(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 January 2015 (15.01.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/006473 A1

(51) International Patent Classification:
H01L 31/00 (2006.01) *H01L 51/00* (2006.01)
C08K 3/10 (2006.01) *C08K 3/04* (2006.01)

(21) International Application Number:
PCT/US2014/045992

(22) International Filing Date:
9 July 2014 (09.07.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/844,223 9 July 2013 (09.07.2013) US

(71) Applicant: **WAKE FOREST UNIVERSITY** [US/US]; 391 Technology Way, Suite 199, Winston-Salem, NC 27101 (US).

(72) Inventor: **CARROLL, David**; 5173 Laurel View Drive, Winston-Salem, NC 27104 (US).

(74) Agents: **WIMBISH, J., Clinton** et al.; Smith Moore Leatherwood LLP, 101 North Tryon Street, Suite 1300, Charlotte, NC 28246 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

[Continued on next page]

(54) Title: PHASE SEPARATED COMPOSITE LAYERS AND APPLICATIONS THEREOF

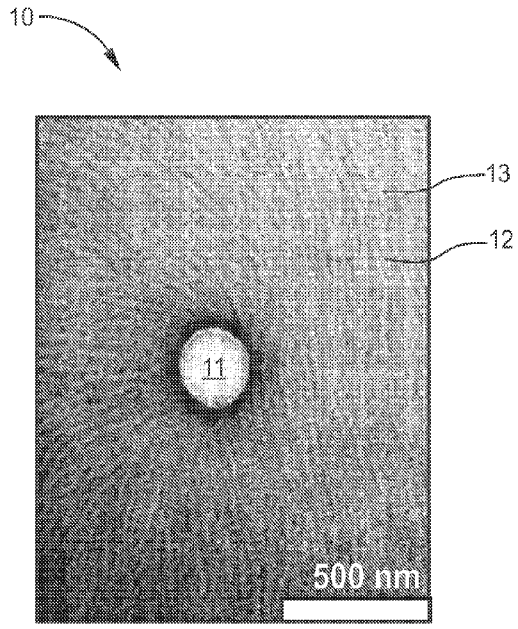


FIGURE 1

(57) Abstract: In one aspect, composite layers are described herein demonstrating phase-separated architectures which, in some embodiments, can mitigate performance disadvantages of prior organic layers of optoelectronic devices. A composite organic layer described herein comprises nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils radiating from the nanocluster nodes.

WO 2015/006473 A1

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

PHASE SEPARATED COMPOSITE LAYERS AND APPLICATIONS THEREOF

RELATED APPLICATION DATA

The present application claims priority pursuant to 35 U.S.C.§ 119(e) to United States Provisional Patent Application Serial Number 61/844,223 filed July 9, 2013 which is incorporated herein by reference in its entirety.

FIELD

The present invention relates to nanocomposite films and, in particular, to nanocomposite films demonstrating phase-separated architectures.

BACKGROUND

Organic thin films continue to be heavily investigated for application in a variety of fields including organic light emitting devices (OLEDs), photovoltaic devices and organic photodetectors. Materials used to construct organic optoelectronic devices are relatively inexpensive in comparison to their inorganic counterparts, thereby providing cost advantages over optoelectronic devices manufactured with inorganic materials. Moreover, organic materials provide desirable physical properties, such as mechanical flexibility, permitting device constructions not attainable with rigid crystalline materials.

Organic thin films, however, suffer from performance disadvantages in comparison to crystalline inorganic materials. For example, some organic photovoltaic devices demonstrate efficiencies of 1% or less. Low efficiencies often displayed in organic photovoltaic devices result from a severe scale mismatch between exciton diffusion length (L_D) and organic layer thickness. Efficient absorption of visible electromagnetic radiation generally requires organic film thickness of 500 nm or more. This thickness greatly exceeds exciton diffusion length which is typically about 50 nm, often resulting in exciton recombination. Given the disparity in performance, organic photovoltaic devices have encountered significant difficulty in challenging traditional inorganic devices.

SUMMARY

In one aspect, composite layers are described herein demonstrating phase-separated architectures which, in some embodiments, can mitigate performance disadvantages of prior

organic layers of optoelectronic devices. A composite organic layer described herein comprises nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils around or radiating from the nanocluster nodes. In some embodiments, for example, the carbon nanofibrils radiate a distance of at least 500 nm or at least 1 μm from the nanocluster nodes providing enhanced pathways for exciton dissociation and transport.

In another aspect, photovoltaic apparatus are described herein. A photovoltaic apparatus comprises first and second electrodes and a photosensitive layer positioned between the first and second electrodes, the photosensitive layer comprising nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils around or radiating from the nanocluster nodes.

In a further aspect, methods of producing composite layers are described herein. A method of producing a composite layer comprises mixing inorganic nanoparticles, conjugated polymeric phase and carbon nanoparticles in an organic solvent, aggregating the inorganic nanoparticles in the conjugated polymeric phase to provide nanocluster nodes and phase separating the carbon nanoparticles from the conjugated polymeric phase as lamellar structures of carbon nanofibrils around or radiating from the nanocluster nodes during removal of the organic solvent.

These and other embodiments are further described in the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a transmission electron microscopy (TEM) image of a section of a composite layer according to one embodiment described herein.

Figure 2 is a sectional TEM image of a comparative layer formed of conjugated polymer and carbon nanoparticles not employing nanocluster nodes.

Figures 3(a)-(d) are sectional TEM images of composite layers according to some embodiments described herein.

Figures 4(a)-(c) are sectional TEM images of composite layers according to some embodiments described herein.

Figure 5 is a histogram detailing nanofibril width in response to inorganic nanoparticle loading in composite layers according to some embodiments described herein.

Figures 6(a)-(d) are sectional TEM images of composite layers according to some embodiments described herein.

Figure 7 is a histogram detailing nanofibril width in response to organic solvent removal rate in composite layers according to some embodiments described herein.

Figures 8(a)-(b) are current density plots for photovoltaic apparatus employing various composite layers described herein relative to a comparative photovoltaic apparatus.

Figures 8(c)-(d) illustrate EQE and IQE of photovoltaic apparatus employing various composite layers described herein relative to a comparative photovoltaic apparatus.

Figures 9(a)-(b) are sectional TEM images of composite layers according to some embodiments described herein.

Figure 9(c) is a sectional TEM images of a composite layer wherein inorganic nanoparticles are not present.

DETAILED DESCRIPTION

Embodiments described herein can be understood more readily by reference to the following detailed description and examples and their previous and following descriptions. Elements, apparatus and methods described herein, however, are not limited to the specific embodiments presented in the detailed description and examples. It should be recognized that these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations will be readily apparent to those of skill in the art without departing from the spirit and scope of the invention.

I. Composite Layers

Composite layers are described herein demonstrating phase-separated architectures. Such phase-separated architectures, in some embodiments, can mitigate performance disadvantages of prior organic layers of optoelectronic devices. For example, phase-separated architectures of composite layers described herein can provide enhanced pathways for exciton separation and collection in photovoltaic apparatus, thereby realizing enhanced efficiencies.

A composite organic layer described herein comprises nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils radiating from the nanocluster nodes. Figure 1 is a TEM image of a section of a composite layer according to one embodiment described herein. As illustrated in Figure 1, the composite layer section (10) comprises a nanoparticle cluster (11) and lamellar structures of carbon nanofibrils (12) radiating from the nanoparticle cluster (11). In the embodiment of Figure 1, the carbon nanofibrils (12) are formed of fullerene conjugate 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)C_{61} (PCBM) phase separated from the conjugated polymeric host (13) of poly[4,4-didodecyl pentaleno[1,2-b]dithiophene-co-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione. The carbon nanofibrils (12) extend outward from the nanocluster (11) distances well in excess of 500 nm. Further, the conjugated polymeric host (13) can also form nanofibrils alternating with the carbon nanofibrils (12) in the lamellar structure.

Turning now to specific components, a composite layer described herein comprises a conjugated polymeric host. The conjugated polymeric host can be formed of any conjugated polymer operable to participate in the formation of lamellar structures described herein. In some embodiments, for example, suitable conjugated polymer demonstrates a surface energy less than nanoparticles forming the nanoparticle cluster. Further, the conjugated polymer host and carbon nanoparticles demonstrate a difference in surface energies sufficient to induce phase separation in the presence of the nanocluster nodes. For example, in some embodiments, the conjugated polymer host exhibits a surface energy less than the carbon nanoparticles. As discussed further herein, conjugated polymer surface energies can be altered and/or tailored by the presence of hydrophobic or hydrophilic side chains of the conjugated polymer.

