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(54) Title: NICKEL OXIDE DECORATED GRAPHENE OXIDE NANOCOMPOSITE AS A HOLE TRANSPORT LAYER AND METHOD OF MANUFACTURING THE SAME

(57) Abstract: A method provides a GO: NiO_x nanocomposite based film for an optoelectronic device. The method includes preparing a GO solution in a first alcohol solvent by oxidization of a graphite, preparing a NiO_x solution in a second alcohol solvent by a solvothermal method, conducting decoration of NiO_x onto GO nanosheet structure (NSs) by blending the GO solution and the NiO_x solution to obtain a GO: NiO_x solution, and forming the GO: NiO_x nanocomposite based film by using the GO: NiO_x solution.



DESCRIPTION

NICKEL OXIDE DECORATED GRAPHENE OXIDE NANOCOMPOSITE AS
A HOLE TRANSPORT LAYER AND METHOD OF MANUFACTURING THE
SAME

FIELD OF THE INVENTION

The present invention generally relates to optoelectronics, and more particularly, to a nickel oxide decorated graphene oxide and methods thereof.

BACKGROUND OF THE INVENTION

Taking the advantage of the elimination of both hygroscopic acidic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) and the easily oxidized low work function (WF) cathode, inverted organic solar cells (OSCs) with prolonged stability have been widely adopted. A conventional transition metal oxide of molybdenum oxide (MoO_3), has been widely used as a hole transport layer (HTL) on top of an organic active layer (hereafter named as a top HTL) in inverted OSCs. However, MoO_3 shows n-type semiconductor characteristics serving as equivalent HTL with poor electron blocking ability and electron conductivity. Easily synthesized and low-cost graphene oxide (GO), with a p-type electrical characteristics, has also been used in inverted OSCs. However, typical functionalization of epoxy, hydroxyl and other groups on the basal plane and at the edges of GO could seriously degrade the conductivity. As a result, most reported optimized thickness of GO functioning as an HTL in inverted OSCs is only 1-2 nm, which is the thickness of a few layers of GO sheets. Therefore, it is a concern to control the thickness of GO in mass production. Besides, the underneath active layer will easily be exposed to the metal electrode and electrons may easily tunnel through the extremely thin interface layer. Both issues cause poor electron blocking ability and induce surface recombination, which degrades the fill factor (FF) of fabricated OSCs. To date, there is still a shortage of solution-processed p-type semiconductor functioning as the top HTL with good conductivity to address the needs of emerging organic optoelectronics.

Solution processed nickel oxide (NiO_x where x is a positive number) has been proven to be a p-type semiconductor with the advantages of good conductivity and electron blocking ability. However, most reported NiO_x HTL application involves post-treatments including oxygen-plasma treatment, ultraviolet ozone (UVO) treatment or annealing at high temperatures.

5 These post-treatments would seriously damage the organic active layer as they would destroy the π -conjugation system of organic semiconductors and degrade polymers. Thus, these NiO_x HTL preparation methods are not compatible with top HTL application in inverted OSCs. Recently, post-treatment-free solution-processed NiO_x nanoparticles (NPs) have been reported for HTL application. However, the NiO_x NPs can only be well dispersed into water, which hinders its
10 application in inverted OSCs due to the poor wetting property of water on a hydrophobic active layer surface.

SUMMARY OF THE INVENTION

Embodiments of the subject invention provide a novel and advantageous optoelectronic
15 device that includes a nickel oxide decorated by a graphene oxide as a nanocomposite based HTL, thereby providing high performance inverted OSCs.

In an embodiment, a method of preparing a GO:NiO_x based film (i.e., GO:NiO_x nanocomposite film) for an optoelectronic device can comprise preparing a GO solution in a first alcohol solvent by oxidization of a graphite, preparing a NiO_x solution in a second alcohol
20 solvent by a solvothermal method, conducting decoration of NiO_x onto GO nanosheet structure (NSs) by blending the GO solution and the NiO_x solution to obtain a GO:NiO_x nanocomposite solution, and forming the GO:NiO_x nanocomposite based film by using this solution.

In another embodiment, an optoelectronic device can comprise a first electrode layer, an electron transport layer on the first electrode layer, an organic active layer disposed on the first
25 electron transport layer, a hole transport layer disposed on the organic active layer and including a GO:NiO_x nanocomposite, and a second electrode layer disposed on the hole transport layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a shows photographs of NiO_x NPs, L-GO NSs, H-GO NSs and L-GO: NiO_x and H-GO: NiO_x nanocomposite in ethanol in accordance with an example embodiment.

FIG. 1b shows C 1s XPS spectrum of L-GO and H-GO in accordance with an example embodiment.

FIG. 1c shows FTIR spectrum of L-GO and H-GO (normalized at 1625 cm^{-1}) in accordance with an example embodiment.

FIG. 2a shows a Transmission electron microscopy (TEM) image of L-GO NSs in accordance with an example embodiment.

FIG. 2b shows a TEM image of NiO_x NPs decorated L-GO NSs nanocomposite in accordance with an example embodiment.

FIG. 2c shows a TEM image of H-GO: NiO_x aggregates in accordance with an example embodiment.

FIG. 2d shows a SEM image of L-GO: NiO_x film in accordance with an example embodiment.

FIG. 3a shows the structure of a solar cell (ITO/ZnO/PTB7-Th:PC₇₁BM/HTL/Ag) in accordance with an example embodiment.

FIG. 3b shows the structure of a solar cell (ITO/ZnO/PBDB-T:ITIC/HTL/Ag) in accordance with an example embodiment.

FIG. 3c shows the structure of a solar cell (ITO/ZnO/PBDB-T:IT-M/HTL/Ag) in accordance with an example embodiment.

FIG. 4a is a graph illustrating the current density-voltage (J - V) characteristics under AM1.5G solar spectrum with light intensity of 100 mW/cm^2 of inverted OSCs with a structure of ITO/ZnO/PTB7-Th:PC₇₁BM/L-GO: NiO_x /Ag compared with the control device with a structure of ITO/ZnO/PTB7-Th:PC₇₁BM/L-GO/Ag according to one or more embodiments.

