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(54) Title: TRANSPARENT ELECTRODES

(57) Abstract: Provided herein a transparent conductive material comprising non-covalent hybrids comprising carbon nanotubes (CNTs) and at least one anthraquinone derivative, and to transparent electrodes comprising thereof.



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TRANSPARENT ELECTRODES

FIELD OF THE INVENTION

[001] This disclosure is directed to a transparent conductive material comprising non-covalent hybrids comprising carbon nanotubes (CNTs) and at least one anthraquinone derivative, and to transparent electrodes comprising thereof.

BACKGROUND OF THE INVENTION

[002] CNTs are used to produce high quality electrodes and can enhance properties of various materials (e.g., polymers). CNTs, both multiwalled (MWCNTs) and single walled (SWCNTs) become readily available and inexpensive due to recent large-scale production. Yet, CNTs have a high tendency for bundling, which impedes their dispersion in liquid (solvents) and solid (polymer) media. This issue limits the ability to fabricate materials with improved properties conveniently and cost-efficiently. This issue is a central challenge in the field.

[003] In the past the inventors used perylene diimide derivatives for CNT dispersions in solution, however, dispersion at concentration above 0.2g/l could not be obtained in neat water, and in most organic solvents.

[004] Although CNTs are known for their diverse electrical properties, providing reliable macroscopic platforms with which to exploit these properties is yet to be fully realized, until now. The presently disclosed subject matter relates to transparent conductive materials and electrodes derived therefrom, based on CNT hybrids, which can be readily transferred on to other transparent substrates. The ability to use CNT-based transparent materials and electrodes on transparent substrates provides a versatile platform for many applications.

[005] A goal of the present application is to provide transparent conductive materials and transparent conductive electrodes, based on CNTs, which are readily fabricated, easily transferrable and integrated with various transparent, flexible, bendable, stretchable and inflatable platforms.

SUMMARY OF THE INVENTION

[006] In one embodiment the presently disclosed subject matter provides a transparent conductive material comprising non-covalent hybrids comprising carbon nanotubes (CNTs) and at least one anthraquinone or derivative thereof. In one embodiment the transparent conductive material comprises CNTs which are single-walled, multi-walled or a combination thereof. In one

embodiment the transparent conductive material comprises CNTs which are single-walled. In one embodiment the transparent conductive material comprises an anthraquinone or derivative thereof which is purpurin or alizarin or a combination thereof. In one embodiment the transparent conductive material is in a form selected from a list comprising: a membrane, dispersion, buckypaper, bulk material, coating, film, paste, paint, gel, powder or aerogel. In one embodiment the transparent conductive material comprises CNTs which are doped. In one embodiment the transparent conductive material is porous. In one embodiment the transparent conductive material has a transmittance of between 50 to 100 % in the UV-visible range. In one embodiment the transparent conductive material has a thickness ranging between 1 and 1000 nm.

[007] In one embodiment the transparent conductive material has a conductance which is maintained upon flexing, bending, stretching and/or inflation. In one embodiment the maintained conductance refers to the conductance not dropping to zero upon flexing, bending, stretching and/or inflating i.e., it is non-zero and can conduct electricity even though the material has been deformed.

[008] In one embodiment the presently disclosed subject matter provides a transparent conductive electrode comprising a transparent conductive material, further comprising a substrate wherein the transparent conductive material is disposed on a substrate. In one embodiment the transparent conductive electrode has a substrate which is transparent or translucent. In one embodiment the transparent conductive electrode comprises a substrate which is stretchable, bendable, flexible and/or inflatable. In one embodiment the transparent conductive electrode comprises a substrate selected from a group comprising: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylon, nylon 6, nylon 6,6, polyamide, aramids, polytetrafluoroethylene (PTFE), thermoplastics, thermoplastic polyurethanes (TPU), polystyrene, polychlorotrifluoroethylene (PCTFE), phenol-formaldehyde resin, para-aramid fiber, para-aramid, polyethylene terephthalate (PET), polychloroprene, meta-aramid polymer, polyacrylonitrile (PAN), polyamide 11 & 12, copolyamid, polyimide, aromatic polyester, polyester, ABS, poly-p-phenylene-2,6-benzobisoxazole (PBO), polyolefins, aromatic polymers, poly(methyl methacrylate) (PMMA), polyether ether ketone (PEEK), polyethylene glycol (PEG), polylactic acid (PLA), halogenated polymers and their combination and/or copolymers. In one embodiment the transparent conductive electrode comprises a substrate selected from a group comprising: fabric, paper, stretchable textile or an elastomer. In one embodiment the transparent conductive electrode comprises a substrate wherein the elastomer is selected from a group comprising: latex, rubber, polyurethane and/or silicone. In one embodiment the transparent conductive electrode comprises a substrate which is glass, silicon and/or silicon oxide.

[009] In one embodiment the presently disclosed subject matter provides a composite electrode comprising a first conductive transparent material, further comprising at least one additional transparent conductive material, and wherein the first transparent conductive material is connected to the at least one additional transparent conductive material in series and/or parallel. In one embodiment the composite electrode comprising a first transparent electrode and further comprising at least one additional transparent conductive electrode, and wherein the first transparent conductive electrode is connected to the at least one additional transparent electrode in series and/or parallel.

[0010] In one embodiment the presently disclosed subject matter provides a method of preparing a transparent conductive electrode, the method comprising:

- optionally grinding carbon nanotubes (CNTs);
- mixing the CNTs and anthraquinone or derivative thereof in a sonication bath in an aqueous solvent or an organic solvent, forming a hybrid solution;
- diluting the hybrid solution;
- vacuum filtering the hybrid solution through a porous medium forming conductive solid deposits disposed thereon;
- placing the porous medium with the conductive solid deposits disposed thereon into a liquid bath wherein the conductive solid deposits detach from the porous medium resulting in the conductive solid deposits remaining on the surface of the liquid bath and the porous medium sinking to the base of the liquid bath;
- removing the porous medium from the liquid bath;
- placing a substrate at the base of the liquid bath;
- removing liquid from the liquid bath until the conductive solid deposits are disposed on the substrate resulting in a transparent conductive electrode; and
- optionally drying the transparent conductive electrode.

[0011] In one embodiment the method comprises CNTs which are single-walled, multi-walled or a combination thereof. In one embodiment the method comprises CNTs which are single-walled. In one embodiment the method comprises CNTs which are doped. In one embodiment of the method the anthraquinone derivative is purpurin or alizarin or a combination thereof.

[0012] In one embodiment of the method the organic solvent is selected from a group comprising: chloroform, methylene chloride, carbon tetrachloride dichloroethane, glyme, diglyme, triglyme, triethylene glycol, trichloroethane, tertbutyl methyl ether, tetrachloro ethane, acetone, THF, DMSO, toluene, benzene, alcohol, isopropyl alcohol (IPA), chlorobenzene, acetonitrile, dioxane, ether, NMP, DME, DMF, ethyl-acetate or combination thereof. In one embodiment of the method

the hybrid solution has a CNT concentration of between 1 wt% to 99 wt%. In one embodiment of the method the porous medium is selected from a group comprising: filter paper, transfer membrane, polyvinylidene difluoride (PVDF) filter/membrane, polytetrafluoroethylene (PTFE) membrane, microporous membranes, mesoporous membranes, microporous membranes, organic-based membranes, inorganic-based membranes, nitrocellulose membranes (NC) and polysilsesquioxane (PSQ) membranes.

[0013] In one embodiment of the method the conductive solid deposits are in the form selected from a group comprising: a membrane, buckypaper, bulk material, coating, film, thin film, paste, paint, gel, powder or aerogel. In one embodiment of the method the liquid bath is a water bath. In one embodiment of the method the substrate is transparent or translucent. In one embodiment of the method the substrate is stretchable, bendable, flexible and/or inflatable. In one embodiment of the method the substrate is selected from a group comprising: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylon, nylon 6, nylon 6,6, polyamide, aramids, polytetrafluoroethylene (PTFE), thermoplastics, thermoplastic polyurethanes (TPU), polystyrene, polychlorotrifluoroethylene (PCTFE), phenol-formaldehyde resin, para-aramid fiber, para-aramid, polyethylene terephthalate (PET), polychloroprene, meta-aramid polymer, polyacrylonitrile (PAN), polyamide 11 & 12, copolyamid, polyimide, aromatic polyester, polyester, ABS, poly-p-phenylene-2,6-benzobisoxazole (PBO), polyolefins, aromatic polymers, poly(methyl methacrylate) (PMMA), polyether ether ketone (PEEK), polyethylene glycol (PEG), polylactic acid (PLA), halogenated polymers and their combination and/or copolymers.

[0014] In one embodiment of the method the substrate is selected from a group comprising: fabric, paper, stretchable textile or an elastomer. In one embodiment of the method the elastomer is selected from a group comprising: latex, rubber, polyurethane and/or silicone. In one embodiment of the method the substrate is glass, silicon and/or silicon oxide. In one embodiment of the method the drying comprises any of the following: drying with nitrogen flow, drying within a dry box, drying with vacuum, drying with heating or any combination thereof.

[0015] In one embodiment the presently disclosed subject matter provides a transparent conductive electrode produced by any of the methods detailed herein.

BRIEF DESCRIPTION OF THE FIGURES

[0016] The subject matter regarded as the present invention is particularly pointed out and distinctly claimed in the concluding portion of the specification. The present invention, however, both as to organization and method of operation, together with objects, features, and advantages

thereof, may best be understood by reference to the following detailed description when read with the accompanying drawings in which:

[0017] **Figures 1A-1C:** (Figure 1A) presents a SEM image of a polyethylene (PE) sheet covered from both sides with a SWCNT-alizarin hybrid as described in Example 2; (Figure 1B) SEM image of the cross-section of the same sheet illustrating the double-sided coating; (Figure 1C) zoom-in on the area in the dashed-line rectangle in (Figure 1B). Illustrating the PE-SWCNT-alizarin composite with a thickness of 93-103 μm and the layers of the SWCNT-alizarin hybrid with an average thickness of 10 ± 3 μm .

[0018] **Figures 2A-2E** present a picture of dispersions in different organic solvents before and after bath sonication, demonstrating a more homogeneous dispersion and more stable, following the sonication step: (Figure 2A) MWCNT in ACN, left blank and right with purpurin prior 15 min bath sonication; (Figures 2B-2E) MWCNT in different solvents, right blank and left with purpurin after 14 h after bath sonication (Figure 2B) ACN; (Figure 2C) acetone; (Figure 2D) EA; (Figure 2E) THF.

[0019] **Figures 3A-3E** represent (Figure 3A) a SEM image of a non-woven polypropylene (PP) sheet covered from one side with a SWCNT-alizarin hybrid; (Figure 3B) SEM image of the cross-section of the same sheet illustrating also the coating of the internal PP fibers with up to several hundreds of nm of the SWCNT hybrid; (Figure 3C) A zoom-in on a cross-sectioned PP fiber and its SWCNT hybrid coating; (Figure 3D) A zoom-in on the area in the dashed-line rectangle in (Figure 3C); (Figure 3E) A zoom-in on the area in the dashed-line rectangle in Figure 3D.

[0020] **Figure 4** represents one embodiment of a method for manufacturing transparent conductive electrodes.

[0021] **Figures 5A-5G** exemplifies some embodiments of single-walled carbon nanotube (SWCNT) transparent conductive electrodes (TCE) on polyethylene terephthalate (PET). Figure 5A shows a photograph of a TCE in front of a fire hazard symbol demonstrating that the TCE is transparent. Figure 5B shows a transparent conductive material on a flexible substrate. Figure 5C shows a circular TCE floating on water/liquid with filter paper at the base of the water/liquid bath. Figure 5D shows a transmission electron microscope image (TEM) of a TCE (enlargement of Figure 5G). Figure 5E Transmission spectrum of a typical SWCNTs-TCE on a quartz substrate. Figure 5F shows SEM image of the SWCNTs-TCE on a quartz substrate after washing with DMSO. Figure 5G TEM image of an ultrathin SWCNTs-TCE on a carbon grid. The arrows indicate the presence of large SWCNTs bundles and iron catalyst.

[0022] **Figures 6A** depicts a graphical example of the sheet resistance of a TCE at different supernatant volumes. **Figure 6B** depicts a graphical example of the transmittance of a SWCNT TCE, fabricated from 400 μl of supernatant solution in the 350 to 800 nm range.

[0023] **Figure 7A** illustrates a schematic of multiple (stand-alone) conductive membranes connected in series forming a composite electrode. **Figure 7B** illustrates a schematic of multiple conductive membranes disposed on separate substrates, connected in series. **Figure 7C** illustrates a schematic of multiple (stand-alone) conductive membranes stacked in parallel.

[0024] **Figures 8A-8C** depict in Figure 8A the structures of anthraquinone-based small-molecule dyes used for SWCNTs exfoliation: Alizarin, Purpurin, Quinizarin, Dantron, and Alizarin Red S. Figure 8B presents a picture of SWCNT–dye dispersions after sonication and centrifugation; and Figure 8C present a Vacuum-filtered SWCNT–dye dispersion supernatants, showing purpurin was the most successful in exfoliating SWCNTs.

[0025] **Figures 9A-9B** depict schematic fabrication process of Purpurin-BP. Figure 9A presents a Bundled SWCNTs powder and purpurin (1,2,4-trihydroxyanthraquinone) were added to a basic aqueous solution. The solution was then bath sonicated to disperse the SWCNTs, centrifuged, and vacuum filtered to provide a self-standing SWCNTs BP. The BP was then soaked in DMSO to remove excess purpurin. The final product was a flexible BP, which could be crumpled to a ball and restored to its original form without visible structural damage. Figure 9B- presents formation of transparent conductive electrodes (TCE) by mixing bundled semiconducting (sc), metallic (m) SWCNTs and purpurin following the process presented in Figure 9A to obtain a flexible, transparent, high conductive and high strength TCE.

[0026] **Figures 10A-10D** depict SEM images and EDS spectra of EtOH-BP (Figures 10A and 10B) and Purpurin-BP (Figure 10C and 10D) The SEM images show a reduction in the diameters of the SWCNT bundles of the SWCNTs exfoliated with purpurin compared to EtOH. The EDS shows a rise in the oxygen content for the Purpurin-BP compared to the EtOH-BP.

[0027] **Figures 11A-11B** show a graphical representation of the thermal stability of CNT-purpurin hybrids using thermogravimetric analysis (TGA). Figure 11A shows a thermogravimetric analysis (TGA) of purpurin powder, pristine-BP and purpurin-BP. Figure 11B shows the data from Figure 8A but plots the derivative of the weight % as a function of temperature (derivative TGA (DTGA)) spectra of EtOH-BP, Purpurin-BP and purpurin powder.

[0028] **Figures 12A-12G** depict Raman spectroscopy of the buckypapers (BPs). Three excitation wavelengths of 532, 633, and 785 nm were used, and the spectrum for each excitation wavelength is the summation of twelve spectra taken from different areas of the BPs. At 532 nm, peaks characteristic of purpurin are observed in the spectrum of Purpurin-BP but not in the spectrum of EtOH-BP (Figure 12G-see box). The radial breathing mode (RBM) region (**Figures 12A-12C**) provides information about the diameter and the chirality of the SWCNTs. The S and M areas indicate frequencies assigned to s-SWCNTs and m-SWCNTs, respectively. The D- and G-bands in the Raman spectra of EtOH-BP and Purpurin-BP at excitation wavelengths of 532, 633, and 785

nm are presented in Figures 12D-12F. Figure 12G presents Raman spectra of EtOH-BP, Purpurin-BP, and purpurin powder at an excitation wavelength of 532 nm.

[0029] **Figures 13A-13C** depict high resolution XPS spectra of the (Figure 13A) C 1s energy region of EtOH-BP, Purpurin-BP, and purpurin powder (the arrows highlight the shift in the sp^2 carbon BE and the increase in signal intensity associated with the C–O bonds of Purpurin-BP, respectively); (Figure 13B) O 1s energy region for two BPs (colored regions show the deconvolution of the Purpurin-BP signal into C–O and C=O components). (Figure 13C) UPS spectra and resulting work functions (inset) of EtOH-BP and Purpurin-BP (with respect to fermi energy, E_F).

[0030] **Figure 14** depicts X-ray photoelectron spectroscopy (XPS) survey spectra of Purpurin-BP and EtOH-BP. For clarity, the spectrum of Purpurin-BP is shifted in the intensity scale (arbitrary units).

[0031] **Figure 15** depicts geometries (GFN2-xTB) of the most stable conformers of purpurin, purpurinate (mono anion of purpurin), and purpurindiate (dianion of purpurin) and their complexes with (8,8) and (10,6) SWCNTs.

[0032] **Figures 16A-16B** depict a summary of the effects of the two fabrication steps – centrifugation and DMSO wash – on the properties of purpurin-based BPs. (**Figure 16A**) shows the different BPs, where ✓ and ✗ indicate whether or not the step was done during the BP fabrication. (**Figure 16B**) The electrical conductivity of different BPs and (**Figure 16C**) the representative stress–strain curve of the BPs; see also Table 5.

[0033] **Figure 17** depicts the ultimate tensile strength (UTS, MPa) versus electrical conductivity ($S\ cm^{-1}$) of EtOH-BP, Purpurin-BP, P-BP_n ($n = 1-3$), and previously reported solution-processed BPs without any post-treatment. **left**: reported BPs fabricated using SWCNT dispersion in organic solvents without adding surfactant. **middle**: reported BPs fabricated using SWCNT dispersion in an aqueous solution with the addition of surfactants. **right**: BPs fabricated using SWCNT dispersion in an aqueous solution with the addition of purpurin.

[0034] **Figure 18** depicts transmittance at 550 nm versus sheet resistance of unwashed and DMSO-washed SWCNT-purpurin based TCEs. The curve represents a “Figure of Merit” (FoM) value of 20. For the DMSO-washed TCEs, there is an increase in the FoM from 4.5 to 13 as the thickness increases.

[0035] **Figure 19** depicts transmittance at 550 nm versus sheet resistance of SWCNTs-purpurin TCEs from the study, reported undoped SWCNT-based TCEs, and ITO. The curve marks FoM = 20.

[0036] It will be appreciated that for simplicity and clarity of illustration, elements shown in the figures have not necessarily been drawn to scale. For example, the dimensions of some of the elements may be exaggerated relative to other elements for clarity. Further, where considered appropriate, reference numerals may be repeated among the figures to indicate corresponding or analogous elements.

DETAILED DESCRIPTION OF THE INVENTION

[0037] In the following detailed description, numerous specific details are set forth in order to provide a thorough understanding of the invention. However, it will be understood by those skilled in the art that the present invention may be practiced without these specific details. In other instances, well-known methods, procedures, and components have not been described in detail so as not to obscure the present invention.

[0038] The superior mechanical and electrical properties of carbon nanotubes (CNTs) are uniquely advantageous for enhancing mechanical and electrical properties of composites (e.g., polymer/CNT ones) that have a broad applicability as electrodes, reinforced materials, antistatic/EMI shielding materials, electro-optical applications and construction materials. Noncovalent molecular attachment to carbon nanotubes (CNTs) has become a preferred approach for overcoming the dominant tendency of CNTs for aggregation, without harming CNT mechanical and electrical properties (as typical of covalent modifications). The presently disclosed subject matter provides a hybrid of inexpensive aromatic molecules and CNTs which noncovalently modify CNTs for efficient and stable dispersions in a broad variety of solvents, solvent mixtures and polymers. The resulting CNT materials can be utilized for the fabrication of electrodes, sensors, and composites with improved mechanical and electrical properties.

Transparent conductive electrode based on nanotubes and their preparation thereof

[0039] Transparent conductive electrodes (TCEs) provide a versatile platform for electro-optic applications due to their exceptional electrical, optical and mechanical characteristics. The present disclosure provides macroscopic electrodes comprising nanotubes in various structural forms. Preferably, the nanotubes disclosed herein are based on carbon. Generally, the present disclosure provides a transparent conductive material disposed on a substrate forming transparent conductive electrode (TCE). The specific properties and use of each component may be tailored and optimized for specific applications, as will become apparent.

[0040] In some embodiments the transparent conductive material and/or TCE's electrical conductivity and/or transmittance is controlled by adjusting the volume and/or concentration of

the (hybrid) solution, which is used to fabricate a transparent conductive material, which is then disposed on a transparent substrate forming a TCE.

[0041] In some embodiments transparent conductive material and/or TCEs comprise non-covalent hybrids comprising single-walled carbon nanotubes (SWCNTs), carbon nanotubes (CNTs) and multi-walled carbon nanotubes (MWCNTs) or combinations thereof and at least one aromatic compound. In other embodiments transparent conductive material and/or TCEs comprise non-covalent hybrids comprising single-walled carbon nanotubes (SWCNTs) and at least one aromatic compound. Numerous examples of suitable materials are disclosed throughout the description, but are not limited to these examples alone.

[0042] In some embodiments, the processes for the preparation of transparent conductive material and/or TCEs are shown in **Figure 4**. It will be appreciated by an expert in the art that other intermediate stages can be added to improve and/or optimize the process to acquire transparent conductive material and the resulting TCEs with particular characteristics such as conductivity, sheet resistance, mechanical properties, transmittance, thermal and chemical stability and other characteristics. Furthermore, in some embodiments, stages shown in Figure 4 can be removed to still achieve transparent conductive material and a resulting TCE, dependent on several factors such as the composition of the hybrid solution, parameters of the filtration process, porous medium that is used, etc. “Porous” or “porous medium” as used herein refers to a material wherein liquid and/or gas can pass through it.