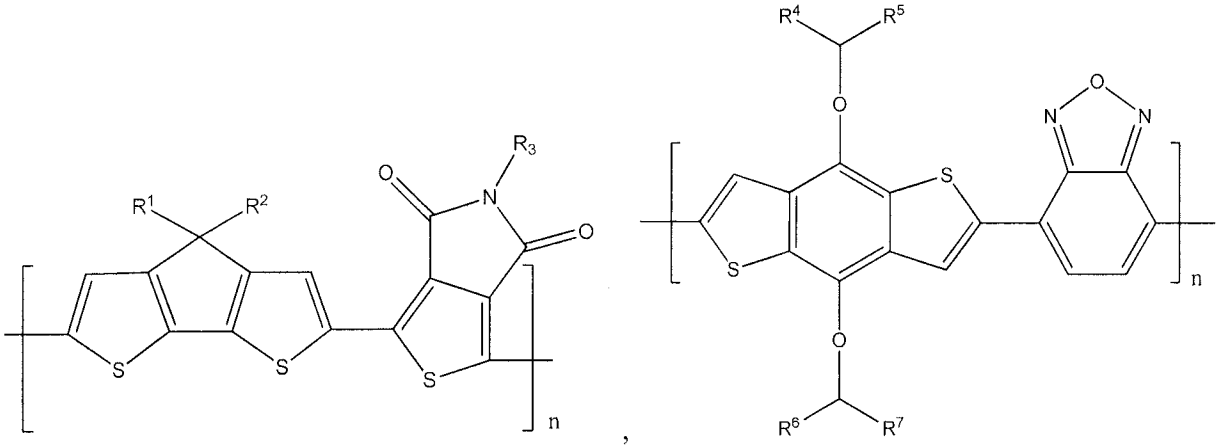
In some embodiments, the conjugated polymeric host can comprise polythiophenes, polythiophene derivatives or mixtures thereof. Polythiophene derivatives can include mono- or di-thiophenes coupled with thienopyrrole moieties, benzoxadiazole moieties or benzothiadiazole moieties. Further, polythiophenes can be provided hydrocarbon and/or alkoxide side chains of suitable length for tailoring surface energy of the polymer for phase separation and/or interaction with carbon nanoparticles forming the carbon nanofibrils. Conjugated polymer side chains can be linear, branched or cyclic and generally formed of at least 10 carbon atoms. In some embodiments, hydrocarbon side chains incorporate 12-20 carbon atoms. Table I provides several

polythiophenes that may be used in the conjugated polymeric phase according to some embodiments herein.

Table I – Polythiophenes of Conjugated Polymeric Phase

poly[4,4-didodecyl pentaleno[1,2-b]dithiophene-co-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione
poly[4,8-bis(1-pentylhexyloxy)-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl-alt-2,1,3-benzoxadiazole-4,7-diyl
poly(3-cyclohexyl-4-methylthiophene)
poly(3-cyclohexylthiophene-2,5-diyl)
poly(3-decyloxythiophene-2,5-diyl)
poly(3-octylthiophene-2,5-diyl-*co*-3-decyloxythiophene-2,5-diyl)
poly(3-decylthiophene-2,5-diyl)
poly[(2,5-didecyloxy-1,4-phenylene)-alt-(2,5-thienylene)]

Further, polythiophene of the conjugated polymeric phase can have a structure selected from Formulas I and II below.



(I) (II)

wherein R^1, R^2 and R^3 are selected from the group consisting of C_8-C_{20} alkyl, C_8-C_{20} alkenyl, cycloalkyl, aryl, heteroaryl, alkyl-aryl, alkyl-heteroaryl and alkyl-cycloalkyl and R^4, R^5, R^6 and R^7 are selected from the group consisting of hydrogen, C_4-C_{20} alkyl, C_4-C_{20} alkenyl, cycloalkyl, aryl, heteroaryl, alkyl-aryl, alkyl-heteroaryl and alkyl-cycloalkyl.

The conjugated polymeric host can also be formed of other conjugated or semiconducting polymers demonstrating sufficient difference in surface energy with the carbon nanoparticles or other electrically conductive nanoparticles to induce phase separation in the presence of the nanocluster nodes. For example, the polymeric host may be formed of semiconducting polymers including phenylene vinylenes, such as poly(phenylene vinylene) and poly(*p*-phenylene

vinylene) (PPV), and derivatives thereof. In some embodiments, semiconducting polymers can comprise poly fluorenes, naphthalenes, and derivatives thereof. In some embodiments, semiconducting polymers comprise poly(2-vinylpyridine) (P2VP), polyamides, poly(N-vinylcarbazole) (PVCZ), polypyrrole (PPy), and polyaniline (PAn). In some embodiments, a semiconducting polymer comprises poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT).

As described herein, the conjugated polymeric host can exhibit a surface energy lower than the carbon nanoparticles, resulting in phase separation with the carbon nanoparticles in the presence of the nanocluster nodes. Hydrophobic or hydrophilic side chains can be used to modify the surface energy of the conjugated polymeric host. For example, branched alkyl or alkenyl side chains can be employed to lower the polar component of the conjugated polymer surface energy. In some embodiments, suitable conjugated polymeric hosts have a polar component contributing from 1% to 9% of the total polymer surface energy. In some embodiments, the polar component of suitable conjugated polymer contributes 1-5% of the total polymer surface energy.

The conjugated polymeric host can be present in the composite layer in any amount not inconsistent with the objectives of the present invention. The conjugated polymeric host, for example, can be present in the composite layer in an amount of 20-80 wt.%. In some embodiments, the conjugated polymeric host is present in an amount of 30-70 wt.% or 40-60 wt.%.

As described herein, nanocluster nodes are disposed in the conjugated polymeric host. Nanocluster nodes can be formed of a material having a higher surface energy than the conjugated polymeric host leading to clustering of the material when contacted with the polymeric host. Nanocluster nodes, for example, can be formed of inorganic nanoparticles. Higher surface energy of the inorganic nanoparticles induces aggregation of the nanopartilces into nanoclusters in the conjugated polymeric host. Inorganic nanoparticles can comprise metal nanoparticles, metal oxide nanoparticles, semiconductor nanoparticles or mixtures thereof. In some embodiments, metal nanoparticles are transition metal nanoparticles. Additionally, metal oxide nanoparticles can comprise transition metal oxides. Transition metal oxides can include oxides of metallic elements of Groups IIB-VIB of the Periodic Table. Metal oxides can also

include alkaline earth metal oxides. In some embodiments, for example, metal oxide nanoparticles are ZnO and TiO_2.

As with the conjugated polymeric host, the inorganic nanoparticles exhibit a surface energy suitable for forming the phase separated compositions described herein. In some embodiments, inorganic nanoparticles with exceedingly high surface energy, such as silver oxide nanoparticles, preclude formation of phase separated lamella structures. However, lower surface energy nanoparticles including ZnO, TiO_2 and similar species, are suitable for phase separated compositions described herein.

Nanoparticles forming nanocluster nodes in the conjugated polymeric host can have any size and shape not inconsistent with the objectives of the present invention. In some embodiments, nanoparticles of a nanocluster have an average size ranging from 5-30 nm or 10-20 nm. Further, nanocluster nodes in the conjugated polymeric host can have average diameter of 100-500 nm. Moreover, nanocluster nodes can demonstrate a variety of geometries including spherical, elliptical or irregular shape. Nanocluster nodes can generally be present in the conjugated polymeric host in an amount of 0.1-10 wt.%. In some embodiments, nanocluster nodes are present in the conjugated polymeric host in an amount of 0.5-5 wt.%.

In addition to nanocluster nodes, carbon nanoparticles are also disposed in the polymeric host, wherein the carbon nanoparticles are phase separated from the conjugated polymeric host forming carbon nanofibrils radiating from the nanocluster nodes. In some embodiments, suitable carbon nanoparticles have surface energy greater than the conjugated polymeric host. Further, the carbon nanoparticles and conjugated polymeric host demonstrate a difference in surface energies sufficient to induce phase separation in the presence of the nanocluster nodes.

Carbon nanoparticles, according to some embodiments, comprise fullerenes and fullerene derivatives. As shown further herein, 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)C_{61} (PCBM) can serve as carbon nanoparticles forming the phase separated nanofibrils. Other fullerene derivatives can include higher order fullerenes (C_{70} and higher) and endometallo-fullerenes (fullerenes having at least one metal atom therein). Carbon nanoparticles can also comprise single-walled carbon nanotubes (SWNT), multi-walled carbon nanotubes (MWNT) or mixtures thereof. Surfaces of carbon nanoparticles can be modified with one or more side chains for tailoring surface energy of the nanoparticles for phase separation and/or interaction with the conjugated polymeric phase.

Carbon nanoparticles are present in the conjugated polymeric host in an amount sufficient to form the phase separated carbon nanofibrils. In some embodiments, carbon nanoparticles are present in the conjugated polymeric host in an amount of 20 to 80 wt.%. Carbon nanoparticles can be present in the conjugated polymeric host in an amount of 30 to 70 wt.% or 35 to 65 wt.%. Further, carbon nanoparticles can be present in the conjugated polymeric host in an amount of 50 to 66 wt.%.

As described herein, the carbon nanoparticles phase separate from the conjugated polymeric phase in the presence of the nanoclusters forming lamellar structures of carbon nanofibrils with the conjugated polymeric phase. The nanofibrils can radiate from the nanoclusters nodes a considerable distance or length into the conjugated polymeric host. In some embodiments, nanofibrils radiate a distance of at least 1 μm from one or more nanocluster nodes. Carbon nanofibrils, in some embodiments, radiate a distance from a nanocluster node a distance provided in Table II.

