



## (51) International Patent Classification:

H01L 21/00 (2006.01)

## (21) International Application Number:

PCT/US2012/029914

## (22) International Filing Date:

21 March 2012 (21.03.2012)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

61/454,636 21 March 2011 (21.03.2011) US

## (72) Inventors; and

(71) Applicants : **KRAMER, Theodore J.** [US/US]; 423 W. 118th Street, Apt. 6A, New York, New York 10027 (US). **HERMAN, Irving P.** [US/US]; 412 Low Library, Mail Code 4308, 535 West 116th Street, New York, New York 10027 (US). **KYMISSIS, Ioannis** [US/US]; 526 W. 113th Street #43, New York, New York 10025 (US).

(74) Agents: **ARORA, Suneel** et al.; P.O. Box 2938, Minneapolis, Minnesota 55402 (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, 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, IS, JP, KE, KG, KM, 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, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, MD, 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, ML, MR, NE, SN, TD, TG).

## Published:

- with international search report (Art. 21(3))
- 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))

(54) Title: ON-SUBSTRATE FABRICATION OF HIGH-SURFACE AREA POLYMER MORPHOLOGY FOR PHOTOACTIVE APPLICATIONS

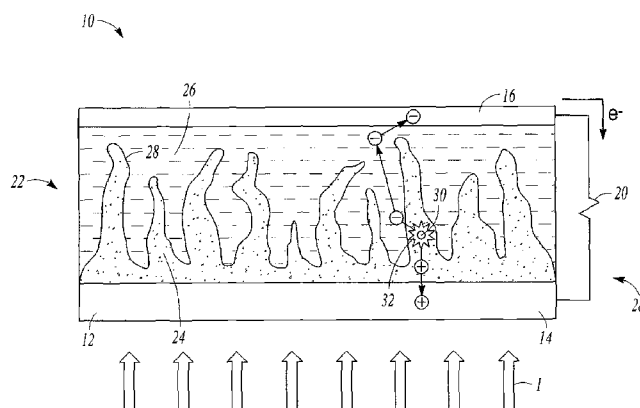


FIG. 1

(57) Abstract: A device can include a substrate and a substantially continuous network of polymer nanostructures coupled to the substrate. A method of making a device can include mixing a first polymer and a second polymer in a solvent to form a solution. The solvent can dissolve each of the first polymer and the second polymer. The solution can be coated onto a substrate. The first polymer can be phase-separated from the second polymer, such as to form a substantially continuous network of nanostructures of the first polymer interlinked with a substantially continuous network of nanostructures of the second polymer. A high-surface area interface can be formed between the substantially continuous network of nanostructures of the first polymer and the substantially continuous network of nanostructures of the second polymer. The second polymer can be removed, such as to expose the high-surface area interface.

## ON-SUBSTRATE FABRICATION OF HIGH-SURFACE AREA POLYMER MORPHOLOGY FOR PHOTOACTIVE APPLICATIONS

### Cross-Reference to Related Patent Documents

5

This patent application claims the benefit of priority, under 35 U.S.C. Section 119(e), to U.S. Provisional Patent Application Serial Number 61/454,636, entitled "ON-CHIP FABRICATION OF HIGH SURFACE AREA POLYMER MORPHOLOGY FOR PHOTOACTIVE APPLICATIONS," filed on MARCH 21, 10 2011 (Attorney Docket No. 2413.131PRV), which application is incorporated by reference herein in its entirety.

### BACKGROUND

Photoactive devices can convert incident light to another form of energy, 15 such as electricity, heat, or light of a different wavelength, or can convert another form of energy to light. A photoactive device can include an interface between a first material and a second material. For example, a photovoltaic device can include a diode junction between an electron donor material and an electron acceptor material. In a photovoltaic device, incident light on the photovoltaic device can 20 excite an electron from the valance band to the conduction band, leaving behind a positively charged hole in the valance band. The bound electron-hole pair can be collectively referred to as an "exciton." The electron and the hole can become separated from each other across the diode junction, with the electron being swept from the electron donor material to the electron acceptor material. For this reason, 25 each unbound electron or unbound hole of an exciton can be referred to as a "charge carrier." A cathode can be electrically connected to the electron acceptor material to collect electrons and pass them through a circuit comprising an electrical load, before returning the electrons to an anode that is electrically connected to the electron donor material where the electrons can rejoin with the holes.

30

## OVERVIEW

In order to increase or maximize the efficiency of photoactive devices, such as photovoltaic devices, it can be desirable to maximize the surface area of contact between the first material and second material of the photoactive device or to  
5 maximize the active volume fraction of the microstructure of each material. Bulk heterojunctions (BHJs) have been developed in an attempt to provide for large surface areas relative to the overall volume of the photoactive device. A BHJ can comprise the first material and second material, generally in the form of polymers, being blended together and then phase-separated to form distinct regions of the first  
10 material and the second material.

The present disclosure is directed to a method for generating a high-surface area or high active-volume fraction morphology and the resulting devices, such as photoactive devices, for example photovoltaic devices, light-emitting diodes, optically active transistors, or other optically active organic devices. The method  
15 can allow for a resulting device having an interconnected high-surface area network of nanostructures, such as nanofibers or nanowires, such as by forming a high-surface area morphology in a first material and depositing a second material over the first material to form a high-surface area interface between the first material and the second material. The high-surface area interface can comprise a plurality of  
20 nanostructures of the first material interlinked with a plurality of nanostructures of the second material.

These and other examples and features of the present photoactive devices and related methods will be set forth in part in the following detailed description. This overview is intended to provide non-limiting examples of the present subject  
25 matter—it is not intended to provide an exclusive or exhaustive explanation. The detailed description below is included to provide further information about the present devices, systems, and methods.

### DETAILED DESCRIPTION

High-surface area or high active-volume fraction structures can be particularly useful for many applications. For example, in a photovoltaic device, a high active-volume fraction of the morphology between the electron donor material and the electron acceptor material can be desirable, such as to increase or maximize external quantum efficiency (EQE) of the resulting solar cell. This disclosure describes structures that can have a high-surface area morphology or a high-active volume morphology as well as apparatuses or devices that can use the high-surface area or high-active volume morphology, such as photoactive devices, for example, a photovoltaic device. This disclosure also describes methods of making the high-surface area or high-active volume morphology.

The structure, apparatus, or device can include a substrate and a substantially continuous network of polymer nanostructures coupled to the substrate. The polymer nanostructures can have a high-surface area or high-active volume morphology that can be suited for a particular application, such as for providing a high-active volume for the morphology of an electron donor phase or electron acceptor phase of a photovoltaic device. The structure, apparatus, or device can also include a mating material that can be in intimate contact with the network of polymer nanostructures, such as to form a high-surface area interface between the network of polymer nanostructures and the mating material. In an example, the network of polymer nanostructures can include either the electron donor material or the electron acceptor material of a photovoltaic device, and the mating material can include the other of the electron donor material or the electron acceptor material of the photovoltaic device.

FIG. 1 is a conceptualized schematic representation of an example of a device comprising a high-surface area or high-active volume morphology structure. FIG. 1 shows an example of a photovoltaic device 10 that can include a substrate 12 on which the high-surface area or high-active volume morphology can be formed. The substrate 12 can include an electrode of a photovoltaic device 10, such as an

anode 14. The substrate 12 can also be transparent or translucent or can otherwise provide access for incident light 1 to reach an interior of the device 19, for example, such as a transparent or translucent layer of indium-tin-oxide (ITO) on a glass substrate 12. A second electrode, such as a cathode 16, can also be included in the photovoltaic device 10. A circuit 18 (e.g., represented in FIG. 1 as an electric load resistance 20) can be connected between the anode 14 and the cathode 16, such as to collect or use electric energy converted by the photovoltaic device 10.

The photovoltaic device 10 can include an active layer 22. The active layer 22 can include a first material 24 and a second material 26. One of the materials 24, 26 can include an electron donor material and the other of the materials 24, 26 can include an electron acceptor material. In an example, the first material 24 can include an electron donor material 24, such as poly(3-hexylthiophene) (P3HT), and the second material 26 can include an electron acceptor material 26, such as phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) or cadmium selenide (CdSe) nanoparticles.

The electron donor material 24 and the electron acceptor material 26 can be in close intimate contact with one another, such as at an interface 28, which can include or be a high-surface area interface. A diode junction can be formed at the interface 28 between the electron donor material 24 and the electron acceptor material 26.

The electron donor material can donate electrons, such as to the electron acceptor material, during operation of the photovoltaic device 10, such as upon exposure to light. An example of such a process is described in more detail below. The electron acceptor material can receive electrons, such as from the electron donor material, such as during operation of the photovoltaic device 10, such as upon exposure to light.

A photovoltaic device 10 can include a diode junction between a “p-type” phase material and an “n-type” phase material. The term “p-type” phase generally refers to a semiconducting material that tends to have more freely available positive charge carriers, referred to as “holes,” and the term “n-type” phase generally refers

to a semiconducting material that tends to have more freely available negative charge carriers, e.g., electrons. When the p-type phase and the n-type phase are brought into intimate contact at the junction, the freely available electrons in the n-type phase are driven to diffuse across the junction to join with freely available  
5 holes in the p-type phase. Similarly, the freely available holes in the p-type phase can transfer across the junction to join with freely available electrons in the n-type phase. The transfer of electrons from the n-type phase to the p-type phase and the transfer of holes from the p-type phase to the n-type phase can create a depletion zone around the junction where neither freely available electrons nor freely  
10 available holes are present. The accumulation of oppositely charged carriers (e.g., the electrons and holes) on opposite sides of the depletion zone can create an electronic field that can act across the junction.

When a photo-generated exciton encounters the field established across the depletion zone there can be an energetic driving force (such as due to columbic  
15 forces or an inherent concentration gradient) for the negatively charged electron to separate from the positively charged hole and for each charge carrier to move independently toward the side of the junction with a complimentary opposite charge and favourable concentration gradient (such as with an electron moving toward the positively charged n-type side of the junction and a hole moving toward the  
20 negatively charged side of the p-type side of the junction).

Operation of the photovoltaic device 10 can occur after the formation of the depletion zone and the electric field described above. The photovoltaic device 10 can be exposed to light, such that photons 30 can be provided to the active layer 22. At least some of the photons 30 can be absorbed at an absorption site 32 by either  
25 the electron donor material 24 or the electron acceptor material 26. In the case of an organic-based photovoltaic device, such as a device using P3HT polymer as the electron donor material 24 and PCBM (the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester) as the electron acceptor material 26, the electron donor material can absorb a large majority of the photons 30. For example, P3HT can

have an optical extinction coefficient that is approximately five times greater than that of PCBM in the visible region of light (e.g., at a wavelength of around 550 nanometers). In an example, up to about 80%, such as up to about 85%, for example up to about 90% of the photons can be absorbed by the electron acceptor material. If the energy of the photon 30 that is absorbed at the absorption site 32 is sufficiently high, e.g., higher than a band gap value of the material absorbing the photon 30, than an exciton, e.g., an electron-hole pair, is formed, which can allow either or both of the electron or hole to move freely.