FIG. 4b is a graph illustrating the PCE of inverted OSCs based on GO and L-GO: NiO_x with different thicknesses (inset shows the cross-section SEM of the device with a structure of ITO/ZnO/PTB7-Th:PC₇₁BM/L-GO: NiO_x /Ag) according to one or more embodiments.

FIG. 5a is a graph illustrating the current density-voltage (J - V) characteristics under AM1.5G solar spectrum with light intensity of 100 mW/cm^2 of inverted OSCs with a structure of

ITO/ZnO/PBDB-T:ITIC/L-GO:NiO_x/Ag compared with the control device with a structure of ITO/ZnO/PBDB-T:ITIC /L-GO/Ag according to one or more embodiments.

FIG. 5b is a graph illustrating the current density-voltage (J - V) characteristics under AM1.5G solar spectrum with light intensity of 100 mW/cm² of inverted OSCs with a structure of ITO/ZnO/PBDB-T:IT-M/L-GO:NiO_x/Ag compared with the control device with a structure of ITO/ZnO/PBDB-T:IT-M/L-GO/Ag according to one or more embodiments.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the subject invention provide a novel and advantageous optoelectronic device that includes a nickel oxide decorated by a graphene oxide as a nanocomposite based HTL, thereby providing high performance inverted OSCs.

Embodiments of the subject invention comprise well intermixed GO:NiO_x nanocomposites in non-aqueous solution that can successfully form efficient top HTL in inverted OSCs. In the embodiments, two approaches are considered to achieve thickness-extended and uniform top HTL from our new solution-processed method. First, the embodiment uses hydrogen bonds between GO NSs and NiO_x NPs to decorate the NiO_x NPs onto GO NSs for realizing the thickness-extended HTL. Second, the embodiment uses the extent of GO oxidation to critically control the dispersion of GO:NiO_x for achieving uniform HTL film. As a result, the embodiments of the subject invention show that the optimized GO:NiO_x nanocomposite film shows about 15 times better conductivity compared with GO films. The long-time concern of too thin GO HTL with typical thickness of only about 2 nm, is addressed by an extension of thickness by about 16 times to as thick as 32 nm. With the enhanced conductivity and electron blocking ability of GO:NiO_x nanocomposite film, the short-current density (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) are all improved in the optimized GO:NiO_x top HTL based inverted OSCs. Overall, a 15% improvement in power conversion efficiency (PCE) is realized by using this GO:NiO_x HTL compared with GO-only based OSCs. Furthermore, this GO:NiO_x nanocomposite HTL is successfully applied to improve the performances of both fullerene and non-fullerene OSCs, which contributes to the robust and practical applications in not only organic optoelectronic devices but also other emerging solution-processed optoelectronics.

Through strategically controlling the hydrogen bond interaction between hydroxyl groups of GO NSs and hydroxyl groups attached to the coordination unsaturated metal atoms of NiO_x , the NiO_x NPs can be decorated onto the GO NSs surface to form the mixed GO:NiO_x nanocomposites. The ethanol dispersible NiO_x NPs are synthesized by a solvothermal method and GO NSs are synthesized by a modified Hummers' method. Specifically, this GO NSs exhibits a low degree of oxidation and is denoted L-GO.

FIG. 1a shows photographs of NiO_x NPs, L-GO NSs, H-GO NSs and L-GO: NiO_x and H-GO: NiO_x nanocomposite in ethanol in accordance with an example embodiment, and FIGs 2a-2d show TEM image and SEM image of L-GO, NiO_x NPs decorated L-GO, H-GO: NiO_x , and L-GO: NiO_x . In particular, the NiO_x NPs solution and L-GO NSs solution are shown in FIG. 1a-I and 1a-II, respectively. The decoration of NiO_x NPs on L-GO NSs has been investigated by transmission electron microscopy (TEM) as shown in FIGs. 2a and 2b. Referring to FIGs 2a-2d, the L-GO NSs exhibit a size around 1-2 μm . After decoration with NiO_x NPs, the TEM images turn out to be shown in FIG. 2b. The black dots are the NiO_x NPs. The profile of nanosheet structure of L-GO is clearly outlined due to the decoration of NiO_x NPs. Consequently, through introducing hydrogen bonds between GO NSs and NiO_x NPs, embodiments of the subject invention successfully realize well-mixed L-GO: NiO_x nanocomposites which can form high quality (dense and well-cover) film as SEM image shown in FIG. 2d, and decent HTL film application potential as described later.

The oxidation degree of GO is demonstrated to be a critical factor to achieve good dispersion of GO:NiO_x nanocomposite for high-quality film. Different from the synthesis process of GO with a low oxidation (i.e. L-GO), an additional pre-oxidation process is introduced during the synthesis, which results in GO with a high oxidation (H-GO). In embodiments of the subject invention, the formation of GO:NiO_x nanocomposite films highly depends on the extent of oxidation of GO as described below. GO can be regarded as graphene NSs functionalized with carboxyl groups, hydroxyl groups, and epoxy groups. The graphene NSs could change from conductive to nearly insulating due to the damage of the conjugated structure. Meanwhile, there is an energy bandgap in GO, which is distinct from that of zero-bandgap graphene. The oxidation degree of GO depends on the density of the functional groups formed on the basal panel. Here, the synthesized GO dispersed in ethanol, with different oxidation degrees, show distinct

appearances. The L-GO solution shows a yellow-like color while the H-GO solution shows slight red-like color, as shown in FIG. 1a-II and a-III.