Table II – Distance or Length of Carbon Nanofibrils (μm)

≥ 1.5
≥ 2
≥ 3
≥ 4
0.5-5
1-5
0.5-10
1-7

In addition to length, phase separated carbon nanofibrils can demonstrate various widths. For example, carbon nanofibrils can have widths ranging from 5 to 30 nm. In some embodiments, carbon nanofibrils have widths of 10 to 20 nm or 10 to 15 nm. As discussed further herein, width of carbon nanofibrils can be controlled by one or more composite layer processing conditions.

In some embodiments, carbon nanoparticles can be replaced with one or more species of inorganic nanoparticles to form electrically conductive or semiconductive inorganic nanofibrils radiating from nanocluster nodes in the conjugated polymeric host. For example, inorganic nanoparticles demonstrating differences in surface energy with the conjugated polymeric host sufficient to induce phase separation into electrically conductive nanofibrils in the presence of

the nanocluster nodes can be used. In some embodiments such nanoparticles comprise semiconducting nanoparticles, including III/V and/or II/VI semiconductor nanoparticles or quantum dots. Further, inorganic nanoparticles can comprise metal nanoparticles, including transition metal nanoparticles.

II. Photovoltaic Apparatus

In another aspect, photovoltaic apparatus are described herein. A photovoltaic apparatus comprises first and second electrodes and a photosensitive layer positioned between the first and second electrodes, the photosensitive layer comprising nanocluster nodes and carbon nanoparticles disposed in a conjugated polymer host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils radiating from the nanocluster nodes.

Turning now to specific components, photovoltaic apparatus comprise first and second electrodes. First and second electrodes can be formed of any electrically conductive material not inconsistent with the objectives of the present invention. First and second electrodes, for example, can be formed of metal or alloy, including aluminum or transition metals or alloys. In some embodiments, one or both of the first and second electrodes are radiation transmissive. A radiation transmissive electrode can be formed of a radiation transmissive conducting oxide. Radiation transmissive conducting oxides, in some embodiments, can comprise indium tin oxide (ITO), gallium indium tin oxide (GITO) or zinc indium tin oxide (ZITO). In another embodiment, a radiation transmissive electrode can comprise a radiation transmissive polymeric material such as polyaniline (PANI) and its chemical relatives. In some embodiments, 3,4-polyethylenedioxythiophene (PEDOT) can be a suitable radiation transmissive polymeric material for the first and/or second electrode. In other embodiments, a radiation transmissive electrode can comprise a metal or carbon nanotube layer having a thickness operable to at least partially pass visible electromagnetic radiation.

In addition to first and second electrodes, photovoltaic apparatus described herein comprise a photosensitive layer comprising nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils radiating from the nanocluster nodes. Components of the photosensitive layer, including the

nanocluster nodes, conjugated polymeric host and carbon nanoparticles, can have compositional parameters and/or properties described for the same in Section I hereinabove. Further, carbon nanofibrils formed by phase separation of the carbon nanoparticles from the conjugated polymeric host can have any properties described in Section I.

Conjugated polymer host of the photosensitive layer can demonstrate various electromagnetic radiation absorption profiles. Conjugated polymer, for example, can be selected to have absorption maxima in the visible region of the electromagnetic spectrum. In some embodiments, conjugated polymer can also absorb wavelengths in the ultraviolet and/or infrared regions of the spectrum. Excitons are generated in the photosensitive layer by absorption of radiation by the conjugated polymeric phase. Further, exciton dissociation can be precipitated at heterojunctions formed between the conjugated polymeric host and carbon nanofibrils of the photosensitive layer. The conjugated polymeric host, for example, serves as a donor material and the carbon nanofibrils serve as the acceptor material, thereby forming heterojunctions operable to for the separation of excitons into holes and electrons.

Given their structure over large distances, carbon nanofibrils of the photosensitive layer facilitate charge transport, thereby enhancing charge collection and efficiency of the photovoltaic apparatus. Further, the photosensitive layer can be made thicker for enhanced absorption characteristics due to the extended structure of the carbon nanofibrils. For example, the photosensitive layer can have a thickness of 200 nm to 1 μm. In some embodiments, the photosensitive organic layer has a thickness in excess of 1 μm.

Photovoltaic apparatus described herein can further comprise additional layers such as one or more exciton blocking layers. An exciton blocking layer (EBL) can act to confine photogenerated excitons to the region near the dissociating interface and prevent parasitic exciton quenching at a photosensitive layer/electrode interface. In addition to limiting the path over which excitons may diffuse, an EBL can additionally act as a diffusion barrier to substances introduced during deposition of the electrodes. In some embodiments, an EBL can have a sufficient thickness to fill pin holes or shorting defects which could otherwise render an organic photovoltaic device inoperable.

An EBL can comprise a polymeric material such as polyethylenedioxythiophene-polystyrenesulfonate (PEDOT:PSS). Alternatively, an EBL can comprise a composite material. For example, an EBL can comprise carbon nanoparticles dispersed in 3,4-

polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS). In another embodiment, an EBL comprises carbon nanoparticles dispersed in poly(vinylidene chloride) and/or copolymers thereof. In further embodiments, EBLs can comprise any polymer having work function energy operable to permit the transport of holes while impeding the passage of electrons. In some embodiments, an EBL may be disposed between the anode and photosensitive layer of the photovoltaic apparatus.

Additionally, one or more layers of metal oxide can be introduced into the photovoltaic architecture. For example, a layer of Li_2O and/or MoO_3 can be positioned between the photosensitive layer and the cathode. Alternatively, a layer of LiF can be positioned between the photosensitive layer and the cathode.

Electrodes of the photovoltaic apparatus, in some embodiments, can serve as support(s) for the photosensitive layer. Alternatively, the photovoltaic construction can be supported by an external substrate. Suitable external substrates can be planar or curved. In some embodiments, an external supporting substrate comprises a planar sheet of glass or plastic. Moreover, an external substrate can have a cylindrical geometry. A cylindrical substrate can be a tube or fiber, such as an optical fiber. In embodiments wherein the support is an optical fiber, electromagnetic radiation can be delivered to the photosensitive layer from the interior of the fiber and/or sides of the fiber. In tubular constructions, various liquids can be flowed through the tube interior for collection of thermal energy. Optical fiber and tubular substrates are described in greater detail in United States Patent Application Serial Numbers 12/298,942 and 13/880,310 respectively.

As described herein, carbon nanofibrils can provide enhanced pathways for exciton separation and collection in photovoltaic apparatus, thereby realizing enhanced efficiencies. For example, a photovoltaic apparatus described herein, in some embodiments, can demonstrate external quantum efficiency (EQE) greater than 20% at one or more wavelengths in the visible spectrum. In some embodiments, a photovoltaic apparatus described herein demonstrates EQE of 20-25% at one more wavelengths in the visible spectrum.

III. Methods of Producing Composite Layers

In a further aspect, methods of producing composite layers are described herein. A method of producing a composite layer comprises mixing inorganic nanoparticles, conjugated polymeric phase and carbon nanoparticles in an organic solvent, aggregating the inorganic

nanoparticles in the conjugated polymeric phase to provide nanocluster nodes and phase separating the carbon nanoparticles from the conjugated polymeric phase as lamellar structures of carbon nanofibrils radiating from the nanocluster nodes during removal of the organic solvent.

Components of methods described herein, including the inorganic nanoparticles, conjugated polymeric phase and carbon nanoparticles, can have compositional parameters and/or properties described for the same in Section I hereinabove. For example, inorganic nanoparticles can comprise transition metal oxide nanoparticles while the conjugated polymeric phase is formed of a polythiophene listed in Table I above, and the carbon nanoparticles comprise fullerenes or fullerene derivatives. Further, nanofibrils formed by phase separation of the carbon nanoparticles from the conjugated polymeric phase can have any properties described in Section I herein.

As discussed further herein, width of the phase separated carbon nanofibrils can be altered depending on various processing conditions, including the removal rate of the organic solvent. For example, nanofibril width can be inversely proportional to solvent removal rate providing the ability to tailor phase separated architectures of the composite layer. Solvent removal rate can be varied by using organic solvents of differing vapor pressure and/or use of differing drying temperatures. In some embodiments, additive(s) can be combined with organic solvent to alter the solvent vapor pressure, producing the desired drying rate and nanofibril morphology.

These and other embodiments are further illustrated by the following non-limiting examples.

EXAMPLE 1 – *Composite Layer*

A composite layer was formed by providing a mixture of zinc oxide (ZnO) nanoparticles (10-20 nm), PCBM and conjugated polymer of poly[4,4-didodecyl pentaleno[1,2-b]dithiophene-co-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione in chlorobenzene solvent. Conjugated polymer and PCBM were present in the mixture in a ratio of 1:1 (polymer:PCBM). Further, ZnO nanoparticles were present in an amount sufficient to achieve about a 1.5 wt.% loading in the final composite layer. The mixture was deposited on a copper grid substrate by spin casting, and the chlorobenzene solvent was removed by drying.