In the case of an absorption site 32 within the electron donor material 24, an electron can tend to be driven toward the interface 28 between the electron donor material 24 and the electron acceptor material 26, due to the electric field that has formed, as described above. The electric field, therefore, can tend to sweep electrons formed as part of excitons in the electron donor material 24 across the interface 28 and into the electron acceptor material 26. Similarly, the electric field can tend to sweep holes that are formed as part of excitons in the electron acceptor material 26 across the interface and into the electron donor material 24. As described above, however, the vast majority of photons 30 are absorbed by the electron donor material 24, so that the primary action of the photovoltaic device 10 can be the sweeping of electrons from the electron donor material 24 to the electron acceptor material 26. For brevity and clarity, the remainder of this description will therefore focus on the movement of electrons, rather than the movement of holes.

The cathode 16 of the photovoltaic device 10 can be electrically coupled to the electron acceptor material 26. The anode 14 of the photovoltaic device 10 can be electrically coupled to the electron donor material 24. When a circuit 18 or electric load 20 is connected across the anode 14 and the cathode 16, the electrons that have been swept into the electron acceptor material 26 can be driven toward the cathode 16, where they can pass through the circuit 18 and return to the anode 14. The electrons can then recombine with holes that were formed as part of excitons in

the electron donor material 24, or with holes that were swept across the interface 28 from excitons formed in the electron acceptor material 26.

In the case of photoactive devices, such as the photovoltaic device 10, one parameter that can be of interest is the active-volume fraction of both the electron  
5 donor material 24 and the electron acceptor material 26. The term “active-volume fraction” as used herein, generally refers to the volume of the material that is within a diffusion length of a charge carrier within the material that absorbs a photon 30. The term “diffusion length,” as it is used herein, generally refers to a length that an  
10 exciton can travel from the absorption site 32 before its constituent charges (i.e. hole and electron) are likely to recombine with an oppositely charged carrier.

The diffusion length is generally material or charge-carrier specific, and in reality is a range of lengths corresponding to the probabilities that a charge carrier will encounter and recombine with an opposite charge carrier within the material. The diffusion length can be statistically characterized as a threshold length wherein  
15 a certain percentage of charge carriers will be presumed to travel, such as a length that the majority of charge carriers will be presumed to have travelled, a length where at least 75% of the charge carriers will be presumed to have travelled, or a length where at least 90% of the charge carriers will be presumed to have travelled. For example, the diffusion length of electrons in poly(3-hexylthiophene) (P3HT),  
20 can be assumed to be up to about 10 nanometers. The diffusion length can be increased with some processing techniques, such as annealing, but for P3HT, 10 nanometers is a widely used and conservative estimate. .

The active volume fraction of a P3HT electron donor material 24, therefore, is the percentage of the P3HT electron donor material 24 that is within 10 nm of an  
25 interface 28 between the P3HT electron donor material 24 and the electron acceptor material 26. The electron acceptor material 26 can be formed into a network of nanostructures, such as a plurality of nanofibers or nanowires 34. The nanowires 34 can be generally cylindrical in shape and each nanowire 34 can be modeled as a circular cylinder. FIG. 2 shows an example of a model cylindrical nanowire 34

having a length L and a radius R. The nanowire 34 can be formed from a P3HT electron donor material 24, and can be surrounded by the electron acceptor material 26. The active volume within the P3HT electron donor material 24 is shown conceptually by region 36 in FIG. 2. The active volume 36 represents the volume of the nanowire 34 that is within the diffusion length of an electron within the P3HT from an outer surface of the nanowire 34, e.g., within a diffusion length from the interface 28 between the electron donor material 24 and the electron acceptor material 26. The active volume fraction (AVF), in this example, is the percentage of the total volume of the nanowire that is occupied by the active volume 36. For a cylinder having a radius R (in nanometers) and a diffusion length  $L_D$  (in nanometers, Equation 1 can be used to calculate the AVF:

$$AVF = \frac{\left(R^2 - (R - L_D)^2\right)}{R^2} \times 100\% \quad [1]$$

According to Equation 1, if the radius R of the cylindrical nanowire 34 is less than or equal to the diffusion length  $L_D$ , the nanowire 34 will have an active-volume fraction of 100%. For a nanowire 34 including P3HT, that means that a radius of 10 nanometers or less will result in an active volume fraction of 100%. In an example, all or the vast majority of the volume of the electron donor material 24 can include or can be formed of nanowires 34, e.g., at least about 95%, at least about 98%, or at least about 99%. Therefore, for P3HT as an electron donor material 24, if the nanowires 34 can be kept to a radius R of 10 nanometers or less, the active volume of the electron donor material 24 will be maximized, such as at or approaching 100%. Similar models and calculations can be made for the electron acceptor material 26 and for other nanostructures or morphologies.

FIG. 3 is a flow diagram of an example of a process 40 for making a structure having a high-surface area or a high-active volume, such as the photovoltaic device 10. FIGS. 4A–4E respectively show examples of individual steps of the process 40 to better illustrate aspects and advantages of the process 40 and the resulting structure.

At 42, a first polymer can be mixed with a second polymer in a solvent to form a solution. The first polymer can be the polymer that can be used to form a desired structure. The second polymer can be a sacrificial polymer that can be used to facilitate formation of the desired structure. In an example of making a photovoltaic device 10, the first polymer can include an electron donor polymer, such as the electron donor material 24, or an electron acceptor polymer, such as the electron acceptor material 26. The solvent used to form the solution can be a good or strong solvent capable of fully or substantially fully dissolving both the first polymer and the sacrificial second polymer.

At 44, the solution of the first polymer, the second polymer, and the solvent can be coated or otherwise formed on a substrate 12, such as by spin casting. FIG. 4A shows an example of a solution 60 of the first polymer, the second polymer, and a solvent being spin casted onto the substrate 12. The solution 60 can be deposited onto the substrate 12 before or while the substrate 12 is rotated at a sufficiently high speed so that a film 62 of the solution 60 is formed evenly or substantially evenly on the substrate. In an example, the substrate can be rotated at a speed that is within a range from 500 RPM to 2000 RPM, such as 1000 RPM. The exact speed of the rotation can depend on the polymers and solvent being cast and on the desired thickness of the resulting film 62. In an example, the film 62 has a resulting thickness that is within a range of from 100 nanometers to 200 nanometers. In an example, if the film 62 is too thick, than a continuous layer of the first polymer or the sacrificial polymer can form close to the substrate. Because a nanostructure morphology does not extend throughout the film thickness, it can lead to a device with increased resistance or poorly utilized regions of the first polymer. In the film 62 is too thin, than the resulting device may not reach an optimum or maximum efficiency.

Coating the solution of the first polymer 64 and the sacrificial polymer 66, such as via spin casting, can result in physisorption of the first polymer onto the substrate 12. As used herein, "physisorption" can refer to a chemical and physical

interaction between a material and a surface, such as between the first polymer 64 and a surface of the substrate 12, where the material can form a conformal and intimate contact with the surface. In an example, the first polymer 64 can achieve a conformal or substantially conformal covering of the substrate 12 and an intimate contact with the substrate 12. It is believed that the use of a good or strong solvent with respect to the first polymer 64 can allow the first polymer 64 an opportunity to rearrange its molecules while it is coming out of solution to conform to the surface of the substrate 12. The presence of a good or strong solvent at the time that the first polymer 64 contacts the substrate 12 can allow the first polymer 64 to self-arrange at the surface of the substrate 12 on all or different length scales, e.g., at a combination of any of the molecular scale, the nanoscale, or the macroscopic scale, such as to provide for the physisorption or the conformal contact with the substrate 12. In contrast, it is believed that when a poor solvent is used, as is often the case with organic photovoltaic systems, the polymer that is suspended in solution can already have a geometric and molecular configuration that is not conducive to making a physisorbed or conformal bond with a surface of the substrate. The strong solvent and the physisorption can make the first polymer 64 more pliable as it is being bonded to the substrate 12 so that physisorption or conformal bonding can occur.

At 46, the first polymer can be phase separated from the sacrificial polymer. FIG. 4B shows an example in which phase separating a first polymer 64 and a sacrificial polymer 66 can result in forming a continuous or substantially continuous network of nanostructures 68 of the first polymer 64 that are interlinked with a network of nanostructures 70 of the sacrificial polymer 66. The nanostructures 68, 70 of each polymer can include nanowires, nanofibers, or other nanostructure types. The term “nanostructures,” such as “nanofibers,” “nanowires,” or “nanoparticles,” as used herein, refer to structures having a size in at least one dimension of less than 100 nanometers. The nanostructures 68, 70 can be modeled as generally cylindrical nanowires, as described above. The phase separating can form a high-surface area

interface 72 between the network of first polymer nanostructures 68 and the network of sacrificial polymer nanostructures 70.

The morphology of the resulting first polymer nanostructures 68 and sacrificial polymer nanostructures 70 can depend on the specific materials used for the first polymer 64 and the sacrificial polymer 66 and the relationship between these polymers. For example, a combination of a first particular first polymer 64, such as P3HT, with a first sacrificial polymer 66, such as polystyrene (PS), can provide for a first morphology, e.g., such as shown in FIG. 4B, while a combination of the P3HT with a different sacrificial polymer 66, such as a polymer having phenyl groups, for example polyphenyl ether, can result in a second morphology that is different from the first morphology. For example, the first morphology created between P3HT and PS can include a network of nanowires, such as the nanowires 68 and 70 having a first diameter and a first length, as shown in FIG. 4B, while the second morphology created between P3HT and polyphenyl ether can comprise a network of nanowires having different lengths, different nanowire diameters, or with nanostructures other than nanowires, such as nanofibers. The choice of solvent that is used to dissolve the first polymer 64 and the sacrificial polymer 66 can also affect the final morphology, but the interaction between the specific first polymer 64 and the specific material of the sacrificial polymer 66 can have a greater affect on final morphology.

A consideration in photoactive devices, such as an organic photovoltaic device (OPV), is the active volume fraction of the resulting network of nanostructures 68. In an example, the morphology of the first polymer 64 after phase-separation from the sacrificial polymer 66, can be identical or substantially the same as the morphology of the first polymer 64 in its final state in the photoactive device. Therefore, in an example, the phase-separation between the first polymer 64 and the sacrificial polymer 66 can be configured so that the resulting network of first polymer nanostructures 68 can have an active volume fraction (AVF) that is higher than a selected threshold, such as an AVF of at least

about 90%, at least about 95%, at least about 96%, at least about 97%, at least about 98%, at least about 99%, or 100%.