[0043] In some embodiments the transparent conductive material, such as buckypaper (BP), can be used as a stand-alone electrode whilst in other embodiments the transparent conductive material is disposed on a substrate forming a TCE. As used herein “buckypaper” refers to a thin sheet made from an aggregate of primarily carbon nanotubes or carbon nanotube grid paper. In some embodiments the transparent conductive material of the TCE can comprise any material form derived from non-covalent hybrid disposed on a transparent substrate. In some embodiments the transparent conductive material takes the form of any of the following structures: a membrane, dispersion, buckypaper, bulk material, coating, a film, thin film, paste, paint, gel, powder or aerogel. As used herein “membrane” refers to a thin sheet of a material. As used herein “transparent conductive material” refers to any nanotube-based hybrid and/or composite material. As used herein “composite” refers to a material made of more than one material, compound, element and the like. As used herein, in some embodiments, the terms “transparent conductive material”, “conductive medium”, “solid deposits” and “conductive solid deposits” may be used interchangeably, as will become clear.

[0044] Some embodiments of the methods for manufacturing transparent conductive materials and the resulting TCEs are now disclosed. First, a supernatant solution **40** comprising SWCNTs in a

solvent is provided. “Supernatant” as defined herein refers to the liquid lying above a solid residue after crystallization, precipitation, centrifugation, or other process. In some embodiments, the supernatant solution **40** comprises a non-covalent hybrid, the non-covalent hybrid preferably comprising carbon nanotubes (CNTs) and at least one aromatic compound. In some embodiments the aromatic compound is selected from the group comprising anthraquinone, acridine, caffeic acid, phenazine, thymolphthalein, aramid nanofiber, their salts thereof and their derivatives thereof. In some embodiments TCEs and the transparent conductive material comprise at least one aromatic compound, their salts and/or derivatives thereof, within the non-covalent hybrid disclosed herein. In some embodiments the aromatic compound is anthraquinone or derivative thereof. In some embodiments the aromatic compound is selected from purpurin or alizarin. In some embodiments the CNTs can be ground and/or milled, as disclosed elsewhere herein. In other embodiments, the supernatant solution **40** is sonicated, as disclosed elsewhere herein. Following the production of a supernatant of SWCNT-anthraquinone (hybrid) solution, it is then diluted forming a diluted hybrid solution **41**, from which a transparent conductive material is formed. In some embodiments, the starting concentration of the diluted hybrid solution **41** determines the mechanical, electrical and optical properties of the resulting transparent conductive material which is produced and can be selected and optimized accordingly. In some embodiments, the diluted hybrid solution **41** then undergoes vacuum filtration **42**. In some embodiments the vacuum filtration action is configured such that nanotubes (e.g., CNTs, SWCNTs, MWCNTs or other), or nanotube hybrids, are caught by filter paper, or other porous media, producing a transparent conductive material such as buckypaper on said filter paper **43**.

[0045] In some embodiments, the substrate onto which the transparent conductive material, such as buckypaper, evaporates onto, thereby forming a thin film/membrane, can be any porous medium upon which nanotubes, and/or nanotube hybrids, are disposed thereon via vacuum-filtration.

[0046] In some embodiments the porous medium (exemplified as filter paper (FP) in **Figure 4**) is selected from a group comprising: filter paper, transfer membrane, polyvinylidene difluoride (PVDF) filter/membrane, polytetrafluoroethylene (PTFE) membrane, microporous membranes (0.2-2nm pores), mesoporous membranes (2-50nm pores), microporous membranes (50-1000nm pores), organic-based membranes, inorganic-based membranes, nitrocellulose (NC) membranes and polysilsesquioxane (PSQ) membranes.

[0047] In some embodiments the porous medium is a transparent substrate. In some embodiments, where the porous medium is a transparent substrate there are no further steps required in the process of forming the TCE, i.e., the transparent conductive material is disposed directly on the porous medium (which is a transparent substrate) during the vacuum filtration step **42**.

[0048] In some embodiments the process for preparation of TCEs comprises first preparing a noncovalent hybrid comprising CNTs and at least one aromatic compound comprising an anthraquinone (for example, alizarin and purpurin). In some embodiments the CNTs are optionally grounded after which the CNTs and at least one aromatic compound is mixed in an aqueous solvent, an organic solvent, or combination thereof and sonicated for a period of time to obtain a dispersion comprising the hybrid wherein the hybrid is subsequently used for the preparation of the transparent conductive material after which TCEs are subsequently formed.

[0049] As used herein “aqueous solvent” or “aqueous solution” refers to any liquid comprising water. In some embodiments aqueous solvent/solution comprises water alone. In some embodiments the aqueous solvent/solution is at a pH of between 9 to 13. In some embodiments the aqueous solvent/solution is at a pH of between 10 to 12.

[0050] Generally, the vacuum filtration step **42** is optimized to produce a transparent conductive material such as buckypaper of a particular thickness disposed upon a porous medium such as filter paper **43**. In some embodiments, the vacuum filtration step **42** can produce any form of conductive solid deposits, disposed on a porous medium such as filter paper **43**, wherein the conductive solid deposits are selected from a list comprising: a membrane, buckypaper, bulk material, coating, film, thin film, paste, paint, gel powder or aerogel.

[0051] As used herein “solid deposits” refers to any solid form which results from vacuum filtration **42**. Solid deposits that are conductive are referred to herein as “conductive solid deposits” or to “transparent conductive material”. The disclosed subject matter relates primarily to conductive solid deposits, however, the principles disclosed in making solid deposits applies to those which are non-conductive as well. The particular form of solid deposits will depend on the starting materials (e.g., a hybrid-nanotube material), vacuum filtration conditions and the likes. In some embodiments this is selected by setting the pressure and the time of operation of the vacuum system accordingly. Furthermore, in some embodiments, the starting concentration of the evaporating solution is selected to optimize the transparent conductive material’s properties. For the purposes of example alone, a high concentration solution which is vacuum filtered at high vacuum will take a shorter amount of time to achieve a buckypaper of a particular thickness in comparison with a lower concentration solution which is vacuum filtered at a lower vacuum.

[0052] However, thickness is not the only characteristic that is considered. In some embodiments, the processes in producing a transparent conductive material such as buckypaper will be selected and optimized to achieve a desired transparency, or a particular sheet-resistance, porosity or mechanical property e.g., flexibility. As used herein “sheet resistance” refers to a measure of the lateral resistance through a thin square of material, i.e., the resistance between opposite sides of a square; it is also commonly defined as the resistivity (ρ) of a material divided by its thickness and

is measured in Ohms per square (Ω/sq). The transmittance of transparent conductive materials, based on different starting materials, will vary. Accordingly, in some embodiments, the materials and method parameters are selected to achieve a desired outcome e.g., transparency. For example, a transparent conductive material comprised of CNT-alizarin hybrid buckypaper/membranes may exhibit high transmittance and low sheet-resistance between 40 – 1000 nm thickness. Thus, method parameters will be selected to ensure that the target thickness range (and desired transmittance/sheet-resistance) is achieved. An expert will be able to utilize the disclosed subject matter herein to optimize the methods and processes to achieve particular characteristics for transparent conductive material and their resulting TCEs.

[0053] For the purposes of example alone, in some embodiments thicker buckypaper membranes transmit less light; a property which can be selected for when optimizing the process for a particular optical use. In some embodiments, the thicker the buckypaper the lower the electrical resistance whereas in other embodiments thicker buckypaper has a higher electrical resistance. Furthermore, in some embodiments, doping of the CNTs and/or selection of particular hybrid combinations modifies the electrical conductivity (and/or (sheet-)resistance), which is selected for in the optimization process.

[0054] In some embodiments the transparent conductive material is a continuous film and in others it is discontinuous. In some embodiments the transparent conductive material is porous. In some embodiments the transparent conductive material is circular but can in principle take on any shape following the methods disclosed herein and subsequent fixation on a porous medium, such as filter paper. In some embodiments the lateral size of the transparent conductive material is in the micrometer range, millimeter range, centimeter range or meter range. The “lateral size”, as used herein refers to the length (or area) of the transparent conductive material from one edge to another edge. However, since the transparent conductive material may not form a uniform shape, the lateral size refers generally to the length scale of the resulting membrane comprising the transparent conductive material. For example, the lateral size of a pad (comprising the transparent conductive material) could be in the centimeter range, whereas its thickness is in the 40 – 1000 nm range.

[0055] In some embodiments a transparent conductive material is disposed on a non-transparent substrate forming a non-transparent conductive electrode. In some embodiments a non-transparent conductive material, formed by the hybrid dispersions disclosed in embodiments herein, is disposed on a transparent or non-transparent substrate forming a non-transparent conductive electrode. In some embodiments the CNT-aromatic compound hybrid forms a conductive hybrid material which is transparent. In some embodiments the CNT-aromatic compound hybrid forms a conductive hybrid material which is translucent or opaque.

[0056] In some embodiments a transparent conductive material is disposed on a transparent substrate forming a transparent conductive electrode (TCE). In some embodiments the thickness of the transparent conductive material of the TCE is less than 50nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 50 and 100 nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 1 and 100nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 100 to 500 nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 500 to 1000 nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 1 to 1000 nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 40 to 1000 nm. In some embodiments the thickness of the transparent conductive material of the TCE is between 1 to 5 microns. In some embodiments the thickness of the transparent conductive material of the TCE is between 1 to 10 microns. In some embodiments the thickness of the transparent conductive material of the TCE is between 10 to 100 microns. In some embodiments the thickness of the transparent conductive material of the TCE is selected to optimize for a particular transmittance.

[0057] In some embodiments the transparent conductive material forms a stand-alone film/membrane/medium which is itself an electrode. In some embodiments the thickness of the stand-alone transparent conductive material is less than 50 nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 50 and 100 nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 1 and 100nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 100 to 500 nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 500 to 1000 nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 1 to 1000 nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 40 to 1000 nm. In some embodiments the thickness of the stand-alone transparent conductive material is between 1 to 5 microns. In some embodiments the thickness of the stand-alone transparent conductive material is between 1 to 10 microns. In some embodiments the thickness of the stand-alone transparent conductive material is between 10 to 100 microns. In some embodiments the thickness of the stand-alone transparent conductive material is selected to optimize for a particular optical transmittance.

[0058] In some embodiments the transparent conductive material, the substrate and/or the transparent conductive electrode allow light to pass through them. As used herein “transmittance” or “optical transmittance” is the ratio of the light passing through a body to that which is incident on it, given as a percentage. As used herein “transparent” refers to allowing light to pass through

a material, normally to a high percentage whereas “translucent” or “semi-transparent” refers to partially allowing light through a material. Generally, as used herein, a transparent material has a higher transmittance than a translucent or semi-transparent material.

[0059] In some embodiments the transmittance refers to the UV-visible range, namely about 350 – 800 nm or just the visible range, which has a slightly smaller range. In other embodiments, the transmittance refers to other wavelength ranges, such as between 300 – 400 nm, 400 – 500 nm, 500 – 600 nm, 600 – 700 nm, 700 – 800 nm or other. Transmittance through transparent conductive materials, substrates and resulting TCEs, will also vary for different wavelengths, as shown in **Figure 6B**. As an example, the transmittance shown in **Figure 6B** varies across a wavelength spectrum of 350 – 800 nm. As an example, the transmittance spectrum of **Figure 6B** can be described as follows: the lowest transmission (about 86 %) occurs at 350 nm, this increases to about 92 % between about 500 to 700 nm and increases to about 94 % between 700 to 800 nm.

[0060] In some embodiments a transparent conductive material is disposed on a transparent substrate forming a transparent conductive electrode (TCE). In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 50% to 100%. In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 60 to 100%. In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 70 to 100%. In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 80 to 100%. In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 90 to 100%. In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 80 to 90%. In some embodiments the transmittance of the transparent conductive material, the substrate or TCE, alone or in combinations thereof, is between 85 to 95%.

[0061] In some embodiments, the concentration of the supernatant solution **40** or diluted hybrid solution **41** (e.g., comprising CNTs with alizarin and/or purpurin) is selected to optimize the sheet resistance, or transmittance, of the resulting transparent conductive material, such as buckypaper, of the TCE. In some embodiments the concentration of CNTs in the supernatant solution **40** or diluted hybrid solution **41** is between 0.05 g/l and 60 g/l. In some embodiments the concentration of CNTs in the supernatant solution **40** or diluted hybrid solution **41** is between 0.05 g/l and 10 g/l. In some embodiments the concentration of CNTs in the supernatant solution **40** or diluted hybrid solution **41** is between 10 g/l and 20 g/l. In some embodiments the concentration of the supernatant solution **40** or diluted hybrid solution **41** is between 20 g/l and 30 g/l. In some

embodiments the concentration of the supernatant solution **40** or diluted hybrid solution **41** is between 30 g/l and 40 g/l. In some embodiments the concentration of the supernatant solution **40** or diluted hybrid solution **41** is between 40 g/l and 50 g/l. In some embodiments the concentration of the supernatant solution **40** or diluted hybrid solution **41** is between 50 g/l and 60 g/l.

[0062] After the buckypaper is formed and is disposed on a porous medium such as filter paper **43** it is then placed in a liquid bath **44** and floats on the surface thereon. In some embodiments the liquid bath **44** is a water bath filled with water. In some embodiments the water can be selected from any of the following non-limiting examples: deionized water, deuterium-depleted water (DDW), filtered water, laboratory grade water, pure/ultrapure water, distilled water and tap water. In some embodiments the buckypaper which is obtained on a porous medium such as filter paper **43** can be floated on the surface of any solution or liquid. The role of step **45** is to separate the buckypaper from the filter paper **43**, which readily occurs due to the low adhesion between the buckypaper and filter paper. The buckypaper subsequently remains free-standing on surface of the liquid (e.g., water) whilst the filter paper sinks to the base of the liquid bath in step **45**. The filter paper is then removed from the liquid bath and a transparent substrate is subsequently placed on the base of the liquid bath, as shown in step **46**. The same principle can be applied to any form of transparent conductive material that forms on a porous medium (such as filter paper), which is subsequently detached. For the purposes of example alone, a bulk material or membrane can form on a filter paper, which is subsequently separated from the filter paper that it was attached to during its initial formation. The form of the transparent conductive material and/or the porous material/medium upon which it forms is not limited to the specific examples disclosed herein, as will become apparent.

[0063] The liquid is subsequently decanted from the bath in step **47**. In some embodiments the liquid is syphoned using standard tubing and pumping methods. In other embodiments the liquid is poured out. In other embodiments the liquid is removed by evaporation under heating. In some embodiments the liquid is evaporated under an air flow (or any other gas). In some embodiments the liquid is removed by vacuum. In some embodiments any combination of the liquid removal methods disclosed herein can be utilized to remove the liquid and subsequently dry the transparent conductive electrode. For the purposes of example alone, in one embodiment the majority of the liquid can be removed by pouring it out, some of the liquid can then be syphoned out, whereas the final remaining liquid can be slowly heated by placing the liquid bath (with TCE) on a hotplate, or otherwise the final remnants of liquid can be removed by drying under nitrogen gas flow, in a dry box or under vacuum conditions, after which the TCE is removed. In some embodiments drying the TCE at the end of the process is optional.

[0064] The resulting TCE **48** comprises the transparent conductive material such as a buckypaper/membrane disposed on a substrate, preferably one that is transparent. In some embodiments the transparent conductive material, such as buckypaper, covers the whole substrate upon which it is disposed whereas in other embodiments the buckypaper partially covers the substrate. In some embodiments the transparent conductive material, such as buckypaper, can be patterned on the transparent substrate and/or form a particular shape thereon.

[0065] Due to the advantageous electrical performance of the transparent conductive material and resulting TCE, in some embodiments the transparent conductive material and/or TCE **48** can be integrated with additional electronic elements such as leads, cables, conducting tape, conducting paint and the likes. In some embodiments the transparent conductive material and/or resulting TCE **48** can be integrated with optical components such as any of the following list comprising: lenses, mirrors, windows, diffusers, optical filters, polaroid, polarizers, beam splitters, prisms, diffraction gratings, gratings, infrared optics, fiber optical components, lasers, coated elements, thin films, transparent materials, translucent materials and diffractive optical elements.

[0066] In some embodiments the transparent conductive material does not comprise a further transparent substrate but is a stand-alone (or free-standing) conducting electrode which can be transferred for use as an electrode. Whereas in other embodiments the transparent conductive material is disposed upon a transparent substrate forming a TCE.

[0067] In some embodiments the transparent conductive material is disposed on a transparent substrate forming the TCE. In some embodiments the transparent conductive material, substrate and TCE are individually, or in combination, stretchable, bendable, flexible and/or inflatable. In some embodiments the electrical, optical and mechanical properties of the transparent conductive materials, substrates and TCEs are not affected, or else deviate partially, upon stretching, bending, flexing and/or inflation. In some embodiments, “deviate partially” can refer to the value of any measured characteristics or properties being $\pm 1\%$, $\pm 5\%$, $\pm 10\%$, $\pm 25\%$ or $\pm 50\%$ of the value of the transparent conductive materials, substrates and TCEs when at rest i.e., not stretched, bent, flexed, inflated, etc.

[0068] In some embodiments the transparent substrate can be of natural or synthetic origin. In some embodiments the transparent substrate comprises any of the following natural materials, but not limited to: natural polymeric material, hemp, shellac, amber, wool, silk, cellulose and natural rubber. In some embodiments the substrate onto which buckypaper is disposed, for example in step **47**, can comprise human tissue, animal tissue, cellulose and biological matter.

[0069] In some embodiments the transparent substrate comprises any of the following, but is not limited to: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylon, nylon 6, nylon 6,6, polyamide, aramids,

polytetrafluoroethylene (PTFE), thermoplastics, thermoplastic polyurethanes (TPU), polystyrene, polychlorotrifluoroethylene (PCTFE), phenol-formaldehyde resin, para-aramid fiber, para-aramid, polyethylene terephthalate (PET), polychloroprene, meta-aramid polymer, polyacrylonitrile (PAN), polyamide 11 & 12, copolyamid, polyimide, aromatic polyester, polyester, ABS, poly-p-phenylene-2,6-benzobisoxazole (PBO), polyolefins, aromatic polymers, poly(methyl methacrylate) (PMMA), polyether ether ketone (PEEK), polyethylene glycol (PEG), polylactic acid (PLA), halogenated polymers and their combination and/or copolymers.

[0070] In other embodiments the transparent substrate is a fabric, paper, stretchable textile or an elastomer such as latex, rubber, polyurethane and/or silicone. Due to the flexible, stretchable and inflatable nature of the transparent conductive material and resulting TCE, some embodiments allow for the transparent conductive material and/or TCE to be bio-compatible with tissues from humans or animals and can be used internally and/or externally therein. In some embodiments the transparent conductive material and/or TCE is embedded within a material or is coated on the surface of a material. In some embodiments, the transparent conductive material and/or TCEs are stacked on top of one another or connected in series with one another. In some embodiments the TCE 48 is heated, post-treated and/or annealed after it is dried.

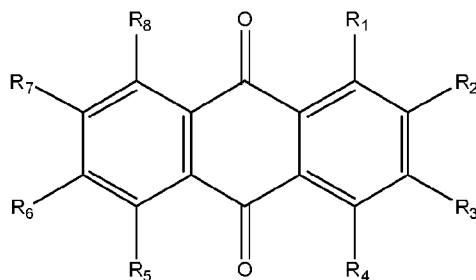
[0071] **Figures 7A-7C** exemplify a number of scenarios wherein transparent stand-alone transparent conductive membranes 701 or transparent conductive electrodes (i.e., those wherein conductive membranes are disposed on transparent substrates, as shown in this example) can be connected to each other, in some embodiments. In one embodiment, to extend the length of conductive membranes, individual units may be joined together in series forming a composite electrode. As used herein “composite electrode” refers to an electrode that is comprised of more than one transparent conductive material (typically in the form of a membrane/film/buckypaper) connected in series and/or parallel. **Figure 7A** shows an extended electrode in series 700 comprising multiple individual transparent conductive membranes 701 with an overlapping portion 702. In principle any number of individual transparent conductive membranes 701 can be joined together in series. In some embodiments the individual transparent conductive membranes 701 are connected in series in a straight light (as see in **Figure 7A**), whereas in other embodiments they are not in straight lines. In some embodiments, conductive extended electrodes in series 700 do not require an additional adhesion material to ensure that they connect. **Figure 7B** illustrates a cross-section of another embodiment of the extended electrodes in series 700 wherein individual transparent conductive membranes 701 are disposed on transparent substrates 702 and are connected in series. In this example, the direction of the conductive membranes is configured such that the conductive regions are in contact and face each other so that they are electrically coupled. In another embodiment, conductive membranes are stacked in parallel 710 with one another and

are thereby electrically coupled, as seen in **Figure 7C**. **Figure 7C** illustrates the conductive membranes **701** as being spaced out (or not in contact), but in some embodiments this is merely a representation that they are stacked in parallel; otherwise, other materials (e.g., dopant, adhesion material, dielectrics) can be placed in-between the conductive membranes depicted therein. According to the exemplified embodiments of **Figures 7A-7C**, the thickness and length of transparent conductive electrodes can be modified by using individual transparent conductive membranes **701** as modular units. In some embodiments, individual transparent conductive membranes **701** adhere together following heating processes or treatment. In other embodiments individual transparent conductive membranes **701** connect to one another by electrostatic and/or van der Waals interaction. The modular platforms shown in **Figures 7A-7C** can be exploited to optimize for a desired length, conductivity, transparency, shape and mechanical properties which comprise conductive membranes and transparent substrates.

Noncovalent hybrid

[0072] In some embodiments, the invention is directed towards noncovalent hybrid comprising carbon nanotubes (CNTs) and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber, their salts thereof and their derivatives thereof. In some embodiments the transparent conductive material, disclosed herein comprises said noncovalent hybrid comprising CNTs and at least one aromatic compound, disclosed hereinabove, forming a conductive electrode. In some embodiments, the transparent conductive material, forming buckypaper, disclosed herein comprises said noncovalent hybrid comprising CNTs and at least one aromatic compound, disclosed hereinabove, wherein the buckypaper and the conductive material are translucent.