The resulting composite layer is illustrated in the TEM sectional view of Figure 1. As illustrated in Figure 1, the composite layer section (10) comprises a nanoparticle cluster (11) and lamellar structures of carbon nanofibrils (12) and conjugated polymer nanofibrils (13) radiating from the nanoparticle cluster (11). In the embodiment of Figure 1, the carbon nanofibrils (12) are formed of fullerene conjugate 1-(3-mehtoxycarbonyl)propyl-1-phenyl-(6,6)C_{61} (PCBM) phase separated from the nanofibrils (13) of the poly[4,4-didodecyl pentaleno[1,2-b]dithiophene-co-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione host. The carbon nanofibrils (12) extend outward from the nanocluster (11) distances well in excess of 500 nm.

A comparative layer was produced in a substantially identical manner, the difference being the absence of ZnO nanoparticles in the mixture. As provided in Figure 2, the resulting layer did not demonstrate any specific phase-separated architectures and mirrored prior organic films incorporating PCBM.

EXAMPLE 2 – *Composite Layer*

A composite layer was formed in accordance with the protocol of Example 1, the difference being the ZnO nanoparticles were present in an amount sufficient to achieve about a 0.75 wt.% loading in the final composite layer. Figures 9(a) and 9(b) are sectional TEM images of the resulting composite layer at differing magnifications. The scale bar in Figure 9(a) is 500 nm, and the scale bar in Figure 9(b) is 2 μm. As illustrated in Figure 9(b), the carbon nanofibrils extend from the ZnO nanoparticle cluster distances on the order of microns. For comparative purposes, a composite layer was prepared in accordance with Example 1, wherein the ZnO nanoparticles were not employed. Absence of the ZnO nanoparticles precluded the formation of lamella structures as show in the TEM of Figure 9(c).

EXAMPLE 3 – *Composite Layer*

A composite layer was formed in accordance with the protocol of Example 1, the difference being the ZnO nanoparticles were replaced with TiO_2 nanoparticles (10-20 nm). The resulting composite layer demonstrated lamellar structures of carbon nanofibrils radiating from nanocluster nodes, similar to that shown in Figure 1.

EXAMPLE 4 – *PCBM Loading in Composite Layer*

Composite layers 3-6 were produced in accordance with Example 1, wherein loading of PCBM in the composite layer was increased to provide conjugated polymer:PCBM ratios of Table III.

Table III – Composite Layer polymer:PCBM ratios

Composite Layer	Conjugated Polymer:PCBM Ratio	Figure
3	1:1	3(a)
4	1:2	3(b)
5	1:3	3(c)
6	1:4	3(d)

As illustrated in Figures 3(a)-(d), the phase separated carbon nanofibrils readily formed at ratios of 1:1 and 1:2. At higher ratios of 1:3 and 1:4, the PCBM begins to crystallize into large clusters losing the nanofibril morphology proximate the nanoclusters. It was noticed, however, that for a ratio of 1:4, the nanofibril morphology was re-established in regions distant from the nanocluster nodes [Figure 3(d)].

EXAMPLE 5 – *Inorganic Nanoparticle Loading in Composite Layer*

Composite layers 7-9 were produced in accordance with Example 1, wherein loading of the ZnO nanoparticles varied according to Table IV, and the conjugated polymer:PCBM ratio was held constant at 1:2 for each composite layer.

Table IV – Composite Layer Inorganic Nanoparticle Loadings

Composite Layer	ZnO Nanoparticle Loading (wt.%)	Figure
7	5	4(a)
8	2.5	4(b)
9	1.2	4(c)

As illustrated in Figures 4(a)-(c), increased ZnO nanoparticle loading increased nanocluster size, which contributed to the conjugated polymer/carbon nanofibril width distribution as provided in Figure 5. As provided in Figure 5, nanocluster size ranged from 148 nm to 799 nm. A statistical study of the conjugated polymer/PCBM nanofibril width radiating from different nanocluster node sizes indicated the fibril patterns displayed a Gaussian distribution typical of a random walk

process. Smaller nanoclusters, for example, produced nanofibrils of reduced with (e.g. 10 nm) while larger nanoclusters produced nanofibrils have width of up to 25 nm.

EXAMPLE 6 – *Solvent Removal Rate*

Composite layers 10-13 were produced in accordance with Example 1, the difference being alteration of the CB solvent as detailed in Table V.

Table V – Solvent Compositional Parameters

Composite Layer	Organic Solvent Composition	Figure
10	1,2-dichlorobenzene (DCB)/chlorobenzene (CB)	6(a)
11	DCB/CB and 1 vol.% 1-chloronaphthalene (CN)	6(b)
12	DCB/CB and 2 vol.% CN	6(c)
13	DCB/CB and 6 vol.% CN	6(d)

As demonstrated in the histogram of Figure 7, the standard deviation of the four organic solvent systems were similar judging from shape of the curves. However, the expectation value shifts from 10-12 nm for fast drying film spin cast form DCB/CB solvent to 14-15 nm for composite layers cast from DCB/CB/2 vol.% CN and up to 16-18 nm for composite layers cast from DCB/CB/6 vol.% CN.

EXAMPLE 7 – *Photovoltaic Apparatus*

Photovoltaic apparatus having the construction listed in Table VI were constructed on ITO substrates. PEDOT:PSS EBLs were deposited on the ITO substrates by spin casting to a thickness of about 80 nm. Photosensitive layers produced in accordance with Example 1 were deposited on the EBLs by spin casting to a thickness of 100 nm. Conjugated polymer of the photosensitive layers was poly[4,4-didodecyl pentaleno[1,2-b]dithiophene-co-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione (P1) and the carbon nanoparticles were PCBM. The ratio of P1:PCBM ratio was 1:2. If present, inorganic nanoparticles forming nanoclusters were ZnO. MoO_3 and Al were deposited over the photosensitive layer.

Table VI – Photovoltaic Apparatus Construction

Photovoltaic Apparatus	Anode	EBL	Photosensitive Layer	Metal Oxide Layer	Cathode
1 (Comparative)	ITO	PEDOT:PSS	P1:PCBM (1:2)	MoO_3	Al
2	ITO	PEDOT:PSS	P1:PCBM (1:2) and 0.1 wt.% ZnO nanoparticles	MoO_3	Al
3	ITO	PEDOT:PSS	P1:PCBM (1:2) and 0.3 wt.% ZnO nanoparticles	MoO_3	Al
4	ITO	PEDOT:PSS	P1:PCBM (1:2) and 0.6 wt.% ZnO nanoparticles	MoO_3	Al
5	ITO	PEDOT:PSS	P1:PCBM (1:2) and 1.2 wt.% ZnO nanoparticles	MoO_3	Al
6	ITO	PEDOT:PSS	P1:PCBM (1:2) and 2.5 wt.% ZnO nanoparticles	MoO_3	Al

The photovoltaic apparatus of Table VI were subsequently tested for current density, EQE and IQE upon exposure to radiation in the visible region of the electromagnetic spectrum. The results are provided in Figures 8(a)-(d). As illustrated in Figures 8(a) and (b), current densities for photovoltaic apparatus employing composite layers described herein comprising phase separated lamellar structures of carbon nanofibrils are substantially higher than the comparative photovoltaic apparatus of P1:PCBM photosensitive layer. Further, the EQE and IQE for the photovoltaic apparatus employing composite layers described herein are 20-92% higher than the comparative photovoltaic apparatus.

EXAMPLE 8 – *Photovoltaic Apparatus*

Photovoltaic apparatus having the construction of Table VI were produced, the difference being the conjugated polymer of the photosensitive layer was changed to poly[4,8-bis(1-pentylhexyloxy)-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl-alt-2,1,3-benzoxadiazole-4,7-diyl. The photovoltaic apparatus were tested for current density, EQE and IQE upon exposure to radiation in the visible region of the electromagnetic spectrum. Results of the testing were similar to those detailed in Example 7.

Various embodiments of the invention have been described in fulfillment of the various objectives of the invention. It should be recognized that these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations

thereof will be readily apparent to those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

1. A composite layer comprising:

nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils radiating from the nanocluster nodes.

2. The composite layer of claim 1, wherein the carbon nanofibrils have a width of 5-25 nm.

3. The composite layer of claim 1, wherein the carbon nanofibrils radiate a distance of 500 nm to 5 μm from the nanocluster nodes.

4. The composite layer of claim 1, wherein the carbon nanofibrils radiate a distance of at least 1 μm from the nanocluster nodes.

5. The composite layer of claim 1, wherein the nanocluster nodes are formed of a material having a surface energy greater than the conjugated polymeric host and carbon nanoparticles.

6. The composite layer of claim 1, wherein the nanocluster nodes are formed of inorganic nanoparticles.

7. The composite layer of claim 5, wherein the inorganic nanoparticles comprise metal or metal oxide nanoparticles.

8. The composite layer of claim 1, wherein the nanocluster nodes have a diameter of 100-500 nm.

9. The composite layer of claim 1, wherein the carbon nanoparticles and conjugated polymeric host demonstrate a difference in surface energies sufficient to induce phase separation in presence of the nanocluster nodes.