For a generally cylindrical nanowire or nanostructure, a primary dimension of interest in establishing or optimizing the active volume fraction is the  
5 nanostructure diameter, such as in relation to the diffusion length of the first polymer material. Therefore, in an example, the phase-separation between the first polymer 64 and the sacrificial polymer 66 can be configured such that the radius of the resulting cylindrical or generally cylindrical nanostructures 68 is as small as is practical in order to achieve an active volume fraction that is equal to or higher than  
10 the desired threshold AVF. In an example, the phase separation can be configured such that the radius is less than or equal to a diffusion length of the first polymer 64 so as to achieve an active volume fraction of 100%.

The phase separation of the first polymer 64 and the sacrificial polymer 66 can be spontaneous, such that the phase separation can occur naturally due to the  
15 physical and chemical interaction between the first polymer 64 and the sacrificial polymer 66. In an example, the phase-separation of the first polymer 64 and the sacrificial polymer 66, and the formation of the first polymer nanostructures 68 and the sacrificial polymer nanostructures 70, can occur via spinoidal decomposition. The phase separation can be facilitated or assisted by other processing. In an  
20 example, at least one of (1) heat annealing of the coated solution and (2) vapor or solvent annealing of the coated solution can be used to facilitate phase separation of the first polymer from the sacrificial polymer, or both. Thermal annealing can include heating the solution film 62 to an elevated temperature that facilitates separation of the polymers. In an example, thermal anneal can provide for enhanced  
25 mobility of individual molecules of the first polymer or the sacrificial polymer, such as by increasing thermal energy of the polymer molecules, allowing the molecules to overcome the energy barrier to movement and reorganization. Thermal annealing also can allow the molecules to attain a higher level of crystallinity. The thermal annealing can also facilitate phase separation of the polymers because the enhance

crystallization of one of the polymers, e.g., the first polymer, can push out the other polymer, e.g., the sacrificial polymer, because the dissimilar structures of the other polymer can interfere with tight packing or stacking of the first polymer's chains. Vapor annealing, sometimes also referred to as solvent annealing, can include

5 exposing the film 62 to an environment that is rich in a vaporized solvent, such that the vaporized solvent is capable of dissolving one or both of the first polymer and the sacrificial second polymer. Vapor annealing can provide for enhanced mobility of the molecules of the first polymer or the sacrificial polymer, or both, to facilitate phase separation, for example by lowering the energy barrier to movement and

10 reorganization of polymer molecules, such as by filling interchain regions with small or highly mobile solvent molecules. The solvent used for vapor annealing can be the same solvent that is used to dissolve the first polymer and the second polymer to form the solution 60. The increased mobility of molecules that can be achieved with thermal annealing or vapor annealing, or both, can allow for the movement of a

15 larger percentage of polymer chains so that the mobile chains can find a lower thermodynamic packing. The film 62 can first be vapor annealed followed by thermal annealing.

At 48 of FIG. 3, the sacrificial polymer can be removed so that the first polymer can be left behind. The sacrificial polymer can be removed such that

20 substantially the entirety of the first polymer morphology can be left behind. If phase separating the first polymer and the sacrificial polymer results in a network of first polymer nanostructures 68 and a network of sacrificial polymer nanostructures 70, removal of the sacrificial polymer can leave behind the network of first polymer nanostructures 68, with the nanostructures 68 having the same or substantially the

25 same structure after the sacrificial polymer is removed as before. The sacrificial polymer can be removed by dissolving the sacrificial polymer.

FIG. 4C shows an example in which a film 74 of the phase-separated first polymer 64 and sacrificial polymer 66 on the substrate 12 can be placed into a bath 76 of a solvent 78. The solvent 78 can dissolve the sacrificial polymer 66, but not

the first polymer 64. The solvent 78 can therefore selectively remove the sacrificial polymer 66, leaving behind the first polymer 64 intact or substantially intact.

At 50 of FIG. 3, a plurality of nanoparticles can be deposited onto the exposed first polymer, such as onto the high-surface area interface. FIG. 4D shows an example of the first polymer 64 with nanoparticles 82 deposited at the interface 72 of the first polymer 64 that was exposed after removal of the sacrificial polymer 66. The amount of nanoparticles 82 deposited onto the first polymer 64 can be a relative small amount, such as only enough nanoparticles 82 to provide for a uniform or substantially uniform monolayer of the nanoparticles 82 at the interface 72.

The nanoparticles 82 can sensitize a photovoltaic device at the interface between an electron donor material and an electron acceptor material, such as to increase adsorption of photons at a particular wavelength or range of wavelengths. Although the use of nanoparticles 82 can be helpful to sensitize a photoactive device to one or more wavelengths of light, such as the wavelengths that are expected to be encountered by the photoactive device, the use of nanoparticles 82 is not required for the resulting device to be used as a photovoltaic device.

The nanoparticles 82 can act similar to a dye, such as by absorbing light at a particular wavelength or range of wavelengths. The wavelength at which a particular nanoparticle 82 will sensitize the photoelectric device can depend on the particle size, e.g., the diameter of a generally spherically-shaped nanoparticle, or on the material of the nanoparticles. For example, a nanoparticle having a size of about 2 nanometers can facilitate absorption at a first range of wavelengths, a nanoparticle having a size of about 3 nanometers can facilitate absorption at a second range of wavelengths, and a nanoparticle having a size of about 4 nanometers can facilitate absorption at a third range of wavelengths. In an example, nanoparticles 82 can be configured to sensitize a photovoltaic device to not only visible wavelengths of light, but also to portions of the non-visible spectrum, such as infrared (IR) light or ultraviolet (UV) light. The nanoparticles 82 can also be configured to sensitize the

photovoltaic device to a wavelength that the electron donor material and the electron acceptor material are unable to absorb due to their band gap values.

A first set of nanoparticles 82 can be sized to facilitate absorption of red light (e.g., light at a wavelength of about 650 nanometers), a second set of  
5 nanoparticles 82 can be sized to facilitate absorption of green light (e.g., light at a wavelength of about 510 nanometers), and a third set of nanoparticles 82 can be sized to facilitate absorption of blue light (e.g., light at a wavelength of about 575 nanometers). Additional sets of nanoparticles 82 can be added to sensitize the photoelectric device to other wavelengths. In an example, the nanoparticles 82,  
10 such as each of the sets of nanoparticles 82, can each be evenly dispersed over the interface 72, such as to sensitize the entire photoelectric device or substantially the entire to the wavelengths of light to which the device will be exposed.

A particular nanoparticle 82 can include a composite nanoparticle. The composite nanoparticle can include an inorganic particle or crystal with a coating or  
15 ligand bound thereto, such as an organic ligand. The coating or ligand can prevent or reduce agglomeration of the nanoparticles 82. A composite nanoparticle can be formed by growing the organic coating or ligand on the inorganic particle or crystal in a solution of a surfactant. The inorganic particle or crystal can comprise at least one of cadmium selenide (CdSe), cadmium sulfide (CdS), lead selenide (PbSe), and  
20 lead sulfide (PbS). Examples of coatings or ligands include, but are not limited to, tri-n-octylphosphene-oxide (TOPO) or pyridine ( $C_5H_5N$ ), an organic ligand that can exhibit a conjugated structure with a delocalized electronic structure, and an inorganic metal-chalcogenide. The nanoparticles 82 can be deposited onto the first polymer 64 by first suspending the nanoparticles 82 in a solvent and then coating  
25 the resulting solution onto the first polymer 64, such as by spin coating the solution. The concentration of the nanoparticles 82 in the solution can be selected to provide for a desired dispersion of the nanoparticles 82 on the first polymer 64. The solvent can dissolve or suspend the nanoparticles 82, without or only slightly or partially dissolving the nanostructures 68 of the first polymer 64. The solvent can include a

mixture of dichlorobenze and diphenyl ether, such as at a concentration of the dichlorobenzene that will not dissolve the first polymer 64. In an example, the mixture is less than 50 % by volume of dichlorobenzene and 50% by volume or greater of diphenyl ether. Other examples of solvents that can be used include a  
5 mixture of dichlorobenze and cyclohexane or a mixture of dichlorobenze and cyclohexane if an organic coating or ligand is used, or a polar solvent if an inorganic coating, like a metal-chalcogenide. The specific solvent used will depend on the type of nanoparticle coating or ligand that is used.

At 52 of FIG. 3, a mating material can be deposited onto the exposed first  
10 polymer. If nanoparticles had been deposited onto the first polymer, then the mating material can be deposited over both the first polymer and the nanoparticles, such that the nanoparticles can be positioned at an interface between the first polymer and the mating material. FIG. 4E shows an example of a mating material  
15 84 that can be deposited onto the network of nanostructures 68 of the first polymer 64 such that the mating material 84 can be in intimate contact with the high-surface area interface 72 of the first polymer 64. The deposited mating material 84 can form a substantially continuous network of nanostructures 86 that can be interlinked with the first polymer nanostructures 68.

The first polymer 64 can include one of an electron donor material and an  
20 electron acceptor material, such as are used in a photovoltaic or other photoactive device. The mating material 84 can include the other of the electron donor material and the electron acceptor material, such that after the mating material 84 is deposited, a photoactive junction can be formed at the interface 72.

Examples of an electron donor polymer that can be used as the first polymer  
25 64 in the process 40 can include, but are not limited to, a semiconductor polymer, such as a polymer having a conjugated structure with a delocalized electronic structure, for example poly(3-hexylthiophene) (P3HT), polyacetylene, and polyphenylene

Examples of an electron acceptor material that can be used as the mating material 84 in the process 40 can include, but are not limited to, phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), C<sub>60</sub>, inorganic nanoparticles that are configured to be an electron acceptor material (e.g., n-type semiconductor), such as via doping, for example CdSe nanoparticles, 2-Vinyl-4,5-dicyanoimidazoles, copper hexadeca fluoro phthalocyanine (F<sub>16</sub>CuPc), and semiconducting carbon nanotubes

Examples of an electron acceptor polymer that can be used as the first polymer 64 in the process 40 can include, but are not limited to one or more polymers that comprise a C<sub>60</sub> pendant group, such as PCBM, 2-Vinyl-4,5-dicyanoimidazoles, and hexadeca fluoro phthalocyanine.

Examples of an electron donor material that can be used as the mating material 84 in the process 40 can include, but are not limited to, the electron donor polymers listed above, such as P3HT.

The mating material 84 can be deposited onto the network of first particle nanostructures 68, such as by any of a variety of methods. The method of depositing the mating material 84 can be selected such that the morphology of the first polymer 64, e.g., the network of first polymer nanostructures 68, is not altered or not substantially altered by depositing the mating material 84. The particular deposition method can depend on any of several factors, including, but not limited to, the specific mating material or materials 84 being used, the specific first polymer 64 being used, and the expected final structure of the deposited mating material 84. For example, if C<sub>60</sub> is being used as the mating material 84, the C<sub>60</sub> material can be deposited by thermal evaporation of the C<sub>60</sub>, which can provide a line-of-sight deposition of the C<sub>60</sub> onto the first polymer 64.

