11 of preparing the reaction mixture, the reaction mixture is prepared by adding the metal salt, the capping agent, the reducing solvent, and the catalyst to the reaction container with a predetermined ratio and mixing them in the reaction container at a room temperature. The reducing solvent reduces the metal salt to a metal. The capping agent grows the reduced metal to have a wire shape.

[106] The metal salt is a compound consisting of metal cation and organic or inorganic anion. For example, the metal cation may be a cation of a metal of Ni, Co, Fe, Pt, Au, Ag, Al, Cr, Cu, Mg, Mn, Mo, Rh, Si, Ta, Ti, W, U, V, Zr, Ge, and so on. The organic or inorganic anion may be $[\text{NO}_3]^-$, $[\text{ClO}_4]^-$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{CH}_3\text{COO}]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{SO}_4]^{2-}$, $[\text{CH}_3\text{COCH}=\text{COCH}_3]^-$, and so on. Two or more metal salts having similar ionization degrees may be mixed and the mixed metal salts may be used. Preferably, a silver salt consisting of cation of silver (Ag^+) and the organic or inorganic anion may

be used.

- [107] The metal salt is dissolved by the reducing solvent, and is decomposed to the metal cation and the organic or inorganic anion. The decomposed metal cation is reduced, and then, is crystallized or grown to the metal nanowire.
- [108] A molar concentration of the metal salt is 0.03 mol/l to 0.4 mol/l. When the molar concentration is below 0.03 mol/l, an output of generated metal nanowire rapidly decreases. When the molar concentration is above 0.4 mol/l, the wires may be aggregated by an overproduction. More preferably, the molar concentration of the metal salt may be 0.05 mol/l to 0.10 mol/l.
- [109] The reducing solvent may be a polar solvent being able to dissolve the metal salt, the catalyst, and the capping agent. The reducing solvent has at least two hydroxyl groups in molecule. For example, a solvent such as a diol, a polyol, a glycol, or so on may be used. The reducing solvent acts as a reducing agent, and reduces the metal salt and forms a metal. As an example, at least one of ethyleneglycol, propyleneglycol, and glycerol may be used. More particularly, at least one of ethyleneglycol, 1, 2-propyleneglycol, 1, 3-propyleneglycol, glycerin, glycerol and diethylglycol may be used.
- [110] The capping agent is a chemical agent firstly interacting with side surfaces of the grown nanowire and being attached to the side surfaces of the grown nanowire so that a surface of a horizontal cross section of the nanowire can be crystallized. That is, the capping agent interacts with the side surface stronger than the surface of the horizontal cross section. Thus, the side surfaces are passivated, while the surface of the horizontal cross section is additionally crystallized to produce the nanowire.
- [111] For the capping agent, a surface-attached polymer such as polyvinylpyrrolidone (PVP), polyvinylalcohol (PVA), polyacrylamide (PAM), polyacrylicacid (PAA), and so on may be used.
- [112] The capping agent is included in an amount of 0.05 to 1.0 parts by weight with respect to 28 parts by weight of the reducing solvent. When the capping agent is included below 0.05 parts by weight, the diameter of the metal nanowire may increase. When the capping agent is included above 1.0 parts by weight, the length of the metal nanowire may largely decrease. The capping agent may be included by 0.05 to 0.5 parts by weight with respect to 28 parts by weight of the reducing solvent.
- [113] The catalyst is a salt additive including a cation and an anion bonded to each other through an ionic bond. The catalyst is separated to ions in the polar solvent such as water, an alcohol, a diol, and a polyol. In this instance, a cation may be an organic material or an inorganic material, and an anion may be generally an inorganic material and has a halogen ion (Cl⁻, Br⁻, F⁻, or so on). Anisotropy nano structures are firstly grown by the catalyst, thereby obtaining the nanowire with a relatively high yield.

- [114] The catalyst may include at least one of a compound where a cation and an anion bonded to each other through an ionic bond and a hydrate thereof. The cation may be a cation of Al, NH₄, Sb, As, Ba, Bi, Cd, Ca, Cr, Co, Cu, Fe, H, Pb, Mg, Hg, Ni, K, Ag, Na, Sr, and/or Zn. The anion may be an anion of C₂H₃O₂, Br, CO₃, Cl, CrO₄, OH, I, NO₃, O, C₂O₄, PO₄, SiO₃, SO₄, S, and/or SO₃.
- [115] A molar concentration of the catalyst may be in a range of 10⁻⁵ mol/l to 10⁻² mol/l. When the molar concentration is below 10⁻⁵ mol/l, the generation of the metal nanowire may be declined by a reduction of an initial nucleation. When the molar concentration is above 10⁻² mol/l, a macro-aggregation may be induced or the surplus catalyst prevents an anisotropic growth of the metal nanowire, the diameter increases, and a generation of spherical particles may increase.
- [116] In the step S21 of synthesizing the metal nanowire, the prepared reaction mixture is reacted in the reaction container. Then, the crystal grows to the metal nanowire through reducing the metal cation and growing crystals from metal nucleation sites through the metal cation. By controlling the reaction temperature and the reaction time as well as the composition of the reaction mixture, the metal nanowire having different diameters with a large diameter and a large aspect ratio is synthesized. According to reaction conditions, the diameter, the length, and properties related the different diameters of the synthesized metal nanowire can be controlled.
- [117] The reaction temperature of the step of synthesizing the metal nanowire may in a range of 110 to 150°C. When the reaction temperature is below 110°C, the time for synthesizing the metal nanowire may increase, an output may decrease. When the reaction temperature is above 150°C, the metal nanowire may be aggregated by an increase of the rapid reaction velocity.
- [118] The reaction time of the step of synthesizing the metal nanowire may be in a range of 3 to 12 hours. When the reaction time is below 3, the grown time of the nanowire may be not sufficient and the length may be small. When the reaction time is above 12, the nanowires may be aggregated by an overproduction.
- [119] In the step of synthesizing the metal nanowire, all materials of a reaction mixture are added to a reaction container and a synthesized reaction is performed at a pressure of an atmospheric pressure or a pressure high than the atmospheric pressure to synthesize the metal nanowire. By using an increased pressure, an evaporation point increases, and thus, the volatilization of the reaction solution can be minimized and a composition of the reaction solution can be maintained. Accordingly, the length of the metal nanowire according to the embodiment is 1.5 times or more the conventional metal nanowire. For increasing the pressure, the reaction container may be sealed, or an inert gas may be injected in the reaction container.
- [120] If the composition of the reaction mixture is changed when the metal nanowire is

synthesized, the length of the synthesized metal nanowire may be varied. When the reaction is generated in the state that the reaction container is sealed, inflow and outflow of substances can be prevented during the reaction, and the constant composition can be maintained. Accordingly, the metal nanowires having uniform lengths can be obtained.

[121] Additives may be added to synthesize the metal nanowire as necessary. For example, a stabilizer such as an antioxidant and so on, a dispersant, a viscosity increasing agent or a thickener, and so on may be further added, however, the embodiment is not limited. For example, so the length of the metal nanowire can be large, HCl or HNO₃ may be included in an amount of 0.1 to 1 parts by weight with respect to all catalysts contained.

[122] The metal nanowire is cooled to a room temperature after the step of synthesizing the metal nanowire, and is cleaned by acetone, ethanol, so on, and then, is purified. Accordingly, the metal nanowire having different diameters with a large diameter and a large aspect ratio can be obtained.

[123] By decreasing the amount of the capping agent and increasing the reaction time compared with the conventional polyol synthesizing method, the capping agent for preventing a growth of side-surfaces of the metal nanowire is sufficient and the first wire portion or part having the first diameter is formed in the beginning of the synthesizing reaction. And then, the growth from the first wire portion or part is continuously generated. Then, in the end of the synthesizing reaction, the amount of the capping agent decrease and the growth of the side-surfaces of the metal nanowire increases, and therefore, a diameter of the metal nanowire increases and thus the second wire portion or part having the second diameter is formed. Accordingly, the metal nanowire including the first wire portion or part and a second wire portion or part extended from the first wire portion or part can be synthesized.

[124] When the metal nanowire is manufactured by a manufacturing method according to an embodiment of the invention, the metal nanowire including wire portions having at least one bent portion, as well as the metal nanowire having different diameters, can be synthesized.

[125] **3) A method for manufacturing a core-shell nanowire having a metal coating**

[126] A method for manufacturing a core-shell nanowire having a metal-compound shell according to an embodiment of the invention includes a step of preparing a nanowire core on a substrate, a step of contacting the nanowire core with a precursor solution for forming a metal-compound shell, and a step of forming a metal-compound shell on the nanowire core by providing growth energy. An absorption ratio of the growth energy to the nanowire core is higher than an absorption ratio of the growth energy to the substrate. After the step of forming the metal-compound shell, a step of cleaning and

nitrogen-drying may be further performed.

- [127] First, a nanowire core is prepared on a substrate. The nanowire core may be formed by directly growing the nanowire core on the substrate. Selectively, the metal nanowire may be prepared by coating the metal nanowire synthesized by the manufacturing method according to the embodiment of the invention on the substrate. The substrate is not limited. For example, the substrate may be a transparent substrate. Also, the substrate may be a substrate providing with an additional layer such as a conductive film or a conductive pattern.
- [128] Next, the nanowire core is contacted with a precursor solution for forming the metal-compound shell. The contacting methods may be varied. For example, the precursor solution may be coated on with the nanowire core on the substrate. Then, the precursor solution may be uniformly and sufficiently contacted to the nanowire core.
- [129] The precursor solution may be distilled water. However, the embodiment is not limited thereto. The precursor solution includes a metal organic compound or its derivatives that is a precursor of the metal compound. The molar concentration of the metal organic compound included in the precursor solution may be in a range of 0.0001 mol/l to 1 mol/l. However, the embodiment is not limited thereto. When the molar concentration of the metal organic compound is below 0.0001 mol/l, the protruded structures may be not sufficient. When the molar concentration of the metal organic compound is above 1 mol/l, the metal compound may be unnecessarily coated on the substrate.
- [130] The precursor solution may further include a growth accelerating agent. A material of the growth accelerating agent is not limited. Preferably, a basic compound or an amine-based compound may be selected. For example, sodium hydroxide, potassium hydroxide, ammonia water, diphenylamine, D-Alanine, D-cysteine, monoethanolamine, monoethylenediamine, S-beta-phenylalanine, chlorophenylamine, and so on may be used. The molar concentration of the growth accelerating agent may be 0.0001 mol/l to 1 mol/l per 1 mol of the metal organic compound included in the precursor solution. When the molar concentration of the growth accelerating agent is below 0.0001 mol/l, the growth velocity is low. The molar concentration of the growth accelerating agent is above 1 mol/l, the protruded structures may be not sufficient or not compete, and the metal compound may be unnecessarily coated on the substrate.
- [131] Next, the metal-compound shell is coated on the nanowire core by providing growth energy. The metal-compound shell is formed by a reduction of a metal organic salt through the growth energy. An absorption ratio of the growth energy to the nanowire core is higher than an absorption ratio of the growth energy to the substrate may be selected in order to suppress the formation of the metal compound on the substrate. For example, the growth energy is an electromagnetic wave including at least one of ul-

traviolet rays, visible rays, and infrared rays. Preferably, a xenon lamp, a halogen lamp, an ultraviolet (UV) lamp, a laser lamp, and an infrared lamp may be used. By using the xenon lamp, xenon light of a range of 50W to 1000W may be irradiated. However, the light having an electric power larger than the range may be used according to a manufacturing area.

- [132] Selectively, energy inducing molecular vibrations may be used. Preferably, microwave energy may be used. The energy of the microwave energy may be in a range of 50 to 200W. However, the energy larger than the range may be used according to a manufacturing area.
- [133] The time of supplying the growth energy is not limited. The time of supplying the growth energy may be in a range of 10 seconds to 5 minutes. However, the time longer than the range may be possible according to a manufacturing area.
- [134] Next, the cleaning and nitrogen-drying may be performed after the metal-compound shell is formed. Alcohol such as ethanol and so on may be used for the cleaning, and nitrogen may be used for the nitrogen-drying. However, the embodiment is not limited thereto.
- [135] Meanwhile, the nanowire core including the metal-compound shell may be manufactured without the substrate. That is, the nanowire core including the metal-compound shell can be obtained by a step of preparing a nanowire core, a step of contacting the nanowire core with a precursor solution for forming a metal-compound shell, and a step of forming a metal-compound shell on the nanowire core by providing growth energy being absorbed to the nanowire core. After the step of forming the metal-compound shell, a step of cleaning and nitrogen-drying may be further performed. In the step of contacting the nanowire core with a precursor solution, the nanowire core may be immersed or dipped into a precursor solution filled in an reaction container.
- [136] On the other hand, as shown in FIG. 14, the nanowire core including the metal-compound shell is formed by a roll-to-roll continuous process. For example, a flexible substrate is transferred by using rollers 30. The nanowire core is firstly formed on the substrate by using a nanowire sprayer 40. And then, the flexible substrate with the nanowire core passes through a dryer 50 and is dried. And then, the precursor solution for forming the metal-compound shell is coated through using a coater 60 so that the precursor can be sufficiently contacted with the nanowire core. And then, the metal-compound shell is coated on the nanowire core by supplying the growth energy through an energy irradiator 70 for applying growth energy. And then, the cleaning and drying is performed by a cleaning and drying apparatus 80, and thus, the substrate coated with the core-shell nanowire including the metal-compound shell can be finally manufactured by the roll-to-roll process.

[137] **(3) A transparent electrode and an organic light emitting diode**

[138] A transparent electrode 300 and an organic light emitting diode 1000 using the metal nanowire or the core-shell nanowire according to an embodiment of the invention are provided. It will be understood that when one element such as a layer, a film, a region or a plate is referred to as being “on” another element, the one element may be directly on the another element, and one or more intervening elements may also be present.

[139] The transparent electrode 300 according to the embodiment of the invention includes a conductor layer 310 provided on a transparent substrate 200 and a transparent electrode layer 320 formed on the conductor layer 310. The conductor layer 310 may include a metal (or core-shell) nanowire 311 according to the embodiment of the invention and metal particles 312 or metal oxide particles 313.

[140] For the nanowire 311 included in the conductor layer 310, the metal (or core-shell) nanowire having the above properties, that is, the metal (or core-shell) nanowire having at least one of bent portion, the metal (or core-shell) nanowire having different diameters, and the core-shell nanowire having the metal coating may be used. The metal (or core-shell) nanowire manufactured by the above-mentioned manufacturing methods may be used.

[141] The metal particle 312 or the metal oxide 313 included in the conductor layer 310 has one or more of conductive materials. For example, the metal particle 312 or the metal oxide particle 313 may include at one selected from a group consisting of silver (Ag), gold (Au), copper (Cu), platinum (Pt), iron (Fe), nickel (Ni), cobalt (Co), zinc (Zn), titanium (Ti), chrome (Cr), aluminum (Al), palladium (Pd), and oxides thereof. However, the embodiment is not limited.

[142] Preferably, silver (Ag) may be used. The silver (Ag) is a metal, and thus, reflects a light. Also, although the silver has low transmittance is low, when the silver faces a second electrode 500 (for example, an aluminum metal electrode) in the organic light emitting diode 1000, and the light can be reflected between the silver and the second electrode 500, and thus, the light loss can be reduced inside the organic light emitting diode.

[143] The transparent substrate 200 may be formed of a material or a mixture including the material. The material may be selected from a group consisting of polyester-based resins including as polyethyleneterephthalate (PET), polybuthyleneterephthalate (PBT), polyarylate, polysulfone-based resins including polysulfone and polyethersulfone (PES), polyetherketone-based resins including polyetherketone (PEK) and polyetheretherketone (PEEK), polycarbonate-based resins, polyolefin acrylic resins, styrene-based resins, cellulose derivatives including cellulose triacetate (TAC), and copolymers thereof.

[144] Also, a transparent substrate may be a silicon substrate, a SOI(Silicon On Insulator)

substrate, a gallium arsenide(GaAs) substrate, a silicon germanium(SiGe) substrate, a ceramic substrate, a quartz substrate, or a glass substrate for lighting. The substrate used for lighting may be unlimitedly used.

- [145] One or more of various transparent and conductive materials may be used for the transparent electrode layer 320. Preferably, one or more of metal oxides including ITO(indium tin oxide), ATO(antimony tin oxide), IZO(indium zinc oxide), AZO(ZnO-Al₂O₃, aluminum-doped zinc oxide), GZO(ZnO-Ga₂O₃, Gallium-doped zinc oxide) and graphene, which has a high transmittance, a high conductivity, and a high heat resistance, may be used for the transparent electrode layer 320.
- [146] The transparent electrode layer 320 may be evenly formed on the conductor layer 310 or formed on the conductor layer 310 with a curve. In the case that the transparent electrode layer 320 is formed with the curve, when a period of the curvature is $R\lambda_a$ and a height of the curvature is R_a , a ratio of $R_a/R\lambda_a$ (that is, a ratio of the height R_a of the curvature with respect to the period $R\lambda_a$ of the curvature) may be 10^{-3} or more. The transparent electrode layer 320 can increase the light-scattering effect, and can protect the nanowire 311, and the metal particle 312 or the metal oxide particle 313.
- [147] Also, the organic light emitting diode 1000 according to the embodiment includes a first electrode 400, a second electrode 500, and an organic light emitting layer 600 between the first electrode 400 and the second electrode 500.
- [148] The first electrode 400 may be a transparent electrode including the metal (or core-shell) nanowire with a large diameter and a large aspect ratio according to embodiments.
- [149] The organic light emitting layer 600 is provided between the first electrode 400 and the second electrode 500, and emits the light by an electric drive between the first electrode 400 and the second electrode 500. The organic light emitting layer 600 has a stacked structure including a light emitting layer 610 and further including at least one selected from a hole injection layer 620, a hole transfer layer 630, an electrode transfer layer 640, and an electrode injection layer 650. A material of the light emitting layer 610 being able to emit light of a visible light range by receiving holes supplied from the hole transfer layer 630 and electrons supplied from the electron transfer layer 640 combining the holes and the electrodes may be used. A material having high quantum efficiency to a fluorescence material or a phosphorescent material may be preferable.
- [150] The second electrode 500 is a reflective electrode. The second electrode 500 may be formed of one or more of an alkali metal, an alkali earth metal, and metals of groups 3 of the periodic table of the elements. That is, the second electrode 500 may be formed of silver (Ag), magnesium (Mg), aluminum, (Al), platinum (Pt), palladium (Pd), gold (Au), nickel (Ni), neodymium (Nd), iridium (Ir), chrome (Cr), lithium (Li) or calcium (Ca), or an alloy thereof. However, the invention is not limited thereto.

- [151] Also, according to an embodiment, an organic light emitting device includes the organic light emitting diode 1000 and a sealing substrate 2000. The organic light emitting diode 1000 includes the transparent substrate 200, the first electrode 400 according to the embodiment, the second electrode 500 facing the first electrode 400, and the organic light emitting layer 600 provided between the first electrode 400 and the second electrode 500.
- [152] The sealing substrate 2000 is provided on the second electrode 500 to cover the organic light emitting diode 1000 on the organic light emitting diode 1000. The sealing substrate 2000 prevents oxygen and water from penetrating through the organic light emitting diode 1000 and protects the organic light emitting diode 1000.
- [153] In the organic light emitting diode used for lighting, inner light extraction efficiency is very important. The transparent electrode according to the embodiment includes the metal (or core-shell) the nanowire according to the embodiment, and thus, the electric conductivity can increase, and the transmittance and the haze are superior. Also, a loss that may be induced by a total reflection of the light generated in the organic light emitting diode due to the reflective index can be reduced, and scattering is induced. Accordingly, the organic light emitting diode and the organic light emitting diode can have the enhanced inner light extraction effect.
- [154] For example, the transparent electrode has a sheet resistance of $50 \Omega/\square$ or less.
- [155] **Advantageous Effects**
- [156] A metal nanowire according to the invention has a large diameter and a large aspect ratio and includes a plurality of wire portions having at least one bent portion. Thus, contact points, contact areas, or a contact probability between the metal nanowires can increase, a sheet resistance can be relatively low, an electric conductivity can be superior, and a light-scattering effect can be achieved.
- [157] Also, a metal nanowire according to the invention has a large diameter and a large aspect ratio and having different diameters. Thus, contact points, contact areas, or a contact probability between the metal nanowires can increase, a sheet resistance can be relatively low, an electric conductivity can be superior, and a light-scattering effect can be achieved.
- [158] In addition, a core-shell nanowire according to the invention has a metal coating. A sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.
- [159] Furthermore, a method for manufacturing a metal nanowire according the invention is an one-pot synthesis. In the method for manufacturing the metal nanowire, a purification of intermediate products is not necessary, and the metal nanowire can be manufactured with a high yield without by-products other than the metal nanowire.