[0073] In some embodiments, the hybrid provided herein comprises carbon nanotubes (CNTs) and anthraquinone, salts thereof or derivatives thereof. In another embodiment, the anthraquinone and derivatives thereof is represented by the structure of formula I:



wherein each of R₁-R₈ is independently hydrogen, hydroxy, alkyl, alkenyl, halide, haloalkyl, CN, COOH, alkyl-COOH, alkylamine, amide, alkylamide, aryl, heteroaryl, cycloalkyl,

heterocycloalkyl, thio (SH), thioalkyl, alkoxy, ether (alkyl-O-alkyl), OR⁹, COR⁹, COOCOR⁹, COOR⁹, OCOR⁹, OCONHR⁹, NHCOOR⁹, NHCONHR⁹, OCOOR⁹, CON(R⁹)₂, SR⁹, SO₂R⁹, SOR⁹, SO₂NH₂, SO₂NH(R⁹), SO₂N(R⁹)₂, NH₂, NH(R⁹), N(R⁹)₂, CONH₂, CONH(R⁹), CON(R⁹)₂, CO(N-heterocycle), NO₂, cyanate, isocyanate, thiocyanate, isothiocyanate, mesylate, tosylate or triflate; wherein R⁹ is H, (C₁-C₁₀)alkyl, (C₁-C₁₀)haloalkyl, (C₃-C₈)cycloalkyl, aryl or heteroaryl, wherein the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups are optionally substituted. Each represents a separate embodiment of this invention. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, each of the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups may be substituted by one or more independently substituents comprising halogen, hydroxy, alkoxy carbonyl, amido, alkylamido, dialkylamido, nitro, amino, alkylamino, dialkylamino, carboxyl, thio or thioalkyl.

[0074] In other embodiments, the carbon nanotube is a multi-walled carbon nanotube. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ of the structure of formula I are each independently a hydrogen. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently hydroxy. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an alkyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an alkenyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a halide. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a haloalkyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a CN. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a COOH. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an alkyl-COOH. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an alkylamine. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an amide. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an aryl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a heteroaryl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a cycloalkyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a heterocycloalkyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a haloalkyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a thio (SH). In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a thioalkyl. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an alkoxy. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an ether (alkyl-O-alkyl). In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ is each independently a OR⁹, wherein R⁹ is H, (C₁-C₁₀)alkyl, (C₁-C₁₀)haloalkyl, (C₃-C₈)cycloalkyl, aryl or heteroaryl, wherein the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups are optionally

[illegible]

SO₂NH₂. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a SO₂NH(R⁹), wherein R⁹ is H, (C₁-C₁₀)alkyl, (C₁-C₁₀)haloalkyl, (C₃-C₈)cycloalkyl, aryl or heteroaryl, wherein the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups are optionally substituted. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a SO₂N(R⁹)₂, wherein R⁹ is H, (C₁-C₁₀)alkyl, (C₁-C₁₀)haloalkyl, (C₃-C₈)cycloalkyl, aryl or heteroaryl, wherein the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups are optionally substituted. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a NH₂. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a NH(R⁹), wherein R⁹ is H, (C₁-C₁₀)alkyl, (C₁-C₁₀)haloalkyl, (C₃-C₈)cycloalkyl, aryl or heteroaryl, wherein the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups are optionally substituted. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a N(R⁹)₂, wherein R⁹ is H, (C₁-C₁₀)alkyl, (C₁-C₁₀)haloalkyl, (C₃-C₈)cycloalkyl, aryl or heteroaryl, wherein the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups are optionally substituted. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a CONH₂. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a haloalkyl CONH(R⁹). In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a CON(R⁹)₂. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a CO(N-heterocycle). In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a NO₂. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a cyanate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an isocyanate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a thiocyanate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently an isothiocyanate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a mesylate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a tosylate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are each independently a triflate. In some embodiments, R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ are not SO₂H. In other embodiments, each of the alkyl, haloalkyl, cycloalkyl, aryl or heteroaryl groups may be substituted by one or more independently substituents comprising halogen, hydroxy, alkoxy, carbonyl, amido, alkylamido, dialkylamido, nitro, amino, alkylamino, dialkylamino, carboxyl, thio or thioalkyl.

[0075] In one embodiment, the hybrid provided herein comprises carbon nanotubes and an anthraquinone, salt thereof or derivative thereof. In one embodiment, the hybrid provided herein comprises carbon nanotubes and an anthraquinone, salt thereof or derivative thereof. In another embodiment the anthraquinone or derivative thereof is represented by the structure of formula I, wherein at least one of R¹-R⁸ of formula I is an hydroxyl. In another embodiment, at least two of

R¹-R⁸ of formula I are hydroxyl. In another embodiment at least three of R¹-R⁸ of formula I are hydroxyl. In one embodiment, the anthraquinone derivative is a dihydroxy or a trihydroxy anthraquinone. In another embodiment, the anthraquinone derivative is purpurin or alizarin. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0076] In some embodiments, the hybrid provided herein comprises carbon nanotubes and an acridine, salt thereof or derivatives thereof. In one embodiment, the acridine derivative is acridine orange. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0077] In some embodiments, the hybrid provided herein comprises carbon nanotubes and a naphthalene disulfonic acid, salt thereof or derivative thereof. In one embodiment, the naphthalene disulfonic acid derivative salt is selected from the group consisting of chromatropic acid disodium salt, 2,6-naphthalenedisulfonic acid sodium salt, 2,7-naphthalenedisulfonic acid sodium salt, 2-(4-nitrophenylazo)chromotropic acid disodium salt (Chromotrope 2B), tetrasodium 4-amino-5-hydroxy-3,6-bis[[4-[[2-(sulphonatooxy)ethyl]sulphonyl]phenyl]azo]naphthalene-2,7-disulphonate (Reactive Black 5), and any combination thereof. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0078] In some embodiments, the hybrid provided herein comprises carbon nanotubes and a caffeic acid, salt thereof or derivative thereof. In other embodiments, the caffeic acid derivative comprises a caffeic ester or a caffeic amide. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0079] In some embodiments, the hybrid provided herein comprises carbon nanotubes and a phenazine, salt thereof or derivative thereof. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0080] In some embodiments, the hybrid provided herein comprises carbon nanotubes and an indigo, salt thereof or derivative thereof. In other embodiments, the indigo derivative comprises indigo carmine. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0081] In some embodiments, the hybrid provided herein comprises carbon nanotubes and a rhodamine, salt thereof or derivative thereof. In other embodiments, the indigo derivative comprises rhodamine 101 inner salt. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0082] In some embodiments, the hybrid provided herein comprises carbon nanotubes and a phenothiazine, salt thereof or derivatives thereof. In other embodiments, the phenothiazine derivative comprises methylene blue. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0083] In some embodiments, the hybrid provided herein comprises carbon nanotubes and a thymolphthalein, salt thereof or derivatives thereof. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0084] In some embodiments, the hybrid provided herein comprises carbon nanotubes and an aramid nanofiber (ANF). Kevlar is a well-known ultra-strong para-aramid synthetic fiber with a high tensile strength-to-weight ratio. The Kevlar fibers can be fragmented into low molecular weight chains and dissolved to form aramid nanofiber (ANF) solution, using DMSO and KOH. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[0085] In some embodiments ANF is added to SWCNTs dispersion following vacuum filtration to obtain SWCNTs-ANF hybrid with improved mechanical properties.

[0086] In one embodiment, presently disclosed subject matter provides a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivative thereof. In another embodiment, the hybrid comprises two, three, four or more different aromatic compounds within the hybrid.

[0087] In some embodiments the hybrid provided herein consists essentially of CNTs and an aromatic compound, salt thereof or derivative thereof. In some embodiments the hybrid provided herein consists essentially of a CNT and at least one aromatic compound, salt thereof or derivative thereof. In some embodiments the hybrid provided herein consists essentially of a CNT and at least one aromatic compound, salt thereof or derivative thereof, wherein the hybrid does not comprise a dispersant.

[0088] In some embodiments, provided herein a noncovalent hybrid consisting essentially of a single-walled carbon nanotube (CNT) and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, caffeic acid, phenazine, thymolphthalein, aramid nanofiber (ANF), their salts thereof and their derivatives thereof.

[0089] A noncovalent hybrid consisting essentially of multi-walled carbon nanotubes (MWCNTs) and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, caffeic acid, safranin, thymolphthalein, aramid nanofiber, their salts thereof and their derivatives thereof.

[0090] In some embodiments, the hybrid provided herein comprises at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof. In other embodiments, the term “*derivative thereof*” comprises a chemical modification of any one of the listed aromatic compounds with one or more functional group or with any chemical group (e.g., hydroxyl, alkyl, aryl, halide, nitro, amine, ester, amide, carboxylic acid or combination thereof). For example, by derivatizing anthraquinone with hydroxyl groups (alizarin, purpurin) a hydrophilic hybrid is obtained. By derivatizing anthraquinone with hydrophobic groups (C₆-C₁₀ alkyls), a hydrophobic hybrid is obtained.

[0091] In some embodiments, the hybrid provided herein comprises at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof. In other embodiments, the salts of any one of the listed aromatic compounds is an organic or inorganic acid salt or an organic or inorganic basic salt.

[0092] Suitable acid salts comprising an inorganic acid or an organic acid. In one embodiment, examples of inorganic acid salts are bisulfates, borates, bromides, chlorides, hemisulfates, hydrobromates, hydrochlorates, 2-hydroxyethylsulfonates (hydroxyethanesulfonates), iodates, iodides, isothionates, nitrate, persulfates, phosphate, sulfates, sulfamates, sulfanilates, sulfonic acids (alkylsulfonates, arylsulfonates, halogen substituted alkylsulfonates, halogen substituted arylsulfonates), sulfonates and thiocyanates.

[0093] In one embodiment, examples of organic acid salts may be selected from aliphatic, cycloaliphatic, aromatic, araliphatic, heterocyclic, carboxylic and sulfonic classes of organic acids, examples of which are acetates, arginines, aspartates, ascorbates, adipates, anthranilate, algenate, alkane carboxylates, substituted alkane carboxylates, alginates, benzenesulfonates, benzoates, bisulfates, butyrates, bicarbonates, bitartrates, carboxilate, citrates, camphorates, camphorsulfonates, cyclohexylsulfamates, cyclopentanepropionates, calcium edetates, camsylates, carbonates, clavulanates, cinnamates, dicarboxylates, digluconates, dodecylsulfonates, dihydrochlorides, decanoates, enanthuates, ethanesulfonates, edetates, edisylates, estolates, esylates, fumarates, formates, fluorides, galacturonate gluconates,

glutamates, glycolates, glucorate, glucoheptanoates, glycerophosphates, gluceptates, glycolylarsanilates, glutarates, glutamate, heptanoates, hexanoates, hydroxymaleates, hydroxycarboxylic acids, hexylresorcinates, hydroxybenzoates, hydroxynaphthoate, hydrofluorate, lactates, lactobionates, laurates, malates, maleates, methylenebis(beta-oxynaphthoate), malonates, mandelates, mesylates, methane sulfonates, methylbromides, methylnitrates, methylsulfonates, monopotassium maleates, mucates, monocarboxylates, nitrates, naphthalenesulfonates, 2-naphthalenesulfonates, nicotines, napsylates, N-methylglucamines, oxalates, octanoates, oleates, pamoates, phenylacetates, picrates, phenylbenzoates, pivalates, propionates, phthalates, phenylacetate, pectinates, phenylpropionates, palmitates, pantothenates, polygalacturates, pyruvates, quinate, salicylates, succinates, stearates, sulfanilate, subacetates, tartarates, theophyllineacetates, p-toluenesulfonates (tosylates), trifluoroacetates, terephthalates, tannates, teoclates, trihaloacetates, triethiodide, tricarboxylates, undecanoates and valerates.

[0094] In one embodiment, examples of inorganic basic salts may be selected from ammonium, alkali metals to include lithium, sodium, potassium, cesium; alkaline earth metals to include calcium, magnesium, aluminium; zinc, barium, cholines, quaternary ammoniums.

[0095] In another embodiment, examples of organic basic salts may be selected from arginine, organic amines to include aliphatic organic amines, alicyclic organic amines, aromatic organic amines, benzathines, *t*-butylamines, benethamines (*N*-benzylphenethylamine), dicyclohexylamines, dimethylamines, diethanolamines, ethanolamines, ethylenediamines, hydrabamines, imidazoles, lysines, methylamines, meglamines, *N*-methyl-D-glucamines, *N,N'*-dibenzylethylenediamines, nicotinamides, organic amines, ornithines, pyridines, picolines, piperazines, procain, tris(hydroxymethyl)methylamines, triethylamines, triethanolamines, trimethylamines, tromethamines and ureas.

[0096] An “alkyl” group refers, in one embodiment, to a saturated aliphatic hydrocarbon, including straight-chain, branched-chain and cyclic alkyl groups. In one embodiment, the alkyl group has 1-12 carbons. In another embodiment, the alkyl group has 1-7 carbons. In another embodiment, the alkyl group has 1-6 carbons. In another embodiment, the alkyl group has 6-12 carbons. In another embodiment, the alkyl group has 8-12 carbons. In another embodiment, the alkyl group has 1-4 carbons. In another embodiment, the alkyl group may be unsubstituted or substituted by one or more groups selected from halogen, hydroxy, alkoxy carbonyl, amido, alkylamido, dialkylamido, nitro, amino, alkylamino, dialkylamino, carboxyl, thio and thioalkyl.

[0097] An “alkenyl” group refers, in another embodiment, to an unsaturated hydrocarbon, including straight chain, branched chain and cyclic groups having one or more double bond. The alkenyl group may have one double bond, two double bonds, three double bonds etc. Examples of alkenyl groups are ethenyl, propenyl, butenyl, cyclohexenyl etc. In one embodiment, the alkenyl

group may be unsubstituted or substituted by one or more groups selected from halogen, hydroxy, alkoxy carbonyl, amido, alkylamido, dialkylamido, nitro, amino, alkylamino, dialkylamino, carboxyl, thio and thioalkyl.

[0098] A “haloalkyl” group refers to an alkyl group as defined above, which is substituted by one or more halogen atoms, in one embodiment by F, in another embodiment by Cl, in another embodiment by Br, in another embodiment by I.

[0099] An “aryl” group refers to an aromatic group having at least one carbocyclic aromatic group or heterocyclic aromatic group, which may be unsubstituted or substituted by one or more groups selected from halogen, haloalkyl, hydroxy, alkoxy carbonyl, amido, alkylamido, dialkylamido, nitro, amino, alkylamino, dialkylamino, carboxy or thio or thioalkyl. Non-limiting examples of aryl rings are phenyl, naphthyl, pyranyl, pyrrolyl, pyrazinyl, pyrimidinyl, pyrazolyl, pyridinyl, furanyl, thiophenyl, thiazolyl, imidazolyl, isoxazolyl, and the like. In one embodiment, the aryl group is a 1-12 membered ring. In another embodiment, the aryl group is a 1-8 membered ring. In another embodiment, the aryl group comprises of 1-4 fused rings.

[00100] In some embodiments, the invention is directed towards noncovalent hybrids comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof.

[00101] In other embodiments, the carbon nanotube is a single-walled carbon nanotube (SWCNT). In other embodiments, the carbon nanotube is a (6,5)-single walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube (MWCNT). In other embodiments, the carbon nanotube is a combination of a multi-walled carbon nanotube (MWCNT) and a single walled carbon nanotube (SWCNT).

[00102] “Carbon nanotubes,” refers herein to tubes comprising carbon with a diameter typically in the nanometer range. In some embodiments “carbon nanotubes” refers to carbon nanotubes which comprise other additional atoms, heteroatoms, elements, compounds and/or materials. In some embodiments CNTs further comprise doping agents, elements and/or additional functional groups. In some embodiments different types of CNTs are used together in any number of combinations to form hybrids and/or hybrid dispersions, including the following non-limiting examples: a combination of carbon-only nanotubes together with doped CNTs, a combination of functionalized CNTs together with non-functionalized CNTs. “Doping”, “doped” and “dopant” refers herein to the addition of atoms, heteroatoms, compounds and/or elements to a material such as CNTs of any variety. In some embodiments doping atoms comprise any of the following non-limiting examples: nitrogen, boron, bismuth, iodine and hydrogen.

[00103] "Single-walled nanotube," as defined herein, refers to a nanotube that does not contain another nanotube.

[00104] "Multi-walled carbon nanotube," refers herein to more than one nanotube within nanotubes (including for example double walled nanotubes).

[00105] In some embodiments, the hybrid of this invention comprises between 1 wt% to 99 wt% of carbon nanotube (CNT). In some embodiments, the hybrid of this invention comprises between 3 wt% to 97 wt% of carbon nanotube (CNT). In some embodiments, the hybrid of this invention comprises between 5 wt% to 95 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 30 wt% to 95wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 50 wt% to 95wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 70 wt% to 95wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 80wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 75wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 70wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 40 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 10 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 15 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 10 wt% to 30 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 5 wt% to 20 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 15 wt% to 60 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 20 wt% to 70 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 35 wt% to 75 wt% of carbon nanotube (CNT). In other embodiments, the hybrid composition comprises between 65 wt% to 70 wt% of carbon nanotube (CNT).

[00106] In some embodiments, the hybrid comprises purpurin and SWCNT. In other embodiments, the hybrid comprises a 1:1 weight ratio of the purpurin and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 95:1 weight ratio of the purpurin and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 50:50 weight ratio of the purpurin and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:1, 1:10, 1:20, 1:30 1:50; 1:70, 1:95 weight ratio of the purpurin and the SWCNT, respectively.

[00107] In some embodiments, the hybrid comprises alizarin and SWCNT. In other embodiments, the hybrid comprises a 1:1 weight ratio of the alizarin and the SWCNT respectively.

In other embodiments, the hybrid comprises a 1:95 to 95:1 weight ratio of the alizarin and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 50:50 weight ratio of the alizarin and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:1, 1:10, 1:20, 1:30 1:50; 1:70, 1:95 weight ratio of the alizarin and the SWCNT, respectively.

[00108] In some embodiments, the hybrid comprises purpurin and MWCNT. In other embodiments, the hybrid comprises a 1:1 weight ratio of the purpurin and the MWCNT. In other embodiments, the hybrid comprises a 1:95 to 95:1 weight ratio of the purpurin and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 50:50 weight ratio of the purpurin and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:1, 1:10, 1:20, 1:30 1:50; 1:70, 1:95 weight ratio of the purpurin and the MWCNT, respectively.

[00109] In some embodiments, the hybrid comprises alizarin and MWCNT. In other embodiments, the hybrid comprises a 1:1 weight ratio of the alizarin and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 95:1 weight ratio of the alizarin and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 50:50 weight ratio of the alizarin and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:1, 1:10, 1:20, 1:30 1:50; 1:70, 1:95 weight ratio of the alizarin and the MWCNT, respectively.

[00110] In some embodiments, the hybrid comprises aramid nanofiber (ANF) and SWCNT. In other embodiments, the hybrid comprises a 1:1 weight ratio of the aramid nanofiber (ANF) and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 95:1 weight ratio of the aramid nanofiber (ANF) and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 50:50 weight ratio of the aramid nanofiber (ANF) and the SWCNT, respectively. In other embodiments, the hybrid comprises a 1:1, 1:10, 1:20, 1:30 1:50; 1:70, 1:95 weight ratio of the aramid nanofiber (ANF) and the SWCNT, respectively.

[00111] In some embodiments, the hybrid comprises aramid nanofiber (ANF) and MWCNT. In other embodiments, the hybrid comprises a 1:1 weight ratio of the aramid nanofiber (ANF) and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 95:1 weight ratio of the aramid nanofiber (ANF) and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:95 to 50:50 weight ratio of the aramid nanofiber (ANF) and the MWCNT, respectively. In other embodiments, the hybrid comprises a 1:1, 1:10, 1:20, 1:30 1:50; 1:70, 1:95 weight ratio of the aramid nanofiber (ANF) and the MWCNT, respectively.

[00112] In some embodiments, the hybrid provided herein is in the form of a dispersion, buckypaper, membrane, film, thin film, a coating, a bulk material, paste, a powder or an aerogel. In other embodiments, the hybrid provided herein is a dispersion in an organic or aqueous solvent. In other embodiments, the hybrid provided herein is a buckypaper or a film. In other embodiments, the hybrid provided herein is used as a coating. In other embodiments, the hybrid provided herein

is a powder. In other embodiments, the hybrid provided herein is a coating. In other embodiments, the hybrid provided herein is a paste. In other embodiments, the hybrid provided herein is an aerogel. In other embodiments, the coating is a powder coating.

[00113] In some embodiments, the hybrid provided herein is conductive.

[00114] In some embodiments, the hybrid provided herein is hydrophilic.

[00115] A “bulk material” refers herein to a material where the hybrid is dispersed in it in 3D.

Process for the Preparation of noncovalent hybrids

[00116] In some embodiments, the presently disclosed subject matter provides a process for the preparation of noncovalent hybrid comprising carbon nanotubes (CNTs) and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof; the process comprises:

- optionally grinding the carbon nanotubes; and
- mixing the carbon nanotubes and the at least one aromatic compound in a sonication bath in an aqueous solvent, an organic solvent, or combination thereof and sonicated for a period of time to obtain a dispersion comprising the hybrid.

[00117] In some embodiments, the presently disclosed subject matter provides a process for the preparation of noncovalent hybrids comprising carbon nanotubes (CNTs) and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof; the process comprises:

- grinding the carbon nanotubes; and
- mixing the carbon nanotubes and the at least one aromatic compound in a sonication bath in an aqueous solvent, an organic solvent, or combination thereof and sonicated for a period of time to obtain a dispersion comprising the hybrid.

[00118] In some embodiments, the mixing step in the sonication bath is for a period of sonication ranging between 15 min to one hour.