FIG. 1b shows C 1s XPS spectrum of L-GO and H-GO in accordance with an example embodiment. FIG. 1c shows FTIR spectrum of L-GO and H-GO (normalized at 1625 cm^{-1}) in accordance with an example embodiment. Referring to FIG. 1b, X-ray photoelectron spectroscopy (XPS) characterization is utilized to determine the oxidation variance results of L-GO and H-GO. XPS spectra of both L-GO and H-GO show C-C (284.8 eV), C-O (286.8 eV) and C=O (288.6 eV) species. However, the peak amplitudes show significant differences in two kinds of GO. In the spectrum of L-GO, the C-C peak is obviously higher than C-O peak while the situation is reversed in the case of H-GO. The ratio between C-C, C-O and C=O is 1:0.54:0.15 for L-GO while the ratio is 1:1.32:0.11 for H-GO. The higher ratio of C-O and C=O over C-C indicates a higher oxidation degree of H-GO, which indeed is mainly attributed to higher concentration of C-O species. Fourier transform infrared spectroscopy (FTIR) has also been used to identify various oxygen functional groups on the carbon basal plane of GO as shown in FIG. 1c. The spectrum is normalized at 1625 cm^{-1} , which arises from asymmetric vibrational stretching of sp^2 -hybridized C=C. The spectrum identifies the presence of carboxyl groups (C=O stretching at 1731 cm^{-1} , O-H of COOH bending at 1400 cm^{-1}), tertiary hydroxyl groups (phenolic C-O at 1227 cm^{-1} and C-O at 1075 cm^{-1}) and epoxy groups (C-O at 1260 cm^{-1}). The relatively strong peak at 1227 cm^{-1} and 1075 cm^{-1} indicates a higher density of hydroxyl groups of H-GO. Both XPS and FTIR spectra indicate that the higher oxidation degree of H-GO mainly originates from a higher density of hydroxyl groups.

For the case of H-GO as shown in FIG. 2c, because of the high density of hydroxyl groups on the GO NSs, the drastic hydrogen bonds induce the shrinking of decorated H-GO NSs. The NiO_x NPs decorated H-GO NSs shrink into aggregates with sizes of several hundred nanometers. These aggregates cannot stably disperse in ethanol and precipitate at the bottom of a vial as shown in FIG. 1a-V. By spin-coating this suspension, the large H-GO: NiO_x aggregates scatter on the underlying substrate which cannot effectively prevent the direct contact of the metal electrode with polymer blend active layer. Consequently, this poorly formed film is not good as an HTL in inverted OSCs as the poor coverage would result in current leakage and serious surface recombination. The well-dispersed NiO_x NPs decorated L-GO NSs can form a high-quality nanocomposite film.

FIGs. 3a-3c show the structure of a solar cell (ITO/ZnO/PTB7-Th:PC₇₁BM/HTL/Ag), a solar cell (ITO/ZnO/PBDB-T:ITIC/HTL/Ag), a solar cell (ITO/ZnO/PBDB-T:IT-M/HTL/Ag) in accordance with an example embodiment, respectively. The solar cell as an optoelectronic device comprises a glass layer, an Indium Tin Oxide (ITO) layer on the glass layer, a Zinc Oxide (ZnO) layer on the ITO layer, an organic active layer on the ZnO layer, and a hole transport layer (HTL) on the organic active layer, and an Ag anode electrode on the HTL. The ITO layer and the ZnO layer function as a cathode electrode. The organic active layer comprises at least one of PTB7-Th:PC₇₁BM, PBDB-T:ITIC, and PBDB-T:IT-M. The Ag anode electrode is configured to transfer a hole h^+ and the ITO layer is configured to transfer an electron e^- .

The HTL comprises a GO:NiO_x nanocomposite in order to extend a thickness of the HTL and to achieve uniform HTL. The GO of the HTL includes a graphene oxide nanosheet structure (GO NSs), the GO NSs has a low degree of oxidation such that the C-C peak of the GO NSs is higher than the C-O peak.

The subject invention includes, but is not limited to, the following exemplified embodiments.

Embodiment 1. A method of preparing a GO:NiO_x based film (GO:NiO_x nanocomposite film) for an optoelectronic device, the method comprising:

preparing a graphene oxide (GO) solution in a first alcohol solvent by oxidization of a graphite;

preparing a nickel oxide (NiO_x) solution in a second alcohol solvent by a solvothermal method;

conducting decoration of NiO_x nanoparticles onto GO nanosheet structure (NSs) by blending the GO solution and the NiO_x solution to obtain a GO:NiO_x nanocomposite solution; and

forming the GO:NiO_x nanocomposite film by using the GO:NiO_x nanocomposite solution.

Embodiment 2. The method of embodiment 1, wherein the GO is a carbon based material binding with functional groups.

Embodiment 3. The method of embodiment 2, wherein the functional groups comprise one or more of hydroxyl groups, carboxyl groups, epoxy groups, amino groups, and sulfonic acid groups.

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Embodiment 4. The method of any of embodiments 1-3, wherein the second alcohol solvent of the solvothermal method includes water, ethanol, methanol, isopropanol, ethylene glycol, glycerin, or a mixture of any thereof.

10 Embodiment 5. The method of any of embodiments 1-4, wherein the NiO_x is a composite consisting essentially of / comprising / consisting of: NiO and other species selected from a group consisting of nickel oxide (Ni_2O_3), nickel oxide hydroxide (NiOOH), and nickel hydroxide $\text{Ni}(\text{OH})_2$.

15 Embodiment 6. The method of any of embodiments 1-5, wherein the NiO_x is non-stoichiometric or shows typical non-stoichiometric property which may have an atomic ratio between nickel and oxygen deviated from 1:1.

20 Embodiment 7. The method of any of embodiments 1-6, wherein the NiO_x possesses a typical p-type semiconductor property.

25 Embodiment 8. The method of any of embodiments 1-7, wherein the first alcohol solvent for the GO solution comprises methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), butanol ($\text{C}_4\text{H}_9\text{OH}$), or a mixture of any thereof.

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Embodiment 9. The method of any of embodiments 1-8, wherein the second alcohol solvent for the NiO_x solution comprises methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), butanol ($\text{C}_4\text{H}_9\text{OH}$), or a mixture of any thereof.

30 Embodiment 10. The method of any of embodiments 1-9, wherein forming the GO:NiO_x nanocomposite based film further includes obtaining a GO:NiO_x nanocomposite based

hole transport layer by using one or more of casting, spin-coating, doctor blading, screen printing, ink jet printing, pad printing, and roll-to-roll technique.

Embodiment 11. The method of any of embodiments 1-10, wherein the
5 optoelectronic device is an device selected from a group consisting of solar cells, phototransistors, photomultipliers, photoresistors, light-emitting diodes, laser diodes and sensors.

Embodiment 12. An optoelectronic device, comprising:
a first electrode layer;
10 an organic active layer disposed on the first electrode layer;
a hole transport layer disposed on the organic active layer and including a GO:NiO_x nanocomposite; and
a second electrode layer disposed on the hole transport layer.