- [160] Also, in a method for manufacturing a metal nanowire according to the invention, volatilization of a reaction mixture can be minimized by adding all of a reaction mixture to a reaction container and reacting with the reaction mixture at a pressure of an atmospheric pressure or a pressure high than the atmospheric pressure. The metal nanowire can be grown to be bent, not to be broken, even the metal nanowire has a large diameter and a large aspect ratio. Thus, the metal nanowire including a plurality of wire portions having at least one bent portion can be manufactured.
- [161] Further, in a method for manufacturing a metal nanowire according to the invention, a side-surface growth of the metal nanowire can be controlled by controlling an amount of a capping agent, and the metal nanowire having different diameters can be manufactured.
- [162] In addition, a method for manufacturing a core-shell nanowire according to the invention can be applied to a metal nanowire including a plurality of wire portions having at least one bent portion and a metal nanowire having different diameters, as well as the known, marketed, or generally used metal nanowire. Thus, a core-shell nanowire having a metal-compound shell can be manufactured.
- [163] Furthermore, according to a method for manufacturing a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion as a conductor layer, the transparent electrode having a transmittance and a haze suitable for an OLED lighting or an organic solar cell at a range of visibly ray can be manufactured.
- [164] Also, according to a method for manufacturing a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and having different diameters as a conductor layer, the transparent electrode having a transmittance and a haze suitable for an OLED lighting or an organic solar cell at a range of visibly ray can be manufactured.
- [165] Furthermore, according to a method for manufacturing a transparent electrode and an organic light emitting diode including a core-shell nanowire having a metal coating, a sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.
- [166] **Embodiment**
- [167] **1) Embodiment 1 to Embodiment 10 - A metal nanowire including a plurality of wire portions having at least one bent portion**
- [168] Embodiment 1
- [169] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1X10⁻³ mol/l of FeCl₃. The reaction mixture was added

into a single container and the single container was sealed, and then, a reaction was generated at 1 atm and 130°C for 5 hours, thereby obtaining silver nanowires including wire portions having at least one bent portion.

[170] Embodiment 2

[171] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1X10⁻³ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 3 atm and 130°C for 5 hours, thereby obtaining silver nanowires including wire portions having at least one bent portion.

[172] Embodiment 3

[173] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1X10⁻³ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 5 atm and 130°C for 5 hours, thereby obtaining silver nanowires including wire portions having at least one bent portion.

[174] Embodiment 4

[175] Silver nanowires including wire portions having at least one bent portion were obtained by the same method according to Embodiment 2, except that the molar concentration of FeCl₃ was 5X10⁻³mol/l and the reaction time is 1 hour.

[176] Embodiment 5

[177] Silver nanowires having wire portion having at least one bent portion were obtained by the same method according to Embodiment 2, except that the molar concentration of FeCl₃ was 5X10⁻³mol/l and the reaction time is 6 hours.

[178] Embodiment 6

[179] Silver nanowires including wire portions having at least one bent portion were obtained by the same method according to Embodiment 2, except that the molar concentration of FeCl₃ was 5X10⁻³mol/l and the reaction time is 12 hours.

[180] Embodiment 7

[181] Silver nanowires having at least one bent portion and having different diameters were obtained by the same method according to Embodiment 2, except that the reaction temperature was 110°C.

[182] Embodiment 8

[183] Silver nanowires having at least one bent portion and having different diameters were obtained by the same method according to Embodiment 2, except that the reaction temperature was 150°C.

[184] Embodiment 9

[185] Silver nanowires having at least one bent portion and having different diameters were obtained by the same method according to Embodiment 2, except that an amount of the

PVP(Mw ~360,000) was 0.8g.

[186] Embodiment 10

[187] Silver nanowires having at least one bent portion and having different diameters were obtained by the same method according to Embodiment 2, except that an amount of the PVP(Mw ~360,000) was 1.5g.

[188] **2) Embodiment 11 to Embodiment 22 - A metal nanowire including having different diameters**

[189] Embodiment 11

[190] A reaction mixture was prepared by mixing 0.2mol/l of AgNO₃, 28g of EG(99.5%), 0.1g of PVP(Mw ~360,000), and 1X10⁻³ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 1 atm and 130°C for 3 hours, thereby obtaining silver nanowires having different diameters.

[191] Embodiment 12

[192] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 11, except that reaction time is 4 hours.

[193] Embodiment 13

[194] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 11, except that reaction time is 5 hours.

[195] Embodiment 14

[196] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 11, except that reaction time is 6 hours.

[197] Embodiment 15

[198] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 11, except that reaction time is 7 hours.

[199] Embodiment 16

[200] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 0.05g of PVP(Mw ~360,000), and 5X10⁻³ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 3 atm and 130°C for 3 hours, thereby obtaining silver nanowires having different diameters.

[201] Embodiment 17

[202] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 11, except that reaction time is 4 hours.

[203] Embodiment 18

[204] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 16, except that reaction time is 5 hours.

[205] Embodiment 19

- [206] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 16, except that reaction time is 6 hours.
- [207] Embodiment 20
- [208] Silver nanowires including wire portions having different diameters were obtained by the same method according to Embodiment 16, except that reaction time is 7 hours.
- [209] Embodiment 21
- [210] A reaction mixture was prepared by mixing 0.1mol/l of AgNO_3 , 28g of EG(99.5%), 0.1g of PVP(Mw ~360,000), and 1×10^{-3} mol/l of FeCl_3 . The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 3 atm and 110°C for 12 hours, thereby obtaining silver nanowires having different diameters and having at least one bent portion.
- [211] Embodiment 22
- [212] A reaction mixture was prepared by mixing 0.1mol/l of AgNO_3 , 28g of EG(99.5%), 0.05g of PVP(Mw ~360,000), and 1×10^{-3} mol/l of FeCl_3 . The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 3 atm and 150°C for 12 hours, thereby obtaining silver nanowires having different diameters and having at least one bent portion.
- [213] **3) Comparative Example 1 to Comparative Example 7**
- [214] Comparative Example 1
- [215] A reaction mixture was prepared by mixing 0.1mol/l of AgNO_3 , 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1×10^{-3} mol/l of FeCl_3 . The reaction mixture was added into a single container and the single container was not sealed, and then, a reaction was generated at 1 atm and 130°C for 5 hours, thereby obtaining silver nanowires.
- [216] Comparative Example 2
- [217] A reaction mixture was prepared by mixing 0.15mol/l of AgNO_3 , 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1×10^{-3} mol/l of FeCl_3 . The reaction mixture was added into a single container and the single container was not sealed, and then, a reaction was generated at 1 atm and 130°C for 5 hours, thereby obtaining silver nanowires.
- [218] Comparative Example 3
- [219] A reaction mixture was prepared by mixing 0.1mol/l of AgNO_3 , 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1×10^{-5} mol/l of FeCl_3 . The reaction mixture was added into a single container and the single container was not sealed, and then, a reaction was generated at 3 atm and 130°C for 5 hours, thereby obtaining silver nanowires.
- [220] Comparative Example 4
- [221] A reaction mixture was prepared by mixing 0.1mol/l of AgNO_3 , 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 5×10^{-5} mol/l of FeCl_3 . The reaction mixture was added into a single container and the single container was not sealed, and then, a reaction was generated at 3 atm and 130°C for 5 hours, thereby obtaining silver nanowires.

[222] Comparative Example 5

[223] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 3g of PVP(Mw ~360,000), and 1X10⁻⁴ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was not sealed, and then, a reaction was generated at 3 atm and 130°C for 5 hours, thereby obtaining silver nanowires.

[224] Comparative Example 6

[225] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 0.5g of PVP(Mw ~360,000), and 1X10⁻³ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 3 atm and 130°C for 2 hours, thereby obtaining silver nanowires.

[226] Comparative Example 7

[227] A reaction mixture was prepared by mixing 0.1mol/l of AgNO₃, 28g of EG(99.5%), 1g of PVP(Mw ~360,000), and 1X10⁻³ mol/l of FeCl₃. The reaction mixture was added into a single container and the single container was sealed, and then, a reaction was generated at 3 atm and 130°C for 1 hour, thereby obtaining silver nanowires.

[228] Table 1

[Table 1]

	amount or concentration of Preparing a reaction mixture				Reaction conditions of Synthesizing silver nanowires			Seal[O] or not- seal[X]
	M.S[mol/l]	R.S[g]	C.A[g]	C[mol/l]	P[atm]	T[hr]	Temp [°C]	
Embodiment 1	0.1	28	3	1X10 ⁻³	1	5	130	O
Embodiment 2	0.1	28	3	1X10 ⁻³	3	5	130	O
Embodiment 3	0.1	28	3	1X10 ⁻³	5	5	130	O
Embodiment 4	0.1	28	3	5X10 ⁻³	3	1	130	O
Embodiment 5	0.1	28	3	5X10 ⁻³	3	6	130	O
Embodiment 6	0.1	28	3	5X10 ⁻³	3	12	130	O
Embodiment 7	0.1	28	3	1X10 ⁻³	3	5	110	O
Embodiment 8	0.1	28	3	1X10 ⁻³	3	5	150	O
Embodiment 9	0.1	28	0.8	1X10 ⁻³	3	5	130	O
Embodiment 10	0.1	28	1.5	1X10 ⁻³	3	5	130	O
Embodiment 11	0.2	28	0.1	1X10 ⁻³	1	3	130	O
Embodiment 12	0.2	28	0.1	1X10 ⁻³	1	4	130	O
Embodiment 13	0.2	28	0.1	1X10 ⁻³	1	5	130	O
Embodiment 14	0.2	28	0.1	1X10 ⁻³	1	6	130	O
Embodiment 15	0.2	28	0.1	1X10 ⁻³	1	7	130	O
Embodiment 16	0.1	28	0.05	5X10 ⁻³	3	3	130	O
Embodiment 17	0.1	28	0.05	5X10 ⁻³	3	4	130	O
Embodiment 18	0.1	28	0.05	5X10 ⁻³	3	5	130	O
Embodiment 19	0.1	28	0.05	5X10 ⁻³	3	6	130	O
Embodiment 20	0.1	28	0.05	5X10 ⁻³	3	7	130	O
Embodiment 21	0.1	28	0.1	1X10 ⁻³	3	12	110	O
Embodiment 22	0.1	28	0.05	1X10 ⁻³	3	12	150	O
Comparative Example 1	0.1	28	3	1X10 ⁻³	1	5	130	X
Comparative	0.15	28	3	1X10 ⁻³	1	5	130	X

Example 2								
Comparative Example 3	0.1	28	3	1×10^{-5}	3	5	130	X
Comparative Example 4	0.1	28	3	5×10^{-5}	3	5	130	X
Comparative Example 5	0.1	28	3	1×10^{-4}	3	5	130	X
Comparative Example 6	0.1	28	0.5	1×10^{-3}	3	2	130	O
Comparative Example 7	0.1	28	1	1×10^{-3}	3	1	130	O

[229] [M.S: a metal salt, R.S: a reducing solution, C.A: a capping agent, C: catalyst, P: pressure, T: time, Temp: Temperature]

[230] **4) Embodiment 23 to Embodiment 32 - A core-shell nanowire having a metal coating**

[231] Embodiment 23

[232] 0.001mol/l of zinc acetate dehydrate and 0.001 mol/l hexamethylenedimaine were added to distilled water to prepare a precursor solution. And then, the precursor solution was coated on a substrate coated with silver nanowires. And then, light was irradiated to the substrate by using a white light source for 5 minutes. After the completion of the reaction, the substrate was washed by using ethanol and was dried by using nitrogen, and thus, the core-shell nanowires were manufactured.

[233] Embodiment 24

[234] Core-shell nanowires were manufactured by the same method according to Embodiment 23, except that the molar concentration of the zinc acetate dehydrate was 0.01mol/l and the amount of the hexamethylenediamine was 0.01mol/l.

[235] Embodiment 25

[236] Core-shell nanowires were manufactured by the same method according to Embodiment 23, except that the molar concentration of the zinc acetate dehydrate was 0.10mol/l and the amount of the hexamethylenediamine was 0.10mol/l.

[237] Embodiment 26

[238] Core-shell nanowires were manufactured by the same method according to Embodiment 23, except that the molar concentration of the zinc acetate dehydrate was 0.50mol/l and the amount of the hexamethylenediamine was 0.50mol/l.

[239] Embodiment 27

[240] Core-shell nanowires were manufactured by the same method according to Em-

bodiment 23, except that the molar concentration of the zinc acetate dehydrate was 1.00mol/l and the amount of the hexamethylenediamine was 1.00mol/l.

[241] Embodiment 28

[242] 0.001mol/l of zinc nitrate and 0.001 mol/l hexamethylenedimaine were added to distilled water to prepare a precursor solution. And then, the precursor solution was coated on a substrate coated with the silver nanowires. And then, microwave of 1000W is applied for 30 seconds. After the completion of the reaction, the substrate was washed by using ethanol and was dried by using nitrogen, and thus, the core-shell nanowires were manufactured.

[243] Embodiment 29

[244] Core-shell nanowires were manufactured by the same method according to Embodiment 28, except that the molar concentration of the zinc nitrate was 0.01mol/l and the amount of the hexamethylenediamine was 0.01mol/l.

[245] Embodiment 30

[246] Core-shell nanowires were manufactured by the same method according to Embodiment 28, except that the molar concentration of the zinc nitrate was 0.10mol/l and the amount of the hexamethylenediamine was 0.10mol/l.

[247] Embodiment 31

[248] Core-shell nanowires were manufactured by the same method according to Embodiment 28, except that the molar concentration of the zinc nitrate was 0.50mol/l and the amount of the hexamethylenediamine was 0.50mol/l.

[249] Embodiment 32

[250] Core-shell nanowires were manufactured by the same method according to Embodiment 28, except that the molar concentration of the zinc nitrate was 1.00mol/l and the amount of the hexamethylenediamine was 1.00mol/l.

[251] Comparative Example 8 to Comparative Example 12

[252] The substrates coated with the silver nanowires according Embodiment 23 to Embodiment 27 before a zinc oxide coating, which were not coated with a zinc oxide, were used as the Comparative Example 8 to Comparative Example 12, respectively.

[253] Comparative Example 13 to Comparative Example 17

[254] The substrates coated with the silver nanowires according Embodiment 28 to Embodiment 32 before a zinc oxide coating, which were not coated with a zinc oxide, were used as the Comparative Example 13 to Comparative Example 17, respectively.

[255] **Test Example**

[256] **1) Measuring a diameter and a length, and calculating an aspect ratio**

[257] The diameters and the lengths of the silver nanowires synthesized according to Embodiments and Comparative Examples were measured, and the aspect ratios were calculated. The result are shown in TABLE 2.

[258] Table 2

[Table 2]

	1 st diameter[n m]	2 nd diameter[μ m]	3 rd diameter[m]	Length [m]	Aspect ratio
Embodiment 1	80			100	1250
Embodiment 2	100			150	1500
Embodiment 3	120			230	1917
Embodiment 4	60			60	1000
Embodiment 5	150			120	800
Embodiment 6	200			230	1150
Embodiment 7	90	0.3-0.9	0.2-0.6	100	1111
Embodiment 8	150	0.4-1.2	0.4-1.0	130	867
Embodiment 9	200			100	500
Embodiment 10	150			100	667
Embodiment 11	50	0.01-0.1		70	1400
Embodiment 12	60	0.02-0.13		100	1667
Embodiment 13	80	0.03-0.15		140	1750
Embodiment 14	80	0.025-0.2	0.025-0.1	150	1875
Embodiment 15	90	0.1-0.3	0.1-0.3	160	1778
Embodiment 16	60	0.03-0.1		50	833
Embodiment 17	70	0.06-0.2		70	1000
Embodiment 18	80	0.1-0.2	0.08-0.15	100	1250
Embodiment 19	100	0.15-0.35	0.08-0.2	120	1200
Embodiment 20	130	0.2-0.5	0.1-0.5	150	1154
Embodiment 21	90	0.3-0.9	0.2-0.6	100	1111
Embodiment 22	150	0.4-1.2	0.4-1.0	130	867
Comparative Example 1	60			40	667
Comparative Example 2	80			40	500
Comparative	50			15	300

Example 3					
Comparative Example 4	55			20	364
Comparative Example 5	60			30	500
Comparative Example 6	150			30	200
Comparative Example 7	100			30	300

[259] As shown in TABLE 2, it can be seen that the silver nanowires according to Embodiments have diameters and lengths larger than diameters and lengths of the silver nanowires according to Comparative Examples. Also, it can be seen that the aspect ratios of the silver nanowires according to Embodiments are generally above 1000.

[260] Also, the silver nanowires according to Embodiment 7, 8 and Embodiment 11 to 22 have a plurality of diameters having a second diameter, a third diameter, and so on. On the other hand, each of the silver nanowires according to Comparative Examples has a uniform diameter.

[261] **2) Analysis of a scanning electron microscopy (SEM)**

[262] FIG. 15 is a photograph of a surface of silver nanowires according to an embodiment of the invention, taken using a scanning electron microscopy. As shown in FIG. 15, the manufactured silver nanowires have a diameter distribution 15a of D1(124.47nm), D2(81.48nm), D3(84.42nm), D4(85.93nm), D5(84.65nm), D6(98.13nm), D7(134.80nm), and D8(67.15nm). That is, the silver nanowires have large diameters. Also, the manufactured silver nanowires have a length distribution 15b of D1(194.79μm), D2(182.86μm), D3(100.14μm), D4(193.74μm), D5(111.31μm), D6(243.61μm), D7(95.14μm), and D8(123.00μm). That is, the silver wires have large lengths.

[263] FIG. 16 is a photograph of silver nanowires having a plurality of wire parts having different diameters according to an embodiment of the invention, taken using a scanning electron microscopy. As shown in FIG. 16, it can be seen that a second part having the second diameter connected to a first part having a first diameter is formed.

[264] **3) Analysis using transmission electron microscope (TEM)**

[265] FIG. 17 and FIG. 18 are photographs of silver nanowires including a plurality of wire portions having at least one bent portion according to an embodiment of the invention, taken using a transmission electron microscopy. The silver nanowires having bent shapes bent to a predetermined direction can be seen. FIG. 19 is a photograph of silver

nanowires not including a plurality of wire portions and not having at least one bent portion as a comparative example, taken using a transmission electron microscopy.

[266] The number of the bent portion and average angle of the bent portion of the silver nanowires including the plurality of wire portion having at least one bent portion are shown in TABLE 3.

[267] Table 3

[Table 3]

	1 st diameter[n m]	2 nd diameter[μm]	3 rd diameter[μm]	Length[μ m]	N.B	A.B[°]
Embodiment 1	80			100	2	155
Embodiment 2	100			150	2	110
Embodiment 3	120			230	3	87
Embodiment 4	60			60	1	150
Embodiment 5	150			120	2	155
Embodiment 6	200			230	2	160
Embodiment 7	90	0.3-0.9	0.2-0.6	100	2	150
Embodiment 8	150	0.4-1.2	0.4-1.0	130	2	160
Embodiment 9	200			100	2	155
Embodiment 10	150			100	2	155
Embodiment 11	50	0.01-0.1		70		
Embodiment 12	60	0.02-0.13		100		
Embodiment 13	80	0.03-0.15		140		
Embodiment 14	80	0.025-0.2	0.025-0.1	150		
Embodiment 15	90	0.1-0.3	0.1-0.3	160		
Embodiment 16	60	0.03-0.1		50		
Embodiment 17	70	0.06-0.2		70		
Embodiment 18	80	0.1-0.2	0.08-0.15	100		
Embodiment 19	100	0.15-0.35	0.08-0.2	120		

Embodiment 20	130	0.2-0.5	0.1-0.5	150		
Embodiment 21	90	0.3-0.9	0.2-0.6	100	2	150
Embodiment 22	150	0.4-1.2	0.4-1.0	130	2	160
Comparative Example 1	60			40		
Comparative Example 2	80			40		
Comparative Example 3	50			15		
Comparative Example 4	55			20		
Comparative Example 5	60			30		
Comparative Example 6	150			30		
Comparative Example 7	100			30		

[268] [N.B: the number of the bent portions, A.B: an average angle of the bent portion]

[269] As shown in TABLE 3, it can be seen that the silver nanowires according to Embodiments generally include two to three bent portions, while the silver nanowires according to Comparative Examples do not include the bent portion. Also, it can be seen that the nanowires according to Embodiments 21 and 22 have different diameters and have at least one bent portion.

[270] **Experimental Example**

[271] **1) Measuring electric conductivity (sheet resistance)**

[272] A sheet resistance of a transparent substrate including silver nanowires according to each Embodiments and Comparative Examples was measured 15 times by using a 4-point probe. An average sheet resistance and a standard deviation were calculated. Also, the average sheet resistance and the standard deviation are shown in TABLE 4.