[00119] In another embodiment the grinding/milling is performed in a solid grinder at between 50-100 krpm for a period of between 2 minutes to 1 hour. In another embodiment, the grinding/milling is performed for a period of between 2 minutes to 10 minutes. The term grinding and milling are used herein interchangeably.

[00120] In some embodiments, the process for the preparation of the hybrid of the presently disclosed subject matter is further purified by centrifugation, filtration, or precipitation to yield homogeneous hybrid.

[00121] In some embodiments, the organic solvent used in the preparation of the hybrid is chloroform, methylene chloride, carbon tetrachloride dichloroethane, glyme, diglyme, triglyme, triethylene glycol, trichloroethane, tertbutyl methyl ether, tetrachloro ethane, acetone, THF, DMSO, toluene, benzene, alcohol, isopropyl alcohol (IPA), chlorobenzene, acetonitrile, dioxane, ether, NMP, DME, DMF, ethyl-acetate or combination thereof. Each represents a separate embodiment of this invention.

[00122] In some embodiments, the process for the preparation of the hybrids provided herein comprises a sonication step. In some embodiments, the sonication step mechanically and chemically alters the CNTs in solution. Bath sonication of CNTs in the presence of aromatic molecules in a preferred solvent disperses the CNTs which enables improved processing by spray-coating, filtration, casting and bulk composite applications.

[00123] In some embodiments, the hybrid prepared by the process provided herein has improved spraying, filtration, or printing properties compared to non-hybrid carbon nanotubes. In some embodiments, the hybrid prepared by the process provided herein has improved spraying, filtration, or printing properties compared to hybrids, where the carbon nanotube was not milled/grinded prior to mixing with an aromatic compound.

[00124] In some embodiments, the aromatic compounds within the hybrids provided herein, modify the surface energy of the adsorbing nanotubes for better solution dispersibility and adhesion.

Composite comprising the noncovalent hybrid provided herein and uses thereof

[00125] Both SWCNT and MWCNT have similar uses as adsorptive materials, conductive fibers, sheets and fabrics, porous electrodes, coatings or membranes, conductive inks, conductive and/or reinforcing additives to material composites, and part of electro-sensing, electro-catalytic or photovoltaic systems. They differ by porosity, electrical and thermal conductivity; chemical, thermal and photonic stability; surface energy; chemical adsorptivity; tensile strength and more. Their specific use may be tailored to a specific application using the hybrids provided herein.

[00126] In some embodiments, the presently disclosed subject matter provides a composite comprising a polymer and a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof

and their derivatives thereof, wherein the composite has improved mechanical and/or conductivity compared to CNT alone (i.e. not a hybrid). In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[00127] In other embodiments, the polymer is any known organic polymer with a melting point higher than 25°C. In other embodiments, the polymers comprise polyethylene, polypropylene, ABS, nylons, polystyrene, polyvinyl chloride, polylactic acid, polyurethanes, polyester, epoxy resin, poly acrylates, PEEK and more (e.g., any polymer that can be used in a 3D printer), their combinations and/or copolymers.

[00128] In some embodiments, the presently disclosed subject matter provides a porous electrode for electrochemical application, comprising a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof. In other embodiments, the electrochemical application comprises circular voltammetry, a sensor, an energy storage, and an energy conversion. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[00129] In some embodiments, the hybrid provided herein is used for the preparation of electrodes. In other embodiments, the hybrid provided herein is used for the preparation of porous electrodes. In other embodiments, the hybrid provided herein is used for the preparation of transparent electrodes.

[00130] In one embodiment, the electrode comprises the hybrid provided herein and/or nanoparticles and/or polymers in a way that will enable appropriate surface energy, selectivity, surface area, porosity, and chemical and thermal stability needed for their utilization in the mentioned systems.

[00131] In some embodiments, the presently disclosed subject matter provides a stretchable, bendable, flexible and/or inflatable material comprising a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof.

[00132] In other embodiments, the hybrid is conductive, and the conductivity of the hybrid is maintained upon stretching, bending, flexing or inflation of the material or substrate it is disposed thereon. In other embodiments, the material or substrate is coated by the hybrid. In other

embodiments, the hybrid is embedded within the material. In other embodiments, the hybrid is a coating on the surface of the material. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[00133] In other embodiments, the stretchable, bendable flexible and/or inflatable material is a fabric, a stretchable textile, a paper, or an elastomer (e.g., latex, rubber, polyurethane, silicone). In other embodiments, the elastomer is latex, rubber, polyurethane or silicone.

[00134] In some embodiments, the presently disclosed subject matter provides an EMI (electromagnetic interference) shielding and electromagnetic radiation absorbers comprising a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof. In other embodiments, the electrochemical application comprises circular voltammetry, a sensor, energy storage, and energy conversion, wherein the hybrid is conductive in the infrared and microwave ranges. The EMI shielding or the electromagnetic radiation absorbers are made of conductive CNT hybrids. EMI shields are faraday cages constructed around a device or an object needed to be shielded from EMI. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[00135] In some embodiments, the presently disclosed subject matter provides a construction material, wherein the construction material comprises a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof, wherein the hybrid reinforces the construction material compared to CNTs alone (not a hybrid). In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[00136] In another embodiment, the hybrid provided herein is embedded within the construction material. In another embodiment, the construction material is coated by the hybrid. In other embodiments, the construction material comprises concrete, a gypsum or construction polymers. In other embodiments, the construction polymers comprise polyethylene, polypropylene, ABS, nylons, polystyrene, polyvinyl chloride, polylactic acid, polyurethanes, polyester, epoxy resin, poly acrylates, PEEK and more (e.g., any polymer that can be used in a 3D printer) and their combination and/or copolymers.

[00137] In some embodiments, the hybrid provided herein is used for the preparation of construction material.

[00138] In other embodiments the hybrid is embedded in glass made by xerogel methods.

[00139] In some embodiments, the presently disclosed subject matter provides a dispersion comprising a noncovalent hybrid comprising carbon nanotubes and at least one aromatic compound, wherein the aromatic compound is selected from the group consisting of anthraquinone or derivative thereof, acridine, naphthalene disulfonic acid, caffeic acid, phenazine, indigo, rhodamine, phenothiazine, thymolphthalein, aramid nanofiber (ANF) their salts thereof and their derivatives thereof in organic or aqueous solvent. In other embodiments, the carbon nanotube is a single-walled carbon nanotube. In other embodiments, the carbon nanotube is a multi-walled carbon nanotube.

[00140] In other embodiments, the dispersion dispersibility of CNTs in organic solvents and water is up to 2 g/l.

[00141] In other embodiments, the dispersion is filtered on a filter paper forming a hydrophilic or a hydrophobic buckypaper on the filter paper. The hydrophobicity or hydrophilicity is determined by the properties of the aromatic compounds within the hybrids. In one embodiment, the buckypaper is hydrophilic and is used for water-oil separation or desiccation. In one embodiment, the buckypaper is hydrophobic and is used for protecting surfaces from humidity and liquid water, water soluble materials (e.g., self-cleaning surfaces), while staying permeable to other gases or organic liquids. The hydrophobic buckyball can be used also for protecting a substrate from regular organic materials that are not polyhalogenated.

[00142] In some embodiments a hybrid dispersion is applied on solid surfaces such as non-limiting examples comprising: glass, silicon oxide, PP, PVC, PET and paper by drop casting, dipping, spray coating, filtration, printing or powder coating to form conductive hybrid films on solid surfaces (substrates). In other embodiments the film can be transferred to another solid surface by hot press. In other embodiments, the film is transferred as exemplified in Example 1 and Example 2.

[00143] In some embodiments a hybrid dispersion is applied on solid surfaces which are transparent, translucent or opaque. In some embodiments a hybrid dispersion is applied on solid surfaces which are stretchable, bendable, flexible and/or inflatable.

[00144] In one embodiment, the terms “a” or “an” as used herein, refer to at least one, or multiples of the indicated element, which may be present in any desired order of magnitude, to suit a particular application, as will be appreciated by the skilled artisan. In one embodiment, the terms “about”, “approximately” or the symbol “~” may comprise a deviance from the indicated term of + 1 %, or in some embodiments, - 1 %, or in some embodiments, ± 2.5 %, or in some

embodiments, $\pm 5\%$, or in some embodiments, $\pm 7.5\%$, or in some embodiments, $\pm 10\%$, or in some embodiments, $\pm 15\%$, or in some embodiments, $\pm 20\%$, or in some embodiments, $\pm 25\%$.

[00145] The following examples are to be considered merely as illustrative and non-limiting in nature. It will be apparent to one skilled in the art to which the present invention pertains that many modifications, permutations, and variations may be made without departing from the scope of the invention.

EXAMPLES

Materials

[00146] SWCNTs (Tuball™) were purchased from OCSiAl (1.2-2 nm diameter, 5 μ m length, and $>80\%$ purity). Purpurin was purchased from Chem-Impex International ($\geq 95\%$ by HPLC). Ethanol and methanol were purchased from Bio-Lab (Israel). Acetone was purchased from Gadot Group (Israel), and dimethylsulphoxide (DMSO) was purchased from J. T. Baker. Polyvinylidene fluoride (PVDF) filter paper (0.45 μ m pore size) was purchased from Merck Millipore. Cellulose acetate (CA) filter paper (0.22 μ m pore size) was purchased from filtraTECH.

Fabrication of Purpurin-BPs

[00147] 60 mg of purpurin powder, 60 mL of doubly-distilled water (DDW), and 2 mL of 1 M NaOH solution were mixed in a 250 mL glass bottle with 12 mg of SWCNT powder. The bottle was then bath sonicated (DSC-120H, MRC, Israel) in cold water (5-15 °C) for 30 min and then centrifuged (5810R, Eppendorf) at 4000 rpm (1840g) for 15 min at room temperature. The top 2/3 of the supernatant was carefully decanted. The supernatant was vacuum filtered through a PVDF membrane, which was then washed with DDW and methanol. After washing, the resulting BP was roll-pressed using an office laminator (Eclips-PDA3-330C, Israel). The BP was easily separated from the filter paper after drying in an oven (5 min, 120 °C). The BP was transferred to a bottle with 30 mL of DMSO and shaken overnight on a low-speed orbital shaker (60 rpm, Orbit LS, Labnet). **To remove the DMSO, the BP washed with acetone and oven-dried (5 min, 120 °C).**

Fabrication of EtOH- buckypaper (BPs)

[00148] 12 mg of SWCNT powder and 60 mL of EtOH were mixed in a 250-mL glass bottle. The bottle was then bath sonicated in cold water (5-15 °C) for 30 min, vacuum filtered through PVDF filter paper, and then roll-pressed. After short oven-drying (5 min, 120 °C), the BP easily separated from the filter paper.

Fabrication of SWCNT-TCEs

[00149] 400-700 μ L of the SWCNTs-purpurin supernatant was added to 30 mL of DDW and vacuum filtered through hydrophilic CA filter paper. The filter paper was submerged in a petri

dish filled with DDW, the TCE separated from the filter paper and floated on the water surface. The DDW was decanted off, and the TCE was placed on a transparent substrate (glass, quartz, or PET) and oven dried at 120 °C for 30 minutes resulting in adhesion of the TCE to the substrate. The TCE was then immersed in DMSO (30 min) and acetone (5 min) and then oven dried (5 min, 120 °C).

Characterization

[00150] Scanning electron microscope (SEM) imaging was performed using a Zeiss Sigma 500 SEM operating at 1-3 kV. Energy dispersive spectroscopy (EDS) spectra were obtained using a four-quadrant detector (Bruker QUANTAX FlatQUAD) installed on a Zeiss Ultra 55 high-resolution SEM. Elemental analysis was performed with a landing voltage of 2-3 kV and a 30 μm aperture at high current mode. Hypermaps of different regions of interest were acquired for 3-5 minutes (2-3 million counts per spectrum).

[00151] Thermogravimetric analysis (TGA) measurements were conducted using an SDT Q 600 thermal analyzer (TA instruments) with an airflow rate of 100 mL/min and a heating rate of 10 °C/min.

[00152] Raman scattering measurements in the range of 70-3200 cm^{-1} of sample films were collected in the backscattering mode using a LabRAM HR Evolution (Horiba, France) confocal microspectrometer equipped with multiple lasers that give the option of tuning the laser power. For the experiments here, lasers at 532, 633, and 785 nm were used. The maximum incident power on the sample was 1-2 mW with a submicron spot size. The Raman spectra were collected by a 1024 $\times$ 256 pixel open electrode front-illuminated CCD camera (Syncerity, Horiba, USA) cooled to -60 °C. The spectra reported are averages of laser exposure times of 20-50 s to achieve the best signal-to-noise ratio (SNR). The spectra were baseline corrected.

[00153] X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed using a Kratos AXIS ULTRA system with a concentric hemispherical analyzer for photoexcited electron detection. A 75 W monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) was used with detection pass energies of 20-80 eV. Curve fitting analysis was based on linear or Shirley background subtraction and application of Gaussian–Lorentzian line shapes. UPS was measured with a helium discharge lamp using the He I (21.22 eV) and He II (40.8 eV) radiation lines. All UPS spectra were measured with a -9 V bias applied to the sample to detect photoemission onset at low kinetic energies.

[00154] Tensile test experiments were performed using an Instron Model 5965 Materials Testing System equipped with a 10 N load cell on buckypaper (BP) strips 4-6 mm in width and >25 mm in length. At least nine specimens were measured for each BP. The deformation rate was

0.2 mm/min. The sample thickness and width were measured using a digital micrometer and a digital caliper, respectively.

[00155] Electrical conductivity was measured using a Jandel cylindrical four-point collinear probe equipped with a Keithley 2401 Source Meter. For each sample, at least ten points were measured.

[00156] Ultraviolet–visible–near infrared (UV–vis–NIR) transmission spectra were measured with a Cary 5000 spectrometer (Agilent) using quartz or glass substrates.

[00157] Transmission electron microscopy (TEM) imaging was carried out at liquid nitrogen temperature on a Titan Krios G3i instrument (Thermo Fisher Scientific) operating at 300 kV. The samples on 300-mesh copper grids coated with Holey carbon were introduced into the TEM using an Autoloader. Images were recorded using a Gatan K3 direct detection camera. The total electron dose per image did not exceed $420 \text{ e}^-/\text{\AA}^2$.

Computational Methods

[00158] Grimme and coworkers' semiempirical method specifically designed for geometries, frequencies and non-covalent interactions (GFN2-xTB) was used using the code provided by the authors (XTB version 6.5.1); GFN2-xTB includes a D4 empirical dispersion correction (*vide infra*), and solvation effects were modelled using an analytical linearized Poisson–Boltzmann (ALPB) model with water as the solvent. Their CREST (version 2.12) tool was used to find the lowest-energy conformer of purpurin and to find its lowest-energy protonations and deprotonations. A number of the geometry optimizations of the complexes with the carbon nanotubes were plagued with small imaginary frequencies ($<25i \text{ cm}^{-1}$), which were ignored; the complex of purpurin with CNT(10,6) had a larger, persistent imaginary frequency of $67i \text{ cm}^{-1}$. The structure of the anion (purpurinate) was found by finding the lowest-energy deprotonation of the neutral species while the lowest-energy structure of the dianion (purpurindiate) was found by finding the lowest-energy protonation of the trianion.

[00159] Accurate energies were obtained with ORCA versions 5.0.3. Adamo and Barone's hybrid version (*i.e.*, PBE0) of the Perdew–Burke–Ernzerhof exchange–correlation functional (PBE) was used. With this functional, the second revision (def2) of Ahlrichs and coworkers' basis sets (def2-SVP) basis set was used. Weigend *et al.*'s “universal” Coulomb fitting basis set (def2/J) was used in order to increase the computational efficiency of the calculations. The resolution of the identity–chain of spheres exchange (RIJCOSX) approximation in conjunction with the def2-SVP/C correlation-fitting auxiliary basis set was used to further improve computational efficiency. An empirical dispersion correction was added, specifically the fourth version of Grimme's dispersion correction (D4). Bulk solvent effects were approximated by using a polarizable continuum model (PCM), specifically the integral equation formalism model (IEF-PCM) with

water (unless stated otherwise) as the solvent as in the experiments. Specifically, Truhlar's empirically parameterized version Solvation Model Density (SMD) was used.

[00160] The CNT fragments (each ~ 25 Å in length) based on the geometry/symmetry relations derived by Qin¹⁴⁰ were built using the nanotube utility in SAMSON version 2.0.1 and were capped with hydrogen atoms.

[00161] The Löwdin partial atomic charges were calculated as part of the PBE0/def2-SVP energy calculations.

EXAMPLE 1

A Hybrid of Alizarin and Single Wall Carbon Nano Tube (SWCNT)-Maintaining Conductivity upon Stretch

[00162] 20 mg of SWCNT (Tuball[®]) (from a 6 g batch milled for 2 minutes at 77 krpm, concentration of 0.5 g/l) and 20 mg alizarin were mixed in 40 mL isopropyl alcohol (IPA) in a bath-sonicated for 30 min. The dispersion was spray-coated on a 10×21 cm paper sheet in several layers where a heat gun was used to dry each layer. One side of a 20×3 cm commercial two-sided polyurethane gel elastomeric ribbon was taped on the length of the paper. The paper with the tape was passed through a laminator (hot press, at room temperature) in order to apply uniform pressure. Afterwards the tape was detached from the face of the paper sheet, and the CNT hybrid was fully transferred to it. The initial measured resistance from one end to another was 250 Ω. The same tape then was stretched to ca. 30 cm, and the obtained measured resistance was 14 kΩ. The tape was additionally stretched to 123 cm and the measured resistance rose to 150 kΩ. Surface fiber alignment by swiping the tape with a finger pressure from end to end (while wearing nitrile rubber gloves) resulted in the 3-fold resistance decrease to 56 kΩ (Table 1). This behavior indicates that the hybrid conductive material remains conductive upon stretching the substrate (By changing the average distance between the CNTs, starting with 0.1 mg/cm² then the elastomer was stretched by 600%).

Table 1: Resistance of elastomeric ribbon coated by hybrid of this invention following stretch.

Length of polyurethane gel elastomeric ribbon	Resistance
20 cm (initial length)	250 Ω
30 cm	14 kΩ
123 cm	150 kΩ
123 cm after surface fiber alignment	56 kΩ

EXAMPLE 2**A Hybrid of Alizarin and Single Wall Carbon Nano Tube (SWCNT) on a PE substrate via Transfer of Hybrid Coating Surface (Figures 1A-1C).**

[00163] A paper sheet was covered with Tuball® SWCNT-alizarin noncovalent hybrid which was obtained by the same method as described in Example 1. The paper sheet was folded in two along its width. A 5×5 cm piece of a commercial polyethylene (PE) sheet (87.5±1 μm thick) was sandwiched between the CNT hybrid-covered face of the paper sandwiched again between two PET sheets (100 μm thick) and passed through a desktop laminator heated to 140 °C (hot roll press), it was repeated 10 times (see Table 2 for thickness of the CNT hybrid-coated paper after thermal laminator treatment). The CNT hybrid was completely transferred to the surfaces of the PE. The conductivity from end to end, after finger pressure strokes (with a gloved hand) all over the surface was measured to be in the range of 60-110 Ω.

Table 2: Measured thicknesses of components in the PE composite production.

[μm]	PE sheet	PE with CNT hybrid
Sample 1	87.5±1 μm	107±4 μm
Sample 2	87.5±1 μm	106±3 μm

[00164] The paper and the PE covered surfaces can be utilized as pressure sensors when two covered surfaces are laid facing each other. Pressure application on the sheets resulted in resistivity reduction e.g., 10×5 cm area the resistance went from ca. 300 Ω to ca. 250 Ω and 215 Ω when weights of 340 g and 1200g were put on the device, respectively.

EXAMPLE 3**A Hybrid of Purpurin and Multi Wall Carbon Nano Tube (MWCNT)**

[00165] Purpurin and MWCNT (10-20 nm in diameter, 20-30 μm long, from Cheaptubes.com) hybrid noncovalent dispersions were prepared in different solvents (e.g., chloroform, tetrahydrofuran (THF), ethyl acetate (EA), acetone, IPA, acetonitrile (ACN), dimethyl sulfoxide (DMSO) and water (see Figures 2A-2E for comparison of MWCNT dispersion in various solvents). In a typical procedure, 12 mg of MWCNT, 6 mg of purpurin and 12 ml of one of the listed solvents were sonicated together for 15 min. The dispersion was stable for at least 14 hours. The MWCNT dispersion then was vacuum-filtrated and washed with the solvent until the washing solvent was clear. The received hybrid on the filter [buckypaper (BP)] was dried at ambient

temperature and easily peeled off from the PVDF filter membrane. The obtained BP was highly hydrophilic (very small contact angle of a 100 μ l water droplet) and can be used for example for water-oil separation or in desiccation.

[00166] The obtained BP can be easily redispersed (to a concentration of at least 2 mg/ml) for e.g., in isopropanol or water by bath sonication of several minutes, enabling recyclability.

EXAMPLE 4

A Hybrid of Purpurin and Single Wall Carbon Nano Tube (SWCNT)

[00167] Purpurin and SWCNT (Tuball[®] SWCNT) noncovalent hybrid dispersions were prepared. In a typical procedure 12 mg of SWCNT, 6 mg of purpurin and 12 ml of dichlorobenzene (DCB) were bath-sonicated for 30 min. Then 48 ml of DCB were added and sonicated for 15 min. The SWCNT dispersion was filtered through a syringe needle.

[00168] The dispersion was vacuum filtrated and washed with chloroform until the washings were colorless. The received hybrid on the filter (buckypaper, BP) was dried at ambient temperature and easily peeled off from the PVDF filter membrane. The obtained BP was hydrophilic.