Embodiment 13. The optoelectronic device of embodiment 12, wherein the
15 GO:NiO_x nanocomposite includes nickel oxide nanoparticles (NiO_x NPs) and a graphene oxide nanosheet structure (GO NSs).

Embodiment 14. The optoelectronic device of embodiment 13, wherein the GO NSs
20 has a low degree of oxidation of which a C-C peak is higher than a C-O peak.

Embodiment 15. The optoelectronic device of any of embodiments 13-14, wherein the NiO_x NPs and the GO NSs are coupled with each other by hydrogen bonds.

Embodiment 16. The optoelectronic device of any of embodiments 12-15, wherein a
25 thickness of the hole transport layer is in a range of 17 nm to 32 nm.

Embodiment 17. The optoelectronic device of any of embodiments 12-16, wherein the first electrode layer includes an Indium Tin Oxide (ITO) layer and a Zinc Oxide (ZnO) layer.

Embodiment 18. The optoelectronic device of any of embodiments 12-17, wherein the second electrode layer includes an Ag anode electrode.

Embodiment 19. The optoelectronic device of any of embodiments 17-18, further comprising a glass layer disposed on a bottom surface of the ITO layer.

Embodiment 20. The optoelectronic device of any of embodiments 12-19, wherein the organic active layer comprises at least one of PTB7-Th:PC₇₁BM, PBDB-T:ITIC/HTL, and PBDB-T:ITIC.

In any one of the above embodiments, the first alcohol solvent or the second alcohol solvent may comprises alkanol having 1-10 carbon atoms.

In any one of the above embodiments, the thickness of the hole transport layer can be in a range of 8 nm to 64 nm, 12 nm to 48 nm, or 17 nm to 32 nm.

In one embodiments of the present invention, the present invention relates to the use of GO:NiO_x nanocomposite in HTL.

A greater understanding of the present invention and its many advantages may be had from the following examples, given by way of illustration. The following examples show some of the methods, applications, embodiments, and variants of the present invention. They are, of course, not to be considered as limiting the invention. Numerous changes and modifications can be made with respect to the invention.

EXAMPLES

Conventionally, due to the destroying of the sp²-hybridized carbon sheet of graphene caused by functioning groups, including epoxy/hydroxyl groups on the basal plane and carboxylic acid groups at the edge, the GO shows a poor conductivity. This poor conductivity

makes the performance of GO based inverted OSCs very sensitive to the thickness of GO. The examples confirm pristine GO also shows such thickness dependent performance. Taking the case of L-GO as an example, when the thickness is 9.9 nm, the device demonstrates almost zero current due to the very small short-circuit current density (J_{SC}) resulting from the poor conductivity of L-GO. Until only the thickness of L-GO decreases to 4.1 nm, J_{SC} starts to increase to around 10 mA cm⁻². The optimized L-GO thickness is very thin with a value of 2.1 nm and the optimized PCE is 8.80%. When the thickness is further decreased, PCE quickly degrades due to a decrease of open-circuit voltage (V_{OC}). This is caused by the direct contact between Ag anode and active layer induced by the uncompleted coverage of L-GO on the surface of active layer. Consequently, our results confirm the too thin/sensitive thickness issue of GO for OSC applications.

To address the very-thin thickness issue of GO, the embodiments of the subject invention form L-GO and NiO_x (0.5:5 mg mL⁻¹) nanocomposites films prepared by the method described in previous section. The electrical conduction enhancement has been investigated by contact-mode conductive atomic force microscopy (c-AFM). The thickness of L-GO, L-GO:NiO_x and NiO_x is fixed at ~20 nm and the current-voltage (I - V) curves measured by c-AFM. At a bias voltage of -2.0 V, the electric current measured for L-GO, L-GO:NiO_x, NiO_x is 0.06, 3.06, 10.35 nA respectively. Different from stoichiometric NiO, a wide bandgap semiconductor with a low intrinsic conductivity of 10⁻¹³ S cm⁻¹, our non-stoichiometric NiO_x is much more conductive (with a conductivity of 5.10 × 10⁻⁴ S cm⁻¹) due to the introduction of Ni³⁺ induced Ni vacancies. Thus accordingly, after decoration of NiO_x on the L-GO NSs, the conductivity increases to 1.38 × 10⁻⁴ S cm⁻¹, which shows an increasing factor of ~14 compared with pristine L-GO with poor conductivity (9.54 × 10⁻⁶ S cm⁻¹).

Following are examples that illustrate procedures for practicing the invention. These examples should not be construed as limiting.

EXAMPLE 1

This novel GO:NiO_x nanocomposite dispersion was prepared by decorating NiO_x NPs onto GO NSs in ethanol. 1 g graphite and 0.5 g sodium nitrate (NaNO₃) was stirred with concentrated sulfuric acid (H₂SO₄, 98%, 25 mL) under ice bath. Then 3 g potassium permanganate (KMnO₄) was slowly added into the mixture to prevent a rapid rise of temperature.

After stirring under ice bath for 2 h, the reaction mixture was heated to 35 °C for 1 h. The slurry was quenched by a mixture of 200 mL deionized (DI) water and 10 mL concentrated H₂SO₄. Finally, 10 mL hydrogen peroxide (H₂O₂, 30%) was added to form the L-GO dispersion. The dispersion was centrifuged at 6000 rpm for 10 min. The precipitate was washed by DI water and ethanol for 3 times respectively. Finally, the precipitate was dispersed into ethanol to get the L-GO in ethanol. For the H-GO synthesis, 1 g graphite was ultrasonic treated with 7.5 mL concentrated H₂SO₄ for 8 h. The pre-oxidized graphite was washed by water and dried before conducting the same reaction process of L-GO to get the H-GO in ethanol. 0.13 g nickel acetylacetonate (Ni(acac)₃) and 14 mL *tert*-butanol were stirred at 700 rpm for 30 min and transferred into a 20 mL Teflon autoclave liner. The autoclave was thermal treated in a muffle furnace by 220 °C for 20 h. After cooling down, the resultant suspension was centrifuged at 15,000 rpm for 10 min. Supernatant was removed and the synthesized NiO_x NPs were dried by vacuum treatment. The NiO_x NPs were decorated onto GO NSs with a weight ratio of 5:0.5 mg mL⁻¹ to form the GO:NiO_x nanocomposite dispersion. The dispersion can be spin-coated onto a substrate to form the GO:NiO_x nanocomposite film.