[273] Table 4

[Table 4]

	average sheet resistance($\Omega/\square$)	Standard deviation
Embodiment 1	25	7.5
Embodiment 2	21	6.3
Embodiment 3	40	12
Embodiment 4	80	24
Embodiment 5	82	24.6
Embodiment 6	42	12.6
Embodiment 7	27	8.1
Embodiment 8	37	11.1
Embodiment 9	29	8.7
Embodiment 10	42	12.6
Embodiment 11	108	20.4
Embodiment 12	97	18.9
Embodiment 13	68	16.7
Embodiment 14	54	13.9
Embodiment 15	40	12.2
Embodiment 16	115	31.1
Embodiment 17	110	29.7
Embodiment 18	48	7.3
Embodiment 19	43	9.7
Embodiment 20	35	8.3
Embodiment 21	27	8.1
Embodiment 22	37	11.1
Comparative Example 1	58	17.4
Comparative Example 2	75	22.5
Comparative Example 3	73	21.9
Comparative Example 4	90	27
Comparative Example 5	120	36
Comparative Example 6	160	48

Comparative Example 7	180	54
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[274] As shown in TABLE 4, the transparent electrodes including the silver nanowires according to Embodiments have sheet resistances of a minimum of $21 \Omega/\square$, a maximum of $115 \Omega/\square$, and an average of $54.9 \Omega/\square$. On the other hand, the transparent electrodes including the silver nanowires according to Comparative Examples have sheet resistances of a minimum of $58 \Omega/\square$, a maximum of $180 \Omega/\square$, and an average of $108 \Omega/\square$. It can be seen that the silver nanowires according to the invention can prevent the sheet resistance from increasing and thus the transparent electrode can have a superior electric conductivity.

[275] **2) Measuring a transmittance and a haze**

[276] A transmittance and a haze of a transparent substrate including silver nanowires according to each Embodiments and Comparative Examples were measured, and the results are shown in TABLE 5. FIG. 20 is graphs of transmittances, wherein (a) of FIG. 20 is a graph of transmittances of a transparent substrate including silver nanowires according to each of Embodiments 11 to 15, and (b) of FIG. 20 is a graph of transmittances of a transparent substrate including silver nanowires according to each of Embodiments 16 to 20. FIG. 21 is graphs of hazes, wherein (a) of FIG. 21 is a graph of a haze of a transparent substrate including silver nanowires according to each of Embodiments 11 to 15, and (b) of FIG. 21 is a graph of a haze of each of a transparent substrate including silver nanowires according to Embodiments 16 to 20.

[277] Table 5

[Table 5]

	transmittance(%)	haze[%]
Embodiment 1	88.3	1.2
Embodiment 2	88.2	1.5
Embodiment 3	88.6	2.2
Embodiment 4	88.8	1.2
Embodiment 5	88.7	1.8
Embodiment 6	88.5	2
Embodiment 7	87.2	10.2
Embodiment 8	87.7	17.4
Embodiment 9	88.3	1.2
Embodiment 10	88.2	1.5
Embodiment 11	86.7	4.5
Embodiment 12	84	8.4
Embodiment 13	85.9	6.1
Embodiment 14	86.9	4.8
Embodiment 15	85.8	6.6
Embodiment 16	85.4	5.9
Embodiment 17	83.2	9.1
Embodiment 18	85.5	7.3
Embodiment 19	82.1	11.2
Embodiment 20	84.3	7.4
Embodiment 21	87.2	10.2
Embodiment 22	87.7	17.4
Comparative Example 1	89.9	1.2
Comparative Example 2	88.7	1.5
Comparative Example 3	89.3	1.3
Comparative Example 4	89.3	1.4
Comparative Example 5	88.2	1.7
Comparative Example 6	87.1	2
Comparative Example 7	87.7	1.6

- [278] The haze may be below 1% when the transparent electrode is used for a display device. On the other hand, when the transparent electrode is used for an OLED lighting (an inner light extraction layer) or an organic solar cell, the haze of 1% or more (more particularly, 5% or more) is necessary. As shown in TABLE 5, the transmittances of the transparent electrodes including the silver nanowires according to Embodiments are similar to those according to Comparative Examples. The hazes of the transparent electrodes including the silver nanowires according to some Embodiments are similar to the those according to Comparative Examples, and the hazes of the transparent electrodes including the silver nanowires according to other Embodiments are high (for example, 10% or more). Thus, the transparent electrode can have properties suitable for an OLED lighting (an inner light extraction layer) or an organic solar cell.
- [279] **3) Experimental Embodiment of Embodiments 23 to 27 and Comparative Examples 8 to 12**
- [280] FIG. 22 and FIG. 23 are scanning electron microscopy photographs of core-shell nanowires according to Embodiments 23 to 27. As shown in FIG. 22 and FIG. 23, it can be seen that metal-compound shells having a plurality of stripe patterns extending in a longitudinal direction of the nanowire are formed.
- [281] Also, FIG. 24 is a photograph for illustrating that a zinc oxide is selectively coated on the nanowire formed on a core-shell nanowire substrate. As shown in FIG. 24, it can be seen that the zinc oxide is selectively coated only on the nanowire.
- [282] FIG. 25 is a graph of sheet resistances of Embodiments. It can be seen that the sheet resistances of the silver nanowires after the coating are similar to the sheet resistances of the silver nanowires before the coating. Also, in some Embodiments, it can be seen that the sheet resistances of the silver nanowires after the coating of the metal-oxide shell are higher than the sheet resistances of the silver nanowires before the coating of the metal-oxide shell.
- [283] Also, FIG. 26 is X-ray diffraction peaks of the core-shell nanowires according to Embodiments. It can be seen that there is a peak of a metal oxide and that an intensity of the peak of the metal oxide increases as a coated amount increases.
- [284] In addition, FIG. 27 to FIG. 29 are graphs of light transmittances of Embodiment 23 to Embodiment 27. It can be seen that the light transmittance can be very superior.
- [285] Further, FIG. 30 to FIG. 32 are graphs of hazes of Embodiment 23 to Embodiment 27. It can be seen that the haze largely increases as the coated amount of the metal oxide shell.
- [286] Also, FIG. 33 is a graph of a photoluminescence (PL) according to each of Embodiments 23 to 25.
- [287] In addition, FIG. 34 is a graph of a sheet resistance with respect to time, according to Embodiment 23 to Embodiment 27. It can be seen that the sheet resistance is generally

maintained as the time goes.

[288] For example, when the core-shell nanowire is coated on a transparent substrate to have a sheet resistance of $1\sim 100(\Omega/\square)$, a haze may be in a range of 5% or more (for example, 20% or more) at a wavelength of 550nm. When the core-shell nanowire is coated on a transparent substrate to have a sheet resistance of $1\sim 100(\Omega/\square)$, a light transmittance may be in a range of 60 to 98% at a wavelength of 550nm.

[289] **4) An exemplary example of Embodiments 28 to 32 and Comparative Examples 13 to 17**

[290] FIG. 35 and FIG. 36 are scanning electron microscopy photographs of core-shell nanowires according to Embodiments 28 to 32. As shown in FIG. 35 and FIG. 36, it can be seen that metal-compound shells having a plurality of stripe patterns extending in a longitudinal direction of the nanowire are formed.

[291] Also, FIG. 37 is a photograph for illustrating that a zinc oxide is selectively coated on the nanowire formed on a core-shell nanowire substrate. As shown in FIG. 37, it can be seen that the zinc oxide is selectively coated only on the nanowire.

[292] FIG. 28 is a graph of sheet resistances of Embodiments of Comparative Examples. It can be seen that the sheet resistances of the silver nanowires after the coating are similar to the sheet resistances of the silver nanowires before the coating. Also, in some Embodiments, it can be seen that the sheet resistances of the silver nanowires after the coating of the metal-oxide shell are higher than the sheet resistances of the silver nanowires before the coating of the metal-oxide shell.

[293] Also, FIG. 39 is X-ray diffraction peaks of the core-shell nanowires according to Embodiments. It can be seen that there is a peak of a metal oxide and that an intensity of the peak of the metal oxide increases as a coated amount increases.

[294] Further, FIG. 40 to FIG. 42 are graphs of hazes of Embodiment 28 to Embodiment 32. It can be seen that the haze largely increases as the coated amount of the metal oxide shell.

[295] In addition, FIG. 43 to FIG. 45 are graphs of light transmittance of Embodiment 28 to Embodiment 32. It can be seen that the light transmittance can be very superior.

[296] Also, FIG. 46 is a graph of a photoluminescence (PL) according to each of Embodiments 28 to 32.

[297] In addition, FIG. 47 is a graph of a sheet resistance with respect to time, according to each of Embodiment 28, 29, and 32. It can be seen that the sheet resistance is generally maintained as the time goes.

[298] For example, when the core-shell nanowire is coated on a transparent substrate to have a sheet resistance of $1\sim 100(\Omega/\square)$, a haze may be in a range of 5% or more (for example, 20% or more) at a wavelength of 550nm. When the core-shell nanowire is coated on a transparent substrate to have a sheet resistance of $1\sim 100(\Omega/\square)$, a light

transmittance may be in a range of 60 to 98% at a wavelength of 550nm.

[299] The above described features, configurations, effects, and the like are included in at least one of the embodiments of the present invention, and should not be limited to only one embodiment. In addition, the features, configurations, effects, and the like as illustrated in each embodiment may be implemented with regard to other embodiments as they are combined with one another or modified by those skilled in the art. Thus, content related to these combinations and modifications should be construed as including in the scope and spirit of the invention as disclosed in the accompanying claims.

[300] **Technical Problem**

[301] The invention has been made in view of the above problems, and it is an object of the invention to provide a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion. Thus, a contact probability between the metal nanowires can increase, an increase of a sheet resistance can be prevented, and an electric conductivity can be superior. Particularly, when the metal nanowire is used for a transparent electrode (particularly, for an OLED lighting, an organic solar cell, and so on), the transparent electrode has a transmittance and a haze suitable for the OLED lighting or the organic solar cell.

[302] Also, it is another object of the invention to provide a metal nanowire having a large diameter and a large aspect ratio and having different diameters. Thus, a contact probability between the metal nanowires can increase, an increase of a sheet resistance can be prevented, and an electric conductivity can be superior. Particularly, when the metal nanowire is used for a transparent electrode (particularly, for an OLED lighting, an organic solar cell, and so on), the transparent electrode has a transmittance and a haze suitable for the OLED lighting or the organic solar cell.

[303] In addition, it is yet another object of the invention to provide a core-shell nanowire having a metal coating. A sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.

[304] Further, it is still another object of the invention to provide a method for manufacturing a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion with a high yield without by-products other than the metal nanowire.

[305] Furthermore, it is yet still another object of the invention to provide a method for manufacturing a metal nanowire having a large diameter and a large aspect ratio and having different diameters with a high yield without by-products other than the metal nanowire.

[306] Also, it is yet still another object of the invention to provide a method for manu-

facturing a core-shell nanowire having a metal coating.

[307] Further, it is yet still another object of the invention to provide a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion as a conductor layer. Thus, an electric conductivity can be superior. Particularly, the transparent electrode has a transmittance and a haze suitable for an OLED lighting or an organic solar cell.

[308] In addition, it is yet still another object of the invention to provide a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and having different diameters as a conductor layer. Thus, an electric conductivity can be superior. Particularly, the transparent electrode has a transmittance and a haze suitable for an OLED lighting or an organic solar cell.

[309] Furthermore, it is yet still another object of the invention to provide a core-shell nanowire having a metal coating as a conductor layer. A sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.

[310] **Technical Solution**

[311] A metal nanowire according to an embodiment includes at least two wire portions. An angle (α) between an n-th wire portion and an (n+1)-th wire portion connected to the n-th wire portion through an n-th bent portion satisfies an inequation of $0^\circ < \alpha < 180^\circ$.

[312] **Advantageous Effects**

[313] A metal nanowire according to the invention has a large diameter and a large aspect ratio and includes a plurality of wire portions having at least one bent portion. Thus, contact points, contact areas, or a contact probability between the metal nanowires can increase, a sheet resistance can be relatively low, an electric conductivity can be superior, and a light-scattering effect can be achieved.

[314] Also, a metal nanowire according to the invention has a large diameter and a large aspect ratio and having different diameters. Thus, contact points, contact areas, or a contact probability between the metal nanowires can increase, a sheet resistance can be relatively low, an electric conductivity can be superior, and a light-scattering effect can be achieved.

[315] In addition, a core-shell nanowire according to the invention has a metal coating. A sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.

- [316] Furthermore, a method for manufacturing a metal nanowire according to the invention is an one-pot synthesis. In the method for manufacturing the metal nanowire, a purification of intermediate products is not necessary, and the metal nanowire can be manufactured with a high yield without by-products other than the metal nanowire.
- [317] Also, in a method for manufacturing a metal nanowire according to the invention, volatilization of a reaction mixture can be minimized by adding all of a reaction mixture to a reaction container and reacting with the reaction mixture at a pressure of an atmospheric pressure or a pressure high than the atmospheric pressure. The metal nanowire can be grown to be bent, not to be broken, even the metal nanowire has a large diameter and a large aspect ratio. Thus, the metal nanowire including a plurality of wire portions having at least one bent portion can be manufactured.
- [318] Further, in a method for manufacturing a metal nanowire according to the invention, a side-surface growth of the metal nanowire can be controlled by controlling an amount of a capping agent, and the metal nanowire having different diameters can be manufactured.
- [319] In addition, a method for manufacturing a core-shell nanowire according to the invention can be applied to a metal nanowire including a plurality of wire portions having at least one bent portion and a metal nanowire having different diameters, as well as the known, marketed, or generally used metal nanowire. Thus, a core-shell nanowire having a metal-compound shell can be manufactured.
- [320] Furthermore, according to a method for manufacturing a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and including a plurality of wire portions having at least one bent portion as a conductor layer, the transparent electrode having a transmittance and a haze suitable for an OLED lighting or an organic solar cell at a range of visibly ray can be manufactured.
- [321] Also, according to a method for manufacturing a transparent electrode and an organic light emitting diode including a metal nanowire having a large diameter and a large aspect ratio and having different diameters as a conductor layer, the transparent electrode having a transmittance and a haze suitable for an OLED lighting or an organic solar cell at a range of visibly ray can be manufactured.
- [322] Furthermore, according to a method for manufacturing a transparent electrode and an organic light emitting diode including a core-shell nanowire having a metal coating, a sulfidation and an oxidation can be prevented and reliability can be enhanced. A light-scattering property can be enhanced, and a high haze can be achieved without largely reducing an electric conductivity and a transmittance.

Brief Description of Drawings

- [323] FIG. 1 illustrates a metal nanowire including two wire portions having a bent portion, according to an embodiment of the invention.
- [324] FIG. 2 illustrates a metal nanowire including a plurality of wire portions having at least one bent portion, according to another embodiment of the invention.
- [325] FIG. 3 illustrates a three-dimensional structure of a metal nanowire including a plurality of wire portions having at least one bent portion, according to yet another embodiment of the invention.
- [326] FIG. 4 illustrates a metal nanowire including a plurality of wire parts having different diameters, wherein the plurality of wire parts including one second wire part, according to yet still another embodiment of the invention.
- [327] FIG. 5 illustrates a metal nanowire including a plurality of wire parts having different diameters according to another embodiment of the invention, wherein (a) illustrates the metal nanowire including a second wire part formed at one end and (b) illustrates the metal nanowire including second wire parts formed at both ends.
- [328] FIG. 6 illustrates wire portions of a metal nanowire having at least one bent portion according to yet still another embodiment of the invention.
- [329] FIG. 7 illustrates the metal nanowire having at least one bent portion according to yet still another embodiment of the invention.
- [330] FIG. 8 illustrates wire parts of a metal nanowire having different diameters according to yet still another embodiment of the invention.
- [331] FIG. 9 illustrates the metal nanowire having different diameters according to yet still another embodiment of the invention.
- [332] FIG. 10 to FIG. 13 schematically illustrate core-shell nanowires according to embodiments of the invention.
- [333] FIG. 14 a schematically view of a roll-to-roll continuation process for forming a core-shell nanowire according to an embodiment of the invention.
- [334] FIG. 15 is a photograph of a surface of silver nanowires according to an embodiment of the invention, taken using a scanning electron microscopy.
- [335] FIG. 16 is a photograph of silver nanowires having a plurality of wire parts having different diameters according to an embodiment of the invention, taken using a scanning electron microscopy.
- [336] FIG. 17 and FIG. 18 are photographs of silver nanowires including a plurality of wire portions having at least one bent portion according to an embodiment of the invention, taken using a transmission electron microscopy.
- [337] FIG. 19 is a photograph of silver nanowires not including a plurality of wire portions and not having at least one bent portion as a comparative example, taken using a transmission electron microscopy.
- [338] FIG. 20 is graphs of transmittances, wherein (a) of FIG. 20 is a graph of a trans-

mittance of a transparent substrate including silver nanowires according to each of Embodiments 11 to 15, and (b) of FIG. 20 is a graph of a transmittance of a transparent substrate including silver nanowires according to each of Embodiments 16 to 20.

- [339] FIG. 21 is graphs of hazes, wherein (a) of FIG. 21 is a graph of a haze of a transparent substrate including silver nanowires according to each of Embodiments 11 to 15, and (b) of FIG. 21 is a graph of a haze of a transparent substrate including silver nanowires according to each of Embodiments 16 to 20.
- [340] FIG. 22 and FIG. 23 are scanning electron microscopy photographs of core-shell nanowires according to Embodiments 23 to 27, wherein (a) of FIG. 22 corresponds to Embodiment 23, (b) of FIG. 22 corresponds to Embodiment 24, (c) of FIG. 23 corresponds to Embodiment 25, (a) of FIG. 23 corresponds to Embodiment 26, and (b) of FIG. 23 corresponds to Embodiment 27.
- [341] FIG. 24 is a photograph for illustrating that a zinc oxide is selectively coated on a nanowire formed on a core-shell nanowire substrate, according to Embodiment 25.
- [342] FIG. 25 is a graph of sheet resistances of each of Embodiments of Comparative Examples.
- [343] FIG. 26 is X-ray diffraction peaks of the core-shell nanowires according to Embodiments, wherein (a) of FIG. 26 corresponds to Embodiment 23, (b) of FIG. 26 corresponds to Embodiment 24, and (c) of FIG. 26 corresponds to Embodiment 27.
- [344] FIG. 27 to FIG. 29 are graphs of light transmittances of Embodiment 23 to Embodiment 27, wherein (a) of FIG. 27 corresponds to Embodiment 23, (b) of FIG. 27 corresponds to Embodiment 24, (a) of FIG. 28 corresponds to Embodiment 25, (b) of FIG. 28 corresponds to Embodiment 26, and 29 corresponds to Embodiment 27.
- [345] FIG. 30 to FIG. 32 are graphs of hazes of Embodiment 23 to Embodiment 27, wherein (a) of FIG. 30 corresponds to Embodiment 23, (b) of FIG. 30 corresponds to Embodiment 24, (a) of FIG. 31 corresponds to Embodiment 25, (b) of FIG. 31 corresponds to Embodiment 26, and FIG. 32 corresponds to Embodiment 27.
- [346] FIG. 33 is a graph of a photoluminescence (PL) according to each of Embodiments 23 to 25, wherein (a) of FIG. 33 corresponds to Embodiment 23, (b) of FIG. 33 corresponds to Embodiment 24, (c) of FIG. 33 corresponds to Embodiment 25.
- [347] FIG. 34 is a graph of a sheet resistance with respect to time, according to each of Embodiment 23 to Embodiment 27.
- [348] FIG. 35 and FIG. 36 are scanning electron microscopy photographs of core-shell nanowires according to Embodiments 28 to 32, wherein (a) of FIG. 35 corresponds to Embodiment 28, (b) of FIG. 35 corresponds to Embodiment 29, (c) of FIG. 35 corresponds to Embodiment 30, (a) of FIG. 36 corresponds to Embodiment 31, and (b) of FIG. 36 corresponds to Embodiment 32.
- [349] FIG. 37 is a photograph for illustrating that a zinc oxide is selectively coated on a

nanowire formed on a core-shell nanowire substrate.

- [350] FIG. 38 is a graph of sheet resistances of each of Embodiments of Comparative Examples.
- [351] FIG. 39 is X-ray diffraction peaks of the core-shell nanowires according to Embodiments, wherein (a) of FIG. 39 corresponds to Embodiment 28, (b) of FIG. 39 corresponds to Embodiment 29, and (c) of FIG. 39 corresponds to Embodiment 32.
- [352] FIG. 40 to FIG. 42 are graphs of hazes of Embodiment 28 to Embodiment 32, wherein (a) of FIG. 40 corresponds to Embodiment 28, (b) of FIG. 40 corresponds to Embodiment 29, (a) of FIG. 41 corresponds to Embodiment 30, (b) of FIG. 41 corresponds to Embodiment 31, and FIG. 42 corresponds to Embodiment 32.
- [353] FIG. 43 to FIG. 45 are graphs of light transmittances of Embodiment 28 to Embodiment 32, wherein (a) of FIG. 43 corresponds to Embodiment 28, (b) of FIG. 43 corresponds to Embodiment 29, (a) of FIG. 44 corresponds to Embodiment 30, (b) of FIG. 44 corresponds to Embodiment 31, and FIG. 45 corresponds to Embodiment 32.
- [354] FIG. 46 is a graph of a photoluminescence (PL) according to Embodiments 28, 29, and 32, wherein (a) of FIG. 46 corresponds to Embodiment 28, (b) of FIG. 46 corresponds to Embodiment 29, (c) of FIG. 46 corresponds to Embodiment 32.
- [355] FIG. 47 is a graph of a sheet resistance with respect to time, according to each of Embodiment 28 to Embodiment 32.