10. The composite layer of claim 1, wherein the carbon nanoparticles comprise PCBM.

11. The composite layer of claim 1, wherein the carbon nanoparticles are present in the layer in an amount sufficient to form the carbon nanofibrils.

12. The composite layer of claim 11, wherein the carbon nanofibrils are present in an amount of 30-66 weight percent of the composite layer.

13. The composite layer of claim 1, wherein the nanoclusters are present in an amount of 0.5 to 5 weight percent of the composite layer.

14. A photovoltaic apparatus comprising:
first and second electrodes; and
a photosensitive layer positioned between the first and second electrodes, the photosensitive layer comprising nanocluster nodes and carbon nanoparticles disposed in a conjugated polymeric host, wherein the carbon nanoparticles are substantially phase separated from the conjugated polymeric host forming lamellar structures of carbon nanofibrils radiating from the nanocluster nodes.

15. The photovoltaic apparatus of claim 14, wherein the carbon nanofibrils have a width of 5-25 nm.

16. The photovoltaic apparatus of claim 14, wherein the carbon nanofibrils radiate a distance of 500 nm to 5 μm from the nanocluster nodes.

17. The photovoltaic apparatus of claim 14, wherein the carbon nanofibrils radiate a distance of at least 1 μm from the nanocluster nodes.

18. The photovoltaic apparatus of claim 14, wherein the nanocluster nodes are formed of a material having a surface energy greater than the conjugated polymeric host and carbon nanoparticles.

19. The photovoltaic apparatus of claim 14, wherein the nanocluster nodes are formed of inorganic nanoparticles.

20. The photovoltaic apparatus of claim 19, wherein the inorganic nanoparticles comprise metal or metal oxide nanoparticles.

21. The photovoltaic apparatus of claim 14, wherein the nanocluster nodes have a diameter of 100-500 nm.

22. The photovoltaic apparatus of claim 14, wherein the photosensitive layer has a thickness of 300 nm to 1 μm.

23. The photovoltaic apparatus of claim 14 having an external quantum efficiency (EQE) greater than 20% at one or more wavelengths in the visible spectrum.

24. A method of producing a composite layer comprising:

mixing inorganic nanoparticles, conjugated polymeric phase and carbon nanopartilces in an organic solvent;

aggregating the inorganic nanoparticles in the conjugated polymeric phase to provide nanocluster nodes; and

phase separating the carbon nanoparticles from the conjugated polymeric phase as lamellar structures of carbon nanofibrils radiating from the nanocluster nodes during removal of the organic solvent.

25. The method of claim 24, wherein the nanofibrils radiate a distance of 500 nm to 5 μm from the nanocluster nodes.

26. The method of claim 24, wherein the nanofibrils radiate a distance of at least 1 μm from the nanocluster nodes.

27. The method of claim 24, wherein the carbon nanoparticles and conjugated polymeric host demonstrate a difference in surface energies sufficient to induce phase separation in the presence of the nanocluster nodes.

28. The method of claim 24, wherein the inorganic nanoparticles comprise metal or metal oxide.

29. The method of claim 24 further comprising altering width of the carbon nanofibrils by altering removal rate of the organic solvent.

30. The method of claim 29, wherein the width of the carbon nanofibrils is inversely proportional to the removal rate of the organic solvent.