EXAMPLE 2

ITO-coated glass substrates with sheet resistance of 15 Ω sq⁻¹ were cleaned and then UVO treated for 15 min. 44 mg zinc acetate dihydrate (Zn(OAc)₂·2H₂O) and 12 μL ethanolamine was dissolved into 2 mL isopropanol (iPA). The solution was spin-coated onto cleaned ITO at 3000 rpm and then annealed at 200 °C for 1 h to form the ZnO electron transport layer (ETL). The polymer donor PTB7-Th and fullerene acceptor PC₇₁BM were purchased from Solarmer Co., Ltd. PTB7-Th:PC₇₁BM (10:15 mg mL⁻¹ in chlorobenzene) with addition of 3% volume ratio 1,8-diiodooctane (DIO) were spin-coated on ZnO at 2000 rpm. DIO was removed by fluxing 150 μL onto the rotating PTB7-Th:PC₇₁BM active layer. L-GO (0.5 mg mL⁻¹), L-GO:NiO_x (0.5:5 mg mL⁻¹) and NiO_x (5 mg mL⁻¹) were spin-coated onto the active layer. Finally, Ag (100 nm) were thermally evaporated through a shadow mask as the top cathode, which defined the device area as 0.06 cm². The OSCs based on PTB7-Th:PC₇₁BM were fabricated by using the inverted structure of ITO/ZnO/PTB7-Th:PC₇₁BM/HTL/Ag as shown in Fig. 3a, and were tested as shown in Table 1.

Table 1. Performance summary of OSCs with a structure of ITO/ZnO/PTB7-Th:PC₇₁BM/HTL/Ag.

HTL	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE _{ave} [PCE _{max}] (%)
L-GO (2.1 nm)	18.39 ± 0.26	0.78 ± 0.01	0.614 ± 0.009	8.80 ± 0.15 [9.01]
L-GO:NiO _x (17 nm)	19.04 ± 0.48	0.78 ± 0.01	0.628 ± 0.009	9.33 ± 0.25 [9.78]
L-GO:NiO _x (21 nm)	19.16 ± 0.33	0.78 ± 0.00	0.651 ± 0.006	9.73 ± 0.08 [9.93]
L-GO:NiO _x (27 nm)	18.34 ± 0.31	0.78 ± 0.01	0.654 ± 0.015	9.36 ± 0.37 [9.77]
L-GO:NiO _x (32 nm)	18.22 ± 0.24	0.78 ± 0.01	0.640 ± 0.022	9.10 ± 0.15 [9.27]
NiO _x (21 nm)	17.63 ± 0.17	0.57 ± 0.02	0.546 ± 0.016	5.52 ± 0.32 [5.71]

5 EXAMPLE 3

The device fabrication process is the same with that in EXAMPLE 2 with replacing the PTB7-Th:PC₇₁BM by PBDB-T:ITIC (10:10 mg mL⁻¹ in chlorobenzene, with addition of 0.5% DIO). The polymer donor PBDB-T and non-fullerene acceptor ITIC were purchased from Solarmer Co., Ltd. DIO was removed by annealing the active layer at 160 °C for 30 min. The OSCs based on PBDB-T:ITIC were fabricated by using the inverted structure of ITO/ZnO/PBDB-T:ITIC/HTL/Ag as shown in Fig. 3b, and were tested as shown in Table 2.

Table 2. Performance summary of OSCs with a structure of ITO/ZnO/PBDB-T:ITIC/HTL/Ag.

HTL	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE _{ave} [PCE _{max}] (%)
GO	16.98 ± 0.31	0.88 ± 0.01	0.621 ± 0.014	9.28 ± 0.22 [9.68]
L-GO:NiO _x	17.59 ± 0.22	0.88 ± 0.01	0.690 ± 0.016	10.68 ± 0.29 [11.12]

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EXAMPLE 4

The device fabrication process is the same with that in EXAMPLE 2 with replacing the PTB7-Th:PC₇₁BM by PBDB-T:IT-M (10:10 mg mL⁻¹ in chlorobenzene, with addition of 1% DIO). The polymer donor PBDB-T and non-fullerene acceptor IT-M were synthesized in Institute of Chemistry, Chinese Academy of Sciences. DIO was removed by annealing the active layer at 160 °C for 30 min. The OSCs based on PBDB-T:IT-M were fabricated by using the inverted structure of ITO/ZnO/PBDB-T:IT-M/HTL/Ag as shown in Fig. 3c, and were tested as shown in Table 3.

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Table 3 Performance summary of the OSC devices with a structure of ITO/ZnO/PBDB-T:IT-M/HTL/Ag.

HTL	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE _{ave} [PCE _{max}] (%)
GO	17.07 ± 0.43	0.91 ± 0.01	0.644 ± 0.010	10.01 ± 0.21 [10.28]
L-GO:NiO _x	17.81 ± 0.33	0.91 ± 0.01	0.706 ± 0.019	11.45 ± 0.44 [12.13]

FIG. 4a shows representative J - V curves of L-GO and L-GO:NiO_x nanocomposite based inverted OSCs and the performances are summarized in Example 1. As discussed above, the L-GO based devices shows an optimized average PCE of 8.80% with an average J_{SC} of 18.39 mA cm⁻², an average V_{OC} of 0.78 V and an average FF of 0.614. The NiO_x based devices show poor V_{OC} due to mismatching WF values. After the decoration of NiO_x on L-GO, the average PCE significantly increases to 9.73% (with best PCE of 9.93%) with an increased average J_{SC} of 19.16 mA cm⁻² and an increased FF of 0.651. The increase of J_{SC} is ascribed to the enhanced conductivity of L-GO:NiO_x nanocomposite compared with bare GO.