EXAMPLE 5

Non-Woven Polypropylene Fabric Coated by Hybrid of This Invention (Figures 3A-3E)

[00169] A 10 cm diameter circle was cut out of a non-woven polypropylene (PP) fabric (40g/m²). The PP circle (310 mg) was placed in vacuum filtration support with the same diameter, and 20 mg of SWCNT (TuballTM) with 20 mg alizarin in 40 ml of isopropyl alcohol was sprayed on it using a spray gun (0.8 mm nozzle at 0.5 bar pressure). After process the PP circle was placed in a 120 °C oven for ca. 5 min. The measured resistance of the diameter of the circle was ca. 400 Ω (due to excess of alizarin). In the next step, the SWCNT hybrid covered PP circle was washed with IPA until the washings were practically colorless. The mass added to the PP circle measured after the washing was ca. 10 mg (~3 w/w%). The PP circle was placed in a 120 °C oven for ca. 5 min. The measured resistance on the covered face on the diameter of the circle was ~40 Ω , while the non-covered face showed irregular conductivity at the range of 1-50x10³ Ω . When the process was repeated on the other side, after the additional washing the total added mass was ca 30 mg

(~4.5 w/w%). The best double-sided sample had resistance on the diameter of the circle, on both sides, of ~15 Ω .

EXAMPLE 6

Transparent conductive electrodes and their preparation

[00170] **Figure 4** illustrates an example of a method for manufacturing transparent conductive electrodes on transparent substrates. The method illustrated in Figure 4 comprises at least the following steps:

- Providing a supernatant solution comprising SWCNTs with anthraquinone derivatives solution (e.g., alizarin and purpurin);
- The solution was then sonicated;
- Said aqueous solution was subsequently diluted;
- A vacuum filtration setup was then performed which directs the evaporated material towards a filter paper (FP) wherein the hybrid noncovalent nanotubes are disposed thereon. The evaporated material forms buckypaper (BP) on the filter paper;
- The buckypaper, disposed on the filter paper, was then floated on a liquid bath (in this case DDW) until the buckypaper detaches from the filter paper. Typically, the filter paper sinks to the base of the liquid bath whereas the buckypaper remains floating on the top;
- The filter paper was then removed from the bath and a transparent substrate was placed at the bottom of the bath instead;
- The water was decanted from the bath, lowering the buckypaper towards the transparent substrate, for example polyethylene terephthalate (PET);
- As the water was removed from the bath, the buckypaper lowers towards the transparent substrate until they come in to contact forming a transparent conductive electrode (TCE). It is noted that the buckypaper itself was a transparent conductive electrode.
- Once all the water was removed the TCE was then taken out the bath and dried.

[00171] **Figure 5A** shows the TCE placed on top of a fire hazard sign, demonstrating its transparency. **Figure 5B** demonstrates the flexibility of TCEs showing a person bending a TCE based on a PET substrate. The high flexibility of the SWCNT-hybrid TCE is one advantage over the brittleness of ITO-based TCEs. **Figure 5C** displays the step of separating the filter paper from the buckypaper. **Figure 5C** shows a transparent purpurin-BP film floating on DDW water whilst the filter paper sinks to the bottom of the liquid bath. The strength of the purpurin-BP was

demonstrated by its ability to remain intact, free-standing, on the surface of the water, showing the strength of inter-(nano)tube interactions in the BP itself. **Figure 5D** displays a TEM image of the TCE, and notably shows its porous structure; seen as gaps in between the nanotubes and nanotube bundles. **Figure 5D** also shows that the bundle thickness is less than 40 nm.

Electro-optical characteristics of TCEs

[00172] **Figures 6A-6B** illustrate the electro-optical performance characteristics of TCEs. **Figure 6A** shows that at low volumes, the amount of SWCNTs was below the percolation threshold, which results in a high sheet resistance (for purpurin-based hybrids). Above the percolation threshold, the sheet resistance was significantly reduced, which, in this example, starts at a volume of 400 μl with a sheet resistance of $131\ \Omega/\square$ (demarcated by a circle in **Figure 6A**). **Figure 6B** shows the transmittance of hybrid(purpurin)-SWCNT-based TCEs prepared using 400 μl of the supernatant solution measured using at a wavelength of range of 350-2000 nm, where the hybrid-SWCNT-based TCE was attached to a glass substrate. The transmittance of the TCE is shown in **Figure 6B** at 550 nm is about 92%. There is an increase in the transmittance at higher wavelengths.

[00173] **Table 3** summarizes the minimum requirements for various applications wherein CNT TCEs are utilized in practical application. T is the transmittance (in percent) and R_s is sheet resistance (measured in Ω/sq) of the TCE. **Table 3** indicates that SWCNT TCEs are suitable for touch panel applications, LCD screens, OLED displays and photovoltaic electrodes.

[00174] **Table 3:** Minimal requirements for the practical application of CNT TCEs

Applications	T (%)	R_s ($\Omega\ \text{sq}^{-1}$)
touch panel	85	500
LCD screen	85	100
OLED display	90	50
photovoltaic electrode	90	10

[00175] Comparing these values with other published TCEs, a figure of merit (FoM) is commonly used to evaluate the TCEs performance (eq. 1):

$$FoM = \frac{\sigma_{dc}}{\sigma_{op}} = \frac{188.5}{(T^{-0.5}-1)R_s} \quad (1)$$

[00176] σ_{dc} is the bulk DC conductivity of the TCE and σ_{op} is the optical conductivity.

[00177] The FoM of the SWCNT-purpurin TCEs is 31.7 ($T=91.5\%$, $R_s=131\ \Omega/\square$) whereas the ITO FoM is 348 ($T=90\%$, $R_s=10\ \Omega/\square$). Comparing this with other SWCNTs TCEs fabricated by solution processes, the highest FoM for undoped SWCNT TCEs is 19.3 while doping increases the FoM to 64.3. Comparing this with dry methods, FoMs of 85 and 139.4 are attained for undoped

and doped SWCNTs TCE, respectively. The doping of SWCNTs networks significantly increases the TCEs electrical conductivity and is also employed in SWCNT-purpurin TCEs.

EXAMPLE 7

Thermal Gravimetric Analysis (TGA)

[00178] TGA measurements were carried out with purpurin powder, pristine buckypaper (BP) and purpurin-BP hybrids which was washed with DMSO. For the BP-purpurin hybrid, after washing with DMSO and drying, the was BP soaked in concentrated hydrochloric acid to remove excess sodium. The BP was then washed with a large amount of DDW. For the TGA measurements the heating rate was set to 10°C/min in an air environment.

[00179] **Figures 11A and 11B** show that Purpurin has two main decomposition peaks at ~300°C and ~500°C. The pristine BP decomposed primarily at ~630°C. The BP-purpurin hybrid has two decomposition peaks, the first is at ~380°C which is attributed to the first decomposition of purpurin. The next peak is at ~670°C and is attributed to the decomposition of the SWCNTs.

[00180] From calculation the weight ratio between purpurin and SWCNTs is ~ 3:2.

EXAMPLE 8:

SWCNT Dispersion and Fabrication of Purpurin/SWCNT Films

[00181] Anthraquinone can interact strongly with SWCNT surface. A selection of anthraquinone dyes were screened to evaluate their efficacy in exfoliating SWCNTs. Purpurin (1,2,4-trihydroxyanthraquinone) was found to be the best (**Figures 8A-8B**). The SWCNTs used in this study are mass-produced, inexpensive Tuball™ SWCNTs in their as-received state; they are highly crystalline SWCNTs with high aspect ratios. The long aspect ratio of Tuball™ SWCNTs induces extended bundling, making their exfoliation more challenging compared to shorter SWCNTs. High-energy tip-sonication gives a higher concentration of exfoliated SWCNTs in the dispersions, but it damages the nanotubes (via sonochemistry) and shortens them. Hence, mild bath sonication and short, low-speed centrifugation were used to preserve the SWCNTs high crystallinity and aspect ratio.

[00182] **Figures 9A** outlines the dispersion preparation and its use for fabrication of the buckypapers (BPs).-An aqueous mixture of SWCNTs, purpurin, and NaOH was bath-sonicated and then centrifuged. The supernatant was separated and vacuum filtered, resulting in a SWCNT film (a “buckypaper” or BP). The BP was roll-pressed to densify the network and then soaked overnight in dimethyl sulfoxide (DMSO) to remove residual purpurin. The BP was then washed with acetone to remove the DMSO and finally dried. The resulting BP exhibits remarkable

flexibility: it can be crumpled into a ball and flattened out maintaining its network integrity without any visible damage (**Figure 9A**). The BP obtained by this method is denoted as Purpurin-BP. A control BP (without purpurin) was prepared in a similar method using ethanol (EtOH-BP). EtOH was chosen as SWCNT dispersions in water were unstable without purpurin.

[00183] Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to study the morphology and elemental composition of the BPs. The SEM images and EDS spectra of EtOH-BP (**Figure 10A and 10B**) and Purpurin-BP (**Figure 10C and 10D**) are shown. The SEM images in **Figures 10A-10D** show a reduction in the diameters of the SWCNT bundles of the SWCNTs exfoliated with purpurin compared to EtOH. The EDS shows a rise in the oxygen content for the Purpurin-BP compared to the EtOH-BP.

[00184] Comparing the morphologies of the two BPs, the diameters of nanotubes in Purpurin-BP are significantly smaller and more uniform than in EtOH-BP, indicating enhanced exfoliation by purpurin. The EDS spectra demonstrate that the BPs mainly consist of C, O, and Fe (iron is used as a catalyst for Tuball™ SWCNT growth and is coated with amorphous carbon in the final SWCNT material). Purpurin-BP has a higher oxygen content than EtOH-BP, and based on the relative O/C ratios in the two BPs, the SWCNTs/purpurin mass ratio is 2.2.

[00185] Thermogravimetric analysis (TGA) of the BPs and purpurin powder further confirms the presence of purpurin in the Purpurin-BP and provides an estimate of the amount of SWCNT-bound purpurin. The TGA and derivative TGA (DTGA) spectra (**Figure 11A-11B**) of the EtOH-BP and the Purpurin-BP show that purpurin remains in the Purpurin-BP, and SWCNT/purpurin mass ratio is 1.8, in good agreement with the EDS results. The estimated Purpurin-BP mass composition is 56.5% SWCNTs, 31.5% purpurin, and 12% iron.

Example 9

Characterization of buckypapers (BPs)

[00186] The BPs from **Example 8** were further characterized using Raman spectroscopy (**Figures 12A-12G**), which provides information about the diameter, chirality, and defects in the SWCNTs. Three excitation wavelengths of 532, 633, and 785 nm were used, and the spectrum for each excitation wavelength is the summation of twelve spectra taken from different areas of the BPs. At 532 nm, peaks characteristic of purpurin are observed in the spectrum of Purpurin-BP but not in the spectrum of EtOH-BP (**Figure 12G**, see box). The radial breathing mode (RBM) region (**Figure 12A-12C**) provides information about the diameter and the chirality of the SWCNTs. The diameter of the SWCNTs (d_t) is 1.1-2.0 nm, as estimated from the RBM frequency using $\omega_{RBM} (cm^{-1}) = 234 / d_t + 10$. The RBM spectra of the Purpurin-BP furthermore display higher content of smaller diameter SWCNTs compared to the EtOH-BP. The colored areas indicate

frequencies assigned to s-SWCNTs and m-SWCNTs according to the Kataura plot. For the Purpurin-BP, there is a significant enhancement of the RBM signal, particularly at 633 and 785 nm excitations, associated with Tuball™ m-SWCNTs. In addition to the RBM peak intensity changes, an upshift of up to 4 cm⁻¹ in the Purpurin-BP is observed, indicative of the strong π - π interactions between purpurin and the SWCNT surface.

[00187] The G- and D-bands of both BPs measured at different excitation wavelengths are shown in (**Figures 12D-12F**). The G-band corresponds to the vibrational mode of the C-C bonds in the hexagonal lattice and is sensitive to the chirality of the SWCNTs. The G-band of SWCNTs is typically split into several bands with a main Lorentzian peak in the high frequencies (G⁺). At lower frequencies, there are usually two or three narrow, symmetric Lorentzian peaks for s-SWCNTs or a Breit–Wigner–Fano (BWF) line shape for m-SWCNTs. The EtOH-BP, with a 2:1 mixture of s- and m-SWCNTs, has a G-band shape that mostly corresponds to s-SWCNTs. The G-band of Purpurin-BP, when excited at 532 or 785 nm, shows a slight increase in the intensity of the lower frequency peaks. At 633 nm excitation, there is a more pronounced change in the lower G-band frequencies, from narrow, symmetric Lorentzian peaks to broader BWF line shapes. The changes in the G-Band and RBM of the Purpurin-BP indicate selective exfoliation of m-SWCNTs, resulting in m-SWCNT-enriched networks. In the D-band, which corresponds to the defects in the hexagonal lattice of the SWCNTs, there is only a minor change between both BPs, which suggests that the exfoliation of the SWCNT bundles using purpurin is due to noncovalent functionalization as the sp²-hybridized carbon structure is preserved.

[00188] The changes in the chemical bonding resulting from exfoliation with purpurin were characterized using X-ray photoelectron spectroscopy (XPS). The survey XPS spectra of the EtOH-BP and Purpurin-BP from Example 8 (**Figure 14**) show three main peaks corresponding to carbon, oxygen, and iron. **Figure 13A** is a high-resolution spectra of the C 1s region for both BPs and purpurin powder. The main peak (sp² carbon, indicated by red arrow) in binding energies (BE) of Purpurin-BP is shifted to lower values by 0.16 eV. Shifts to lower BE have been observed for m-SWCNTs but not for s-SWCNTs, and also for doped SWCNTs. Doping of SWCNTs typically also results in a shift of the G-band in the Raman spectra, which is minor for Purpurin-BP (**Figures 12D-12F**). Thus, this shift in BE is attributed to m-SWCNT enrichment. There is an increase in the intensity of the signals corresponding to carbon-oxygen bonds (indicated by blue arrow) and in the peak associated with C–O and C=O groups in the high-resolution O 1s spectra in Purpurin-BP (**Figure 13B**), consistent with the presence of the adsorbed purpurin.

[00189] Ultraviolet photoelectron spectroscopy (UPS) probes changes in the electronic structure of a material and, thus, would be sensitive to variation in the ratio of m- and s-SWCNTs.

s-SWCNTs usually have lower work functions (WF, 4.0-4.5 eV) than m-SWCNTs (4.4-5.1 eV). The UPS spectra and the resulting WF (**Figure 13A**) show an increase of 0.17 eV in the WF for purpurin-BP, consistent with m-SWCNT enrichment.

Example 10

Model SWCNT/dye System Studies

[00190] To better understand the interaction of purpurin and its anions (purpurinate and purpurindiate) with the SWCNT surface, model SWCNT/dye systems were studied using density functional theory (DFT). A ~25 Å hydrogen-capped fragment of a metallic (8,8) and a semiconducting (10,6) SWCNTs was taken. The geometries of the most stable conformers of the purpurin species and their complexes with SWCNTs are shown in **Figure 15**. The complexation energy (CE) of the different purpurin species (**Table 4**) shows the dominant influence of the London dispersion forces (LDF) in binding the purpurin and its anions to the nanotube. The Raman spectra (*vide supra*) indicates that the exfoliation results from noncovalent functionalization of the SWCNT bundles. These interactions become increasingly stronger with each deprotonation, which is reasonable as the SWCNT π -system can absorb electron density and help stabilize the charged species. A previous DFT study on condensed benzenoid aromatic molecules showed higher adsorption energies with m-SWCNTs due to the favorable parallel alignment for π - π stacking compared to the angled configuration with the s-SWCNTs (Liu, *et al. Phys Chem Chem Phys* **2009**, *11* (33), 7257-7267). The gas-phase charge distribution in the purpurin-SWCNT complexes (**Table 4**), which would approximate the purpurin-SWCNT interactions after removal of the aqueous solvent, shows only a very minor charge transfer. Overall, while DFT indicates significant interactions between purpurin and SWCNTs, the differences between m- and s-SWCNTs are within the expected method error.

[00191] **Table 4:** Calculated complexation energies (CE) of purpurin, purpurinate and purpurindiate with (8,8) and (10,6) SWCNTs in aqueous solution and the gas-phase charge distribution between purpurin and SWCNTs.

SWCNT	dispersant	Complexation Energy (kcal/mol)			Charge Distribution (gas-phase)	
		ΔG_{298} (with LDF)	ΔG_{298} (no LDF)	ΔE_{LDF}	q(SWCNTs)	q(purpurin)
(8,8)	purpurin	-10.7	20.8	-31.5	0.007	-0.007
(10,6)	purpurin	-10.4	20.1	-30.6	-0.007	0.007
(8,8)	purpurinate	-11.5	18.9	-31.9		
(10,6)	purpurinate	-12.3	19.9	-31.2		
(8,8)	purpurindiate	-13.6	18.6	-32.2		
(10,6)	purpurindiate	-14.1	17.6	-31.7		

Example 11

Electrical Conductivity and Mechanical Properties

[00192] There are several steps in the preparation of the BPs (**Figure 10**). To evaluate their relative importance to the process, the electrical conductivity and mechanical properties were measured for the EtOH-BP, and Purpurin-BP, and three other BPs that can be considered as intermediates during the process (**Figure 16A**). The highest electrical conductivity was measured for the Purpurin-BP (**Figure 16B** and **Table 5**). P-BP1 had the lowest electrical conductivity, but washing it with DMSO results in P-BP2 and a 10.9% increase in conductivity. Centrifuging P-BP1 gives P-BP3 and a 26.7% increase in conductivity. Washing and then centrifuging P-BP1 increases the conductivity by 127% (effectively Purpurin-BP).

[00193] **Table 5:** Mechanical properties and electrical conductivity of EtOH-BP, Purpurin-BP, and P-BP_n ($n = 1-3$).

	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Electrical conductivity (S/cm)
EtOH-BP	0.18 ± 0.1	3.9 ± 1.3	3 ± 1	2028 ± 123
Purpurin-BP	0.48 ± 0.1	24.4 ± 9	4.9 ± 1.3	3726 ± 238
P-BP1	0.28 ± 0.1	10.2 ± 4.1	4.9 ± 1.1	1639 ± 324
P-BP2	0.23 ± 0.01	5.05 ± 0.8	3.68 ± 0.5	1817 ± 302
P-BP3	1.3 ± 0.2	44.2 ± 7.7	2.8 ± 0.6	2077 ± 345

[00194] The mechanical properties of the BPs were measured using unidirectional tensile tests, in particular Young's modulus (E), the ultimate tensile strength (UTS), and the elongation at break (**Table 5**, representative stress–strain curves are presented in (**Figure 16C**). Mechanically, EtOH-BP is the weakest, outperformed even by the process intermediates P-BP_n ($n = 1-3$). It is interesting to note that the mechanical properties of P-BP3 are superior to all the other BPs, yet it has much lower electrical conductivity. Purpurin-BP has remarkable mechanical properties that, together with its high electrical conductivity, make it a viable candidate for various applications.

[00195] The increased electrical conductivity and improved mechanical properties of Purpurin-BP over EtOH-BP are additional indications of the efficient exfoliation of the SWCNT bundles by purpurin. Preferable exfoliation of the m-SWCNTs results in a significant increase in the electrical conductivity. The residual purpurin (~31.5% of the Purpurin-BP mass) leads to increased contact resistance between the SWCNTs bundles, evident from the lower electrical conductivity of P-BP2

relative to EtOH-BP even though the P-BP2 has a higher degree of exfoliation. While the removal of purpurin by DMSO increases the electrical conductivity, at the same time it significantly decreases the network strength.

[00196] The electrical conductivity and the mechanical properties of SWCNT networks can be enhanced by different methods, such as removal of catalysts and adsorbed dispersants, SWCNTs alignment, doping, and change of dispersion method. However, these methods require pre- and/or post-treatments, which can be time-consuming and/or require advanced instrumentation.

[00197] **Figure 17** compares the UTS versus electrical conductivity of EtOH-BP, Purpurin-BP, P-BP n ($n = 1-3$), and SWCNT-BPs fabricated by solution processing, randomly oriented and without post treatments reported in other studies. The reported BPs are divided into two groups: SWCNTs dispersed in organic solvents without any dispersant (left) and SWCNTs dispersed in aqueous solution with the addition of surfactants (middle); details of the BPs are summarized in **Table 6**. Exfoliation using surfactants increases the electrical conductivity of the BPs relative to the surfactant-free BPs. The BPs from this study have at least an order of magnitude higher electrical conductivity than the reported BPs; P-BP3 also has superior mechanical strength, but Purpurin-BP has superior electronic properties.

[00198] **Table 6:** Specifications of numerous reported buckypapers (BPs) (solvent used in the preparation and dispersant) and their mechanical properties and electrical conductivity.

	Solvent	Dispersant	Young's modulus (E, GPa)	Ultimate tensile strength (UTS, MPa)	Elongation at break (%)	Electrical conductivity (S/cm)	*Ref.
1	EtOH	none	1.6	28	2.1	20	¹
2	EtOH/ Methanol	none	1.1	20	~1.8	49	²
3	NMP	none	2	22	1.5	50	³
4	Methanol	none	0.37	3.4	1.6	117	⁴
5	DDW	Triton X-100	2.02	15	1.7	150	⁵
6	DDW	Triton X-100	2.24	23.6	~1.8	170	⁶
7	DDW	Triton X-100	1.11	17.8	N/A	449	⁷
8	DDW	SDS	0.66	11	1.7	700	⁸

*References

- (1) Diez-Pascual, *et al. ACS Applied Materials & Interfaces* **2013**, 5 (22), 12107-12119.
- (2) Diez-Pascual, *et al. Composites Part A: Applied Science and Manufacturing* **2012**, 43 (6), 997-1006.
- (3) Khan, *et al. Carbon* **2010**, 48 (10), 2825-2830.
- (4) Jakubinek, *et al. RSC Adv.* **2014**, 4 (101), 57564-57573.
- (5) Chen, *et al. Nanotechnology* **2011**, 22 (48), 485708.
- (6) Park, *et al. Journal of Applied Physics* **2009**, 106 (10), 104310.
- (7) Chu, *et al. Carbon* **2014**, 66, 154-163.