The mating material 84 can be dissolved in a solvent and the solvent can be coated onto the network of first polymer nanostructures 68, followed by removal of the solvent to effect deposition of the mating material 60. Dissolving of the mating material 84 can be particularly effective if the mating material 84 is a polymer or other organic compound, such as phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM),

because the use of a solvent can provide for a good coating of the first polymer nanostructures 68 with the mating material 84. In an example, the solvent that is used to dissolve the mating material 84 is unable to dissolve the first polymer 64, so that the network of first polymer nanostructures 68 can remain while the mating  
5 material 84 is deposited.

The depositing the mating material 84 can provide conformal or substantially conformal coverage of the first polymer 64, and the nanoparticles 82 (if present) by the mating material 84, such as to increase or maximize the area of the junction between the first polymer 64 and the mating material 84 at the interface  
10 72.

At 54 of FIG. 3, an anode can be electrically connected to the electron donor material. At 56, a cathode can be electrically connected to the electron acceptor material. At 58, a circuit or an electrical load can be electrically connected between the anode and the cathode. As described above, FIG. 1 shows an example of a  
15 photovoltaic device 10 in which an anode 14 has been electrically connected to the electron donor material 24, a cathode 16 has been electrically connected to the electron acceptor material 26, and a circuit 18 comprising an electric load 20 has been electrically connected between the anode 14 and the cathode 16.

The process can omit depositing the nanoparticles onto the first polymer (at  
20 50), depositing the mating material onto the first polymer (at 52), electrically connecting an anode to the electron donor material (at 54), electrically connecting a cathode to the electron acceptor material (at 56), and electrically connecting a circuit between the cathode and the anode (at 60). Instead, the process can include forming the morphology of the first polymer desired to be used for an application, for  
25 example for an application in which a high-surface area or a high-active volume can be desirable. For example, the high-surface area morphology of the first polymer 64 can be used for catalysis where the first polymer 64 or another material deposited thereon can act as a catalyst for a fluid-phase (e.g., gas or liquid phase) reaction. The high-surface area interface 72 of the first polymer 64 can also be configured as

a hydrophobic or hydrophilic surface, depending on the material of the first polymer 64. For example, it has been found that when poly(3-hexylthiophene) (P3HT) is used as the first polymer 64 and formed into the network of nanostructures 68, the resulting outer surface 80 (FIG. 4C) of the P3HT first polymer 64 has a water contact angle that is 400% greater than a substantially planar P3HT surface, indicating that the network of P3HT nanostructures 68 is more hydrophobic than the substantially planar P3HT surface. Other materials can be used to make the network of nanostructures 68 so that the outer surface 80 is less hydrophobic or more hydrophilic than the native properties of the first polymer 64.

10           A specific example of the process 40 will now be described with respect to the manufacture of an organic photovoltaic device (OPV). In the example, the first polymer 64 can comprise poly(3-hexylthiophene) (P3HT). The P3HT 64 can be dissolved with polystyrene (PS) as the sacrificial polymer 66 in dichlorobenzene (DCB) as the solvent that dissolves both the P3HT and the PS. The P3HT-PS-DCB solution 60 can be spin-casted onto a substrate 12, such as a patterned indium-tin-oxide (ITO) on glass substrate 12. After spin casting the P3HT-PS-DCB solution onto the ITO substrate 12, the resulting film 62 can be subjected to solvent annealing, also referred to as vapor annealing, by exposing the film 62 to a DCB-rich atmosphere. The film 62 also can be subjected to thermal annealing, such as by heating the film 62 to an elevated temperature of 135 °C. The phase-separated and annealed film 62 can be subjected to a solvent that will dissolve the PS but leave the P3HT, such as a solution of tetrahydrofuran and ethanol in a volume ratio of one part tetrahydrofuran to two parts ethanol, or a solution of dioxane and ethanol in a volume ratio of one part dioxane to two parts ethanol. The resulting structure comprises a network of P3HT nanostructures 68 that can be rinsed of the solvent, such as with pure ethanol.

25           A plurality of cadmium selenide (CdSe) nanoparticles 82 with an organic coating or ligand, such as tri-n-octylphosphine-oxide (TOPO) or pyridine (C<sub>5</sub>H<sub>5</sub>N), can be deposited onto the P3HT nanostructures 68, such as by placing the

nanocrystals in a dichlorobenzene (DCB) and diphenyl ether solvent with a volume concentration of the DCB of less than 50%. The solution of the CdSe nanoparticles, DCB, and the diphenyl ether can be coated onto the P3HT nanostructures 68, such as via spin casting.

5           A mating material 84 can be deposited onto the P3HT nanostructures 68 and nanoparticles 82, where the mating material 84 can comprise an electron acceptor material, such as phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) or cadmium selenide (CdSe) nanocrystals. Both the PCBM and the CdSe nanocrystals can be deposited by dissolving the material in a solvent that will dissolve the mating material 84, but  
10       not the P3HT, such as a solution of DCB and diphenyl ether in a 1:1 volume ratio. The solution of the acceptor material (PCBM or CdSe nanocrystals) can be spin-casted onto the P3HT nanostructures 68 and then baked to remove the solvent, such as at a temperature of 75 °C for about 30 minutes.

          One approach to maximize the active-volume fraction in organic  
15       photovoltaic devices is to form a bulk heterojunction (BHJ). A BHJ can be formed when an electron donor polymer and an electron acceptor material, usually another polymer, are blended together and cast into a film that phase separates. The phase separation of the electron donor polymer and the electron acceptor polymer can form closely intermixed regions of the electron donor material and the electron  
20       acceptor material, wherein the regions are sized on the order of a few nanometers, e.g., 5 nanometers, to about 50 nanometers.

          BHJs can be formed by dissolving both the electron donor polymer and the electron acceptor polymer in a solvent at the same time and casting the donor-acceptor system onto a substrate to form a film wherein the BHJ can form by phase-  
25       separation of the two materials. FIG. 5 is an example of a BHJ 90 formed by this method, where regions 92 of an electron donor polymer are intermixed with regions 94 of an electron acceptor polymer.

          A problem with a BHJ formed by a process of dissolving the electron donor and electron acceptor polymers in a common solvent is the difficulty of matching a

solvent to both the electron donor polymer and the electron acceptor polymer. For example, the solvent may be a good or strong solvent for the electron donor polymer, but a poor or weak solvent for the electron acceptor polymer, or vice versa. Or, in some cases, the only solvent that can dissolve both materials may  
5 actually be a poor solvent for both the electron donor polymer and the electron acceptor polymer. In either case, large quantities of solvent must be used to properly dissolve both the electron donor polymer and the electron acceptor polymer. The use of large quantities of solvent can be inefficient and, in some cases, cost prohibitive. Moreover, this method of forming BHJs can limit the  
10 choices of material combinations that can be used to form the BHJ, since both the electron donor material and the electron acceptor material must be able to be dissolved together.

Another problem associated with a BHJ formed by a process of dissolving the electron donor and electron acceptor polymers in a common solvent is the fact  
15 that many regions of each type of material, either electron donor or electron acceptor, can become isolated from a corresponding electrode. For example, as shown in FIG. 5, region 92A of the electron donor material and region 94A of the electron acceptor material can be completely isolated and surrounded by the other material without a path for charge carriers to take to reach the anode 96 or the  
20 cathode 98, respectively. Also, while a region 92B of the electron donor material is in contact with one of the electrodes, it is only in contact with the cathode 98 and it has no direct path to the anode 96 without having to pass through a junction into the electron acceptor material. Therefore, any holes that are created from an electron-hole pair in the region 92B or are swept into the region 92B cannot reach the anode  
25 96 to recombine with a returning electron. Similarly, while a region 94B of the electron acceptor material is in contact with one of the electrodes, it is only in contact with the anode 96 and has no direct path to the cathode 98, so that any electrons that are created from an electron-hole pair in the region 94B or that are swept into the region 94B cannot reach the cathode 98 so that the electrons from the

region 94B will not flow through a circuit 100 between the cathode 98 and the anode 96.

The process described in this disclosure, such as process 40 of FIG. 3, can avoid or overcome these disadvantages of other approaches to BHJ production.

5 First, the nanostructures of the first polymer, which can be the electron donor material or the electron acceptor material, is formed with the interaction between the first polymer and the sacrificial polymer, not by the interaction with the other material of the BHJ (e.g., with the other of the electron donor material and the electron acceptor material). Because of this, the first polymer, the sacrificial  
10 polymer, and the solvent can be selected so that the morphology of the first polymer can be formed independent of the mating material that forms the other part of the photoactive device. This independent formation of the first polymer nanostructure morphology allows a solvent that is a good or strong solvent for both the first polymer and the sacrificial polymer to be used.

15 The process described in this disclosure can provide several advantages over other techniques for forming BHJ structures. For example, as described in more detail above, the use of a good or strong solvent can allow the first polymer to be physisorbed to the substrate, and thus can form a conformal or substantially conformal bond between the first polymer and the surface of the substrate.

20 Therefore, the first polymer can be bonded to the surface of the substrate better than the electron donor and electron acceptor materials of other approaches to BHJ production.

Second, the process described in this disclosure can also help ensure that all or substantially all of the first polymer nanostructures can be coupled or bonded to  
25 the substrate surface. Because the substrate can serve as an electrode, or can electrically connect the first polymer to an electrode, the coupling or bonding of all or substantially all of the first polymer nanostructures can help ensure that there is a pathway for charge carriers (e.g., electrons or holes) within all or substantially all the nanostructures to reach the substrate. This is in contrast to other BHJ production

processes, in which one or more regions of both the electron donor material and the electron acceptor material can be isolated from their respective electrodes, as described above with respect to regions 92A, 92B, 94A, and 94B (FIG. 5).

Although it is possible for regions of the first polymer to be isolated from the substrate during phase separation of the first polymer from the sacrificial polymer, those isolated regions can become separated from the network of first polymer nanostructures when the sacrificial polymer is removed. The remaining first polymer can remain connected to the substrate throughout the remainder of the process.

10 Third, the process described in this disclosure can separate the formation of the nanostructure morphology of one of the materials of a photoactive device from the deposition of the other material of the photoactive device. Not only can this separation of these process steps allow for the use of a good or strong solvent for the first material, with the advantages described above, but this separation of the process steps can allow for more customization of the materials used in the formation of the photoactive device, allowing for practically unlimited combinations of the electron donor material and the electron acceptor material. Contrast this to other BHJ production methods, in which the combination of materials can be limited to those pairs of electron donor materials and electron acceptor materials that can be co-dissolved in the same solvent. The greater flexibility of the combination of electron donor materials and electron acceptor materials can provide for customization of the resulting photoactive device to the particular intended application or for optimization of the operation of the photoactive device.