FIG. 4b illustrates that the thickness of GO can be significantly increased by using L-GO:NiO_x nanocomposites (formed from strategically adopting the hydrogen bonds between GO NSs and NiO_x NPs). When GO is used as the HTL, the thickness requirement is strict and any small alteration of thickness would degrade the performance obviously. For example, when the thickness increases from 2.1 nm to 3.4 nm by only a 1.3 nm increment, the average PCE degrades to 4.23%, less than half of the optimized average PCE (8.80%). However, replacing L-GO with L-GO:NiO_x nanocomposite will significantly diminish the thickness-dependent sensitivity. When thickness of L-GO:NiO_x nanocomposite is 21 nm, the devices show an optimized average PCE of 9.73%. When the thickness is increased to 32 nm (over 15 times of the bare L-GO thickness), the average PCE is 9.10% which is still better than the pristine L-GO case.

FIG. 5a and 5b illustrate that our newly developed L-GO:NiO_x nanocomposite HTL can also serve as efficient HTL for non-fullerene OSCs. By using the combination of the polymer donor named poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)-co-(1,3-di(5-thiophene-2-yl)-5,7-bis(2-ethylhexyl)-benzo[1,2-c:4,5-c']dithiophene-4,8-dione)] (PBDB-T) and the non-fullerene acceptor 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-

indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d':2',3'-d']-s-indaceno[1,2-b:5,6-b']-dithiophene (ITIC), the average PCE of L-GO:NiO_x nanocomposite based devices can reach at 10.68% (with best PCE of 11.12%). By using the combination of PBDB-T and methyl groups modulated ITIC (IT-M), the averaged PCE of GO:NiO_x nanocomposite based devices can reach at 11.45% (with best PCE of 12.13%). The weak energy loss in the charge transfer process of PBDB-T:IT-M results a higher V_{OC} (~ 0.91 V) compared with PBDB-T:IT-M based devices. The optimized photovoltaic parameters and representative $J-V$ characteristics are summarized in Example 2 and 3, respectively. In PBDB-T:ITIC system, the L-GO:NiO_x nanocomposite OSCs show a higher average PCE of 10.68% compared with 9.28% of GO OSCs. The 15.0% improvement in PCE is mainly attributed to increasing of both J_{SC} and FF. Similarly, in PBDB-T:IT-M system, the average PCE of GO:NiO_x nanocomposite based devices shows a 14.4% improvement compared with GO based devices (from 10.01% to 11.45%). The improvement of J_{SC} (from 17.07 mA cm⁻² to 17.81 mA cm⁻²) and FF (from 0.644 to 0.706) contributes to this PCE improvement.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

CLAIMS

What is claimed is:

1. A method of preparing a GO:NiO_x nanocomposite based film for an optoelectronic device, the method comprising:

preparing a graphene oxide GO solution in a first alcohol solvent by oxidization of graphite;

preparing a nickel oxide NiO_x solution in a second alcohol solvent by a solvothermal method;

conducting decoration of NiO_x nanoparticles onto GO nanosheet structure NSs by blending the GO solution and the NiO_x solution to obtain a GO:NiO_x nanocomposite solution; and

forming the GO:NiO_x nanocomposite film by using the GO:NiO_x nanocomposite solution,

where x is a positive number.

2. The method of claim 1,

wherein the GO is a carbon based material binding with functional groups; or

wherein the GO is a carbon based material binding with functional groups comprising one or more of hydroxyl groups, carboxyl groups, epoxy groups, amino groups, and sulfonic acid groups; or

wherein the second alcohol solvent of the solvothermal method includes water, ethanol, methanol, isopropanol, ethylene glycol, glycerin, or a mixture of any thereof; or

wherein the NiO_x is a composite comprising or consisting of NiO and other species selected from a group consisting of Ni_2O_3 , nickel oxide hydroxide, and nickel hydroxide; or

wherein the NiO_x is non-stoichiometric; or

wherein the NiO_x possesses a typical p-type semiconductor property; or

wherein the first alcohol solvent for the GO solution comprises alkanol having 1-10 carbon atoms, or methanol, ethanol, propanol, butanol, or a mixture of any thereof; or

wherein the second alcohol solvent for the NiO_x solution comprises alkanol having 1-10 carbon atoms, or methanol, ethanol, propanol, butanol, or a mixture of any thereof; or

wherein forming the GO:NiO_x nanocomposite film further includes obtaining a GO:NiO_x nanocomposite based hole transport layer by using one or more of casting, spin-coating, doctor blading, screen printing, ink jet printing, pad printing, and roll-to-roll technique; or

wherein the optoelectronic device is an device selected from a group consisting of solar cells, phototransistors, photomultipliers, photoresistors, light-emitting diodes, laser diodes and sensors.

3. An optoelectronic device, comprising:

a first electrode layer;

an organic active layer disposed on the first electrode layer;

5 a hole transport layer disposed on the organic active layer and including a GO:NiO_x nanocomposite; and

a second electrode layer disposed on the hole transport layer,

where x is a positive number.

10 4. The optoelectronic device of claim 3, wherein the GO:NiO_x nanocomposite includes nickel oxide nanoparticles NiO_x NPs and a graphene oxide nanosheet structure GO NSs.

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5. The optoelectronic device of claim 4, wherein the GO NSs has a degree of oxidation of which C-C peak is higher than C-O peak.

6. The optoelectronic device of claim 5, wherein the NiO_x NPs and the GO NSs are coupled with each other by hydrogen bonds.

7. The optoelectronic device of claim 6,
wherein a thickness of the hole transport layer is in a range of 8 nm to 64nm, 12 nm to 48nm, or 17 nm to 32 nm; or
wherein the first electrode layer includes an Indium Tin Oxide ITO layer and a Zinc Oxide layer.

8. The optoelectronic device of claim 7, wherein the second electrode layer includes an Ag anode electrode.

9. The optoelectronic device of claim 8, further comprising a glass layer disposed on a bottom surface of the ITO layer.

10. The optoelectronic device of claim 9, wherein the organic active layer comprises at least one of PTB7-Th:PC₇₁BM, PBDB-T:ITIC/HTL, and PBDB-T:ITIC.