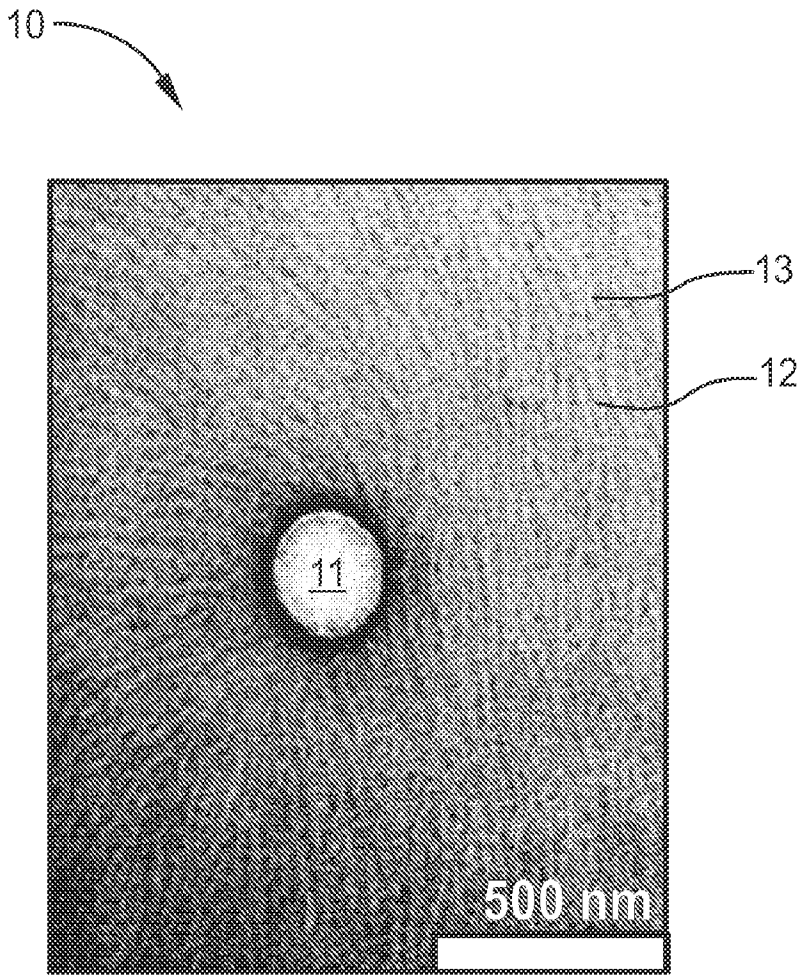


FIGURE 1

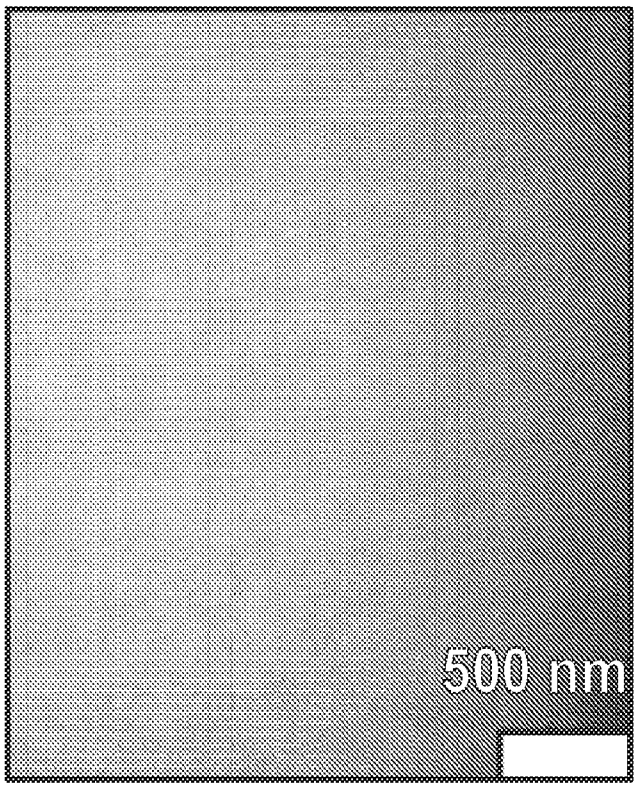


FIGURE 2

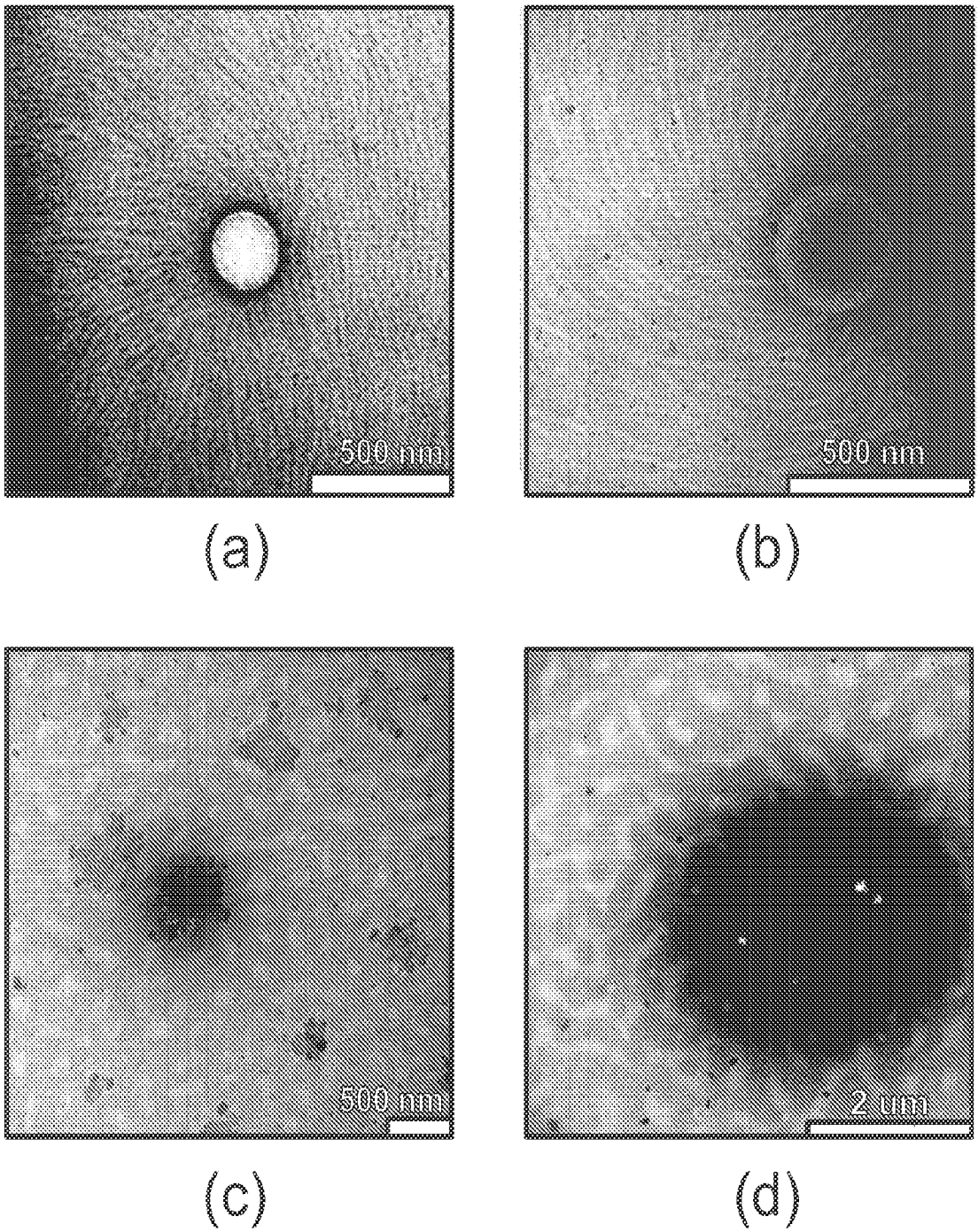


FIGURE 3

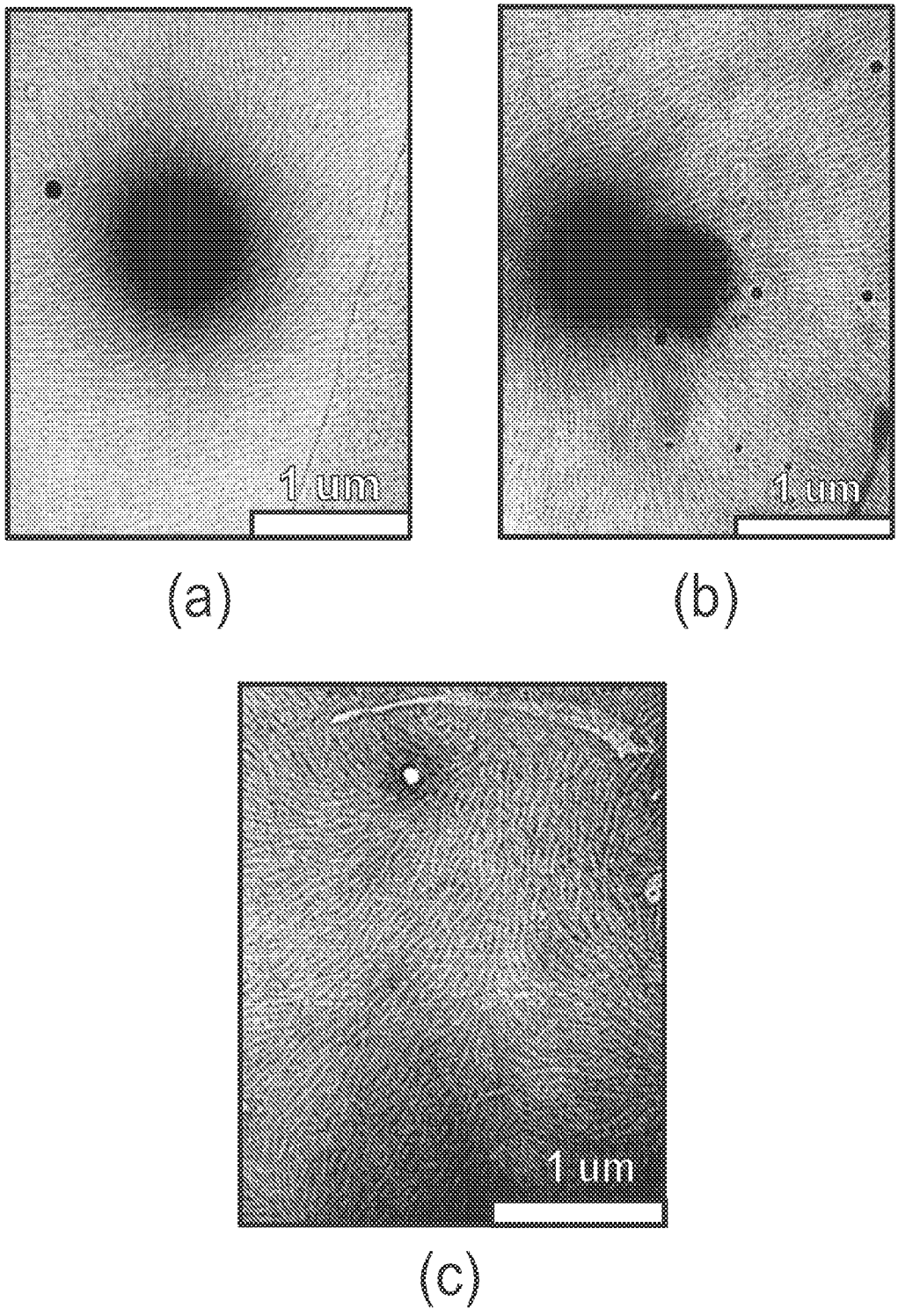


FIGURE 4

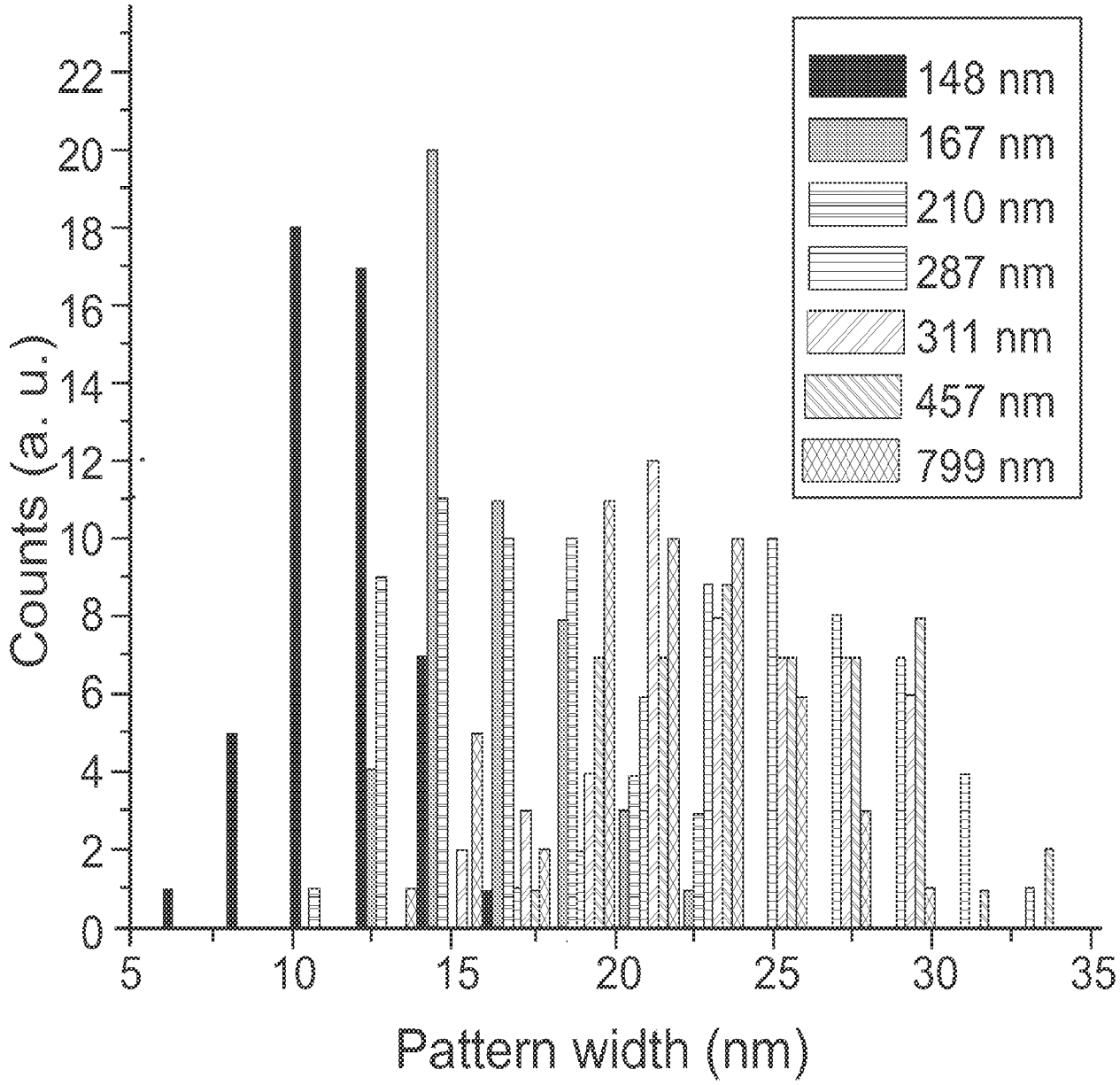

148 nm
167 nm
210 nm
287 nm
311 nm
457 nm
799 nm
Counts (a. u.)
0
2
4
6
8
10
12
14
16
18
20
22
5
10
15
20
25
30
35
Pattern width (nm)