25 Fourth, the process described in this disclosure can allow for the deposition of nanoparticles at the interface of the electron donor material and the electron acceptor material, so that the photovoltaic device will be sensitized at or proximate to the junction by all or substantially all of the nanoparticles that are deposited onto the device. Previous methods of forming BJHs, where the electron donor material and the electron acceptor material were cast together, could only add nanoparticles

to the blend of the electron donor material and the electron acceptor material, resulting in nanoparticles dispersed throughout the phase-separated suspension. This lead to a substantial portion of the nanoparticles being located away from the junction where the nanoparticles cannot provide as efficient of sensitizing to a particular wavelength, and in some cases, where the nanoparticles can provide no sensitizing at all.

BHJs can also be formed by growing nanostructures, such as nanofibers or nanowires, of one of the materials and then attempting to coat or deposit the formed nanostructures onto a substrate. The other material of the BHJ can then be deposited onto the nanostructures. This method of forming BHJs may solve some of the problems of other approaches to BHJ production, such as by decoupling the placement of the donor and acceptor materials of an eventual BHJ structure, allowing for customization of the materials that form the BHJ. However, previously demonstrated techniques for creating nanostructures in solution required a large volume of solvent to create a relatively small amount of nanostructures that can eventually be cast onto a device substrate. The technique described in this disclosure allows for a relatively concentrate solution of both the first material of the BHJ and the sacrificial polymer to be prepared in a common solvent, meaning much less solvent is needed to form the morphology of the first polymer compared to the weak solvents that are required for other approaches to BHJ production. The reduced solvent usage of the process of this disclosure can therefore provide for a more economical manufacture of a photoactive device compared to other approaches to making BHJ by separate production of polymer nanostructures.

Moreover, attempting to coat or deposit the grown nanostructures may not provide for adequate bonding or attachment to the substrate. The grown nanostructures can be deposited by first suspending the grown nanostructures in a weak solvent and then drop coating or spin casting the solvent and nanostructure suspension onto the substrate, which can provide for at least partial attachment of some of the nanostructures to the substrate. However, the use of pre-formed and

substantially rigid nanostructures is unlikely to create a conformal or bond between nanostructure and substrate, greatly reducing the area of intimate physisorption and reducing the quality of electrical contact between the pre-formed nanostructures and the substrate surface. Rather, the pre-fabricated nanostructures form sporadic  
5 attachment to the substrate, such as through point contact and bonding of each nanostructure. The strong or good solvents that can be used with the process of this disclosure cannot be used for the method of applying pre-formed (e.g., solution grown) nanostructure to a substrate, because the strong solvent would dissolve the nanostructure, resulting in the application of a planar film that does not provide the  
10 utility of a nanostructured film.

#### EXAMPLE

A solution of highly monodisperse polystyrene (PS) from Polymer Standards Service-USA, Amherst, MA, USA, and poly(3-hexylthiophene) (P3HT) from Luminescent Technologies Corp., Hsinchu, Taiwan was dissolved in  
15 dichlorobenzene (DCB) under inert conditions in a nitrogen (N<sub>2</sub>) filled glove box. After stirring over an extended period, e.g., up to 24 hours, at room temperature each solution was spun-cast at 1000 RPM for 60 seconds on poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) coated substrates. For morphology studies silicon wafers with native oxide were used as substrates.  
20 Patterned indium tin oxide (ITO) on glass was used as the substrate for device measurements.

Immediately after spin-casting, the films were subjected to a one hour room temperature solvent annealing treatment in a DCB-rich atmosphere. Next, the films were baked at 135 °C for 30 minutes. After baking, the films were submersed in a  
25 1:2 solution (on a volume basis) of tetrahydrofuran:ethanol for 30 minutes to remove the PS phase. The resulting P3HT films were then rinsed in pure ethanol, followed by drying at 70 degrees C for 30 minutes.

The resulting morphology of the P3HT was investigated using a Hitachi Model S-4700 scanning electron microscope (SEM), Hitachi High-Technologies

American Inc., Pleasanton, CA, USA, operated at 10 kV. To improve contrast samples were coated with approximately 18 angstroms of Au-Pd prior to SEM imaging. Surface contact measurements using both water and methyl alcohol served as an indicator of the effective surface area factor ( $\text{cm}^2$  of P3HT per ( $\text{areal cm}^2$ )).

5           The influence of the P3HT:PS ratio on the P3HT nanofiber morphology was explored by holding P3HT concentration constant at 15 mg/ml and varying the concentration of PS (molecular weight (MW) of 10.4 kg/mol) from 15 mg/ml to 60 mg/ml (resulting in the mass ratio of PS:P3HT being varied from 1:1 to 4:1). The effect of PS MW on P3HT morphology was investigated by holding the P3HT:PS  
10   mass ratio constant at 1:2 (45 mg/ml total solids) and increasing the PS MW from 6.2 kg/mol to 96 kg/mol.

          Small angle x-ray scattering (SAXS) measurements were performed at the Stanford Linear Accelerator Center (beam line 11-3) in order to investigate molecular packing within the P3HT nanofibers as well as the PS matrix. An  
15   incident angle of 0.12 degrees was used to obtain SAXS data from films of pure P3HT, pure PS (10.4k MW), blended films of PS and P3HT, as well as P3HT nanowire mats. The SAXS data showed that the P3HT nanofibers are highly crystalline and therefore expected to have good electrical characteristics. Therefore, blending and phase-separating the sacrificial PS with P3HT, followed by removal of  
20   the PS does not appear to adversely affect molecular packing of the P3HT, such that the P3HT is expected to have good electrical characteristics.

          Photovoltaic devices were fabricated by spin-coating an acceptor material onto the P3HT nanofiber mats. The acceptor phase solution was made by dissolving 15 mg/ml of either PCBM from Luminescent Technologies, Corp., Hsinchu, Taiwan  
25   or pyridine-capped CdSe nanocrystals (~ 3.5 nm diameter) in an orthogonal solvent consisting of 1:1 DCB:Diphenylether. The CdSe nanocrystals were formed by injecting a mixture of dimethylcadmium, trioctylphosphine-selendie, and trioctylphosphine into a molten bath of trioctylphosphine oxide held at a temperature of 350 °C. The CdSe nanoparticles were coated with pyridine (Sigma-

Aldrich Co. LLC (St. Louis, MO, USA). These solutions were spin casted onto either planar P3HT films or P3HT nanofiber mats at 800 RPM for 60 seconds and subsequently baked at 75 °C for 30 minutes.

### Results

5           FIG. 6 shows the morphology that results from a typical 1:1 blend of P3HT and PS (10.4 kg/mol) after removal of the PS phase. As shown in FIG. 6, regions of P3HT nanofiber exist as isolated pockets surrounded by a planar P3HT film. At P3HT fractions of less than 50 wt. % (e.g., a P3HT:PS mass ratio of less than 1:1) we find that there is an inversion of this structure where the majority of the film (> 10 50%) develops a nanofiber morphology leaving small mesas of planar P3HT that protrude above the planar mat by approximately 60 nm. As P3HT weight fraction is reduced the fraction of the substrate covered in nanofiber mat steadily increase. FIG. 7 shows an approximately linear relationship between nanofiber coverage and initial P3HT weight fraction in the initial polymer blend. Although SEM studies may 15 indicate that low weight fractions of P3HT in the initial blend (< 20 wt. %) produces the largest fraction of nanofiber morphology, surface contact angle measurements indicate a maximum effective surface area for films initially containing 30 wt. % P3HT. This is consistent with atomic force microscope (AFM) measurements that show films initially consisting of less than 30 wt. % P3HT lead to nanofiber mats 20 that are very thin and may leave regions of exposed substrate. Therefore, a weight percentage of 30 wt. % P3HT in the initial mixture appears to be a good composition for the formation of P3HT nanofiber mats.

The effect of PS molecular weight on P3HT nanofiber morphology was also investigated by holding the P3HT:PS ratio constant at 30 wt. % P3HT while varying 25 the PS molecular weight from 6.4 kg/mol to 96 kg/mol. At low PS MW values (6.4 kg/mol) the eventual P3HT film exhibits relatively few planar mesas and is dominated by a nanofiber mat morphology. However, the P3HT nanofiber mat is relatively thin. At higher PS Mw values (> 10k kg/mol) the final P3HT morphology is relatively constant and is characterized by nanowires covering approximately 80–

90 % of the substrate surface. However, for high PS MW it takes longer to remove the PS phase. For PS MW of 19kg/mol and greater it is possible to identify regions of the film in which PS removal has not yet been completed after attempting to dissolve the PS for 30 min. If the same films are subjected to a second 30 min  
5 immersion in a fresh solution of the selective solvent, all films reach a similar morphology.

The above results suggest that the formation of P3HT nanofibers is driven by the crystallization of the P3HT phase and the corresponding exclusion of the PS phase from the P3HT crystallites. At low P3HT fractions this leads to a large  
10 number of small P3HT crystals that are surrounded by a continuous matrix of PS. Upon removal of the PS phase, some of the P3HT is left unsupported and is lost to the PS-selective solvent. In order to attain a continuous and interconnected P3HT nanowire mat it is important to have sufficient P3HT in the initial blend that during phase separation and drying adjacent P3HT domains impinge upon one another.  
15 This type of crystallite percolation can occur at P3HT fractions of greater than 20 wt. %. The MW of the PS sacrificial phase has relatively little influence on the eventual film morphology. The tendency of high MW PS to leave planar regions may be the result of reduced PS solubility in the PS selective solvent, or partial entrapment of large PS molecules by the insoluble P3HT phase.

20 SAXS measurements demonstrate that the P3HT nanowire films exhibit a high degree of ordering in the out of plane direction. Annealed P3HT/PS blends show ordering in the out of plane direction corresponding to P3HT interchain stacking. The PS phase produces a diffuse diffraction pattern characteristic of an amorphous polymer. Upon removal of the PS phase the out of plane P3HT ordering  
25 persists. Comparison to planar P3HT films confirms that the blending and phase-separation process and subsequent removal of the sacrificial PS does not interfere with an apparently strong interaction of P3HT with the substrate.

Photovoltaic device measurements of the devices made from the P3HT nanowire films and of control devices made from planar P3HT films were taken.

The devices made with nanowire morphology demonstrated an increase in short-circuit current ( $J_{SC}$ ) of as much as 400% compared to devices with a planar P3HT film. The P3HT nanowire electron donor material back-filled with PCBM or CdSe nanocrystals also demonstrated an increase of photoconversion efficiency of 800% and 300%, respectively, compared to devices with a planar P3HT film.

To better illustrate the photoactive devices and methods of making a photoactive device, a non-limiting list of examples is now provided:

Example 1 can include subject matter (such as an apparatus, a device, a method, or one or more means for performing acts), such as can include or use a device comprising a substrate. A continuous or substantially continuous network of polymer nanostructures can be coupled to the substrate.