Claims

- [Claim 1] A metal nanowire comprising at least two wire portions, wherein an angle (α) between an n-th wire portion and an (n+1)-th wire portion connected to the n-th wire portion through an n-th bent portion satisfies the following Inequation 1.
[Inequation 1] $0^\circ < \alpha < 180^\circ$
- [Claim 2] The metal nanowire according to claim 1, wherein the angle (α) between the n-th wire portion and the (n+1)-th wire portion satisfies an inequation of $130^\circ \leq \alpha \leq 170^\circ$.
- [Claim 3] The metal nanowire according to claim 1, further comprising:
an (n+2)-th wire portion connected to the (n+1)-th wire portion through an (n+1)-th bent portion,
wherein, when a plane comprising the n-th wire portion and the (n+1)-th wire portion is an A plane and a plane comprising the (n+1)-th wire portion and the (n+2)-th wire portion is a B plane, an angle (β) of the B plane with respect to the A plane is in a range of -10° to 10° .
- [Claim 4] The metal nanowire according to claim 2, wherein the metal nanowire has a diameter of 50 to 200nm, and
wherein the metal nanowire has a length of 40 to 300 μ m.
- [Claim 5] The metal nanowire according to claim 2, wherein the metal nanowire has an aspect ratio (length/diameter) of a length to a diameter in a range of 200 to 6000.
- [Claim 6] The metal nanowire according to one of claims 1 to 5, wherein the metal nanowire is a nanowire of a metal selected from a group consisting of Ni, Co, Fe, Pt, Au, Ag, Al, Cr, Cu, Mg, Mn, Mo, Rh, Si, Ta, Ti, W, U, V, Zr, and Ge.
- [Claim 7] The metal nanowire according to one of claims 1 to 5, wherein at least one of the wire portions has at least two different diameters.
- [Claim 8] The metal nanowire according to claim 7, wherein at least one of the wire portions has a first diameter of 50 to 200nm and a second diameter of 150 to 1100nm.
- [Claim 9] The metal nanowire according to one of claims 1 to 5, further comprising:
a metal-compound shell formed on the metal nanowire.
- [Claim 10] The metal nanowire according to claim 9, wherein the metal-compound shell comprises a transparent conductive metal compound.
- [Claim 11] The metal nanowire according to claim 9, wherein the metal-compound

shell has a shape of a plurality of polygons when viewed in a cross-sectional view perpendicular to a length direction of the metal nanowire.

- [Claim 12] The metal nanowire according to claim 11, wherein the number of the plurality of polygons viewed in the cross-sectional is three to six, and wherein, when a side of one of the polygons adjacent to the metal nanowire is a bottom side of the one of the polygons, the bottom side of the one of the polygons has a length (d) of 40nm to 200nm and a height (c) of 10nm to 200nm.
- [Claim 13] The metal nanowire according to claim 11, wherein a ratio (c/a) of the height (c) of one of the polygon to a length (a) of the metal nanowire is in a range of 0.00006 to 0.02.
- [Claim 14] The metal nanowire according to claim 11, wherein a ratio (f/a) of a longest diameter (f) of one of the polygons, when viewed in the cross-sectional view perpendicular to the longitudinal direction of the metal nanowire, to a length (a) of the metal nanowire is in a range of 0.0001 to 0.06.
- [Claim 15] A transparent electrode, comprising:
a conductor layer comprising a metal nanowire; and
a transparent electrode layer formed on the conductor layer,
wherein the metal nanowire comprises at least two wire portions, and
wherein an angle (α) between an n-th wire portion and an (n+1)-th wire portion connected to the n-th wire portion through an n-th bent portion satisfies an inequation of $130^\circ \leq \alpha \leq 170^\circ$.
- [Claim 16] The transparent electrode according to claim 15, wherein the metal nanowire further comprises an (n+2)-th wire portion connected to the (n+1)-th wire portion through an (n+1)-th bent portion, and
wherein, when a plane comprising the n-th wire portion and the (n+1)-th wire portion is an A plane and a plane comprising the (n+1)-th wire portion and the (n+2)-th wire portion is a B plane, an angle (β) of the B plane with respect to the A plane is in a range of -10° to 10° .
- [Claim 17] The transparent electrode according to claim 15, wherein at least one of the wire portions has at least two different diameters, and
wherein at least one of the wire portions has a first diameter of 50 to 200nm and a second diameter of 150 to 1100nm.
- [Claim 18] The transparent electrode according to claims 15, wherein the metal nanowire further comprises a metal-compound shell formed on the metal nanowire, and

wherein the metal-compound shell has a shape of a plurality of polygons when viewed in a cross-sectional view perpendicular to a length direction of the metal nanowire.

[Claim 19]

An organic light emitting diode, comprising:

a transparent substrate;

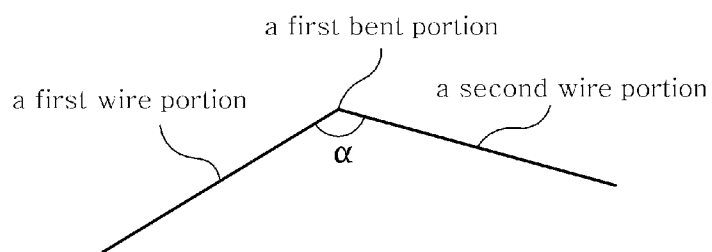
a first electrode provided on the transparent substrate;

a second electrode facing the first electrode; and

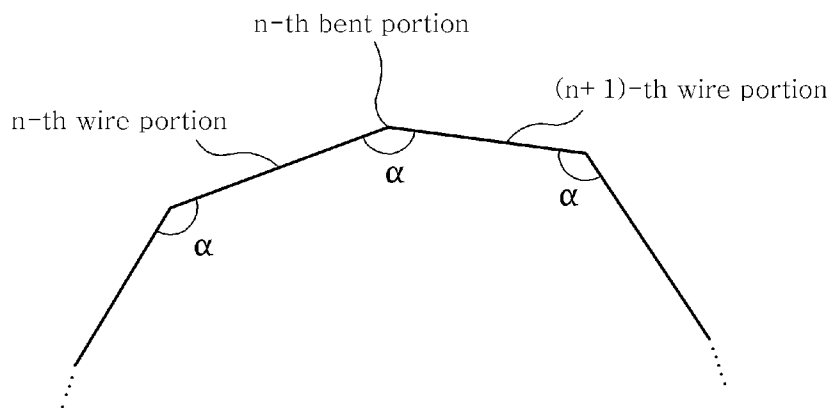
an organic light emitting layer provided between the first electrode and the second electrode,

wherein the first electrode comprises a transparent electrode according to one of claims 15 to 18.

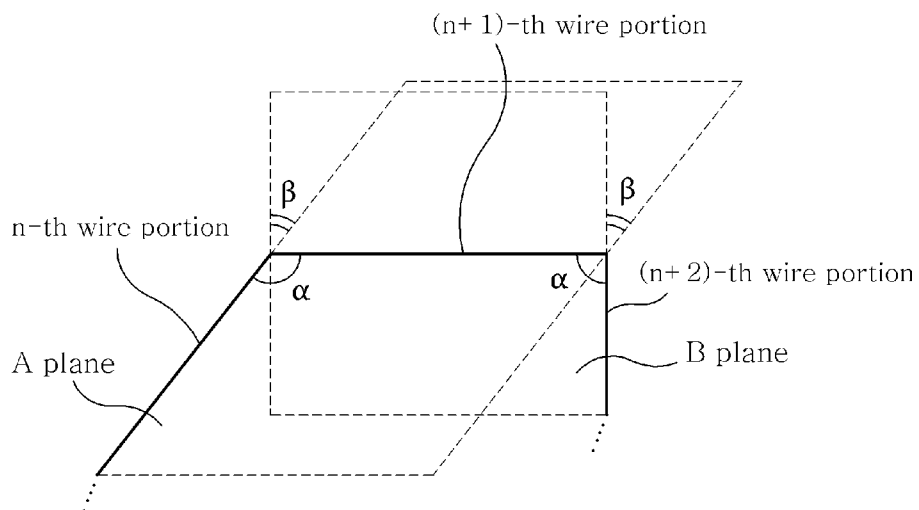
[Fig. 1]



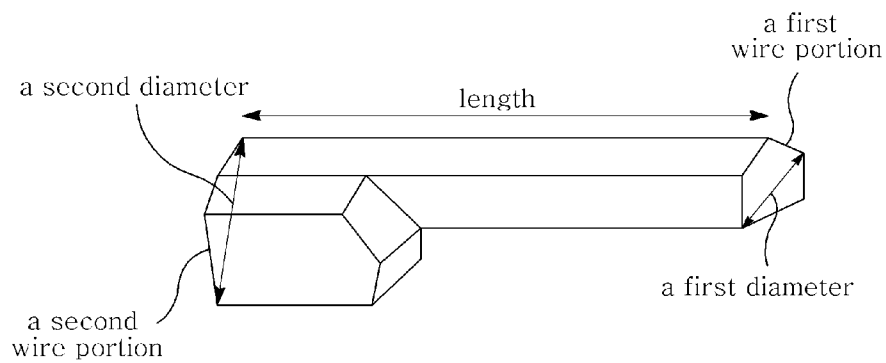
[Fig. 2]



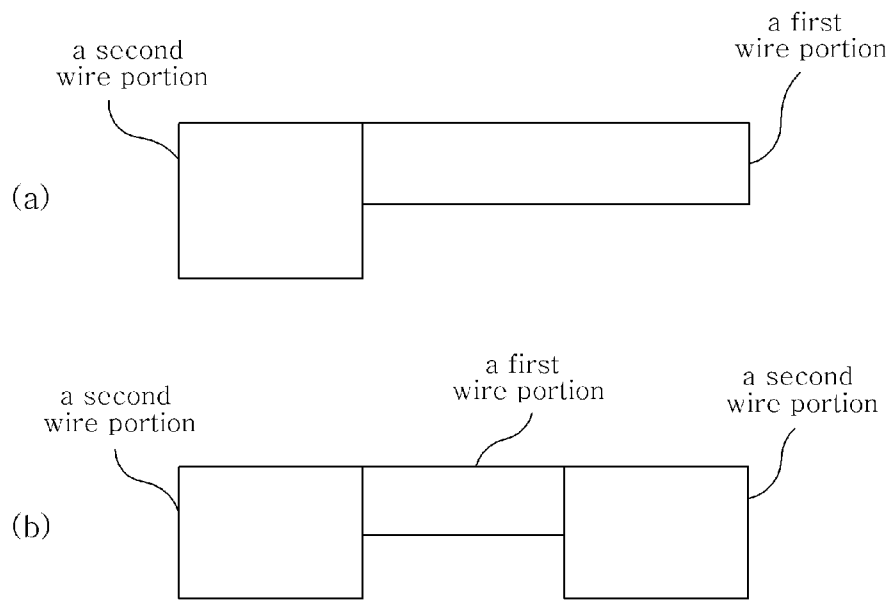
[Fig. 3]



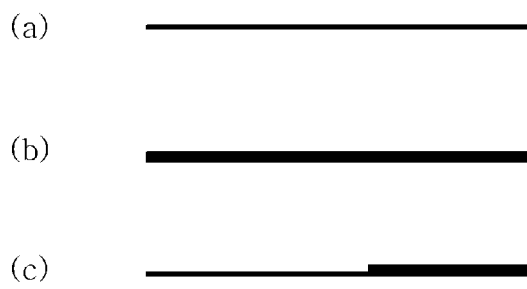
[Fig. 4]



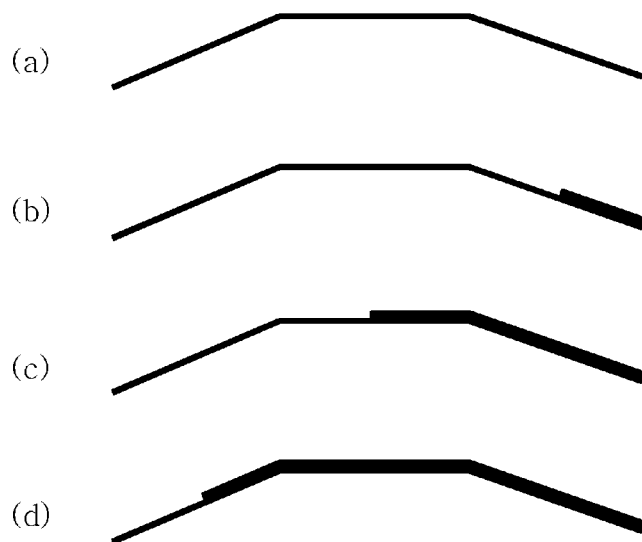
[Fig. 5]



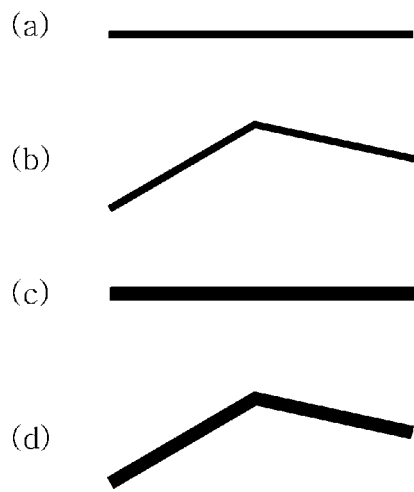
[Fig. 6]



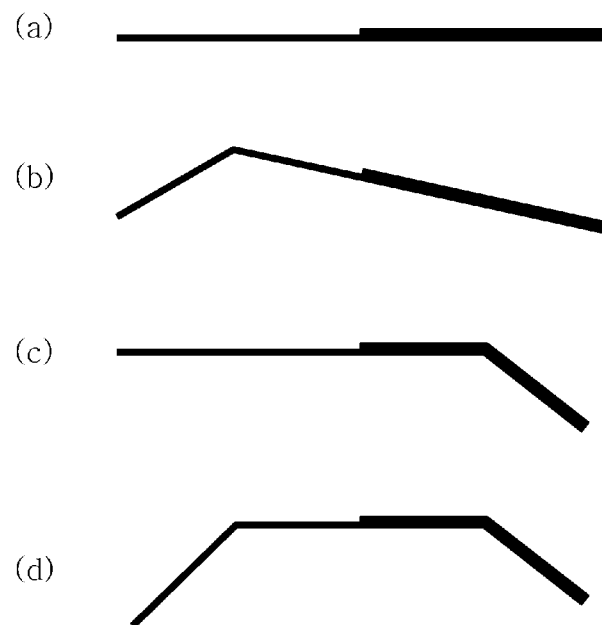
[Fig. 7]



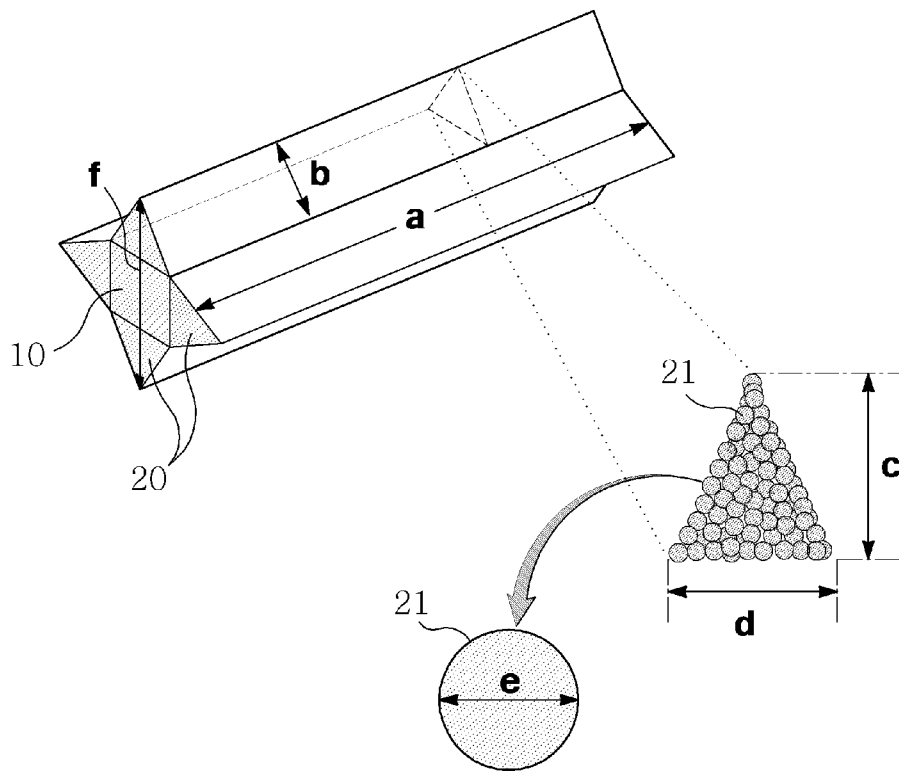
[Fig. 8]



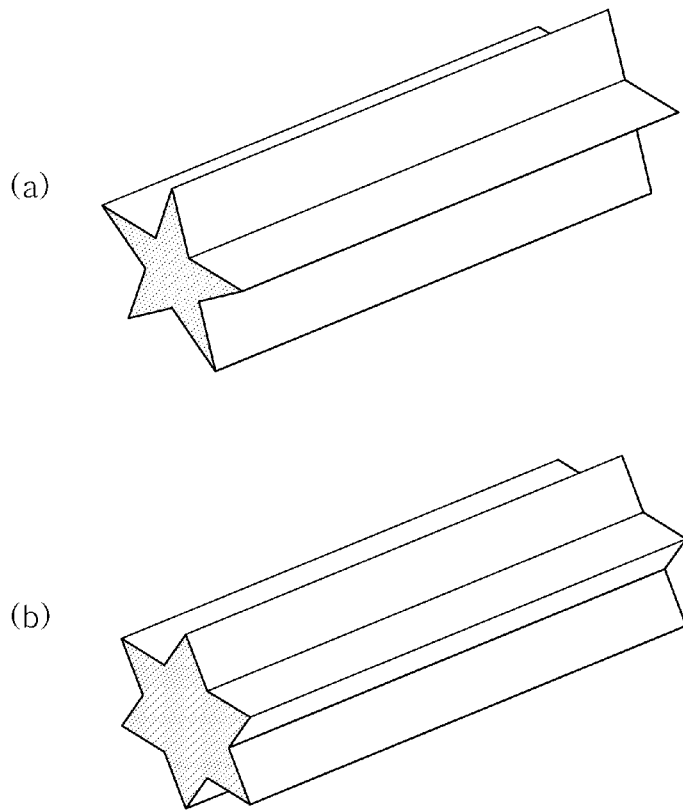
[Fig. 9]



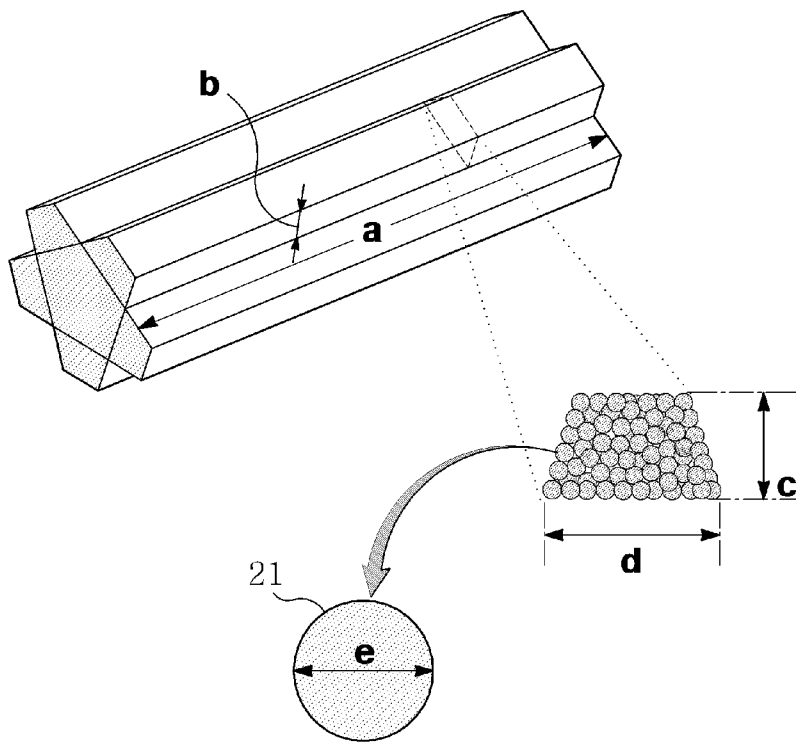
[Fig. 10]



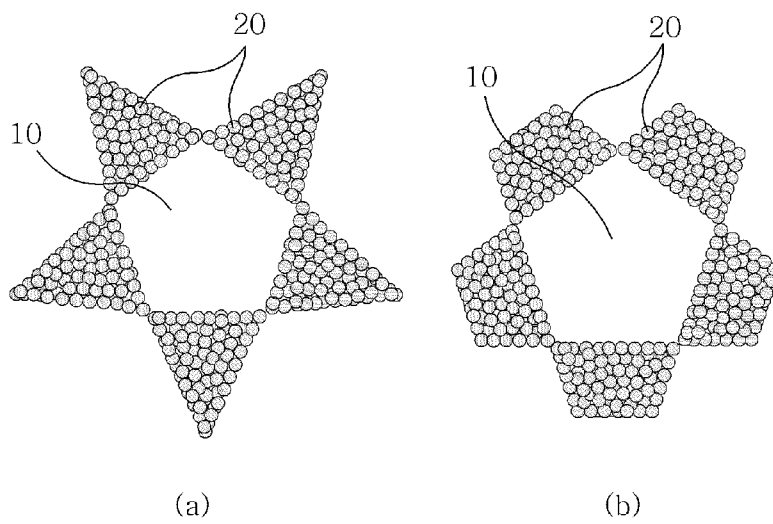
[Fig. 11]