FIGURE 5

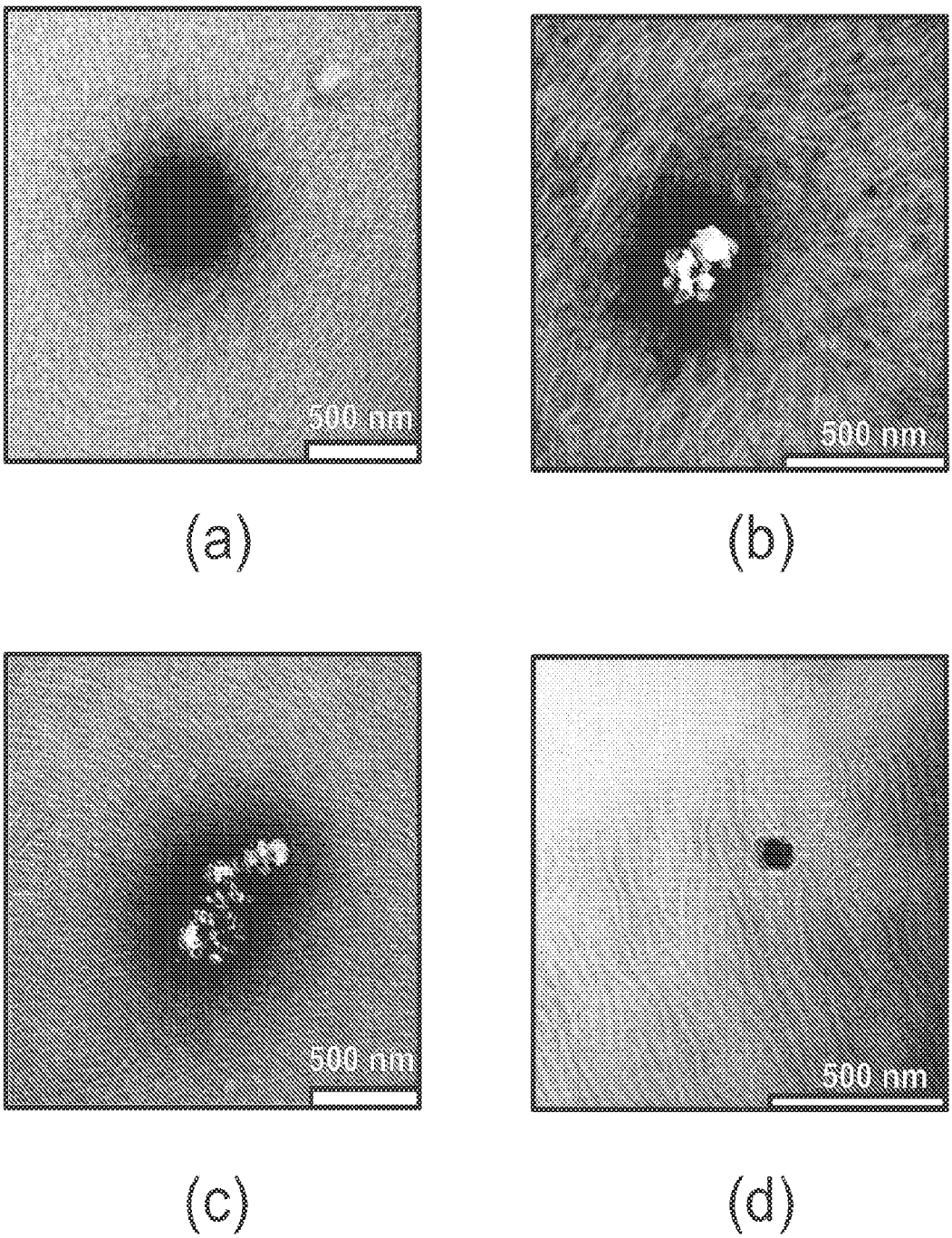


FIGURE 6

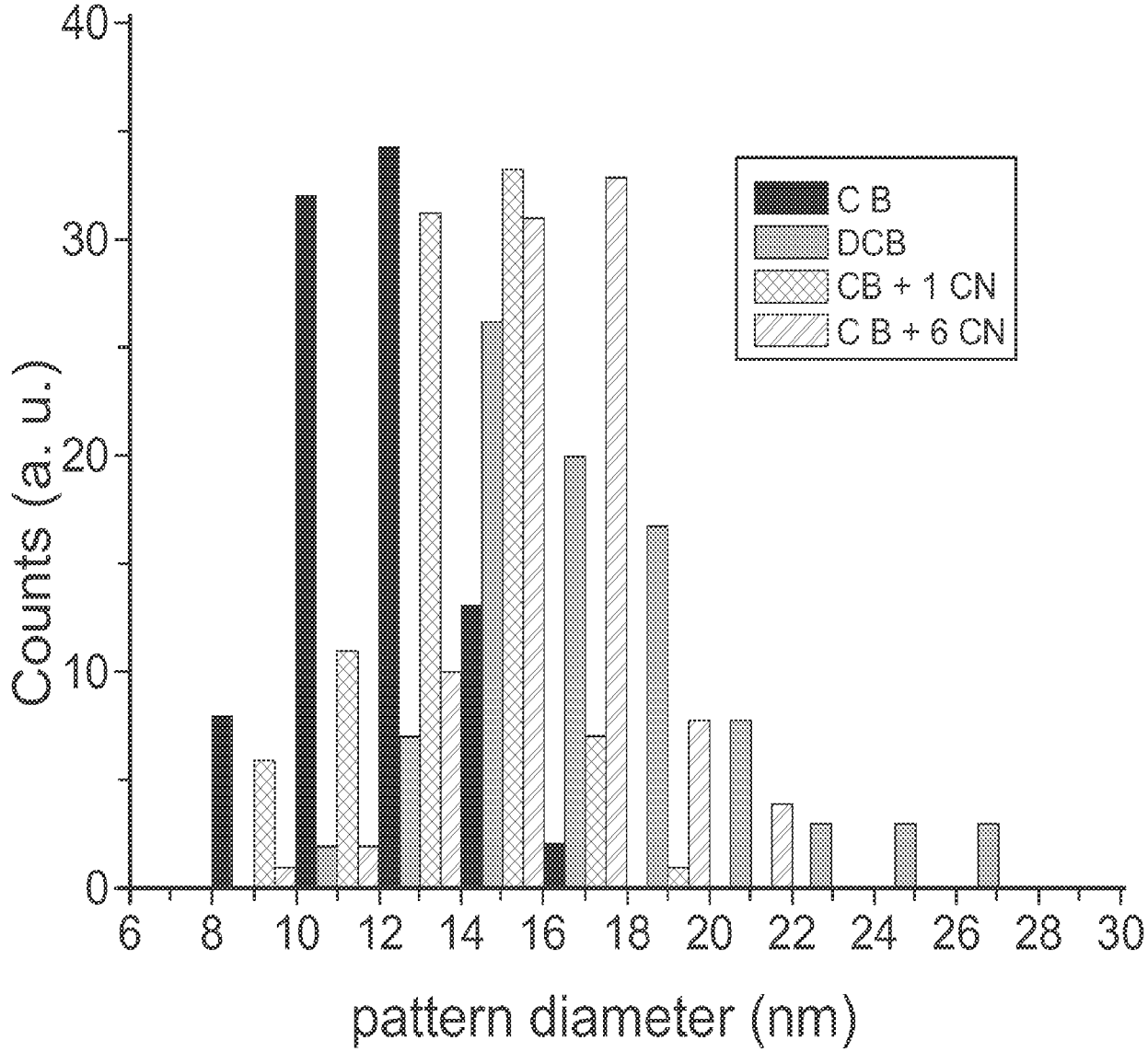

40
30
20
10
0
Counts (a. u.)
6
8
10
12
14
16
18
20
22
24
26
28
30
pattern diameter (nm)
C B
DCB
CB + 1 CN
C B + 6 CN