Example 2 can include, or can optionally be combined with the subject matter of Example 1, to optionally include or use the network of polymer nanostructures being physisorbed to the substrate, such as in an intimate and conformal coupling between the network of polymer nanostructures and the substrate.

Example 3 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1 and 2, to optionally include or use a mating material that can be in intimate contact with the network of polymer nanostructures, such as to form a high-surface area interface between the network of polymer nanostructures and the mating material.

Example 4 can include, or can optionally be combined with the subject matter of Example 3, to optionally include or use the network of polymer nanostructures comprising one of an electron donor material and an electron acceptor material. The mating material can comprise the other of the electron donor material and the electron acceptor material.

Example 5 can include, or can optionally be combined with the subject matter of one or any combination of Examples 3–4, to optionally include or use a plurality of nanoparticles at the high-surface area interface.

Example 6 can include, or can optionally be combined with the subject matter of one or any combination of Examples 3–5, to optionally include or use nanoparticles at the high-surface area interface that can comprise nanocomposite particles comprising inorganic nanocrystals with an organic polymer surface  
5 coating.

Example 7 can include, or can optionally be combined with the subject matter of one or any combination of Examples 3–6, to optionally include or use nanoparticles at the high-surface area interface that can comprise a nanocrystal comprising cadmium selenide.

10 Example 8 can include, or can optionally be combined with the subject matter of one or any combination of Examples 4–7, to optionally include or use the electron donor material comprising poly(3-hexylthiophene).

Example 9 can include, or can optionally be combined with the subject matter of one or any combination of Examples 4–8, to optionally include or use the  
15 electron acceptor material comprising at least one of phenyl-C<sub>61</sub>-butyric acid methyl ester or a plurality of cadmium selenide nanocrystals.

Example 10 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–9, to optionally include or use the network of polymer nanostructures comprising a semiconductor polymer.

20 Example 11 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–10, to include subject matter (such as an apparatus, a device, a method, or one or more means for performing acts), such as can include a method of making a photoactive device. The subject matter can comprise mixing a first polymer and a second polymer in a solvent, such as to  
25 form a solution in which each of the first polymer and the second polymer can be dissolved by the solvent. The solution can be coated onto a substrate. The first polymer can be phase-separated from the second polymer, such as to form a substantially continuous network of nanostructures of the first polymer that can be interlinked with a substantially continuous network of nanostructures of the second

polymer. A high-surface area interface can be formed between the substantially continuous network of nanostructures of the first polymer and the substantially continuous network of nanostructures of the second polymer. The second polymer can be removed to expose the high-surface area interface.

5           Example 12 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1-11, to optionally include phase-separating the first polymer from the second polymer that comprises physisorbing the first polymer to the substrate, such as for forming an intimate and conformal coupling between the network of nanostructures of the first polymer and the  
10    substrate.

          Example 13 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1-12, to optionally include depositing a mating material onto the network of nanostructures of the first polymer such that the mating material can be in intimate contact with the high-surface area  
15    interface.

          Example 14 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1-13, to optionally include the first polymer comprising one of an electron donor material and an electron acceptor material. The mating material can comprise the other of the electron donor material  
20    and the electron acceptor material.

          Example 15 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1-14, to optionally include depositing a plurality of nanoparticles at the high-surface area interface prior to depositing the mating material onto the network of nanostructures of the first  
25    polymer.

          Example 16 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1-15, to optionally include the nanoparticles comprising nanocomposite particles comprising inorganic nanocrystals grafted with an organic polymer ligand.

Example 17 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–16, to optionally include the nanoparticles comprising a nanocrystal comprising cadmium selenide.

5      Example 18 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–17, to optionally include depositing the mating material comprising dissolving the mating material into a second solvent to form a second solution and coating the second solution onto the network of nanostructures of the first polymer.

10      Example 19 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–18, to optionally include phase-separating the sacrificial material and the first material comprising at least one of thermal annealing or vapor annealing the mixture of the first polymer and the second polymer.

15      Example 20 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–19, to optionally include removing the second polymer comprising dissolving the second polymer while leaving the first polymer.

20      Example 21 can include, or can optionally be combined with the subject matter of one or any combination of Examples 1–20, to optionally include the first polymer comprising a semiconductor polymer.

Example 22 can include, or can optionally be combined with any portion or combination of any portions of any one or more of Examples 1-21 to include, subject matter that can include one or means for performing any one or more of the functions of Examples 1-21.

25      In the above detailed description, reference is made to the accompanying drawings that form a part hereof and in which are shown, by way of illustration, specific embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the

invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made.

While a number of embodiments of the invention are described, the above lists are not intended to be exhaustive. Although specific embodiments have been  
5 illustrated and described herein, it will be appreciated by those of ordinary skill in the art that any arrangement that is calculated to achieve the same purpose may be substituted for the specific embodiment shown. This application is intended to cover any adaptations or variations of the present invention. It is to be understood that the above description is intended to be illustrative and not restrictive.

10 The above detailed description includes references to the accompanying drawings, which form a part of the detailed description. The drawings show, by way of illustration, specific embodiments in which the invention can be practiced. These embodiments are also referred to herein as “examples.” Such examples can include elements in addition to those shown or described. However, the present  
15 inventors also contemplate examples in which only those elements shown or described are provided. Moreover, the present inventors also contemplate examples using any combination or permutation of those elements shown or described (or one or more aspects thereof), either with respect to a particular example (or one or more aspects thereof), or with respect to other examples (or one or more aspects thereof)  
20 shown or described herein.

These non-limiting examples can be combined in any permutation or combination.

All publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually  
25 incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference(s) should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

In this document, the terms “a” or “an” are used, as is common in patent documents, to include one or more than one, independent of any other instances or usages of “at least one” or “one or more.” In this document, the term “or” is used to refer to a nonexclusive or, such that “A or B” includes “A but not B,” “B but not A,” and “A and B,” unless otherwise indicated. In the appended claims, the terms “including” and “in which” are used as the plain-English equivalents of the respective terms “comprising” and “wherein.” Also, in the following claims, the terms “including” and “comprising” are open-ended, that is, a system, device, article, or process that includes elements in addition to those listed after such a term in a claim are still deemed to fall within the scope of that claim. Moreover, in the following claims, the terms “first,” “second,” and “third,” etc. are used merely as labels, and are not intended to impose numerical requirements on their objects.

The above description is intended to be illustrative, and not restrictive. For example, the above-described examples (or one or more aspects thereof) may be used in combination with each other. Other embodiments can be used, such as by one of ordinary skill in the art upon reviewing the above description. The Abstract is provided to comply with 37 C.F.R. §1.72(b), to allow the reader to quickly ascertain the nature of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims. Also, in the above Detailed Description, various features may be grouped together to streamline the disclosure. This should not be interpreted as intending that an unclaimed disclosed feature is essential to any claim. Rather, inventive subject matter may lie in less than all features of a particular disclosed embodiment. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment, and it is contemplated that such embodiments can be combined with each other in various combinations or permutations. The scope of the invention should be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

THE CLAIMED INVENTION IS:

1. A device, comprising:  
a substrate; and  
a continuous network of polymer nanostructures coupled to the substrate.
2. The device of claim 1, wherein the network of polymer nanostructures is physisorbed to the substrate in an intimate and conformal coupling between the network of polymer nanostructures and the substrate.
3. The device of claim 1, comprising a mating material in intimate contact with the network of polymer nanostructures to form a high-surface area interface between the network of polymer nanostructures and the mating material.
4. The device of claim 3, wherein the network of polymer nanostructures comprises one of an electron donor material and an electron acceptor material and the mating material comprises the other of the electron donor material and the electron acceptor material.
5. The device of claim 4, comprising a plurality of nanoparticles at the high-surface area interface.
6. The device of claim 5, wherein the nanoparticles comprise nanocomposite particles comprising inorganic nanocrystals with an organic polymer surface coating.
7. The device of claim 5, wherein the nanoparticles comprise a nanocrystal comprising cadmium selenide.

8. The device of claim 4, wherein the electron donor material comprises poly(3-hexylthiophene).
9. The device of claim 4, wherein the electron acceptor material comprises at least one of phenyl-C<sub>61</sub>-butyric acid methyl ester or a plurality of cadmium selenide nanocrystals.
10. The device of any of claim 1, wherein the network of polymer nanostructures comprises a semiconductor polymer.
11. A method of making a photoactive device, the method comprising:
  - mixing a first polymer and a second polymer in a solvent to form a solution in which each of the first polymer and the second polymer is dissolved by the solvent;
  - coating the solution onto a substrate;
  - phase-separating the first polymer from the second polymer to form a substantially continuous network of nanostructures of the first polymer interlinked with a substantially continuous network of nanostructures of the second polymer, forming a high-surface area interface between the substantially continuous network of nanostructures of the first polymer and the substantially continuous network of nanostructures of the second polymer; and
  - removing the second polymer to expose the high-surface area interface.
12. The method of claim 11, wherein phase-separating the first polymer from the second polymer comprises physisorbing the first polymer to the substrate and forming an intimate and conformal coupling between the network of nanostructures of the first polymer and the substrate.

13. The method of claim 11, comprising depositing a mating material onto the network of nanostructures of the first polymer so that the mating material is in intimate contact with the high-surface area interface.

14. The method of claim 13, wherein the first polymer comprises one of an electron donor material and an electron acceptor material and the mating material comprises the other of the electron donor material and the electron acceptor material.

15. The method of claim 13, comprising depositing a plurality of nanoparticles at the high-surface area interface prior to depositing the mating material onto the network of nanostructures of the first polymer.

16. The method of claim 15, wherein the nanoparticles comprise nanocomposite particles comprising inorganic nanocrystals grafted with an organic polymer ligand.

17. The method of claim 15, wherein the nanoparticles comprise a nanocrystal comprising cadmium selenide.

18. The method of claim 13, wherein depositing the mating material comprises dissolving the mating material into a second solvent to form a second solution and coating the second solution onto the network of nanostructures of the first polymer.

19. The method of claim 11, wherein phase-separating the sacrificial material and the first material comprises at least one of thermal annealing or vapor annealing the mixture of the first polymer and the second polymer.

20. The method of claim 11, wherein removing the second polymer comprises dissolving the second polymer while leaving the first polymer.