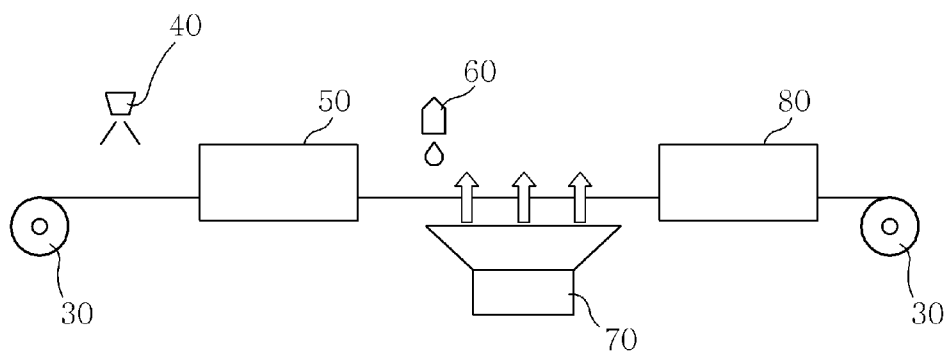
[Fig. 12]



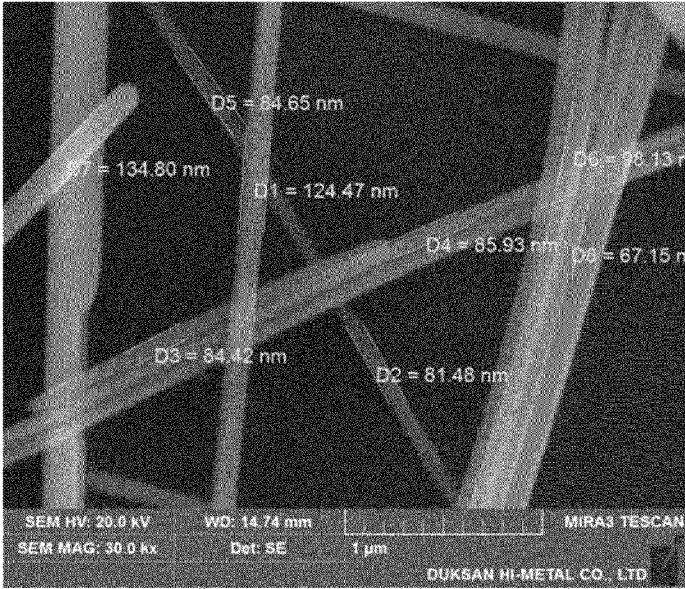
[Fig. 13]



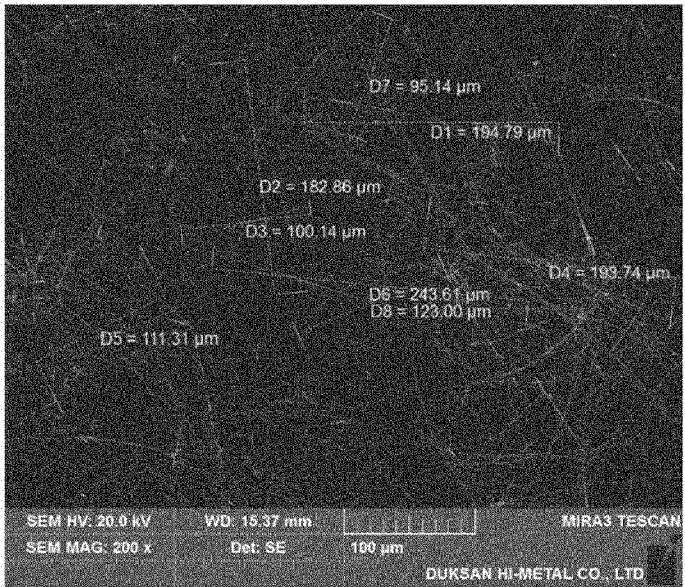
[Fig. 14]



[Fig. 15]

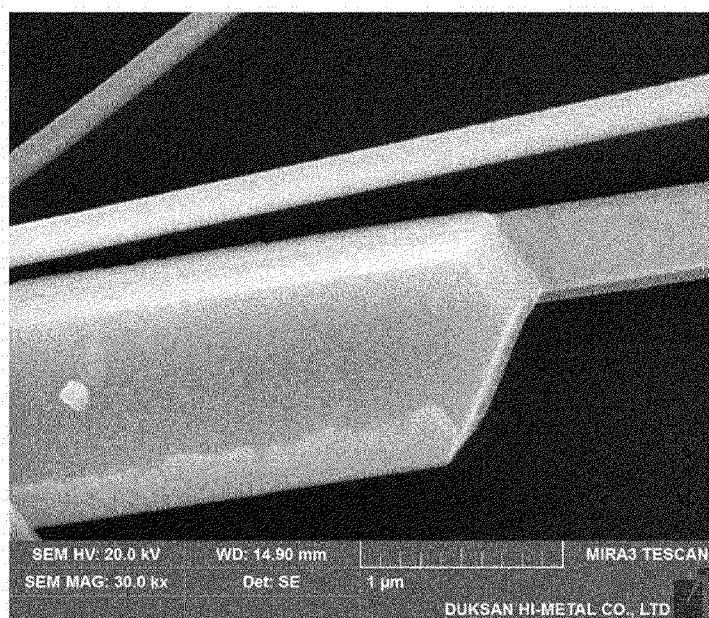


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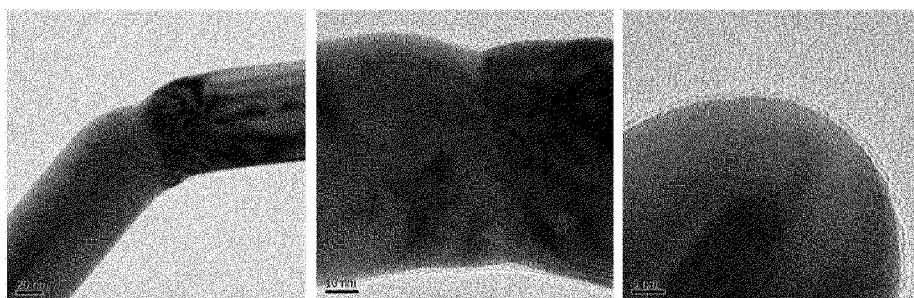


(b)

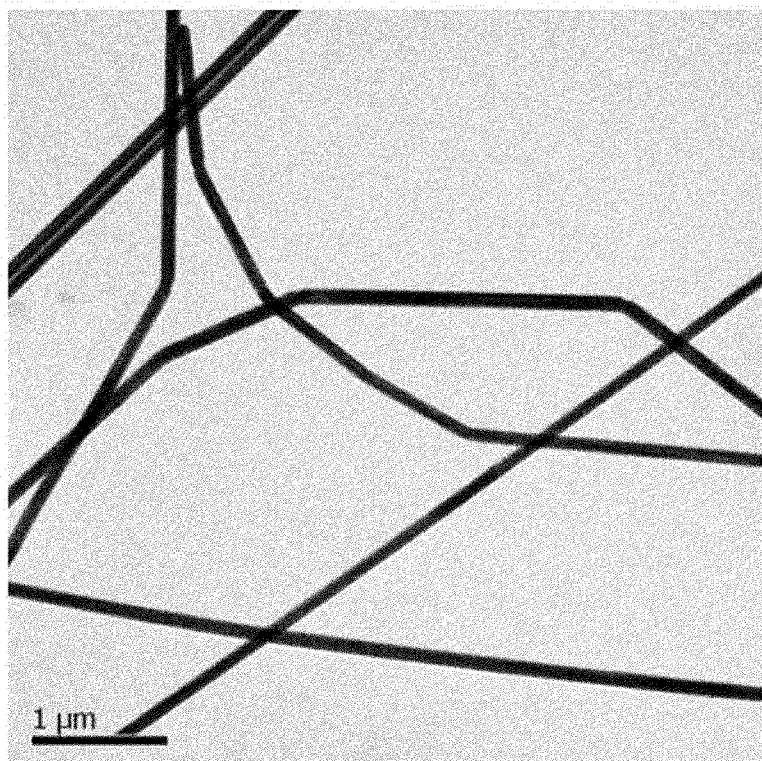
[Fig. 16]



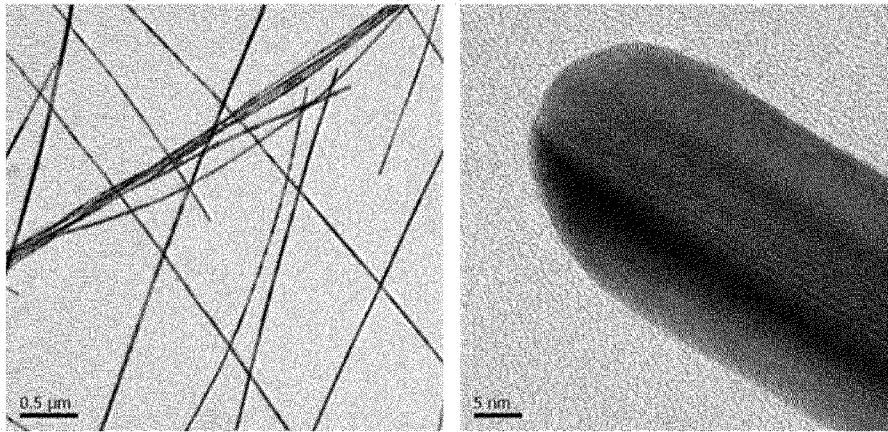
[Fig. 17]



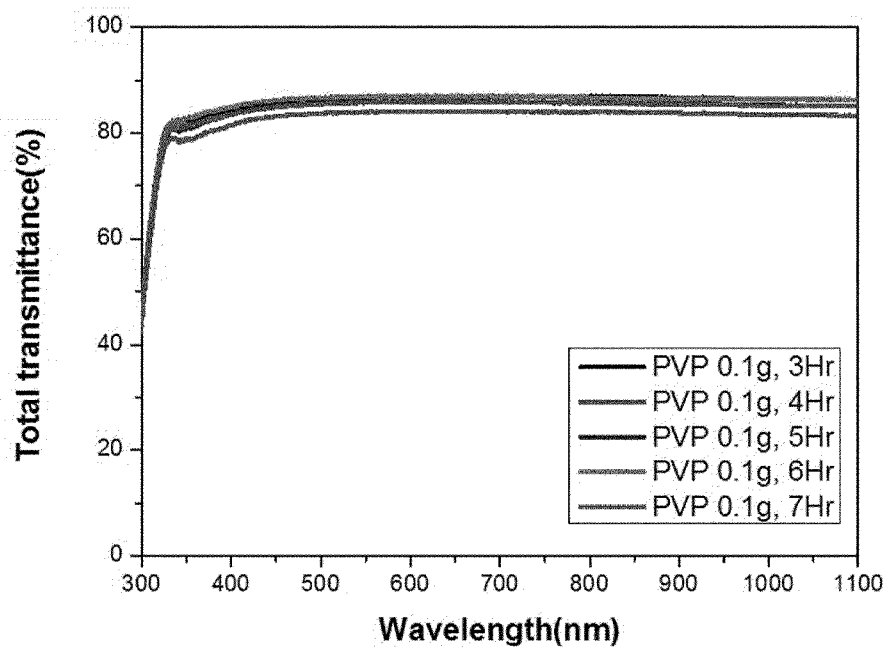
[Fig. 18]



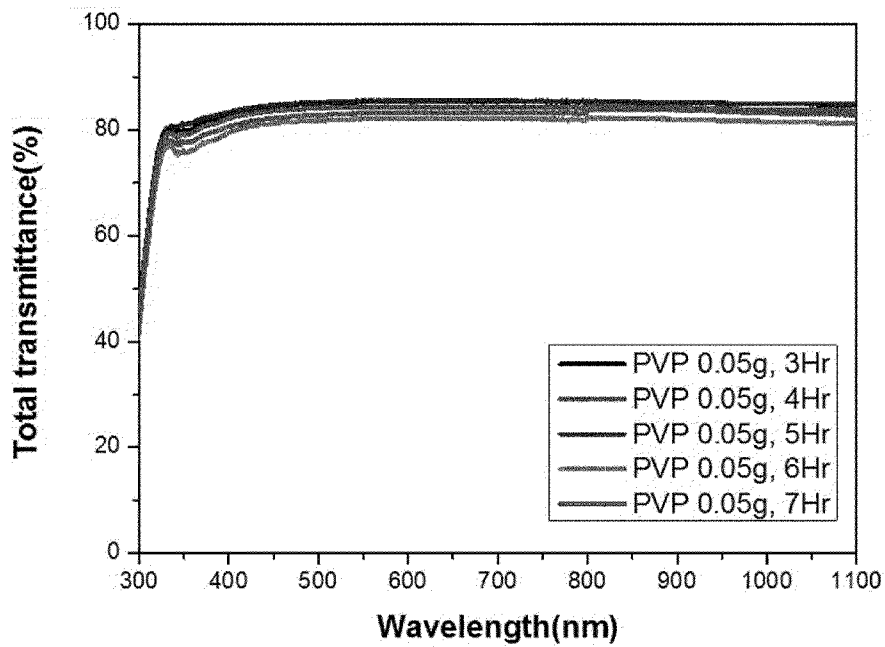
[Fig. 19]



[Fig. 20]

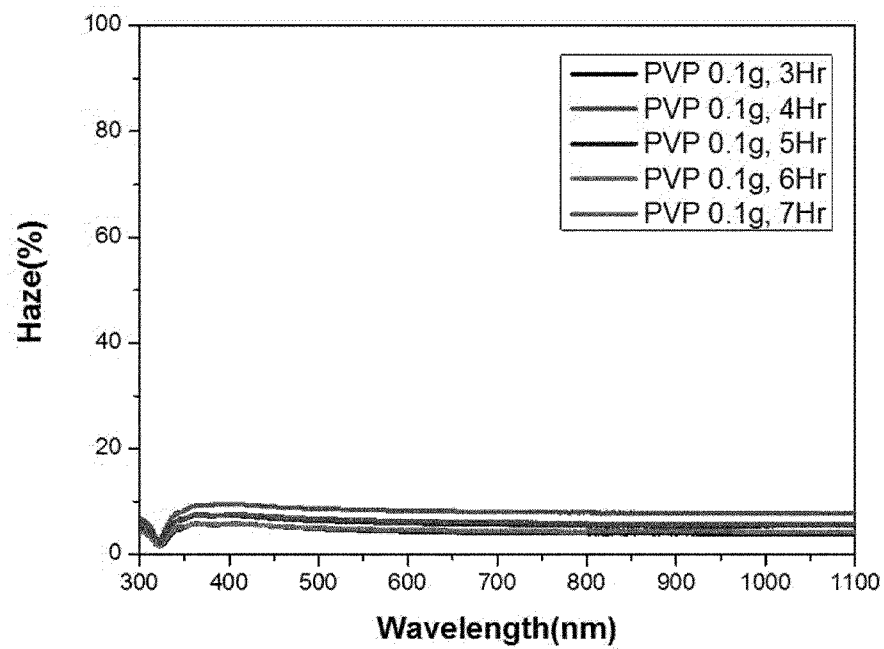


(a)

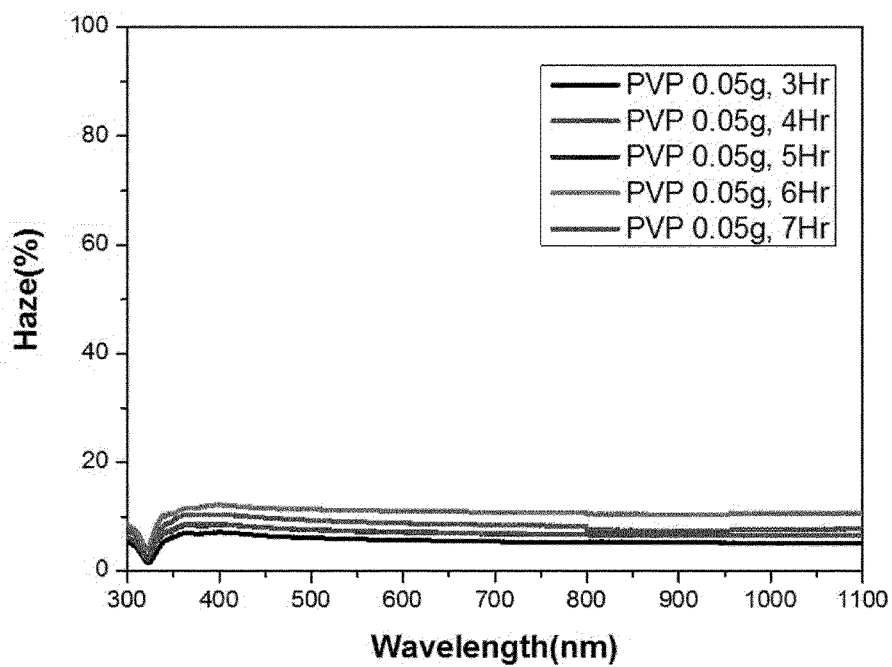


(b)

[Fig. 21]

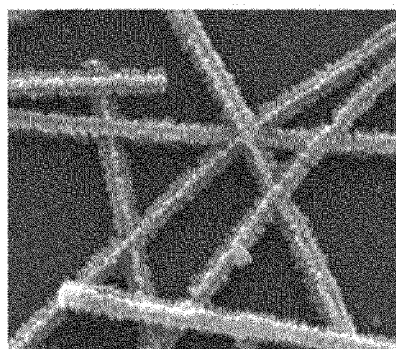
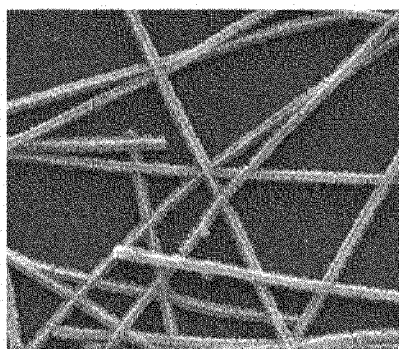


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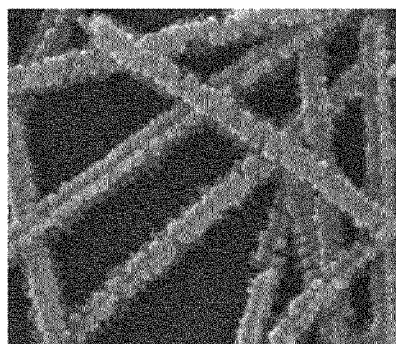
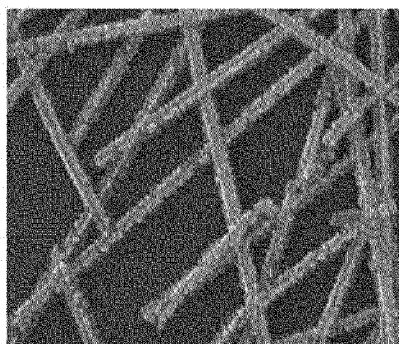


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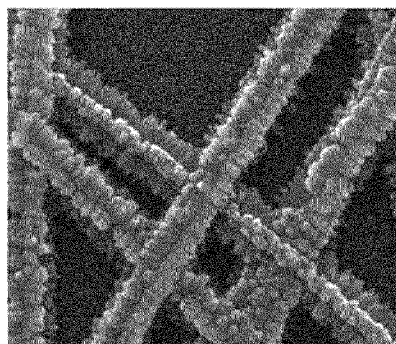
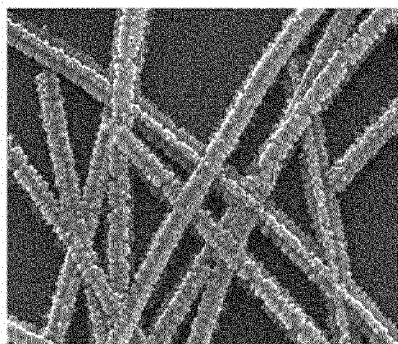
[Fig. 22]



(a)

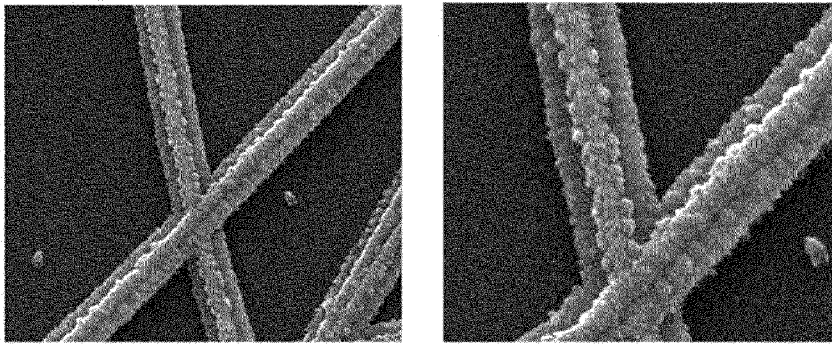


(b)