FIG. 1a

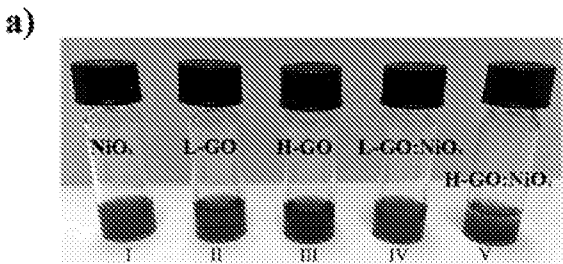


FIG. 1b

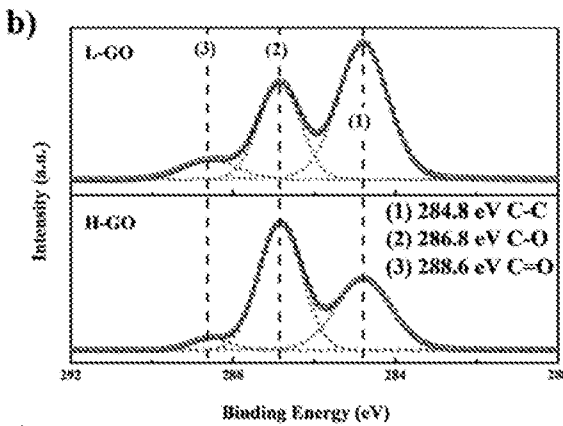


FIG. 1c

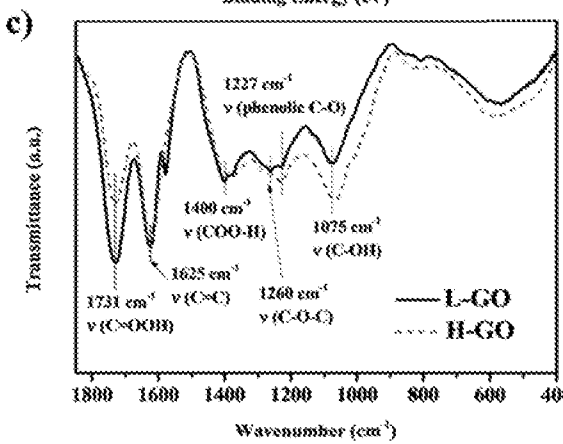


FIG. 2a

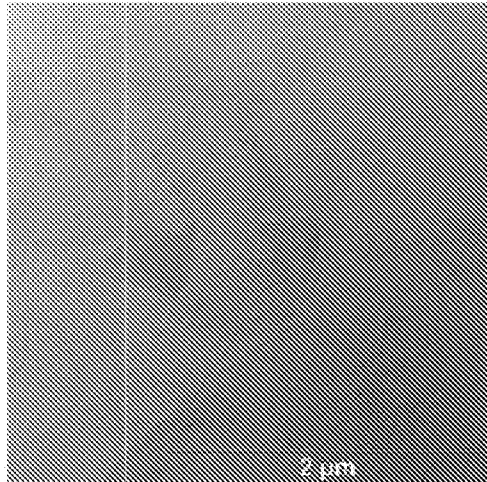
a) L-GO nanosheets

FIG. 2b

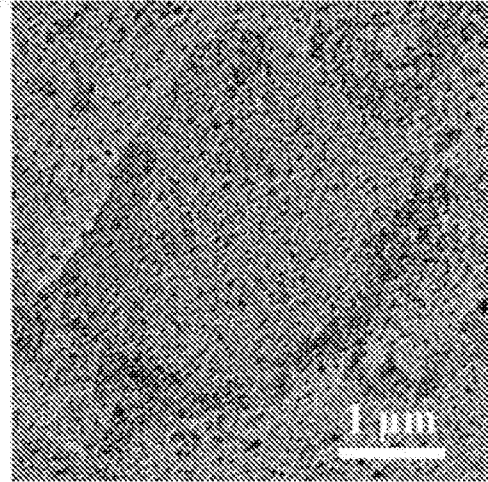
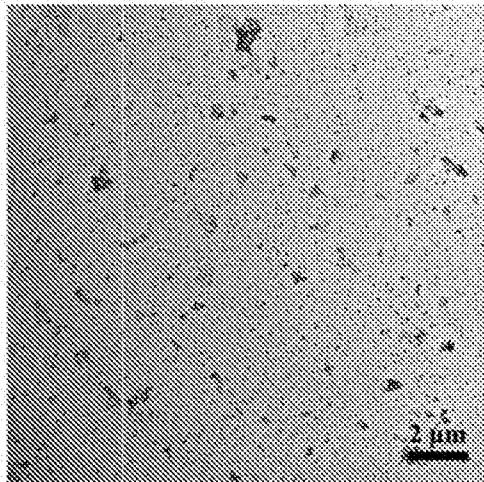
b) NiO_x decorated L-GO nanosheets**c)** H-GO:NiO_x aggregates