21. The method of claim 11, wherein the first polymer comprises a semiconductor polymer.

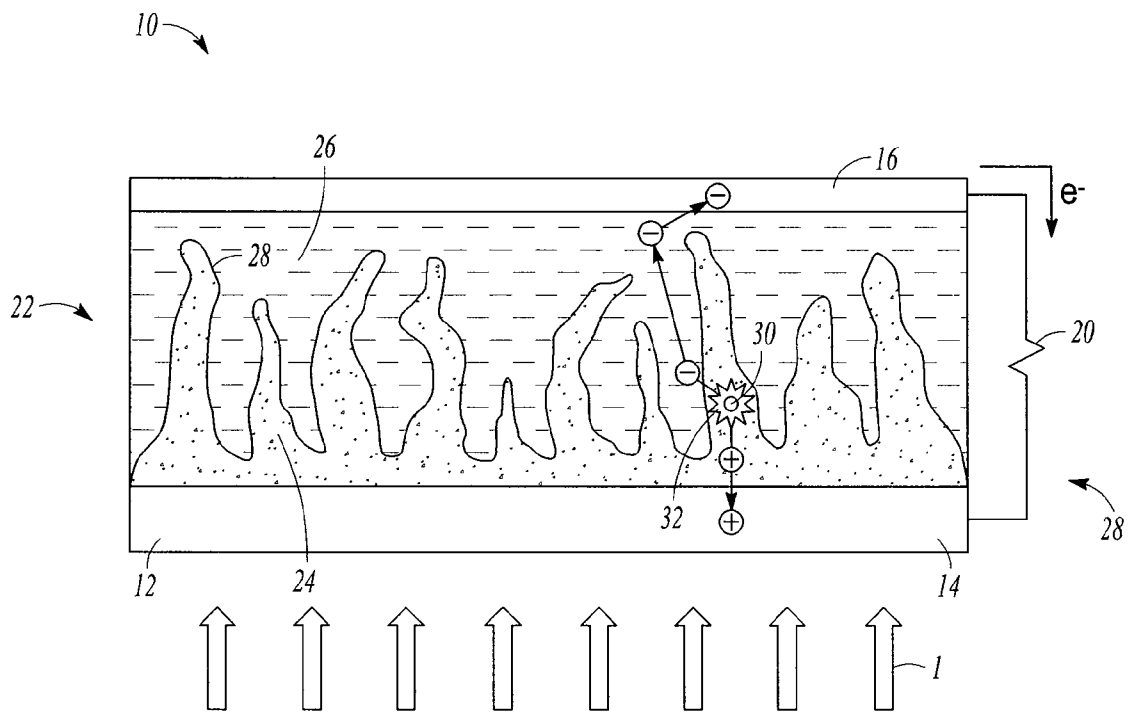


FIG. 1

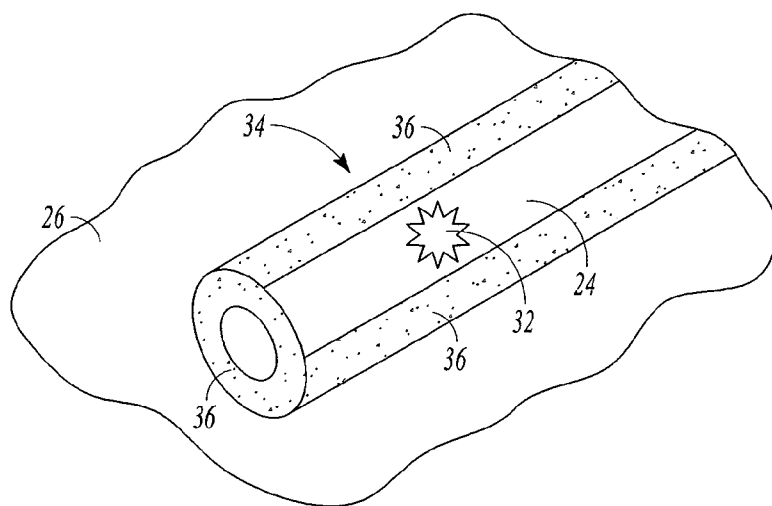
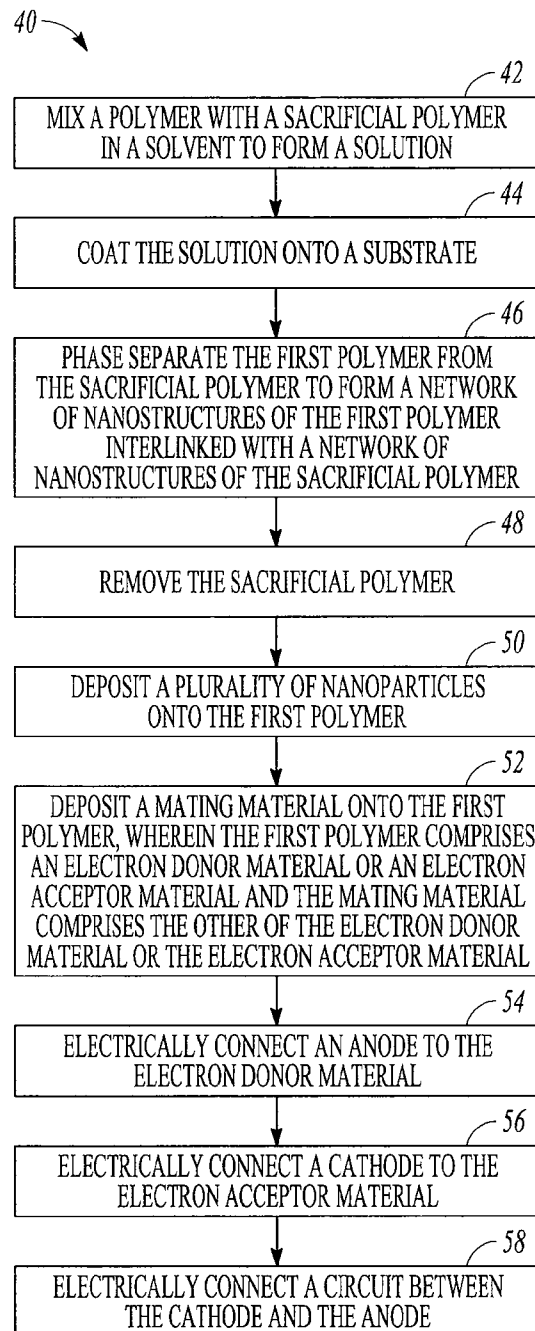
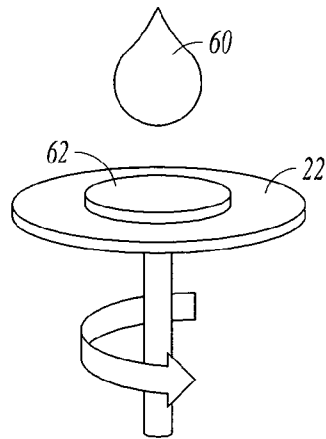
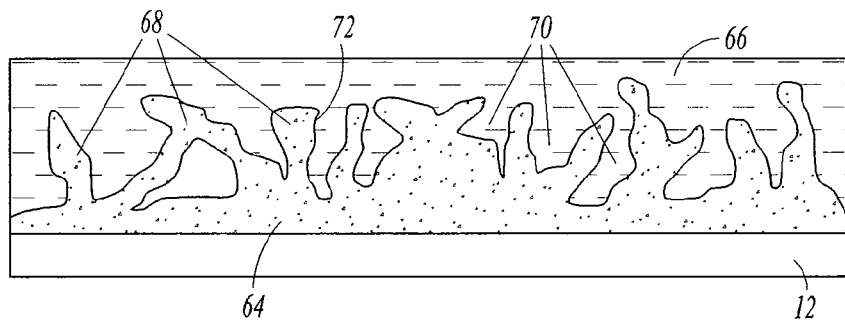