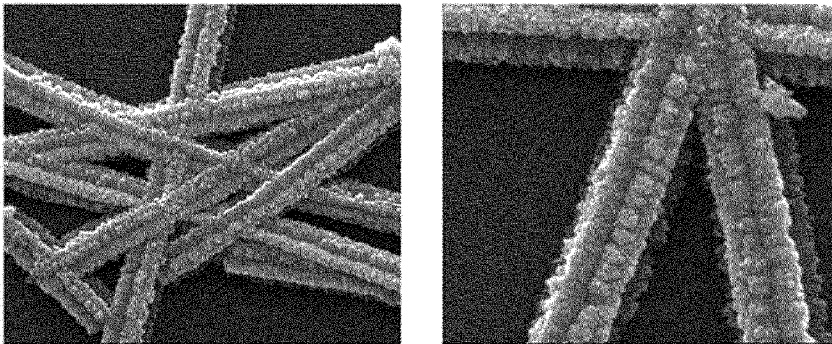


(c)

[Fig. 23]

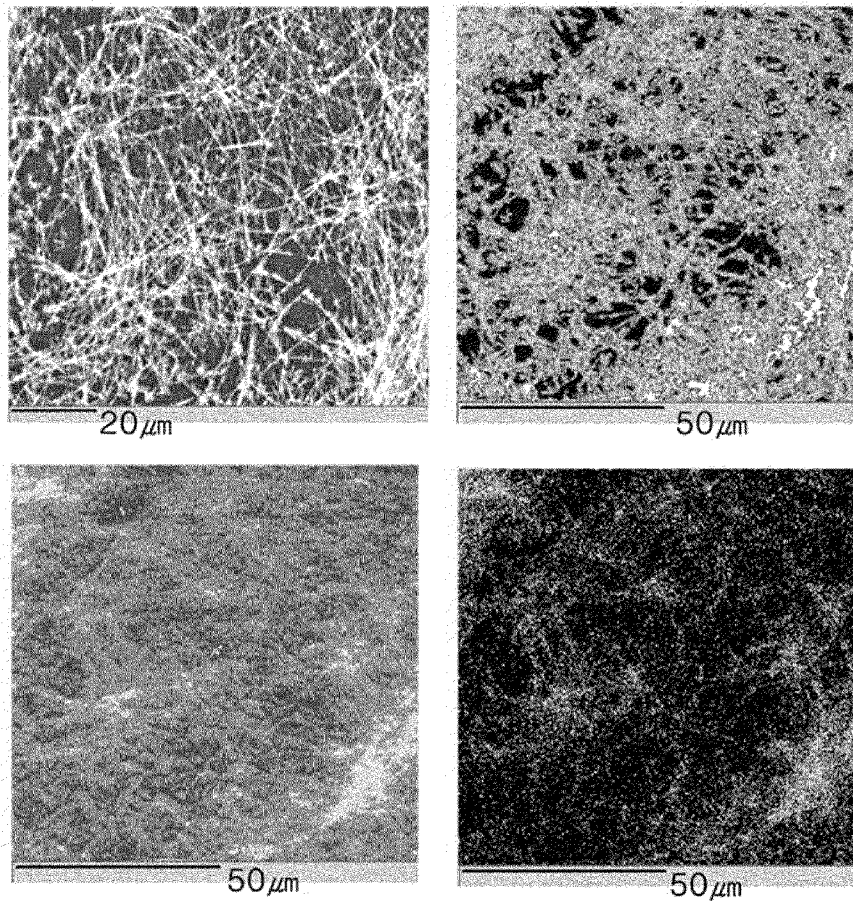


(a)

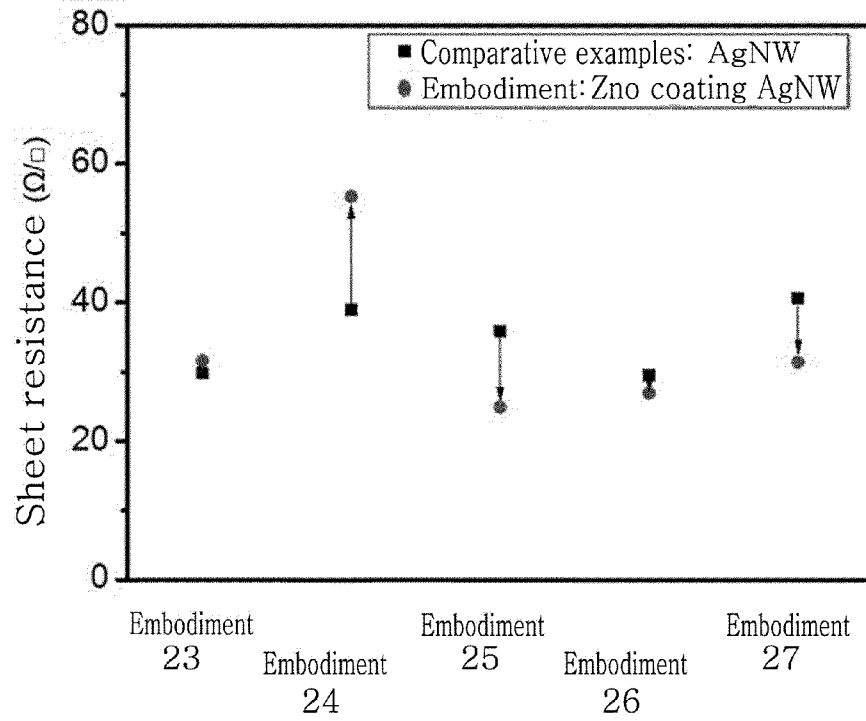


(b)

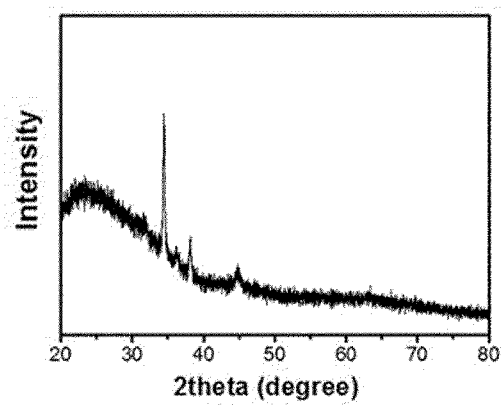
[Fig. 24]



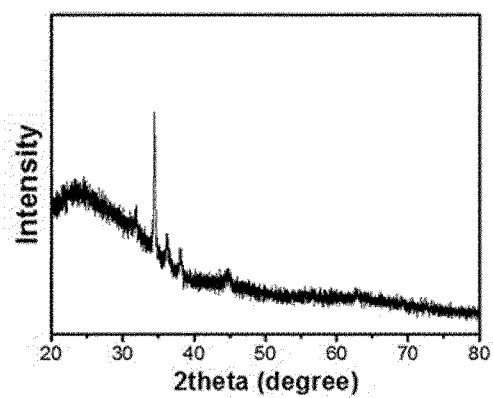
[Fig. 25]



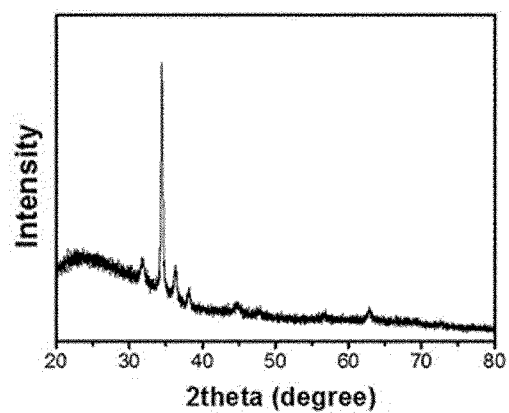
[Fig. 26]



(a)

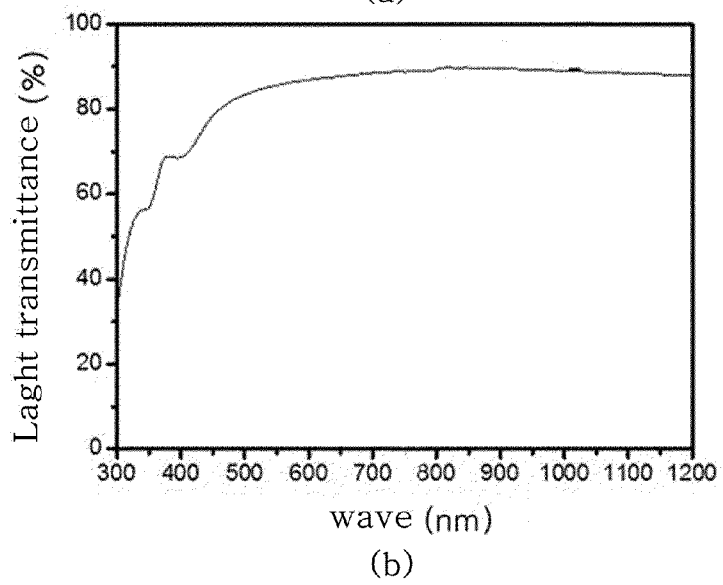
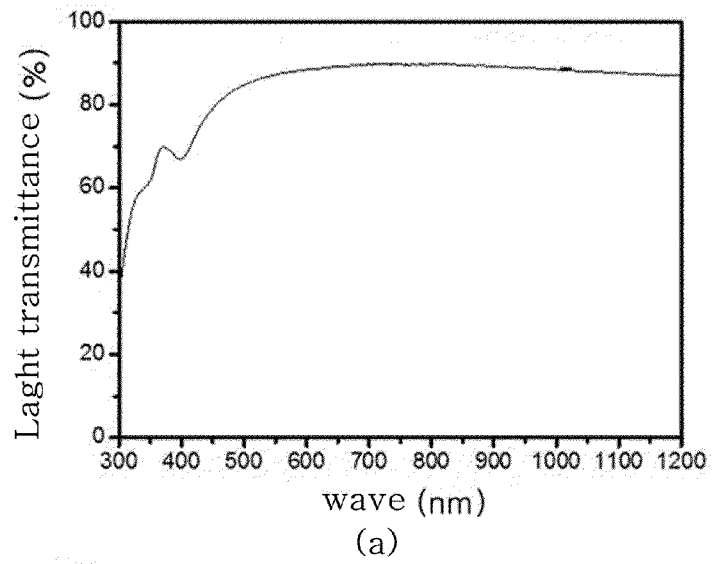


(b)

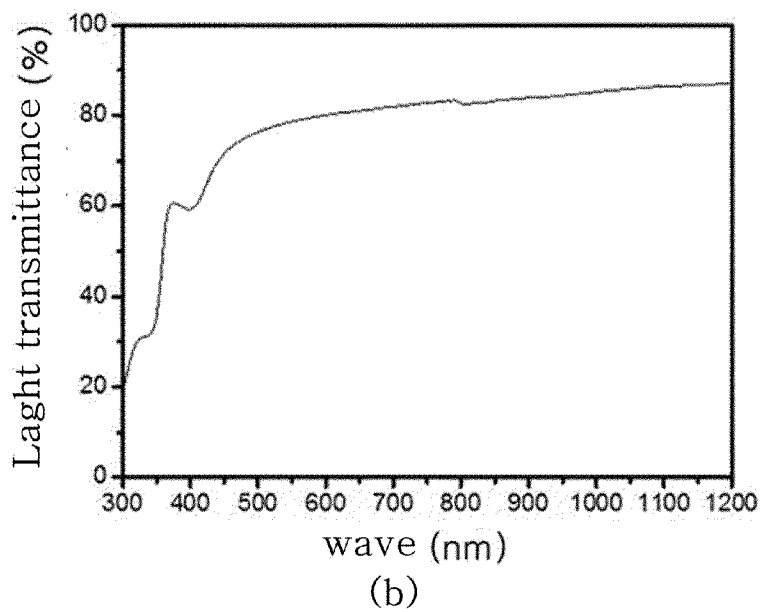
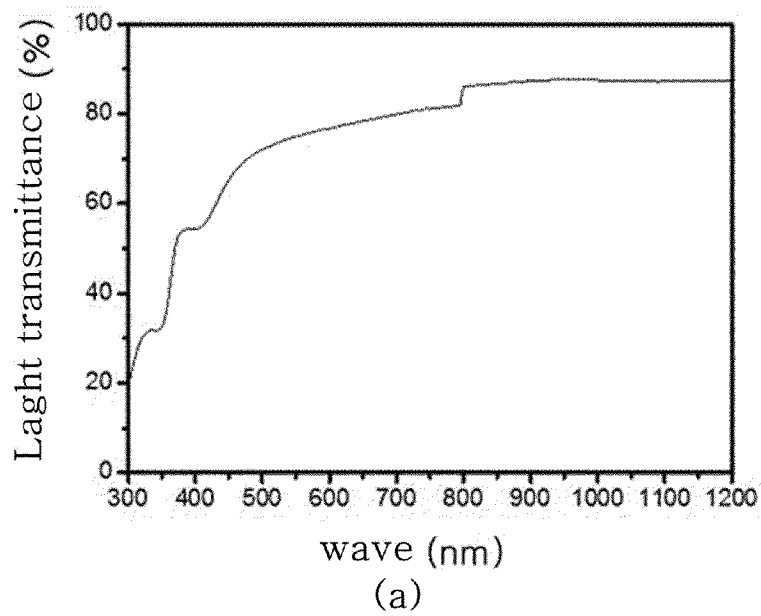


(c)

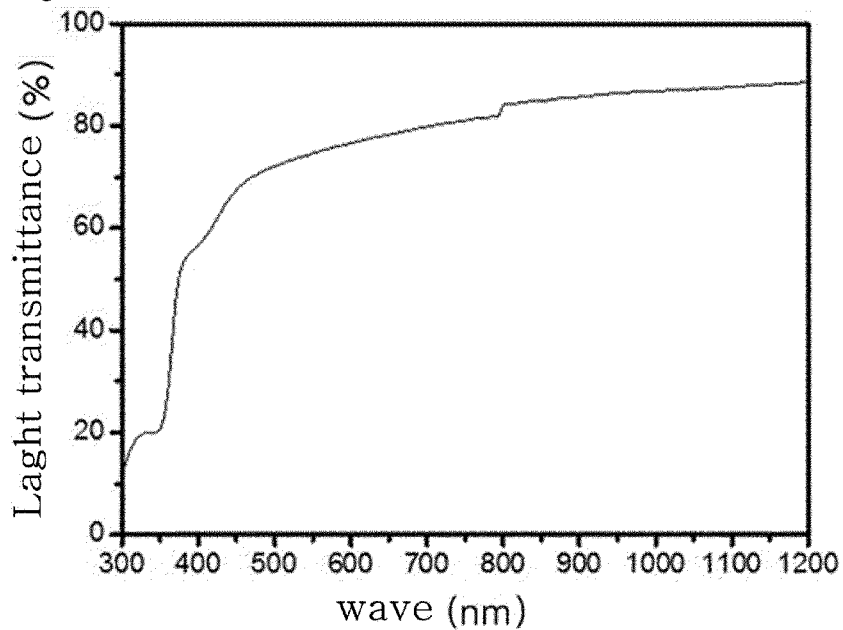
[Fig. 27]



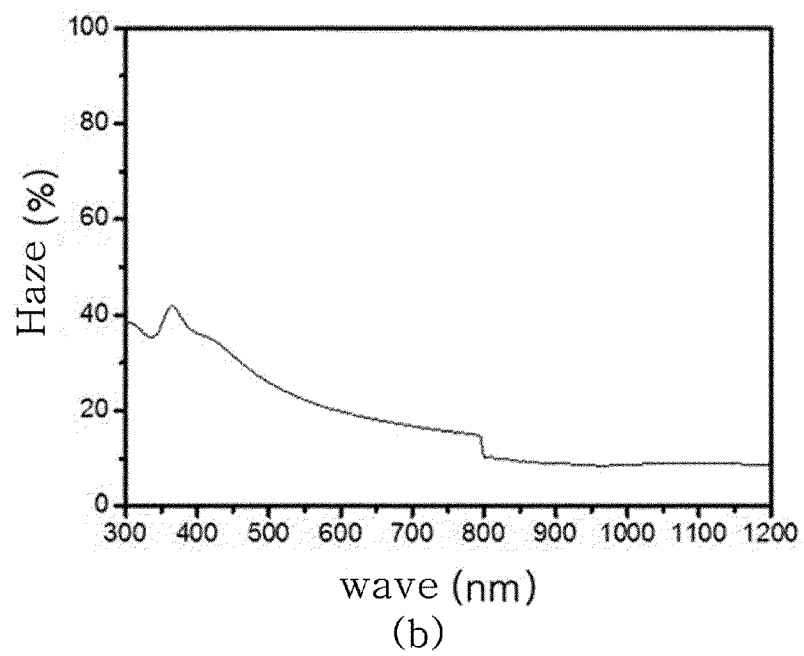
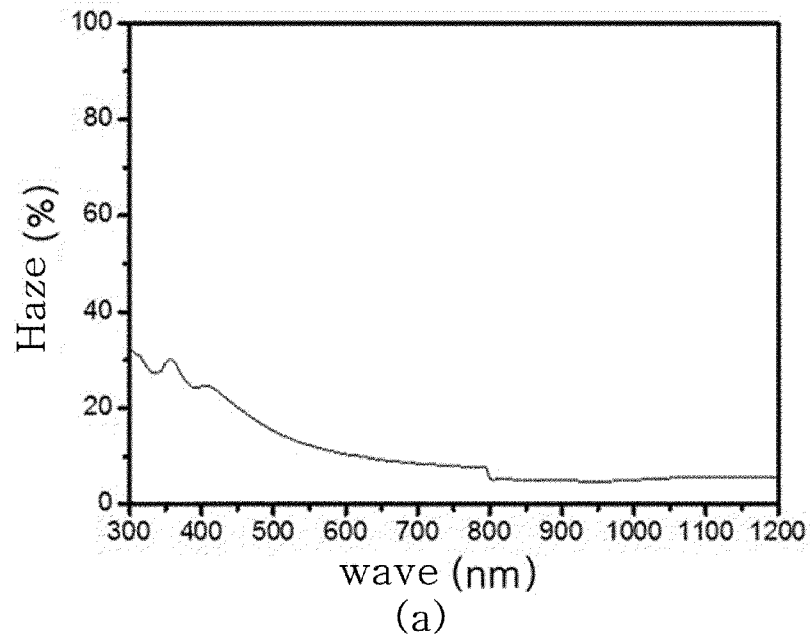
[Fig. 28]



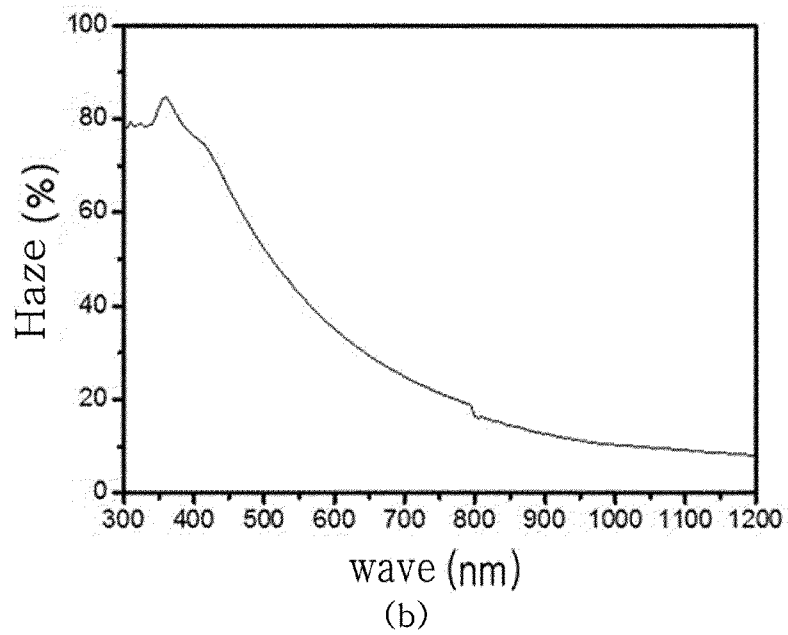
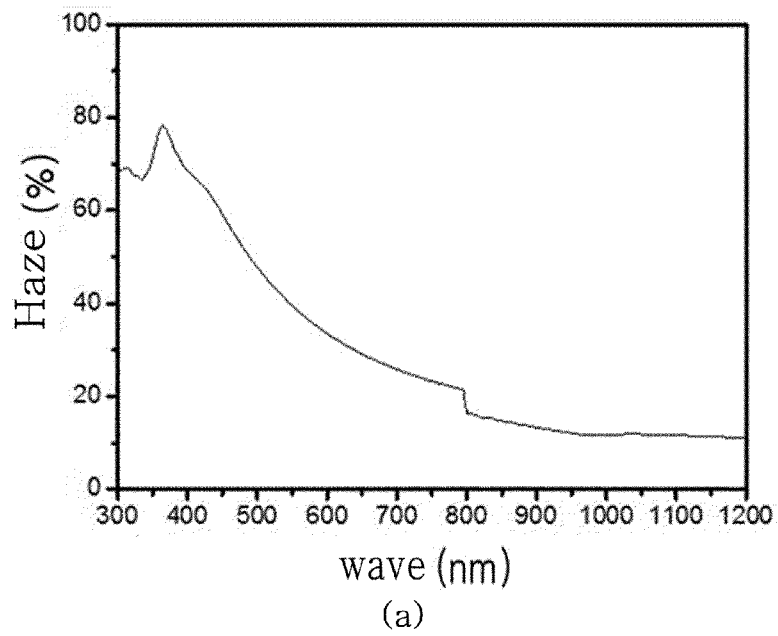
[Fig. 29]