FIGURE 7

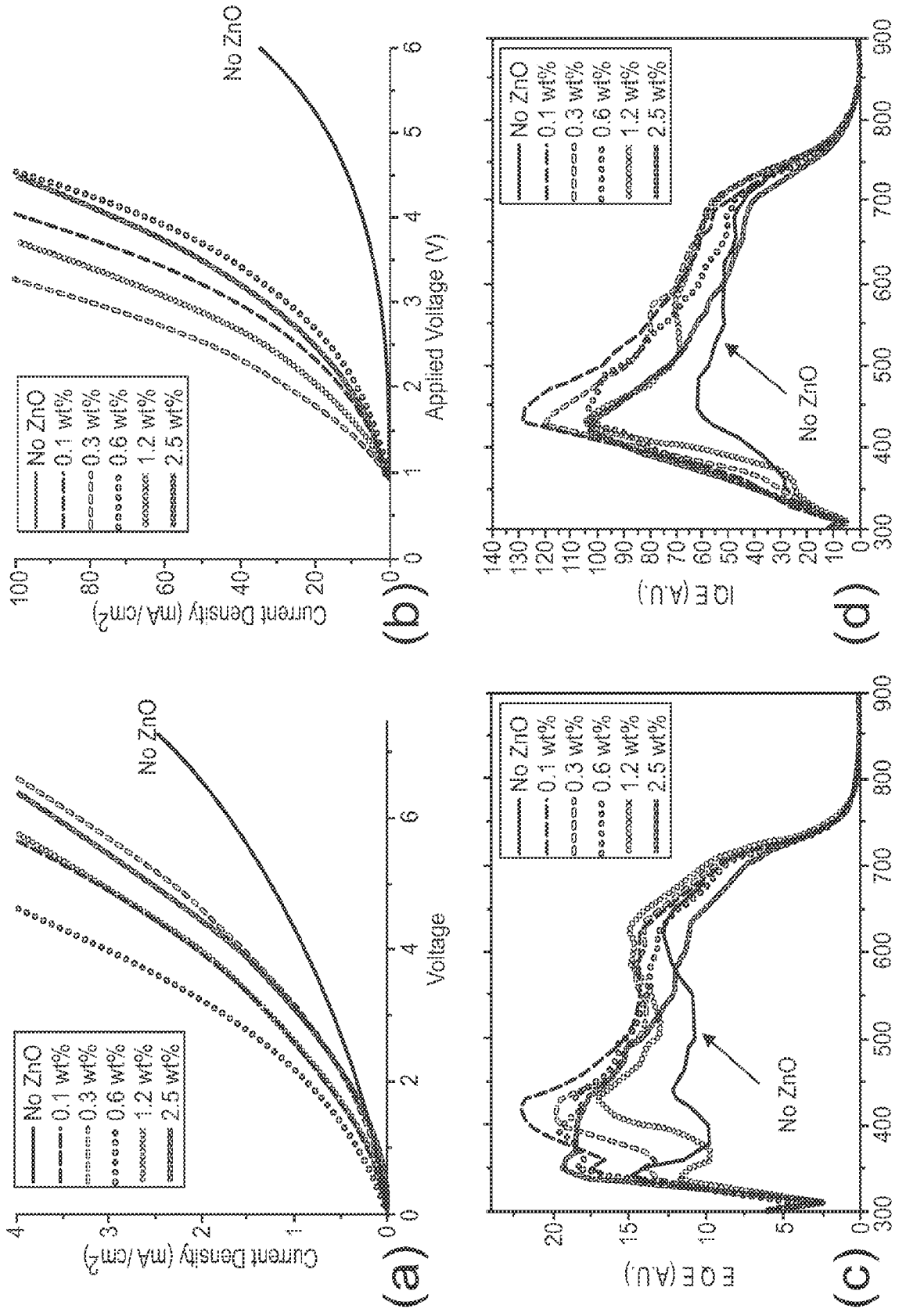

(a)
Current Density (mA/cm²)
Voltage
No ZnO
0.1 wt%
0.3 wt%
0.6 wt%
1.2 wt%
2.5 wt%
(b)
Current Density (mA/cm²)
Applied Voltage (V)
No ZnO
(c)
FQE (A.U.)
No ZnO
(d)
EQE (A.U.)
No ZnO

FIGURE 8

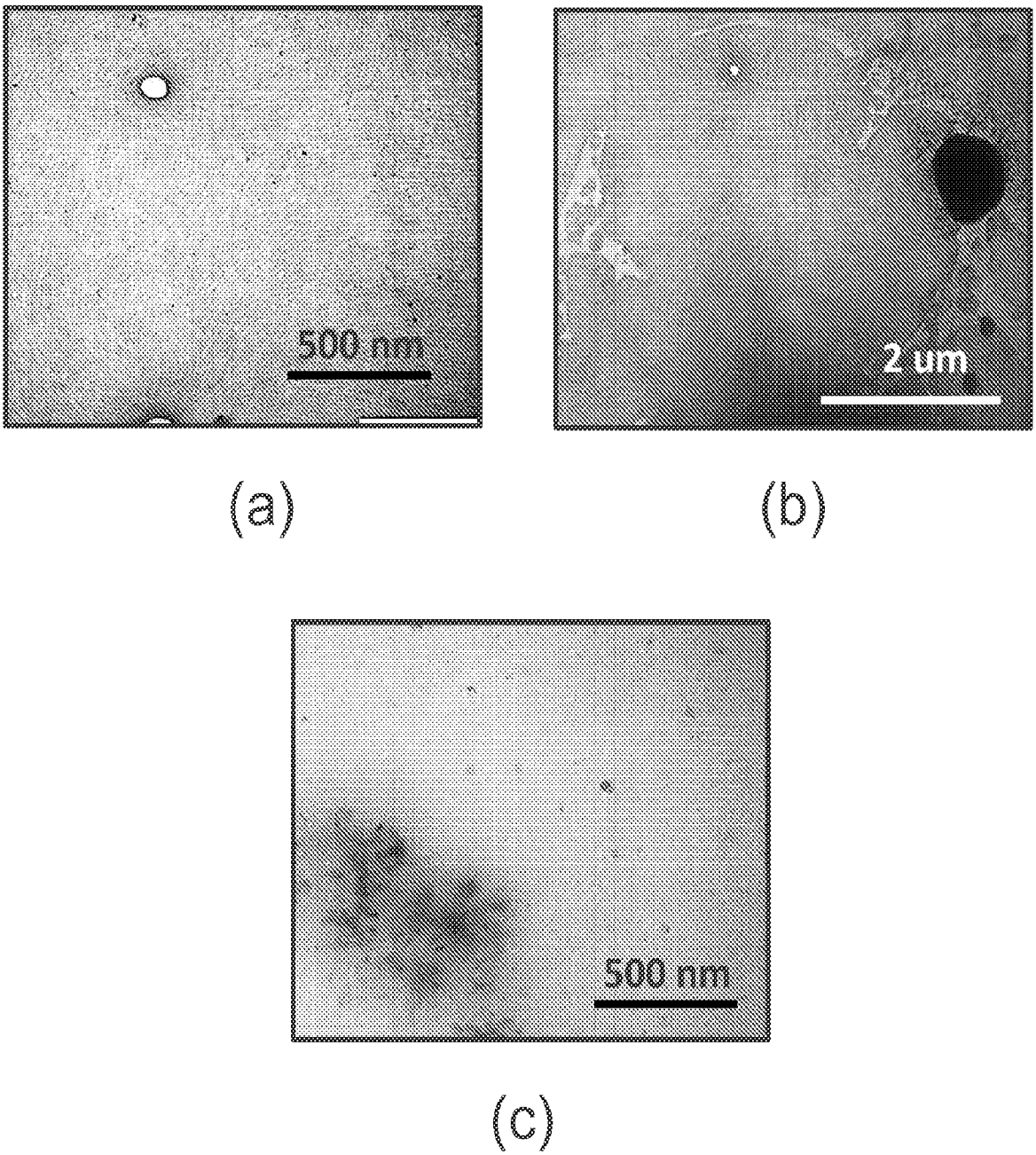


FIGURE 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/045992

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L31/00 C08K3/10 H01L51/00 C08K3/04
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L C08K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/134618 A1 (CARROLL DAVID LOREN [US]) 31 May 2012 (2012-05-31) page 11; claims 12,13	1-30
A	WO 2012/054495 A2 (UNIV WAKE FOREST [US]; CARROLL DAVID L [US]) 26 April 2012 (2012-04-26) page 17, line 17 - line 29	1-30
A	US 2008/149178 A1 (REYES-REYES MARISOL [US] ET AL) 26 June 2008 (2008-06-26) page 7 - page 8; claims 17-27	1-30

☐ 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	Date of mailing of the international search report
24 November 2014	28/11/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Jung, Andreas

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/045992

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012134618 A1	31-05-2012	US 2012134618 A1	31-05-2012
		WO 2010144438 A1	16-12-2010
WO 2012054495 A2	26-04-2012	CA 2814991 A1	26-04-2012
		CN 103270608 A	28-08-2013
		EP 2630666 A2	28-08-2013
		US 2013312801 A1	28-11-2013
		WO 2012054495 A2	26-04-2012
US 2008149178 A1	26-06-2008	NONE	