FIG. 2

*FIG. 3*



**FIG. 4A**



**FIG. 4B**

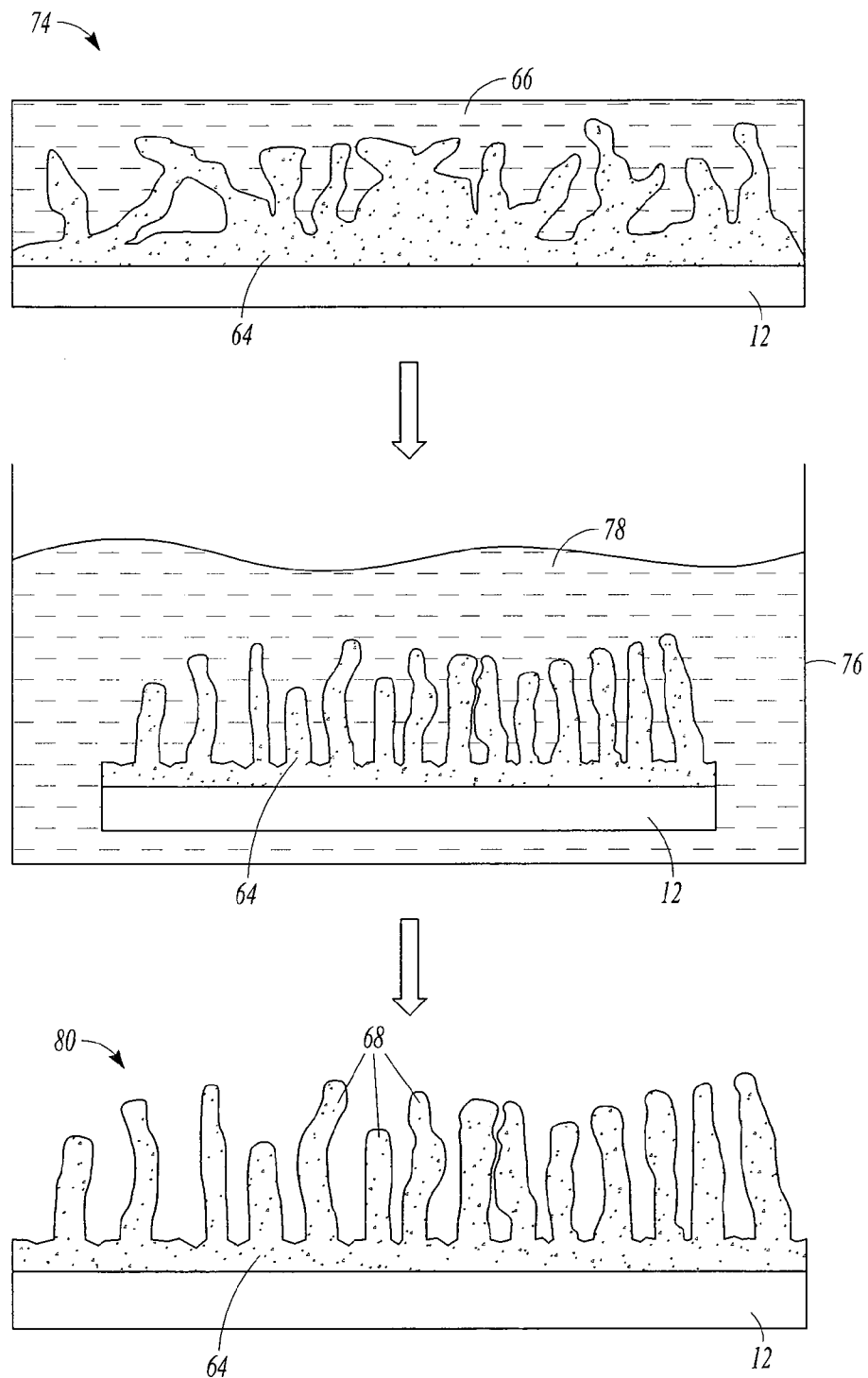


FIG. 4C

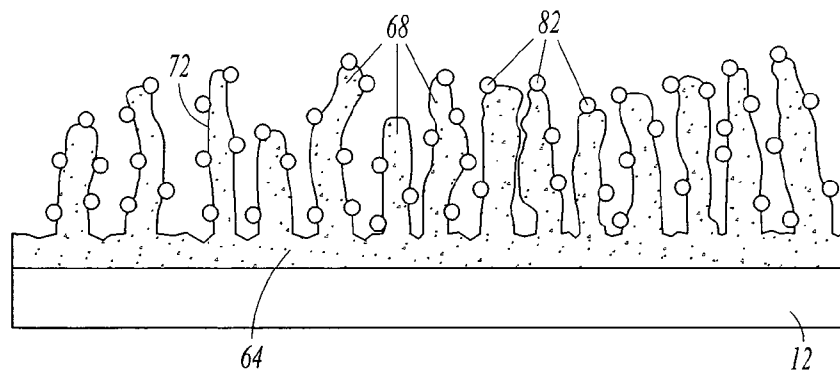


FIG. 4D

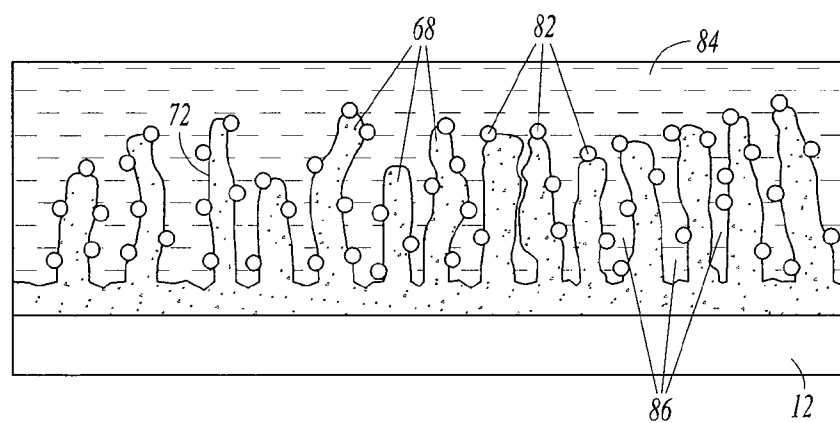


FIG. 4E

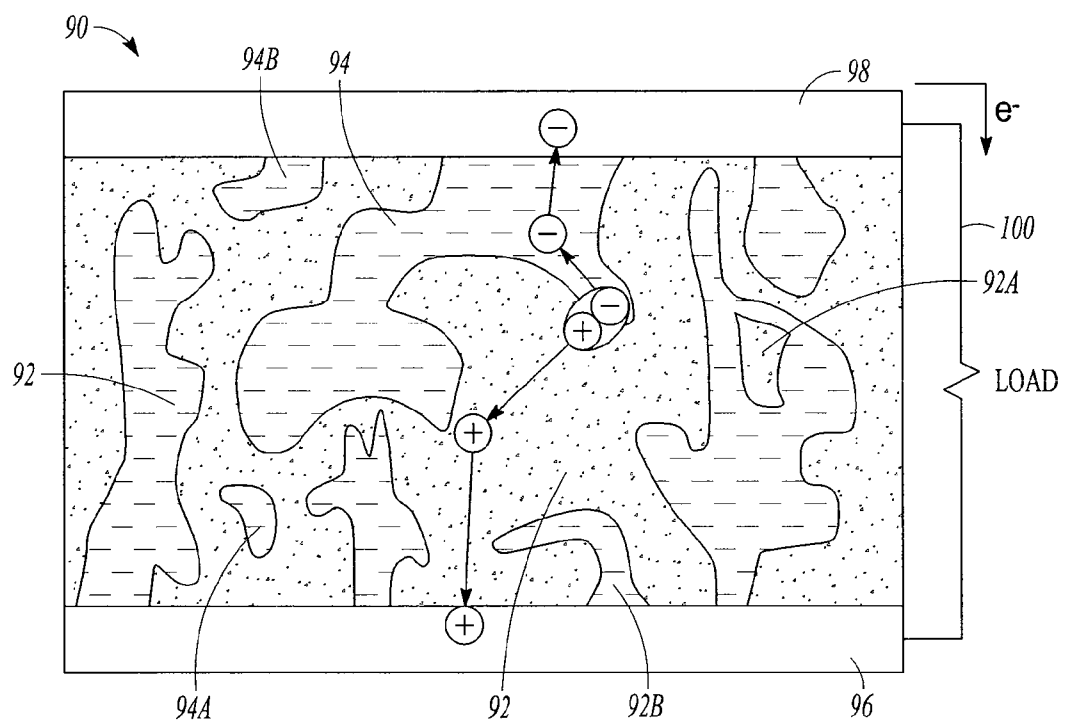
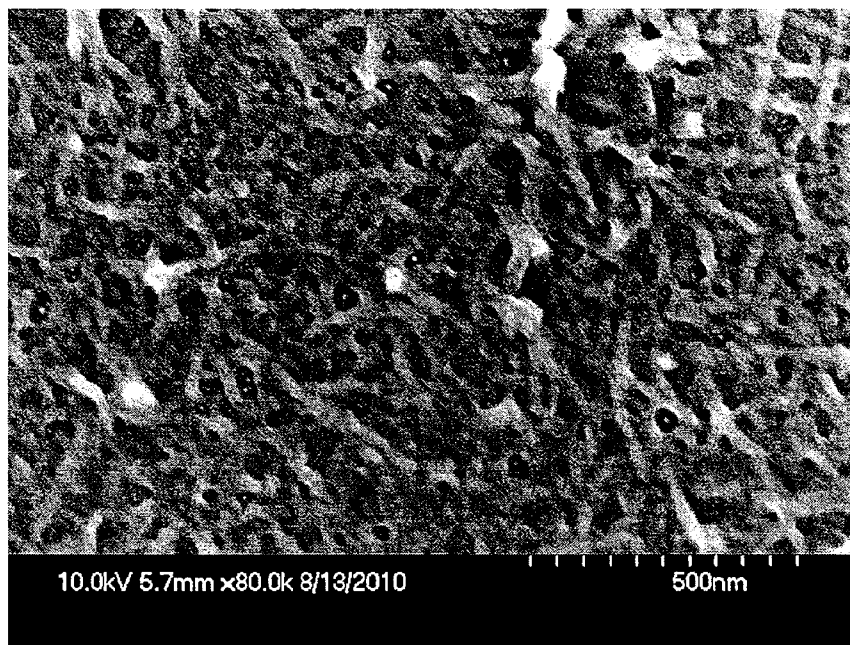
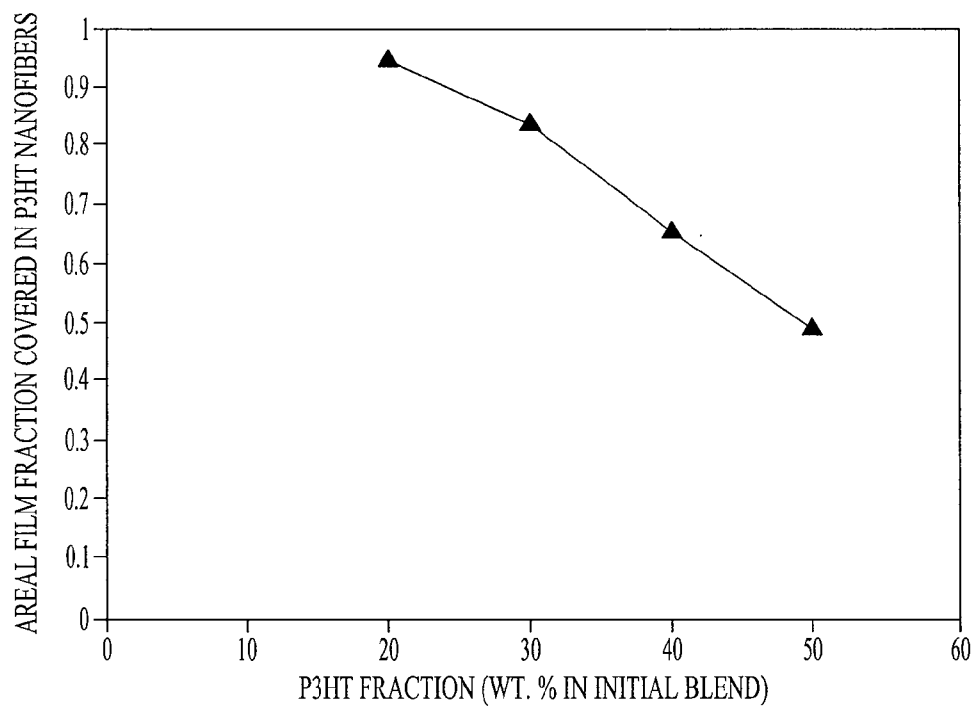


FIG. 5

*FIG. 6**FIG. 7*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/029914

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC(8) - H01L 21/00 (2012.01)<br>USPC - 438/82<br>According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                    |                                                                                                     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC(8) - H01L 21/00, H01L 31/00 (2012.01)<br>USPC - 136/263, 136/264; 438/82, 438/84; 977/948<br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>MicroPatent, Google Patents, Google Scholar                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                    |                                                                                                     |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                    |                                                                                                     |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No.                                                                               |
| X<br>---                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | US 2005/0150541 A1 (SCHER et al) 14 July 2005 (14.07.2005) entire document         | 1,3-11,13-21                                                                                        |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                    | 2,12                                                                                                |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 2011/0045523 A1 (STRANO et al) 24 February 2011 (24.02.2011) entire document    | 2,12                                                                                                |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 7,858,550 B2 (DRESSICK et al) 28 December 2010 (28.12.2010) entire document     | 1-21                                                                                                |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 7,771,512 B2 (NORTON et al) 10 August 2010 (10.08.2010) entire document         | 1-21                                                                                                |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                    |                                                                                                     |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier application or patent but published on or after the international filing date<br>"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)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br>"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<br>"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<br>"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<br>"&" document member of the same patent family |                                                                                    |                                                                                                     |
| Date of the actual completion of the international search<br>26 June 2012                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                    | Date of mailing of the international search report<br><b>13 JUL 2012</b>                            |
| Name and mailing address of the ISA/US<br>Mail Stop PCT, Attn: ISA/US, Commissioner for Patents<br>P.O. Box 1450, Alexandria, Virginia 22313-1450<br>Facsimile No. 571-273-3201                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                    | Authorized officer:<br>Blaine R. Copenheaver<br>PCT Helpdesk: 571-272-4300<br>PCT OSP: 571-272-7774 |