(8) Dettlaff-Weglikowska, *et al. J Am Chem Soc* **2005**, 127 (14), 5125-5131.

Example 12

Transparent Conductive Electrodes (TCEs)

[00199] One application of the SWCNT networks from the study is the preparation of transparent conductive electrodes (TCEs). TCEs are employed in a wide range of applications, including touch screens, OLEDs, and solar cells. TCEs based on SWCNTs can be prepared similarly to the BPs. After initially preparing a BP, albeit at lower concentrations of SWCNT and purpurin, the SWCNT network is separated from the filter paper by submersion in water. The liberated network can then be transferred to a suitable substrate, such as polyethylene terephthalate (PET) or quartz.

[00200] Using a PET substrate, highly transparent and flexible TCEs were obtained (**Figure 5A-5B**). A typical transmittance spectrum of SWCNT-TCE (quartz substrate, **Figure 5E**) shows a high transmittance in the visible spectrum and increased transmittance in the IR region. The absorption at 273 nm is characteristic of SWCNTs and arises due to the π -plasmon resonance. SEM of a DMSO-washed SWCNTs-TCE on quartz shows a porous network structure ((**Figure 5F**). Ultrathin TCEs suitable for transmission electron microscopy (TEM) imaging can be prepared due to the strong SWCNT network. TEM imaging (**Figure 5G**) and higher magnification in (**Figure 5D**) shows the SWCNT bundles with the thicknesses of 10.2 ± 3.1 nm, indicating good exfoliation.

[00201] The optoelectronic performance of TCEs is commonly evaluated using the “figure of merit” (FoM), which is defined as the ratio of the electrical conductivity (σ_{dc}) to optical conductivity (σ_{op}):

$$FoM = \frac{\sigma_{dc}}{\sigma_{op}} = \frac{Z_0}{(T^{-1/2} - 1)2R_s}$$

where T is the transmittance at 550 nm, R_s is the sheet resistance, and $Z_0 = 377 \Omega$ is the impedance of a free space. FoM reflects the balance of electrical and optical quality, and higher values of FoM are indicative of better-performing TCEs. The calculated FoM of the purpurin-based TCEs displays a large difference between the DMSO-washed and the unwashed TCEs. The former shows much lower FoM with large variability, with values of 4.5-13 compared to 20-25 for the unwashed TCEs (**Figure 18**).

[00202] The advantageous performance of these systems is evident from comparing the purpurin-based TCEs to reported SWCNT-based TCEs fabricated by wet processing without any additional doping treatment. In **Figure 19**, the transmittance at 550 nm is plotted against the sheet resistance of the different TCEs, and the curve marks a FoM value of 20, which corresponds to the

lowest FoM value of these purpurin-based TCEs. The optoelectronic performance of the TCEs from this work (highest FoM value of 25) is superior to most TCEs fabricated using solution-processed SWCNTs and close to the best reported wet-processed SWCNT-based TCEs with FoM values of 26 and 30.3. These TCEs were fabricated using enhanced direct-injection pyrolytic synthesis (eDIPS) SWCNTs, which have higher crystallinity than Tuball™ SWCNTs and thus higher conductivity, improving TCE properties.

[00203] Indium tin oxide (ITO) is currently the most employed material for TCEs with 10 Ω/sq sheet resistance at 90% optical transmittance (**Figure 19**, FoM = 348). However, ITO suffers from serious drawbacks, such as its brittle nature, and the scarcity of indium, which makes ITO a high-cost material. Even though the SWCNT-purpurin TCEs in this study have lower optoelectronic performances than ITO, they are nonetheless suitable for implementation in touch panels and LCD screens as they meet the requirements in terms of transmittance and sheet resistance for these applications (**Table 7**) while bypassing the limitations of ITO.

[00204] **Table 7:** The minimal requirements for the practical application of TCEs.

Application	T (%)	R_s ($\Omega \text{ sq}^{-1}$)	FoM
touch panel	85	500	4.5
LCD screen	85	100	22.3
OLED display	90	50	69.7
photovoltaic electrode	90	10	348

[00205] The fabrication of highly electrically conductive and robust SWCNT materials has been demonstrated using purpurin, a common organic dye, as an exfoliating agent in aqueous solution. Strong and selective noncovalent interactions result in high-quality dispersions enriched with metallic SWCNTs. The dispersions enable a solution-based fabrication of flexible BPs and TCEs with improved electrical conductivity. The BPs have enhanced mechanical properties, and the TCEs exhibit excellent optoelectronic performance. The SWCNT-purpurin TCEs have superior optoelectronic performance to other wet-processed Tuball™ SWCNTs-based TCEs. The SWCNT-purpurin TCEs are highly flexible and are prepared via a simple solution-based process and, thus, are an attractive alternative to the more expensive systems currently extensively used in a wide range of industrial applications. The use of strong and selective noncovalent interactions induced by readily available organic molecules in aqueous media allows for the fabrication of materials with superior properties, opening the door to new avenues in the field of carbon nanotube-based materials.

[00206] It is appreciated by persons skilled in the art that the present invention is not limited by what has been particularly shown and described hereinabove. Rather, the scope of the present invention includes both combinations and sub-combinations of various features described hereinabove as well as variations and modifications. Therefore, the invention is not to be constructed as restricted to the particularly described embodiments, and the scope and concept of the invention will be more readily understood by references to the claims, which follow.

CLAIMS

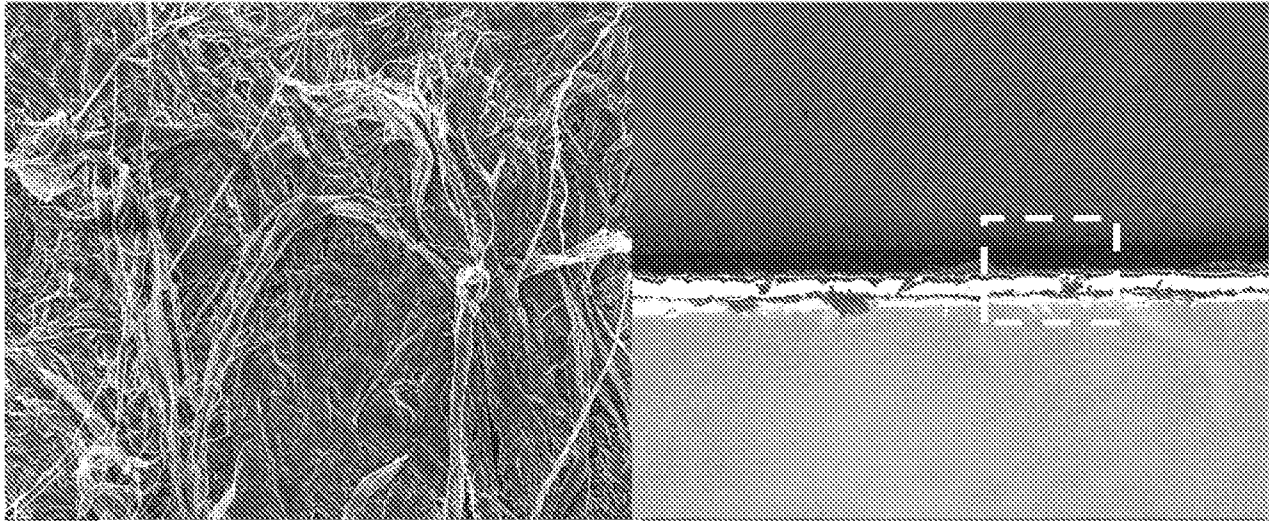
1. A transparent conductive material comprising non-covalent hybrids comprising carbon nanotubes (CNTs) and at least one anthraquinone or derivative thereof.
2. The transparent conductive material of claim 1 wherein said CNTs are single-walled, multi-walled or a combination thereof.
3. The transparent conductive material of claim 1 or 2 wherein said anthraquinone derivative is purpurin or alizarin or a combination thereof.
4. The transparent conductive material of any one of claims 1 to 3 in a form selected from a list comprising: a membrane, dispersion, buckypaper, bulk material, coating, film, paste, paint, gel, powder or aerogel.
5. The transparent conductive material of any one of claims 1 to 4 wherein said CNTs are doped.
6. The transparent conductive material of any one of claims 1 to 5 wherein said transparent conductive material is porous.
7. The transparent conductive material of any one of claims 1 to 6 wherein said transparent conductive material has a transmittance of between 50 to 100 % in the UV-visible range.
8. The transparent conductive material of any one of claims 1 to 7 wherein said transparent conductive material has a thickness ranging between 1 and 1000 nm.
9. The transparent conductive material of any one of claims 1 to 8 wherein said transparent conductive material has a conductance which is maintained upon flexing, bending, stretching and/or inflation.
10. A transparent conductive electrode comprising the transparent conductive material of any one of claims 1 to 9 further comprising a substrate wherein said transparent conductive material is disposed on said substrate.
11. The transparent conductive electrode of claim 10 wherein said substrate is transparent or translucent.
12. The transparent conductive electrode of claim 10 or claim 11 wherein said substrate is stretchable, bendable, flexible and/or inflatable.
13. The transparent conductive electrode of any one of claims 10 to 12 wherein said substrate is selected from a group comprising: low-density polyethylene (LDPE), high-density

polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylon, nylon 6, nylon 6,6, polyamide, aramids, polytetrafluoroethylene (PTFE), thermoplastics, thermoplastic polyurethanes (TPU), polystyrene, polychlorotrifluoroethylene (PCTFE), phenol-formaldehyde resin, para-aramid fibre, para-aramid, polyethylene terephthalate (PET), polychloroprene, meta-aramid polymer, polyacrylonitrile (PAN), polyamide 11 & 12, copolyamid, polyimide, aromatic polyester, polyester, ABS, poly-p-phenylene-2,6-benzobisoxazole (PBO), polyolefins, aromatic polymers, poly(methyl methacrylate) (PMMA), polyether ether ketone (PEEK), polyethylene glycol (PEG), polylactic acid (PLA), halogenated polymers and their combination and/or copolymers.

14. The transparent conductive electrode of any one of claims 10 to 12 wherein the substrate is selected from a group comprising: fabric, paper, stretchable textile or an elastomer.
15. The transparent conductive electrode of claim 14 wherein said elastomer is selected from a group comprising: latex, rubber, polyurethane and/or silicone.
16. The transparent conductive electrode of claim 10 wherein said substrate is glass, silicon and/or silicon oxide.
17. A composite electrode comprising a first transparent conductive material of any one of claims 1 to 9 further comprising at least one additional transparent conductive material of any one of claims 1 to 9 wherein said first transparent conductive material is connected to said at least one additional transparent conductive material in series and/or parallel.
18. A composite electrode comprising a first transparent electrode of any one of claims 10 to 16 further comprising at least one additional transparent conductive electrode of any one of claims 10 to 16 wherein said first transparent conductive electrode is connected to said at least one additional transparent electrode in series and/or parallel.
19. A method of preparing a transparent conductive electrode, said method comprising:
 - optionally grinding carbon nanotubes (CNTs);
 - mixing said CNTs and anthraquinone derivative in a sonication bath in an aqueous solvent or an organic solvent, forming a hybrid solution;
 - diluting said hybrid solution;
 - vacuum filtering said hybrid solution through a porous medium forming conductive solid deposits disposed thereon;

- placing said porous medium with said conductive solid deposits disposed thereon into a liquid bath wherein said conductive solid deposits detach from said porous medium resulting in said conductive solid deposits remaining on the surface of said liquid bath and said porous medium sinking to the base of said liquid bath;
 - removing said porous medium from said liquid bath;
 - placing a substrate at the base of said liquid bath;
 - removing liquid from said liquid bath until said conductive solid deposits are disposed on said substrate resulting in a transparent conductive electrode; and
 - optionally drying said transparent conductive electrode.
20. The method of claim 19 wherein said CNTs are single-walled, multi-walled or a combination thereof.
21. The method of claim 19 or 20 wherein said CNTs are doped.
22. The method of any one of claims 19 to 21 wherein said anthraquinone derivative is purpurin or alizarin or a combination thereof.
23. The method of any one of claims 19 to 22 wherein said organic solvent is selected from a group comprising: chloroform, methylene chloride, carbon tetrachloride dichloroethane, glyme, diglyme, triglyme, triethylene glycol, trichloroethane, tertbutyl methyl ether, tetrachloro ethane, acetone, THF, DMSO, toluene, benzene, alcohol, isopropyl alcohol (IPA), chlorobenzene, acetonitrile, dioxane, ether, NMP, DME, DMF, ethyl-acetate or combination thereof.
24. The method of any one of claims 19 to 23 wherein said hybrid solution has a CNT concentration of between 1 wt% to 99 wt%.
25. The method of any one of claims 19 to 24 wherein said porous medium is selected from a group comprising: filter paper, transfer membrane, polyvinylidene difluoride (PVDF) filter/membrane, polytetrafluoroethylene (PTFE) membrane, microporous membranes, mesoporous membranes, microporous membranes, organic-based membranes, inorganic-based membranes, nitrocellulose membranes (NC) and polysilsesquioxane (PSQ) membranes.
26. The method of any one of claims 19 to 25 wherein said conductive solid deposits are in the form selected from a group comprising: a membrane, buckypaper, bulk material, coating, film, thin film, paste, paint, gel, powder or aerogel.
27. The method of any one of claims 19 to 26 wherein said liquid bath is a water bath.

28. The method of any one of claims 19 to 27 wherein said substrate is transparent or translucent.
29. The method of any one of claims 19 to 28 wherein said substrate is stretchable, bendable, flexible and/or inflatable.
30. The method of any one of claims 19 to 29 wherein said substrate is selected from a group comprising: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylon, nylon 6, nylon 6,6, polyamide, aramids, polytetrafluoroethylene (PTFE), thermoplastics, thermoplastic polyurethanes (TPU), polystyrene, polychlorotrifluoroethylene (PCTFE), phenol-formaldehyde resin, para-aramid fiber, para-aramid, polyethylene terephthalate (PET), polychloroprene, meta-aramid polymer, polyacrylonitrile (PAN), polyamide 11 & 12, copolyamid, polyimide, aromatic polyester, polyester, ABS, poly-p-phenylene-2,6-benzobisoxazole (PBO), polyolefins, aromatic polymers, poly(methyl methacrylate) (PMMA), polyether ether ketone (PEEK), polyethylene glycol (PEG), polylactic acid (PLA), halogenated polymers and their combination and/or copolymers.
31. The method of any one of claims 19 to 30 wherein said substrate is selected from a group comprising: fabric, paper, stretchable textile or an elastomer.
32. The method of claim 31 wherein said elastomer is selected from a group comprising: latex, rubber, polyurethane and/or silicone.
33. The method of any one of claims 19 to 28 wherein said substrate is glass, silicon and/or silicon oxide.
34. The method of any one of claims 19 to 33 wherein said drying comprises any of the following: drying with nitrogen flow, drying within a dry box, drying with vacuum, drying with heating or any combination thereof.
35. A transparent conductive electrode produced by the method of any one of claims 19 to 34.



10μm

100μm

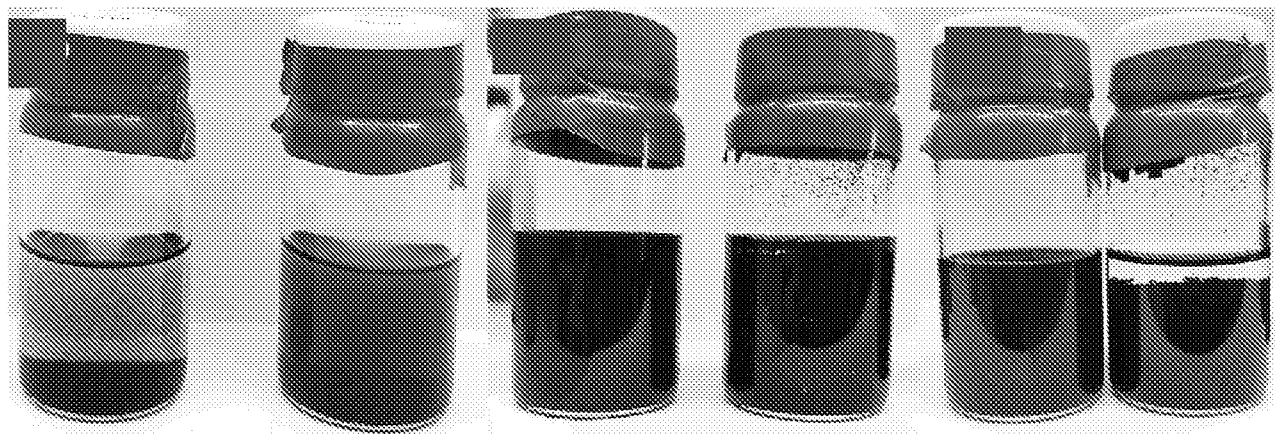
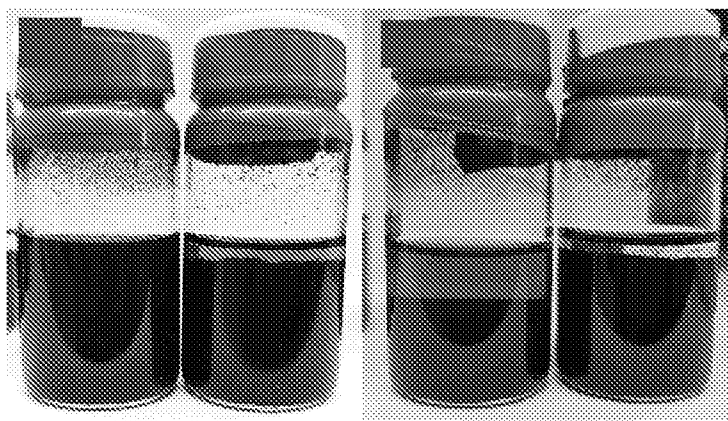
FIGURE 1A