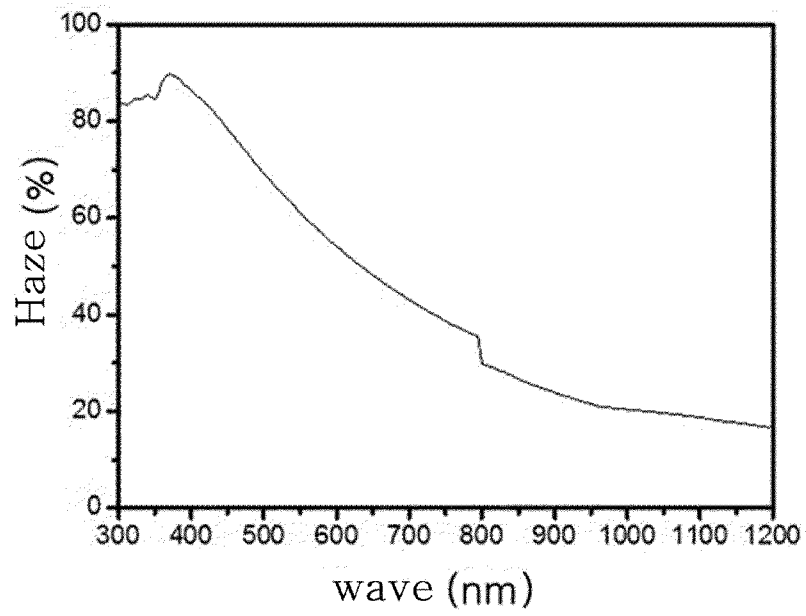
[Fig. 30]



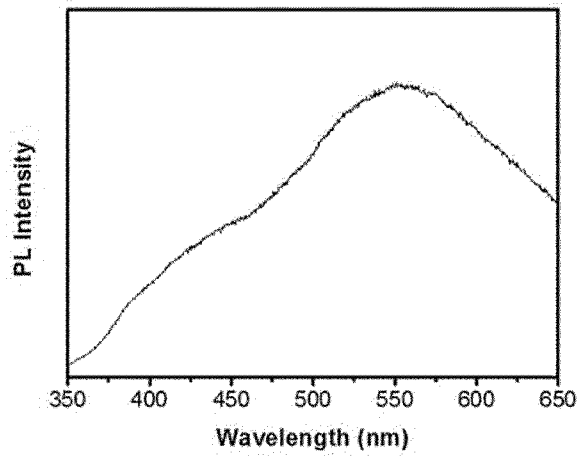
[Fig. 31]



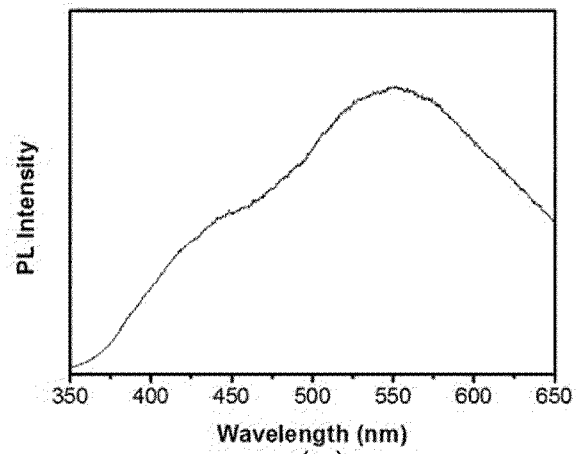
[Fig. 32]



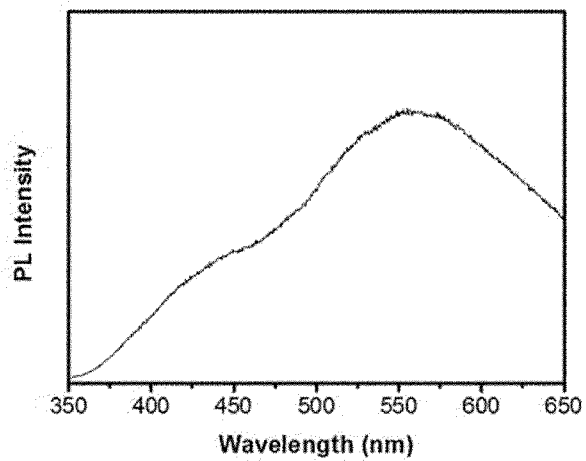
[Fig. 33]



(a)

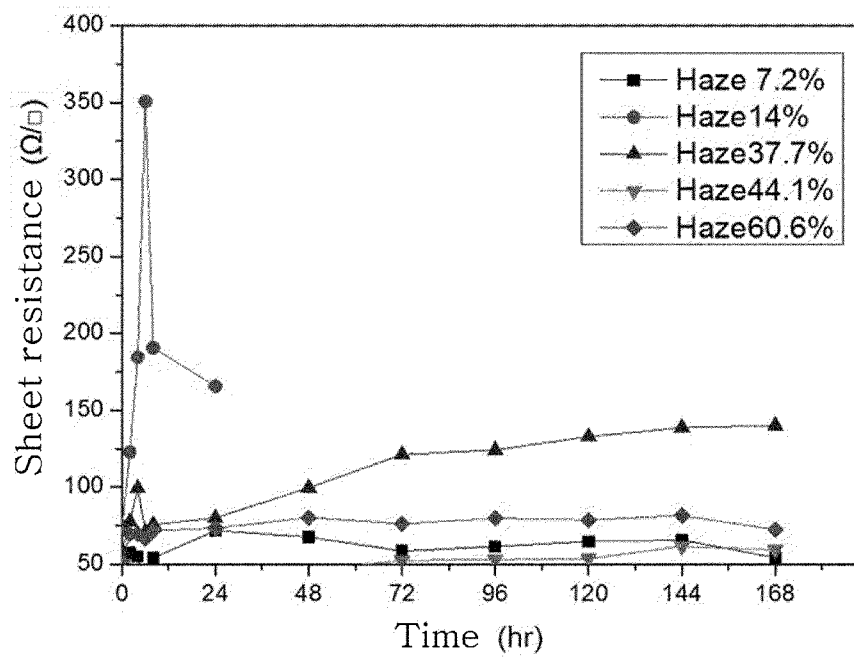


(b)

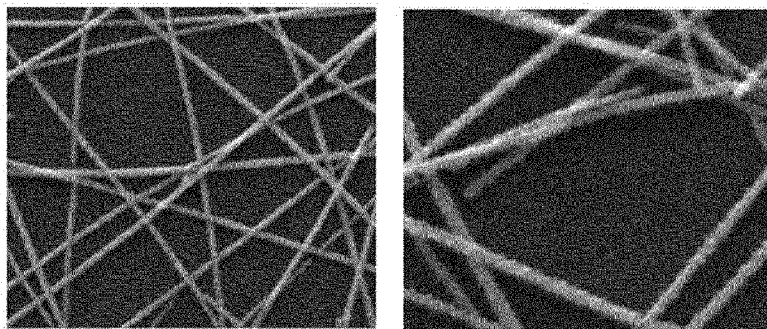


(c)

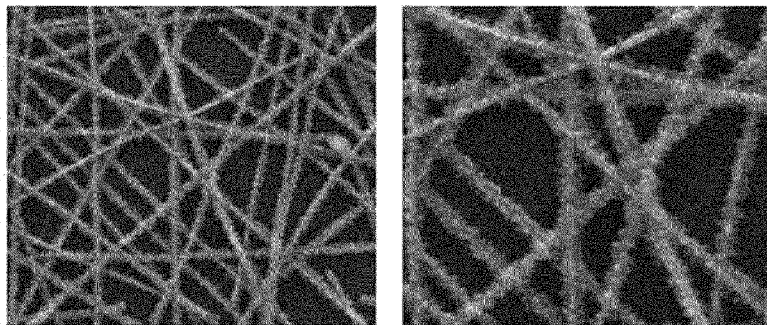
[Fig. 34]



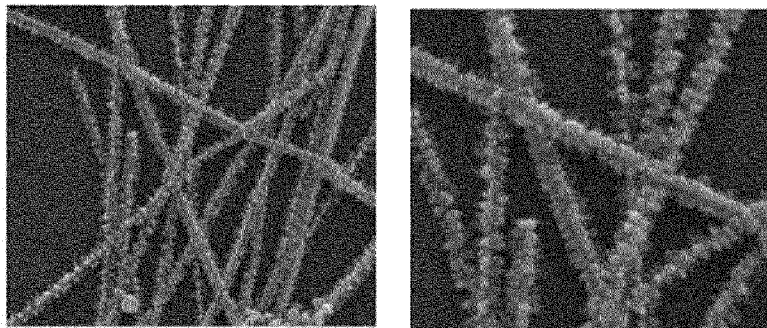
[Fig. 35]



(a)

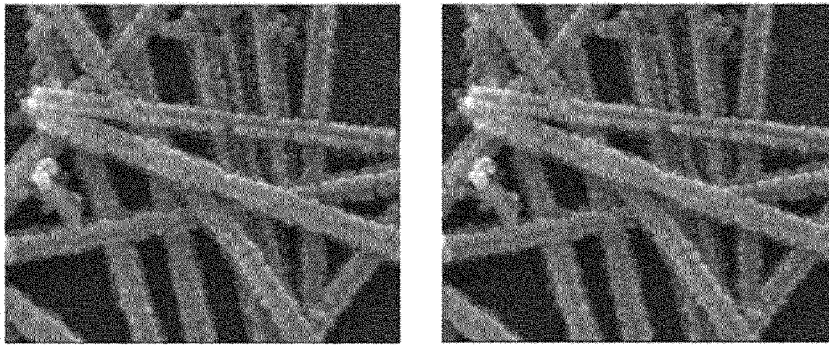


(b)

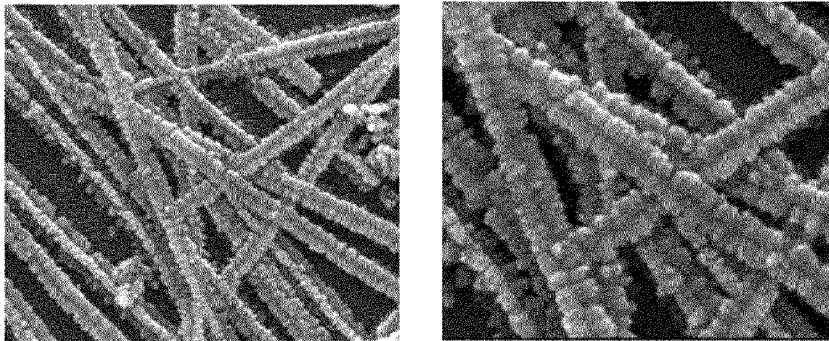


(c)

[Fig. 36]

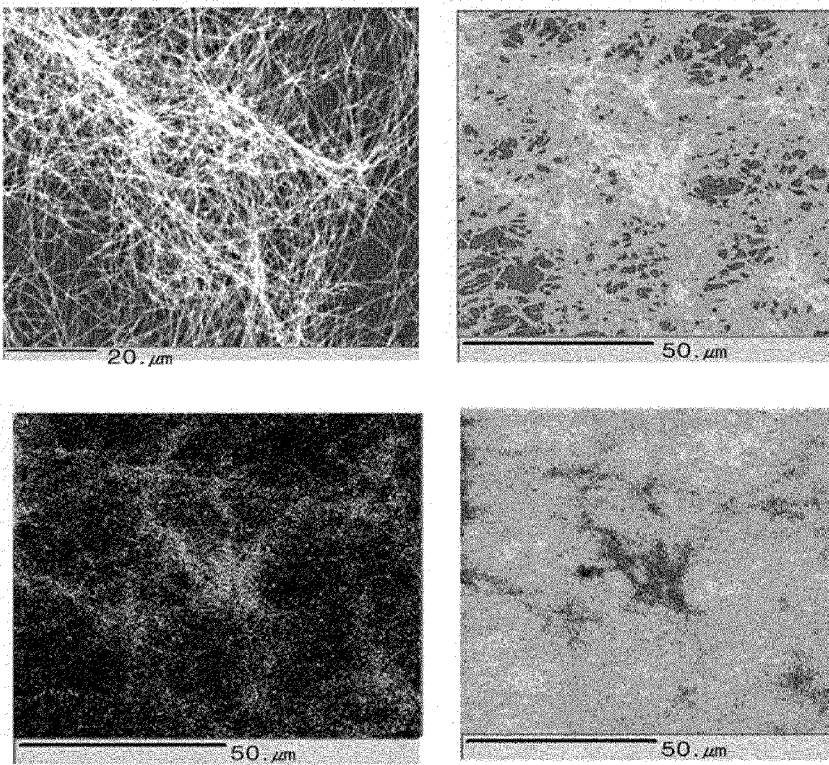


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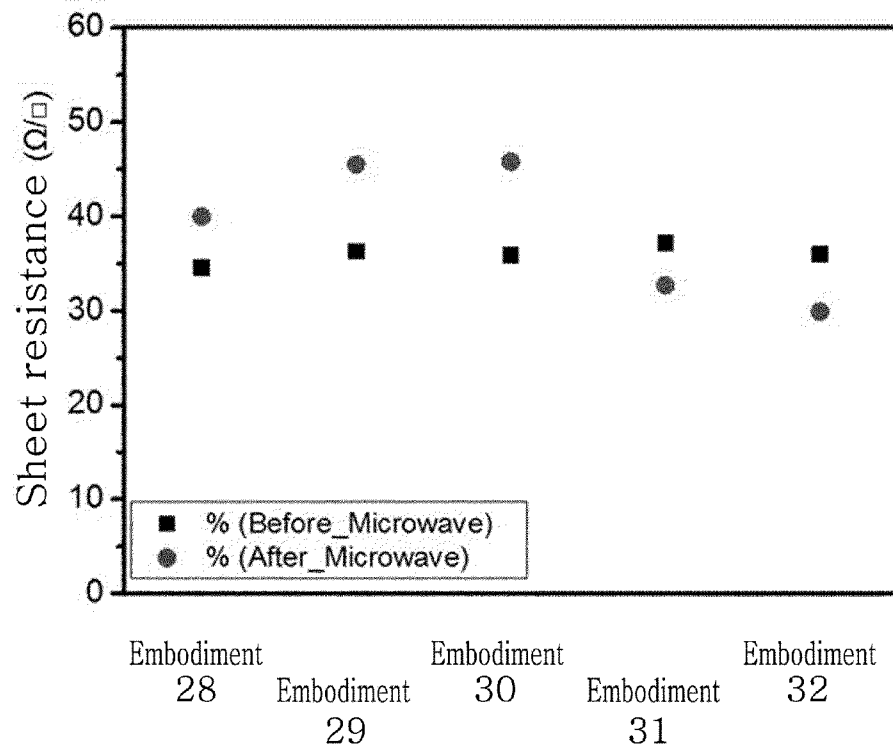


(b)

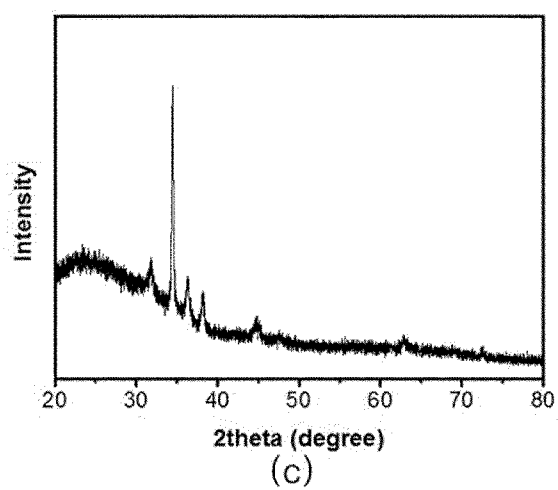
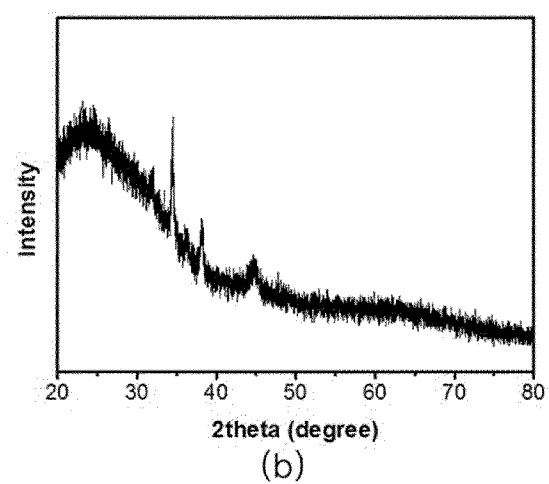
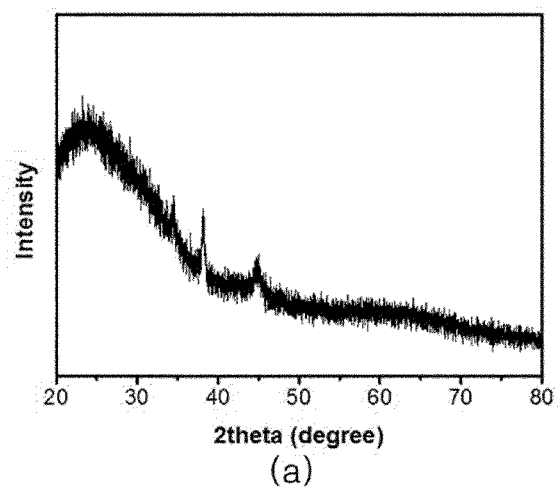
[Fig. 37]



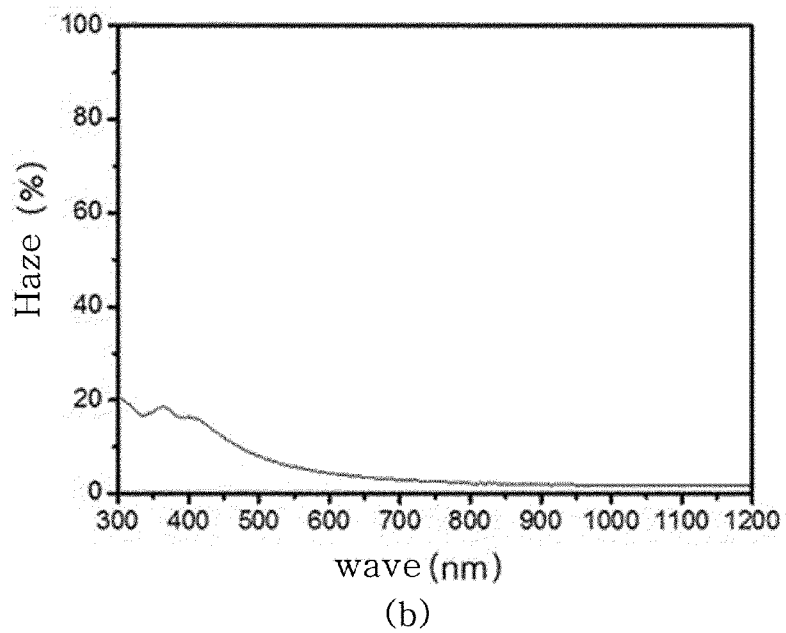
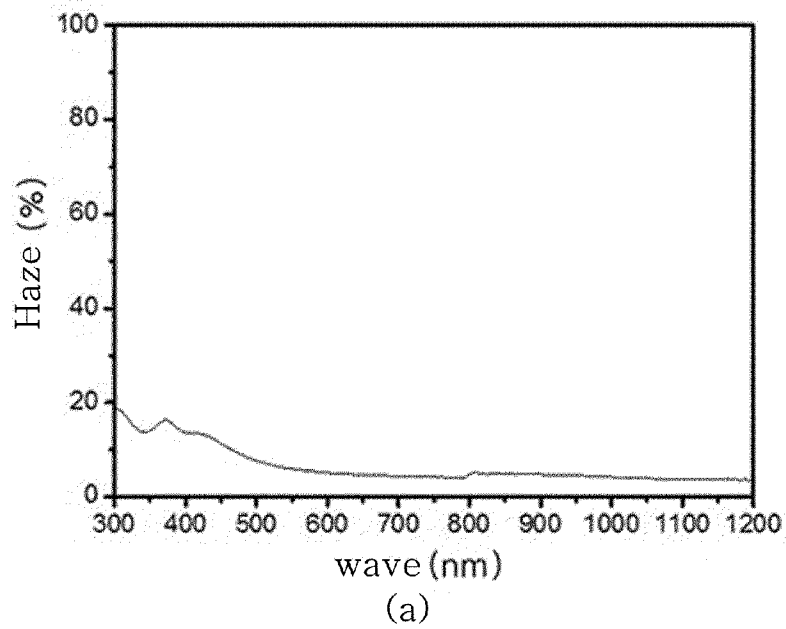
[Fig. 38]