FIG. 2c

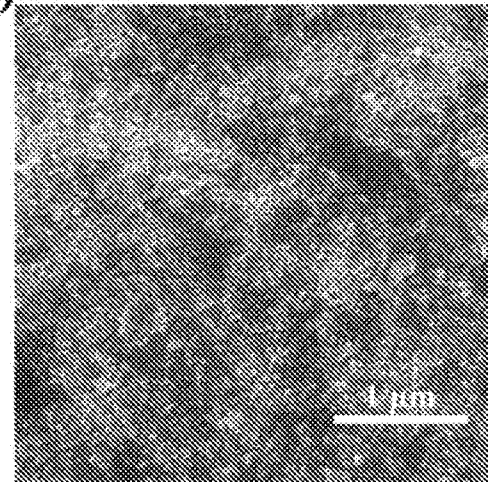
d) L-GO:NiO_x film

FIG. 2d

FIG. 3a

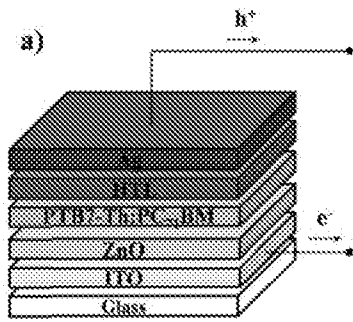


FIG. 3b

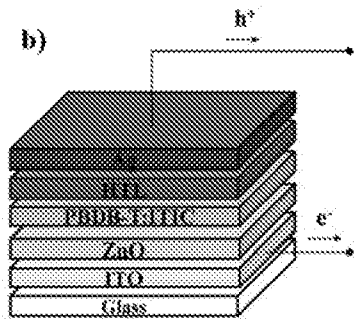


FIG. 3c

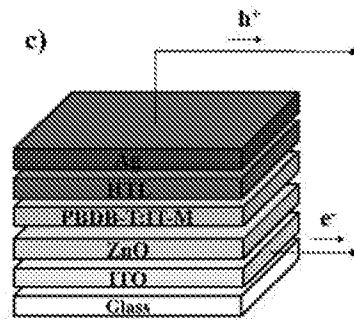


FIG. 4a

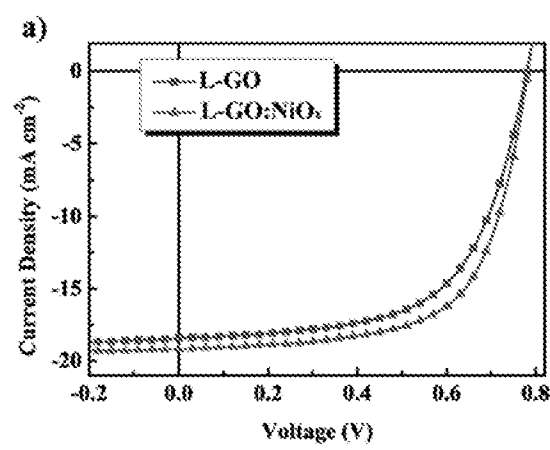


FIG. 4b

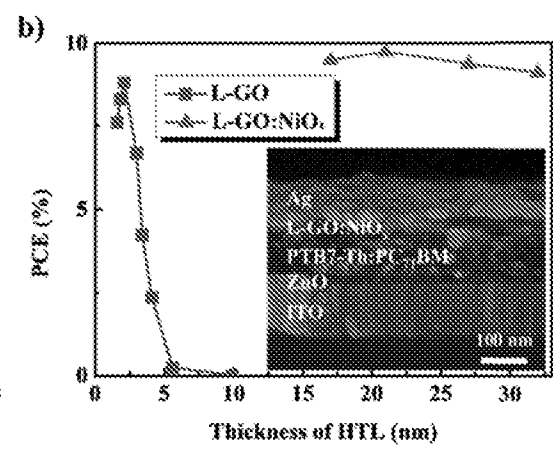


FIG. 5a

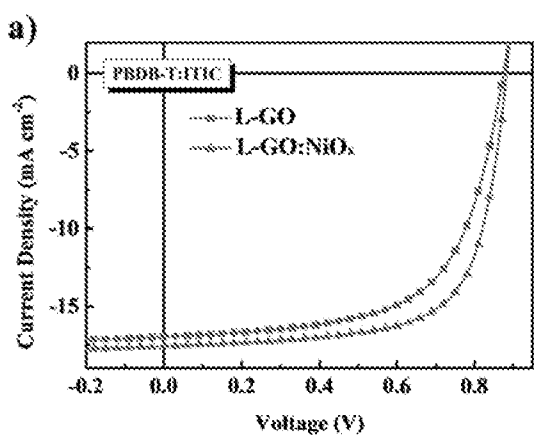
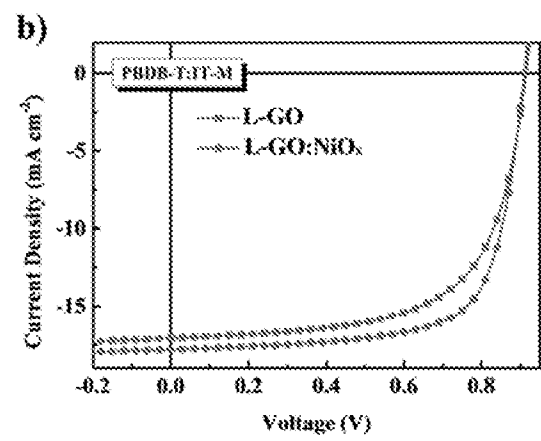


FIG. 5b



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2017/110786

A. CLASSIFICATION OF SUBJECT MATTER		
H01G 11/24(2013.01)i; H01G 11/32(2013.01)i; H01L 51/00(2006.01)i; H01G 11/46(2013.01)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) H01G11/-,H01L51/-		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CNABS;CNTXT;DWPI; graphene oxide, GO, NiO,Ni2O3 nickel oxide,nickel hydroxide, nickel oxide hydroxide,NiOH,nano+, alcohol,+anol,HTL,optoelectr+,hole transport layer,cell,electrode		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 106486291 A (UNIV. ZHEJIANG) 08 March 2017 (2017-03-08) paragraphs [0003] -[0011]	1-2
A	CN 103855307 A (NAT CENT NANOSCIENCE & TECHNOLOGY CHINA) 11 June 2014 (2014-06-11) paragraphs [0006] -[0014]	3-10
A	CN 104801307 A (SHANGHAI ADVANCED RES. INST. CHINESE ACAD.ET AL.) 29 July 2015 (2015-07-29) paragraphs [0005] -[0022]	1-10
A	CN 106229503 A (UNIV. ANHUI NORMAL) 14 December 2016 (2016-12-14) paragraphs [0008] -[0021]	1-10
A	US 2014346408 A1 (ELECTRONICS & TELECOM. RES. INST.) 27 November 2014 (2014-11-27) Abstract, paragraphs [0035] -[0041]and fig.1	1-10
A	US 2011292570 A1 (MAX-PLANCK-GES FOERDERUNG WISSENSCHAFTEN. ET AL.) 01 December 2011 (2011-12-01) paragraphs [0033] -[0062]	1-10
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 10 July 2018		Date of mailing of the international search report 26 July 2018
Name and mailing address of the ISA/CN STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA 6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China		Authorized officer FENG,Xue
Facsimile No. (86-10)62019451		Telephone No. (86-10)53962909

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2017/110786

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	106486291	A	08 March 2017	None			
CN	103855307	A	11 June 2014	None			
CN	104801307	A	29 July 2015	None			
CN	106229503	A	14 December 2016	None			
US	2014346408	A1	27 November 2014	KR	20140137574	A	03 December 2014
US	2011292570	A1	01 December 2011	US	8611070	B2	17 December 2013
				TW	201206712	A	16 February 2012
				TW	I562898	B	21 December 2016