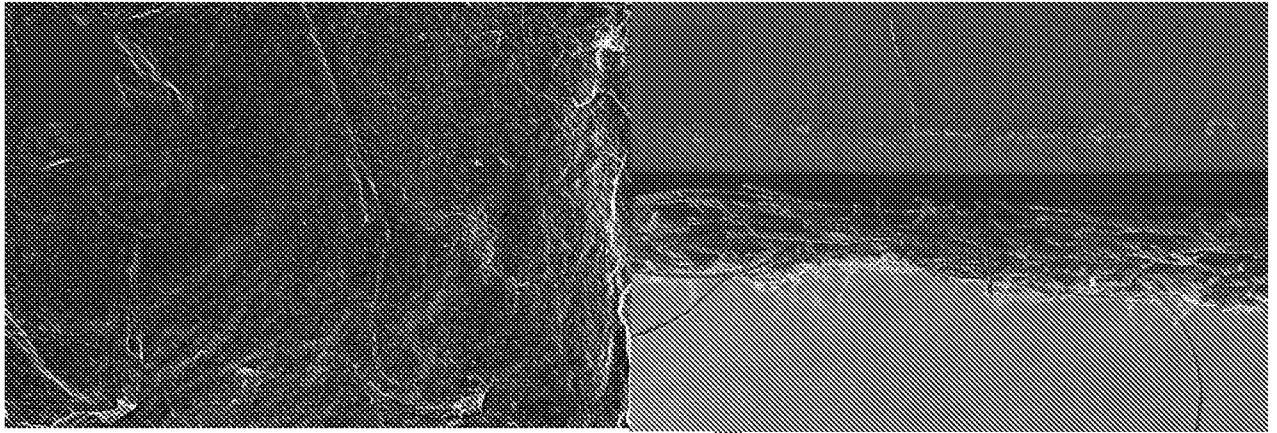
FIGURE 1B



20μm

FIGURE 1C

**FIGURE 2A****FIGURE 2B****FIGURE 2C****FIGURE 2D****FIGURE 2E**

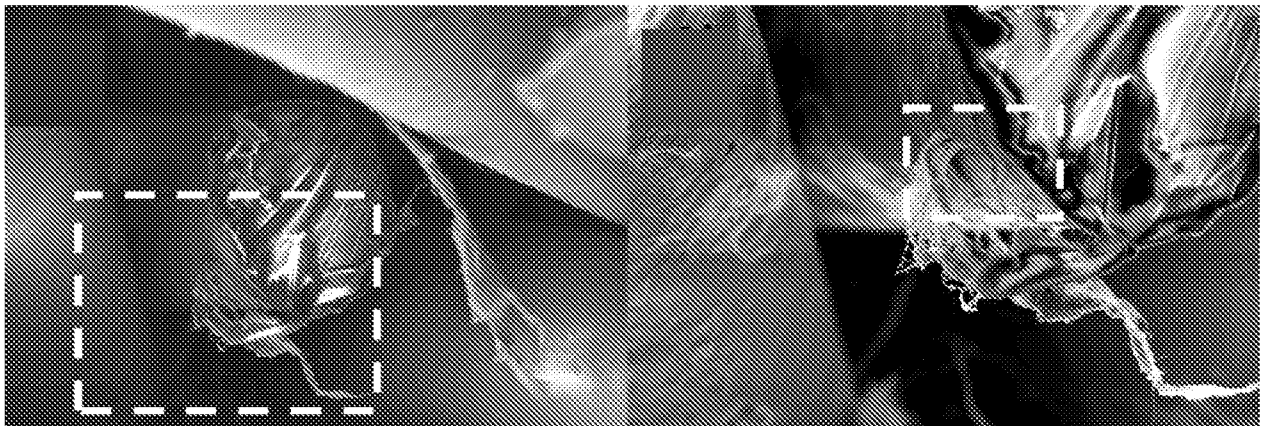


10μm

100μm

FIGURE 3A

FIGURE 3B

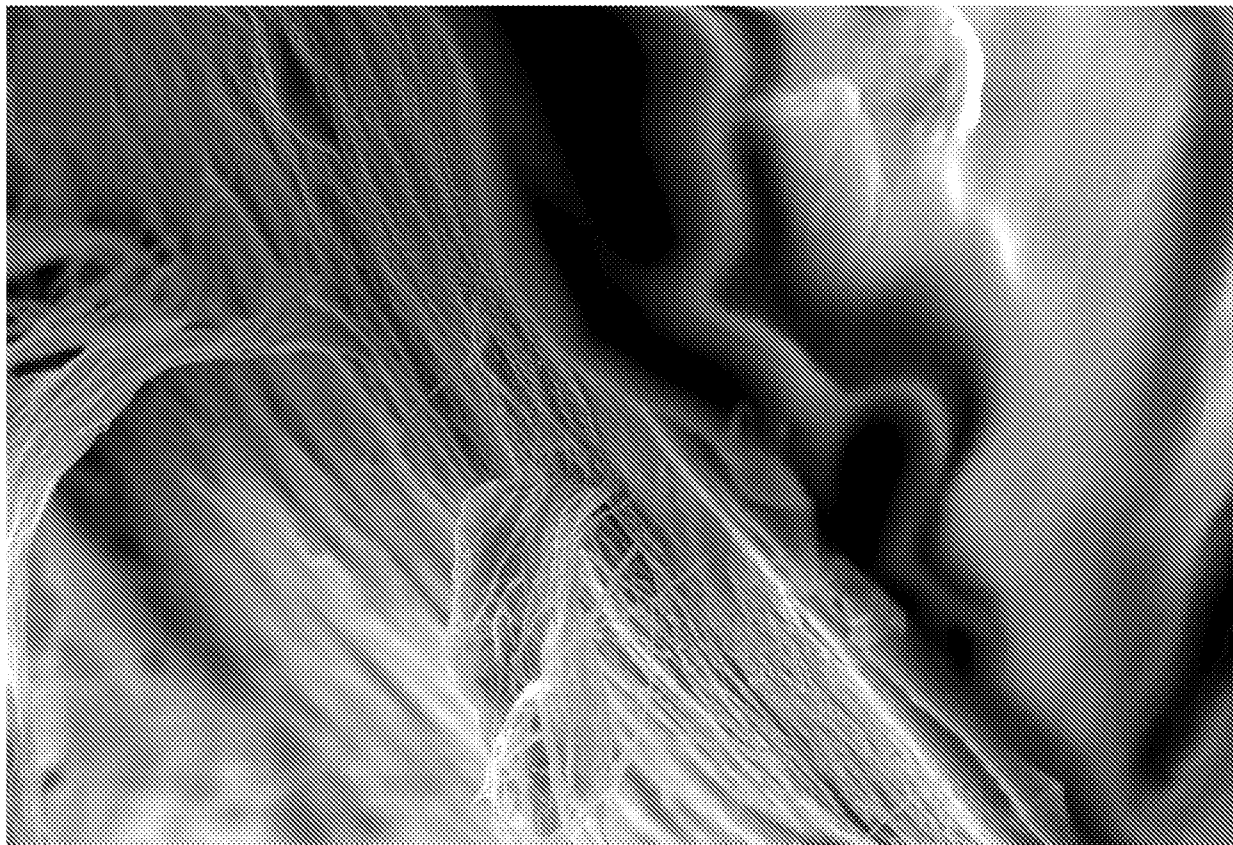


2μm

1μm

FIGURE 3C

FIGURE 3D



300nm

FIGURE 3E

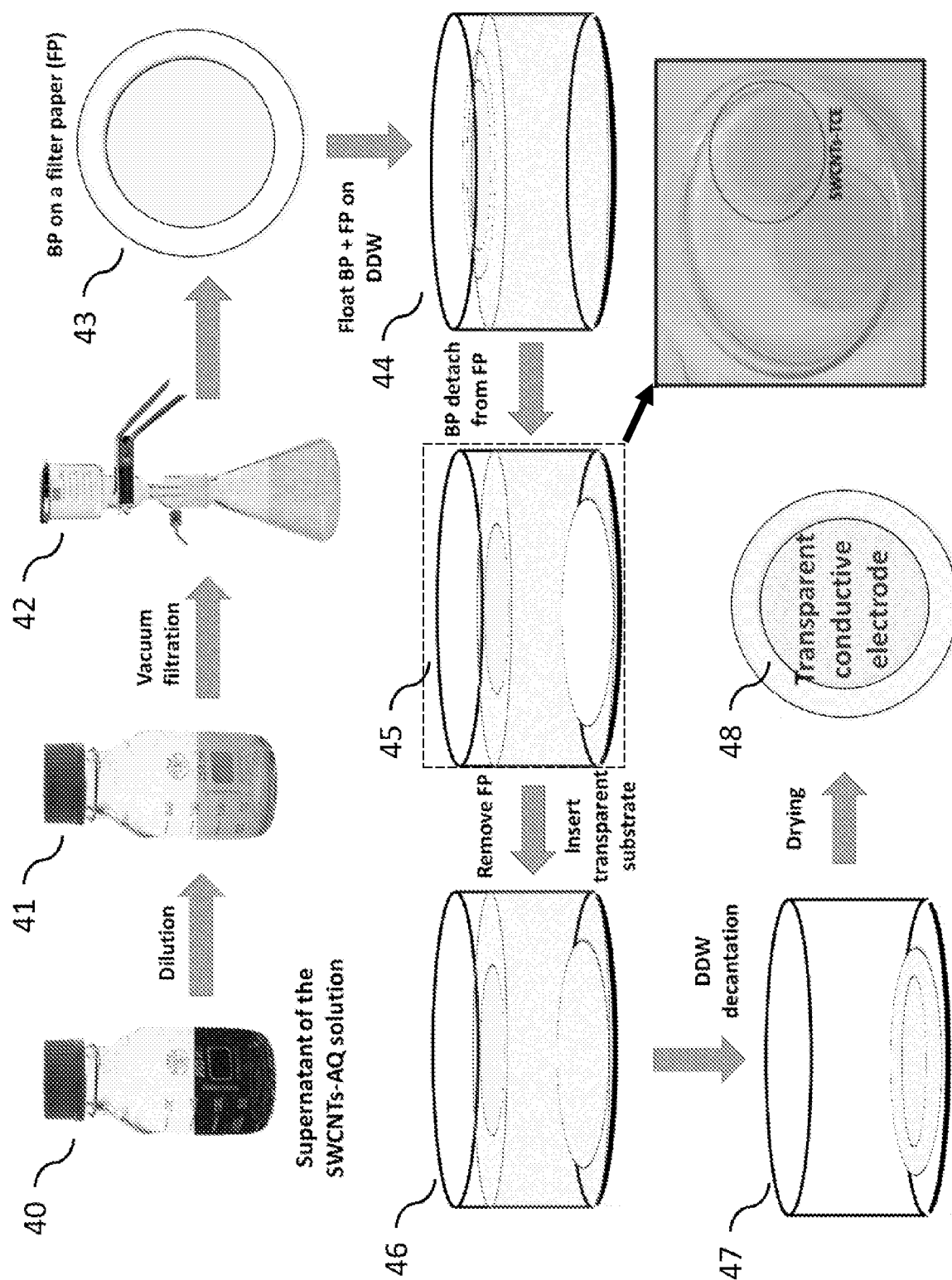
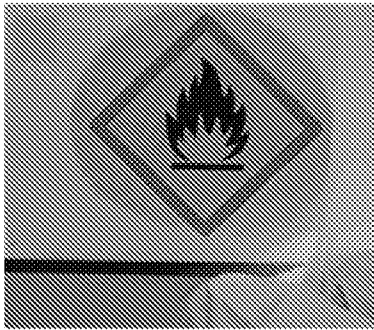
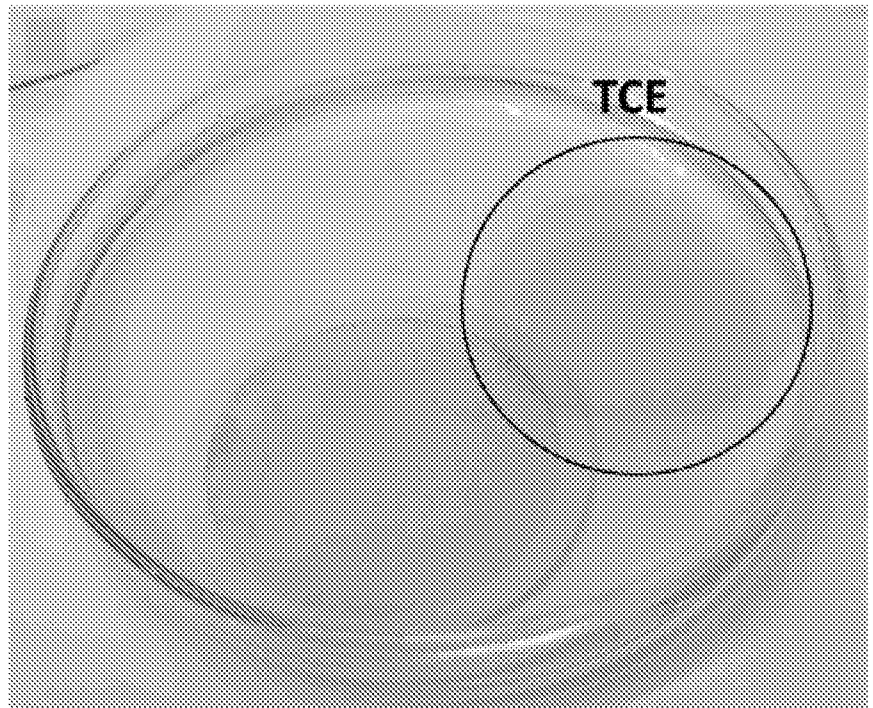
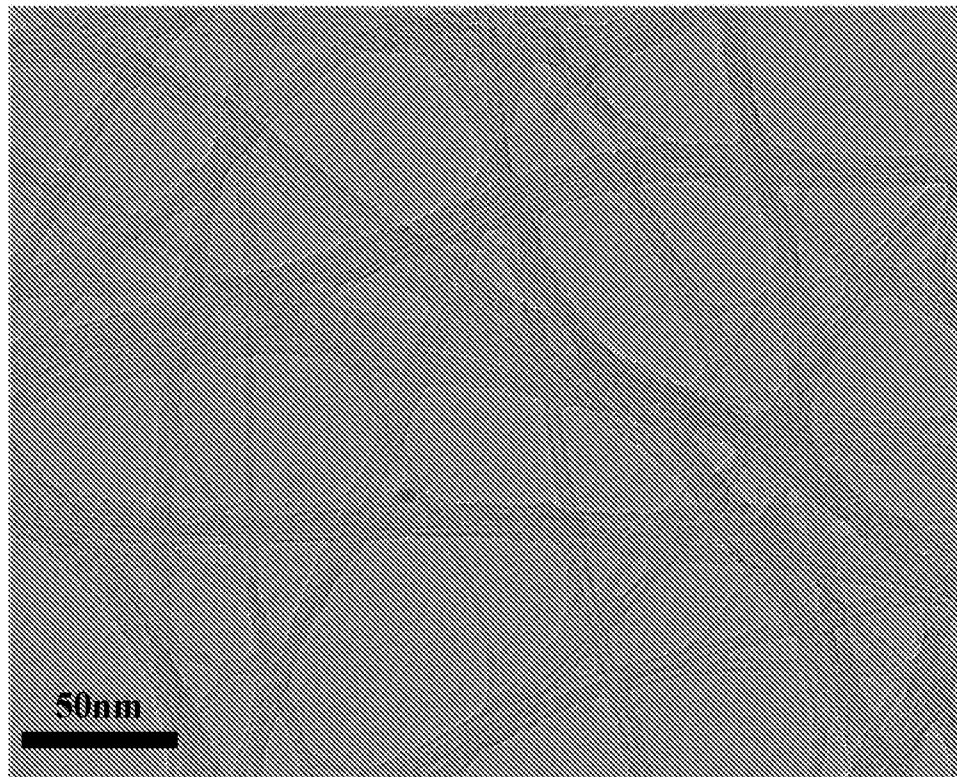


FIGURE 4

FIGURE 5A**FIGURE 5B****FIGURE 5C****FIGURE 5D**

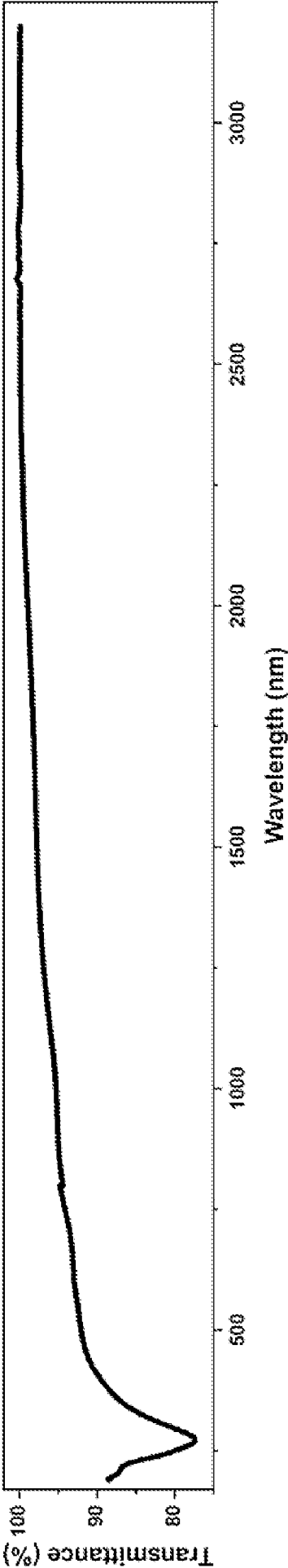
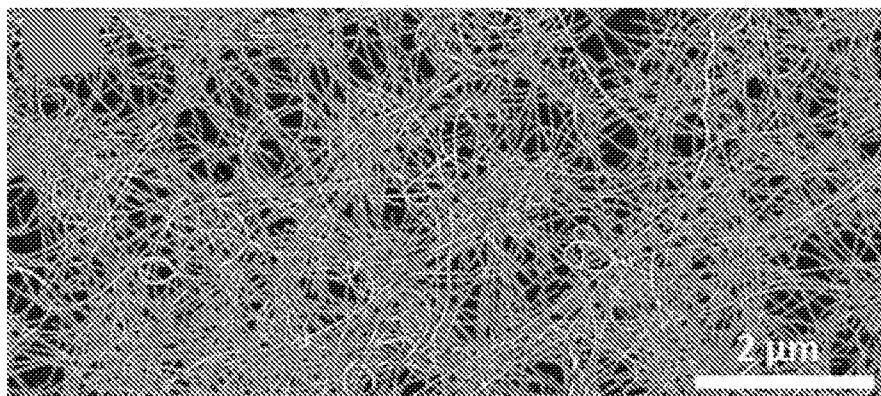
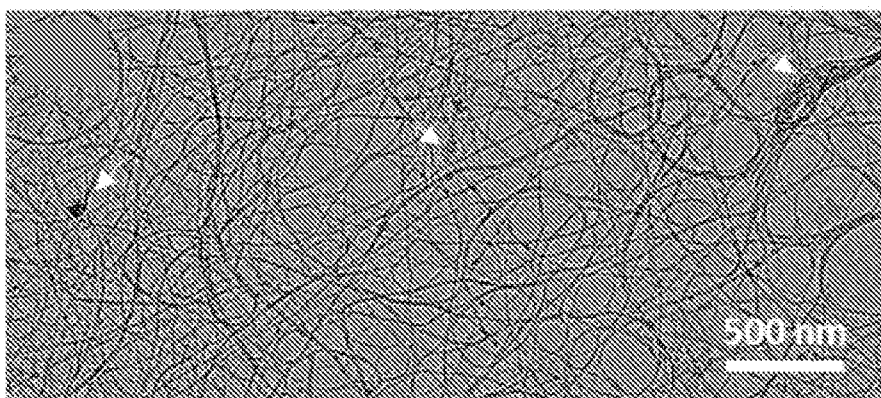
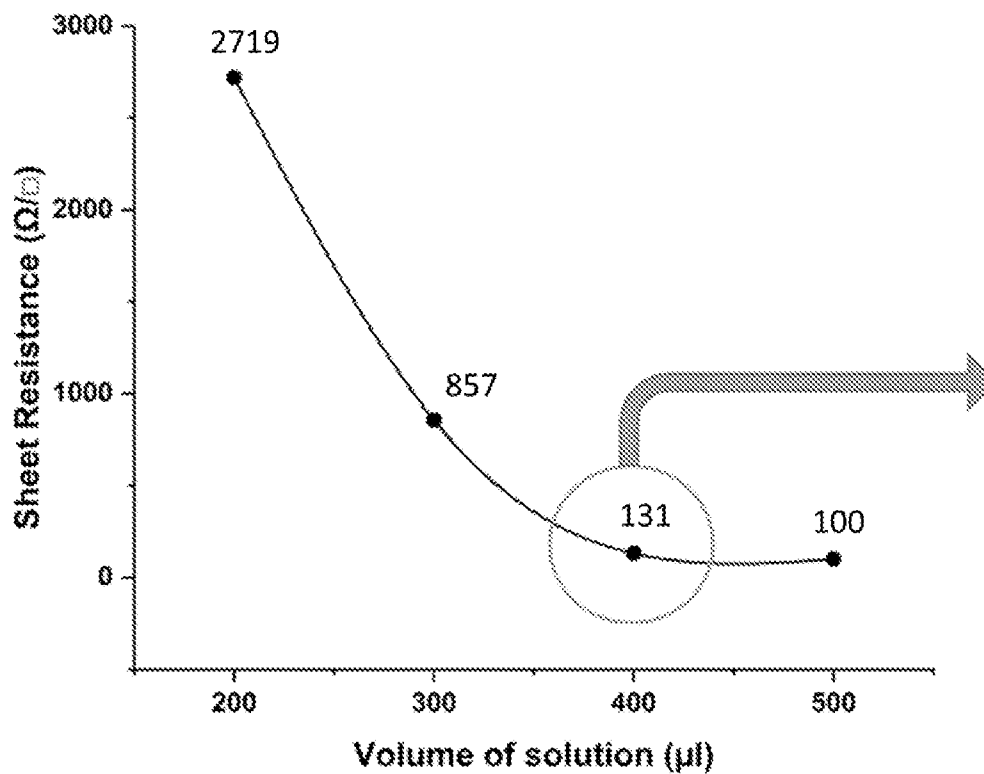
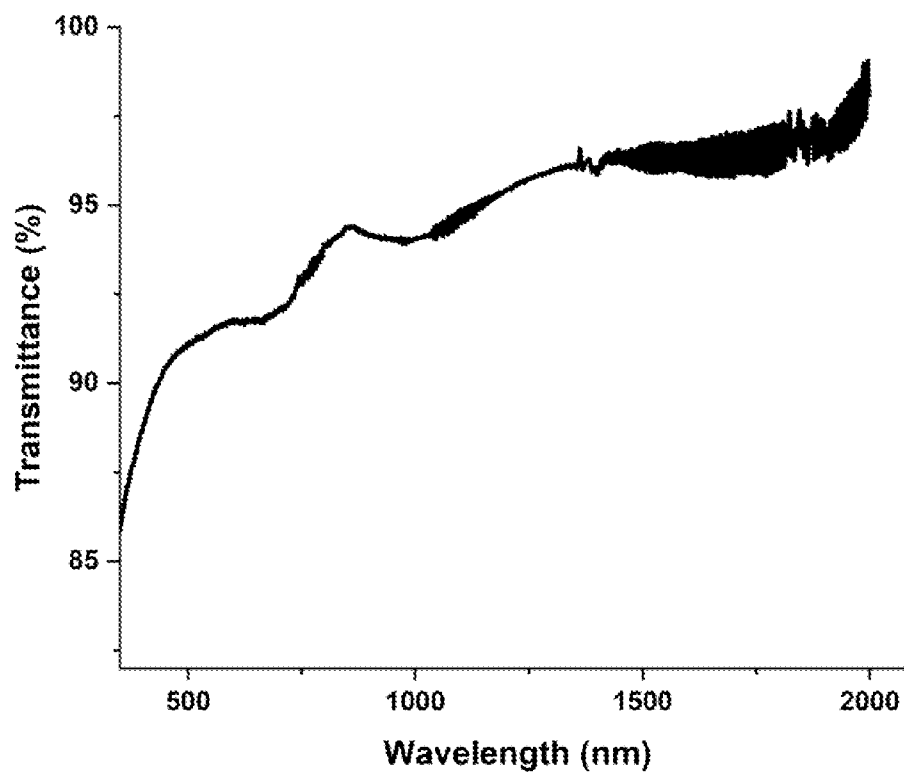