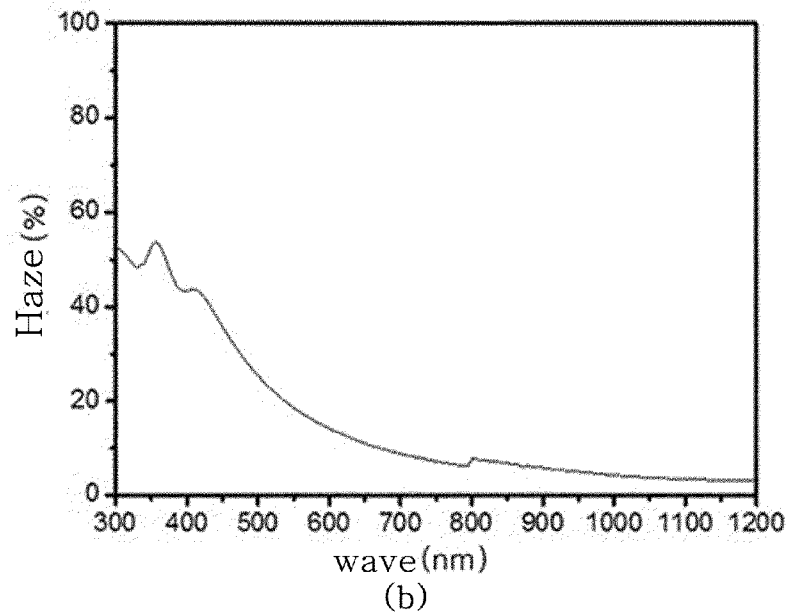
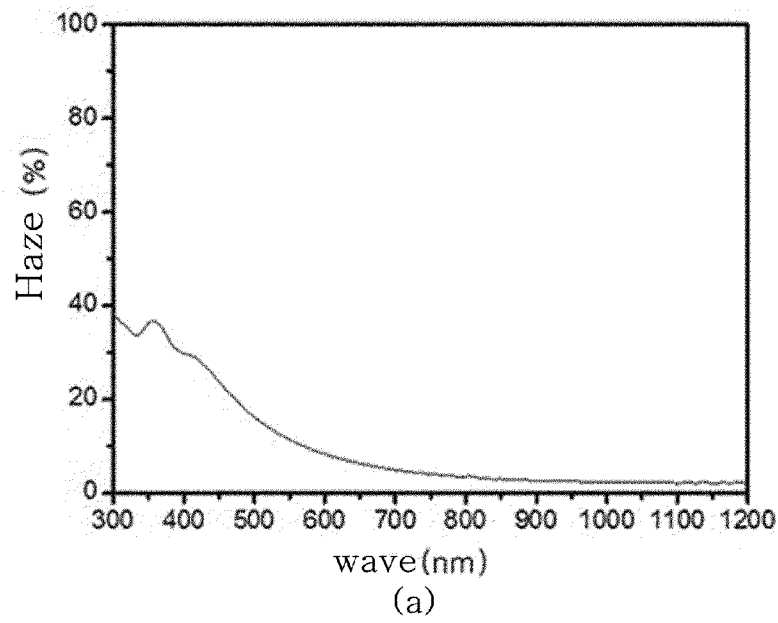
[Fig. 39]



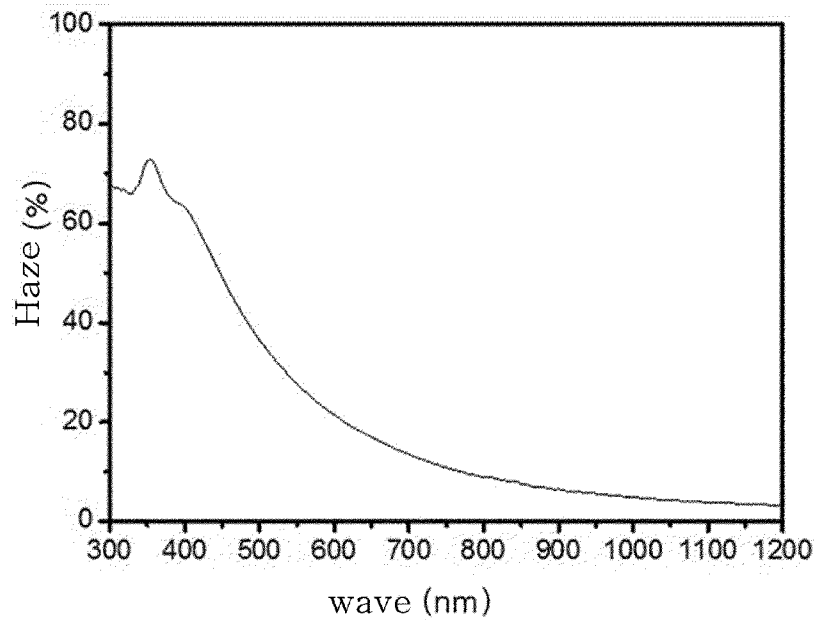
[Fig. 40]



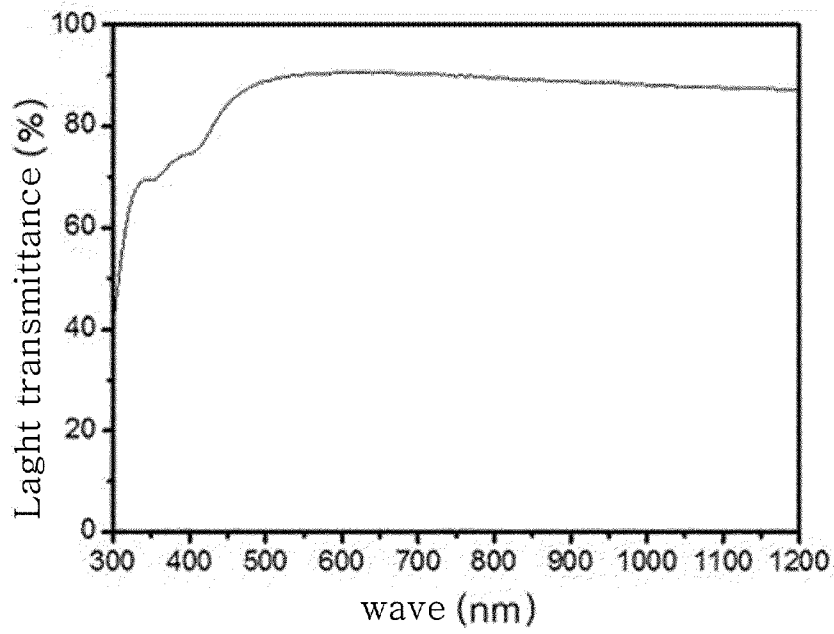
[Fig. 41]



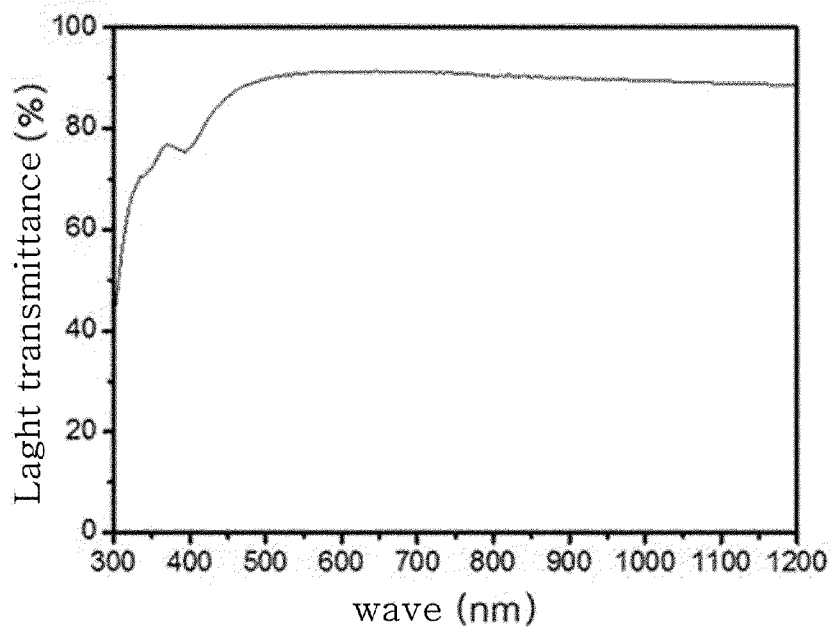
[Fig. 42]



[Fig. 43]

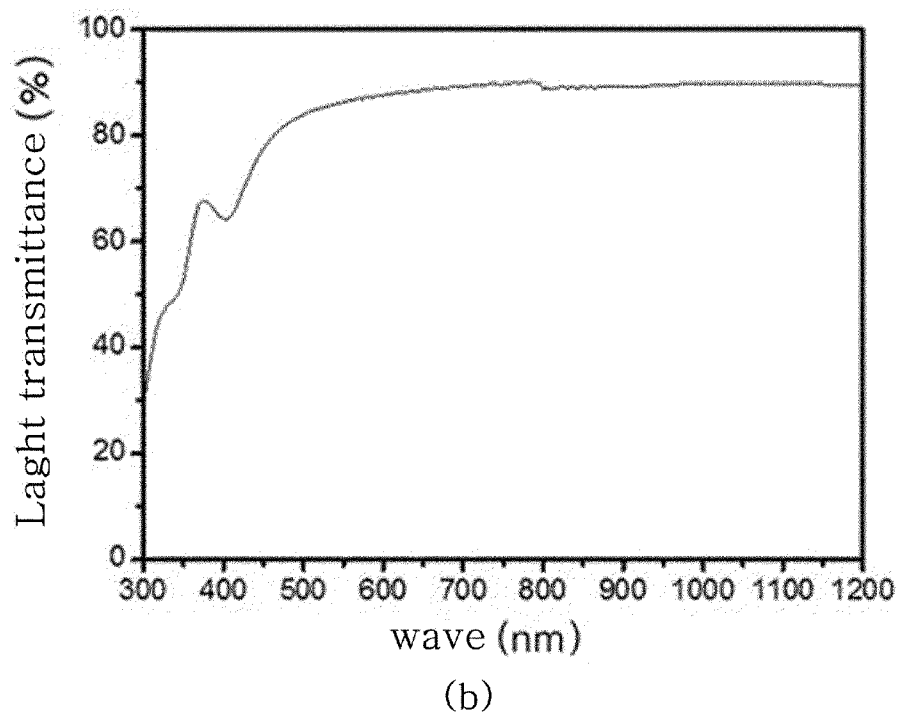
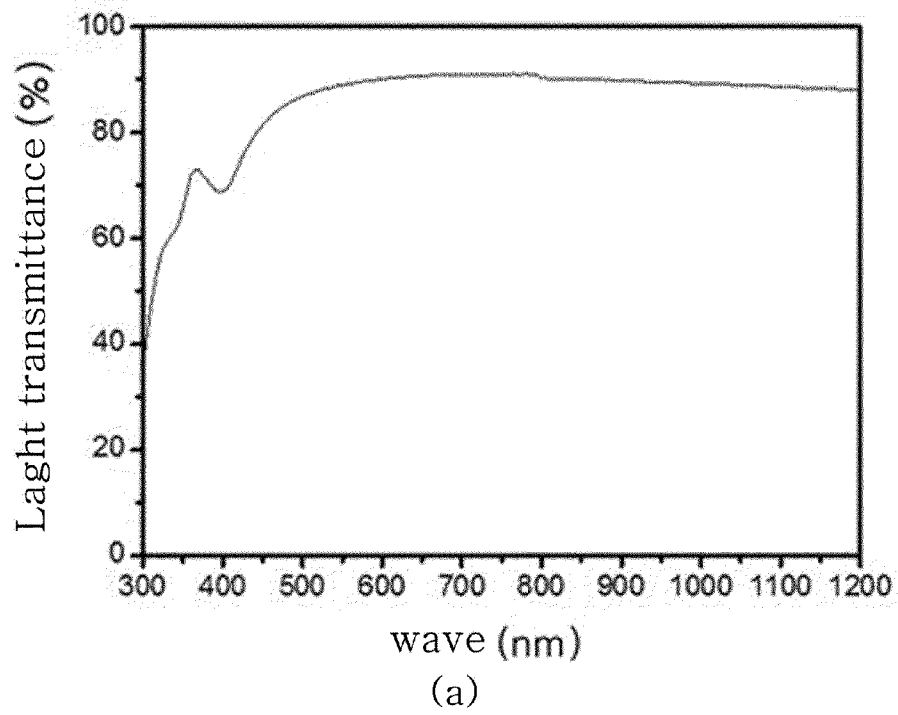


(a)

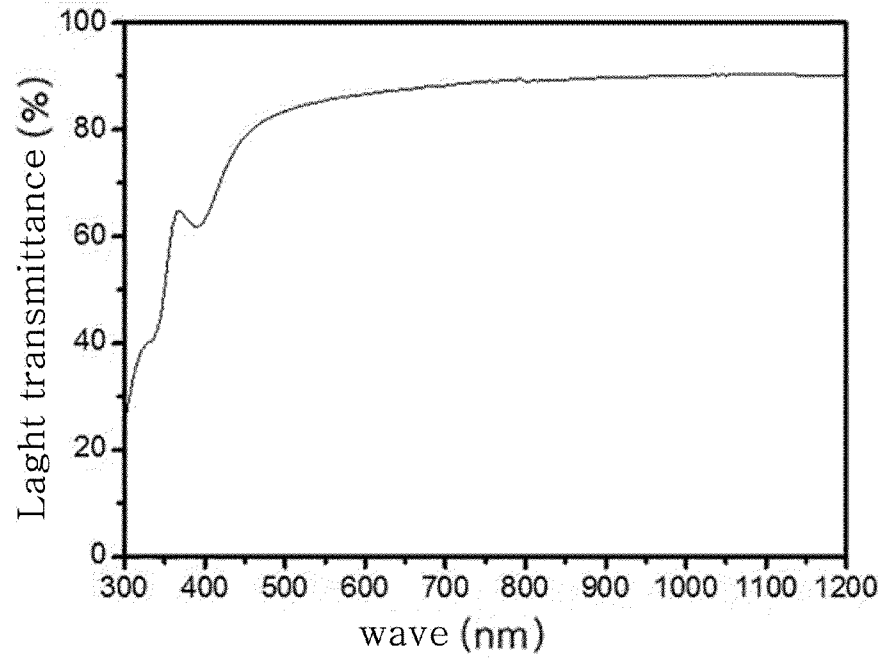


(b)

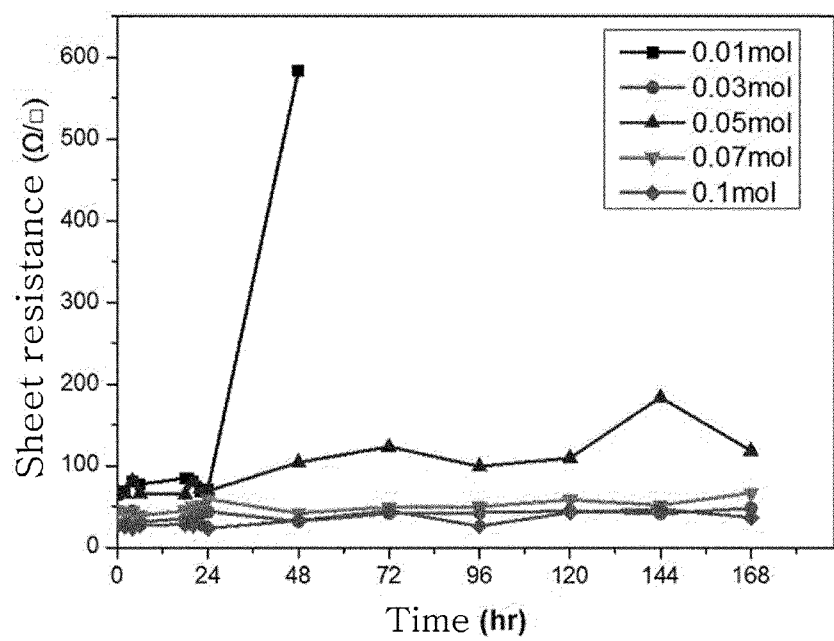
[Fig. 44]



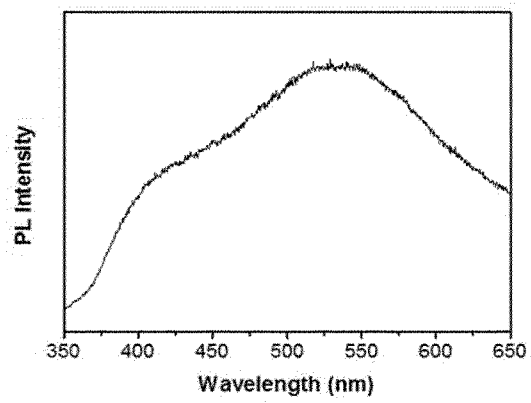
[Fig. 45]



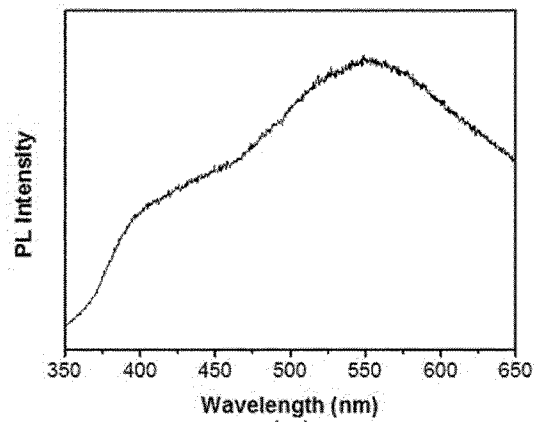
[Fig. 46]



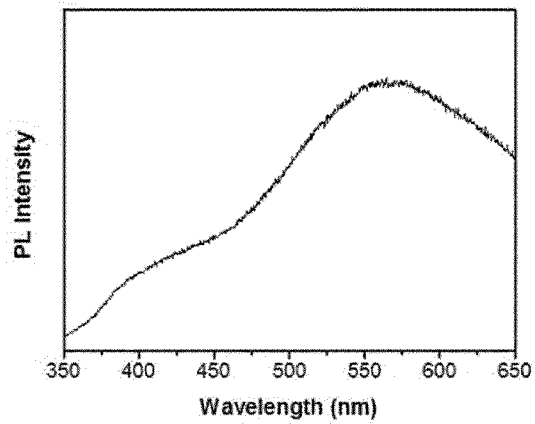
[Fig. 47]



(a)



(b)



(c)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2015/000799**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/02(2006.01)i, H01L 29/66(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)

H01L 21/02; H01B 1/22; B32B 5/16; C21C 1/06; B22F 1/00; B22F 9/24; H01B 5/14; H01B 13/00; H01L 29/66

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, synthesizing, transparent electrode, OLED

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005-0056118 A1 (YOUNAN XIA et al.) 17 March 2005 See paragraph [0073], claims 14, 22 and figures 1-8.	1-19
A	US 2007-0289409 A1 (YOUNAN XIA et al.) 20 December 2007 See abstract, paragraphs [0033]-[0038] and figure 5.	1-19
A	WO 2013-128458 A1 (RAMOT AT TEL-AVIV UNIVERSITY LTD. et al.) 06 September 2013 See abstract, pages 13-15 and claims 1-23.	1-19
A	US 2009-0130433 A1 (HIROSHI TAKADA) 21 May 2009 See paragraphs [0049]-[0076] and claims 1-6.	1-19
A	JP 2012-527071 A (DUPONT TEIJIN FILMS U.S. LIMITED PARTNERSHIP) 01 November 2012 See paragraphs [0009]-[0025] and claims 1-22.	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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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

30 September 2015 (30.09.2015)

Date of mailing of the international search report

30 September 2015 (30.09.2015)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2015/000799

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005-0056118 A1	17/03/2005	US 2009-0282948 A1 US 7585349 B2	19/11/2009 08/09/2009
US 2007-0289409 A1	20/12/2007	US 8114187 B2	14/02/2012
WO 2013-128458 A1	06/09/2013	CN 104508758 A EP 2820657 A1 US 2015-0104936 A1	08/04/2015 07/01/2015 16/04/2015
US 2009-0130433 A1	21/05/2009	US 8052773 B2 WO 2009-063744 A1	08/11/2011 22/05/2009
JP 2012-527071 A	01/11/2012	CN 102421600 A CN 102421600 B EP 2429819 A1 EP 2500171 A2 GB 0908300 D0 JP 5712205 B2 KR 10-2012-0087804 A TW 201106383 A US 2012-0118617 A1 WO 2010-130986 A1	18/04/2012 25/03/2015 21/03/2012 19/09/2012 24/06/2009 07/05/2015 07/08/2012 16/02/2011 17/05/2012 18/11/2010