FIGURE 5E

**FIGURE 5F****FIGURE 5G**

**FIGURE 6A****FIGURE 6B**

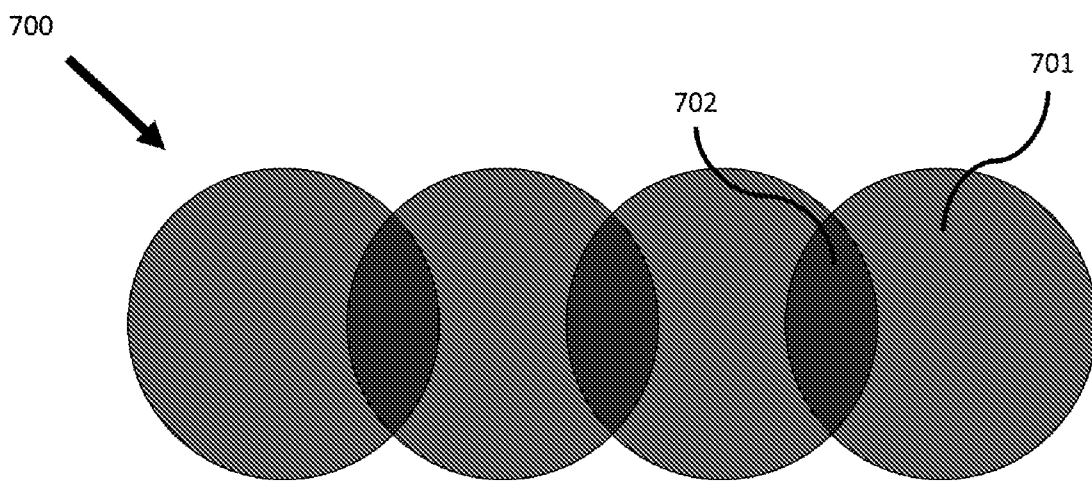


FIGURE 7A



FIGURE 7B

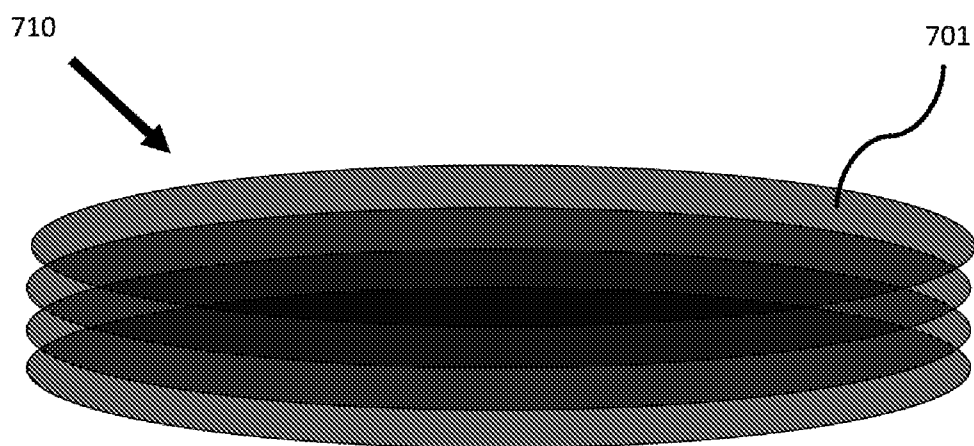
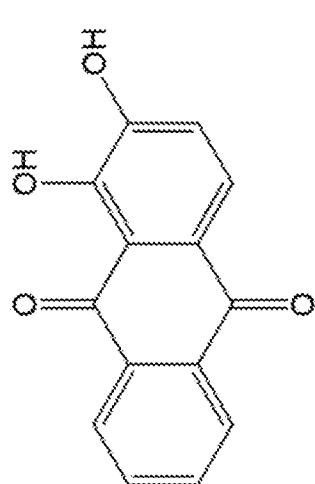
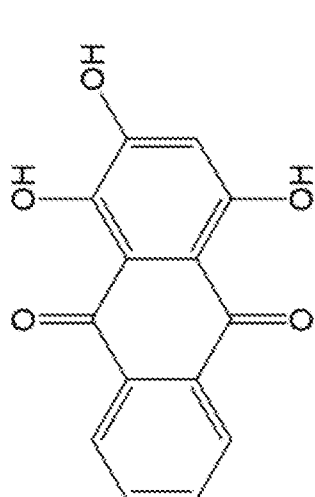


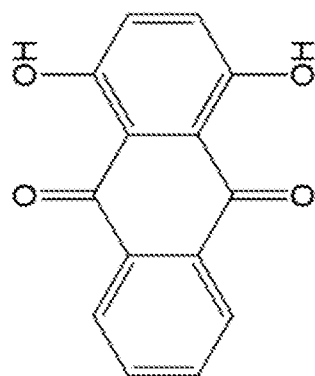
FIGURE 7C



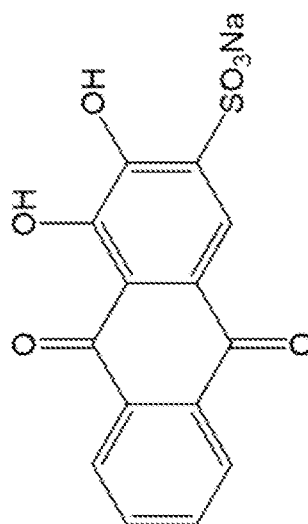
1,2-dihydroxyanthraquinone
Alizarin



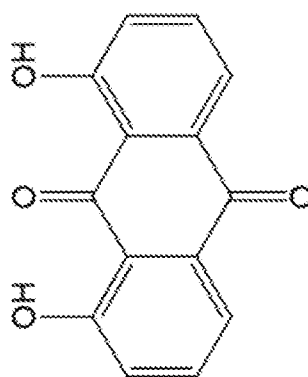
1,2,4-trihydroxyanthraquinone
Purpurin



1,4-dihydroxyanthraquinone
Quinizarin

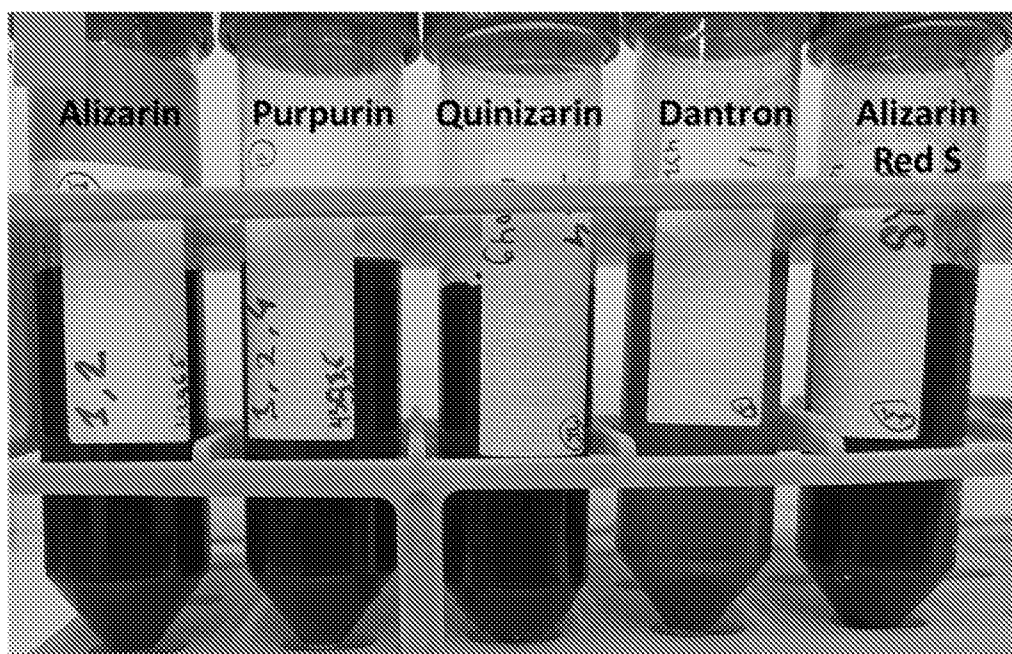
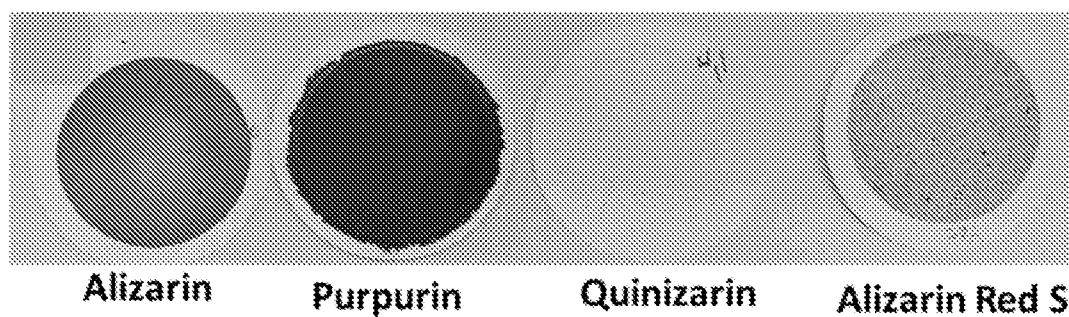


3,4-Dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2-sulfonic acid
Alizarin Red S



1,8-dihydroxyanthraquinone
Dantron

FIGURE 8A

**FIGURE 8B****FIGURE 8C**

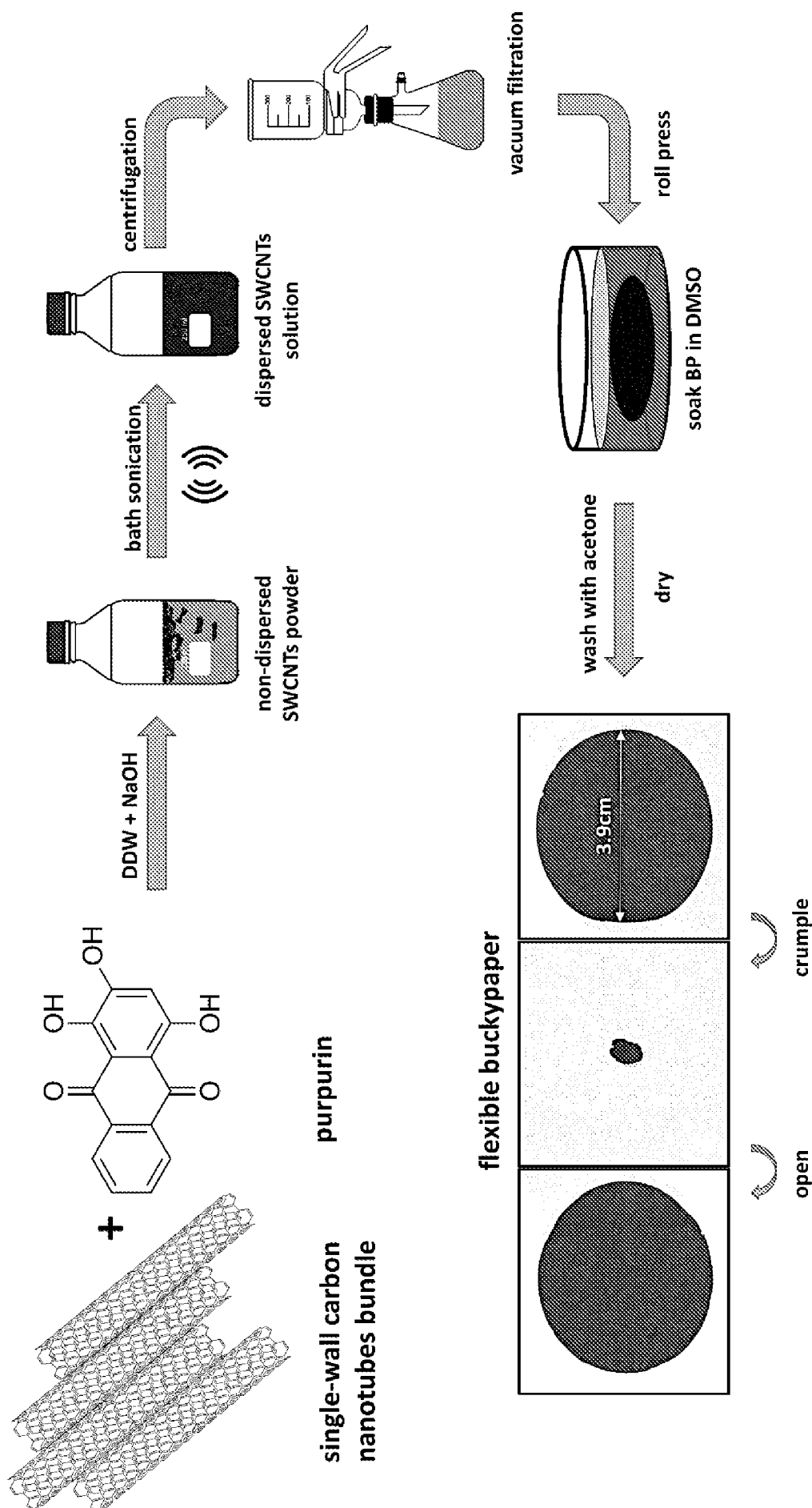


FIGURE 9A

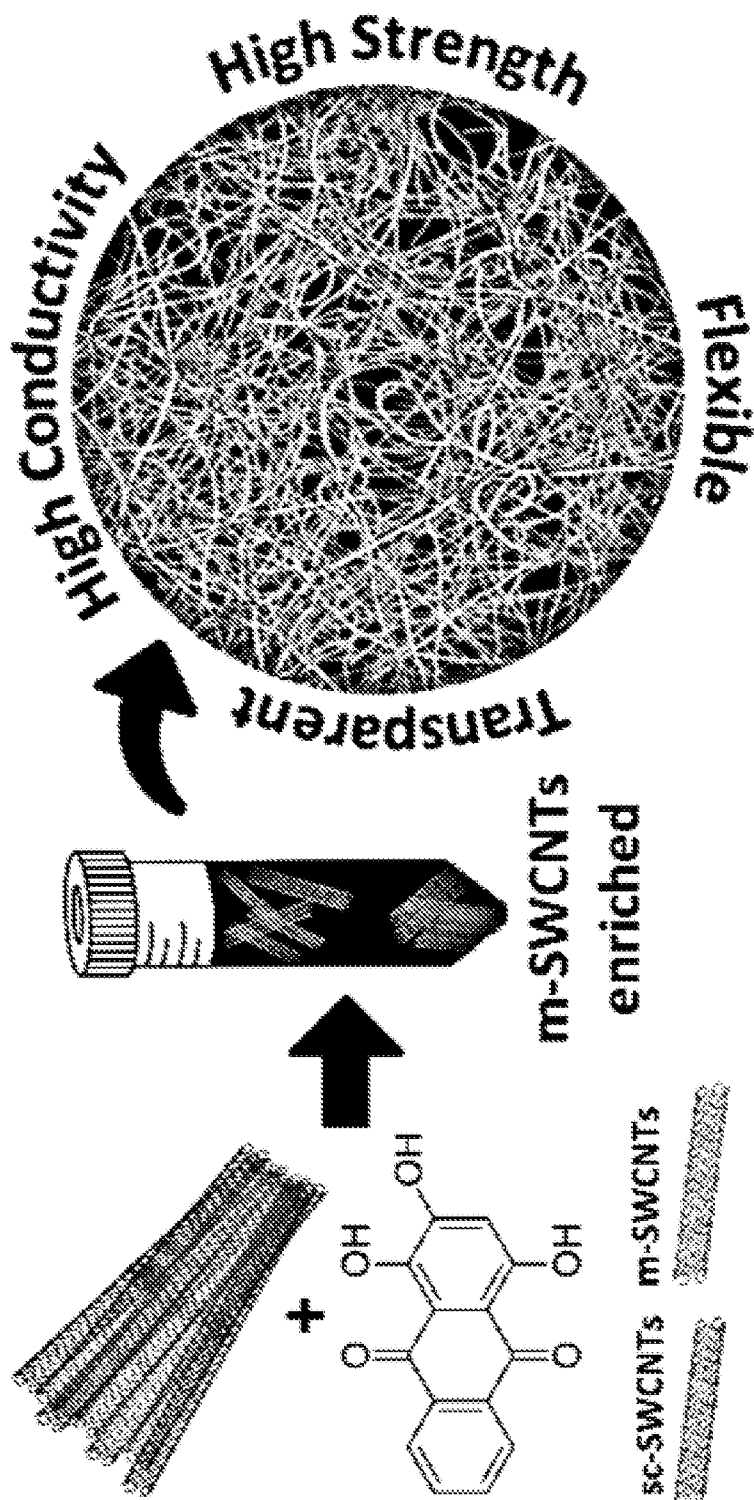


FIGURE 9B

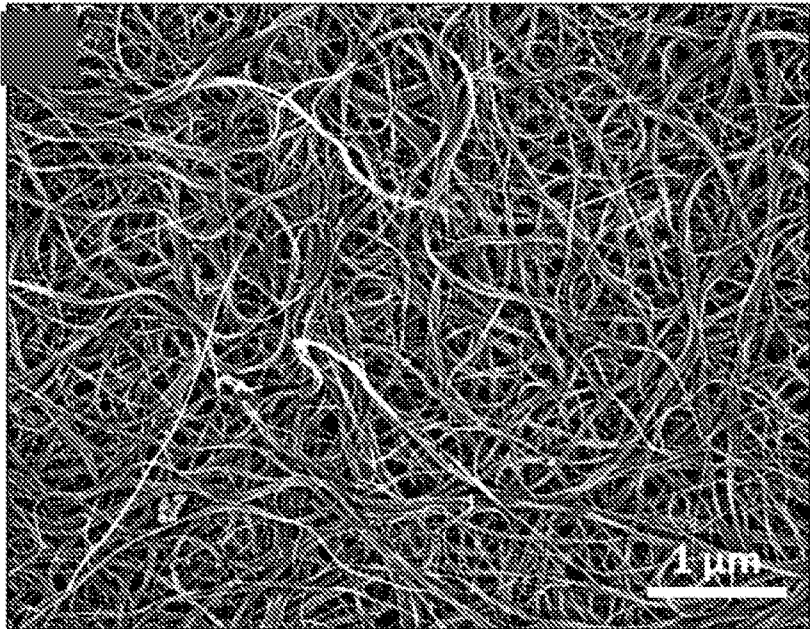


FIGURE 10A

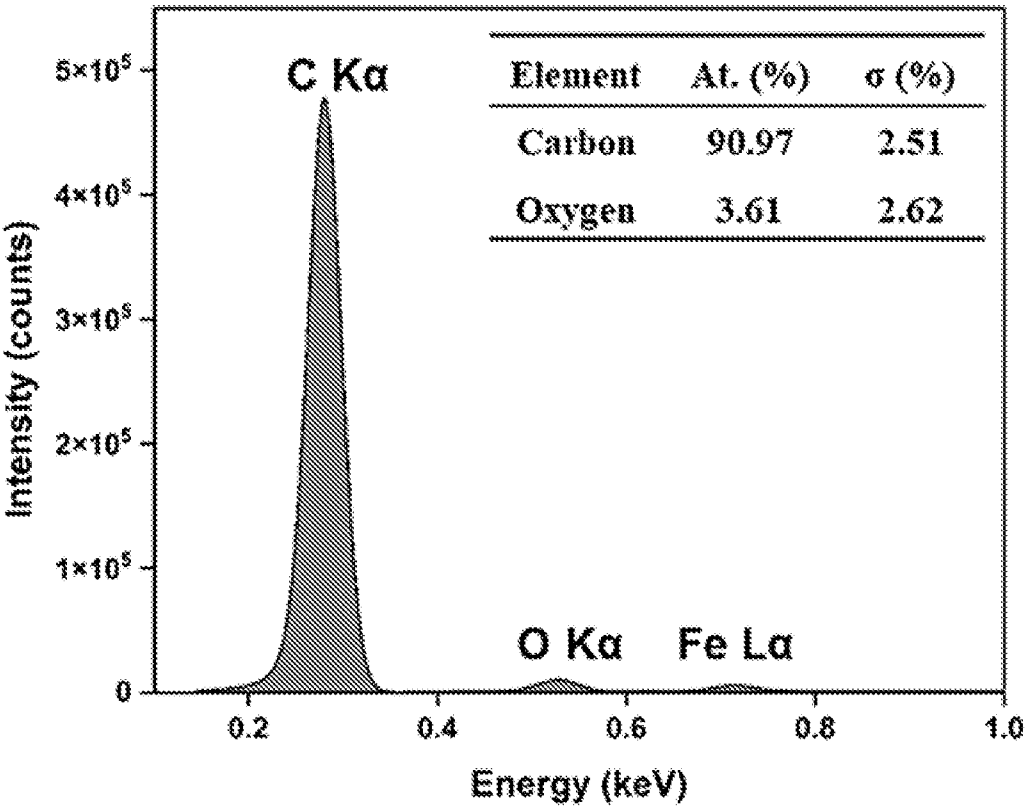


FIGURE 10B

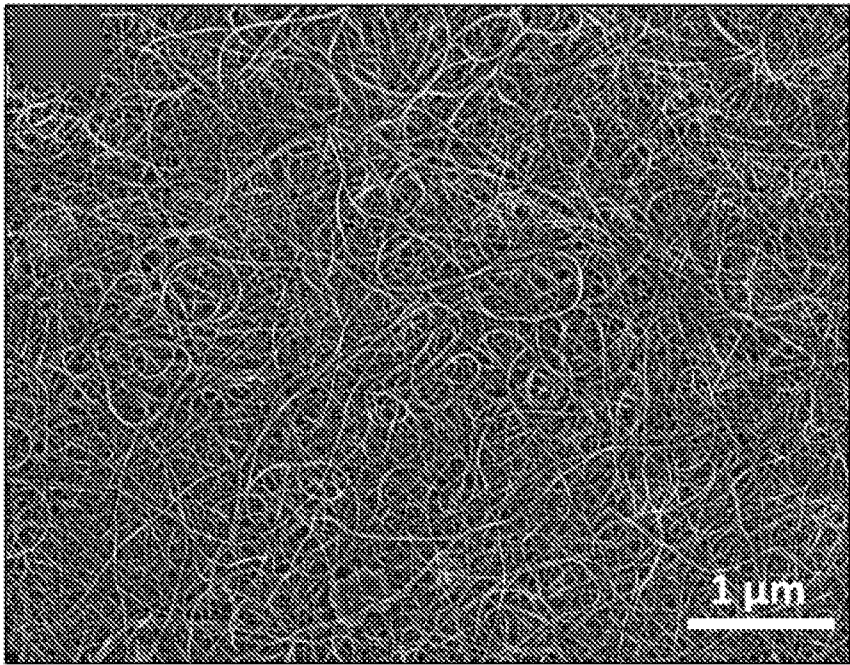


FIGURE 10C

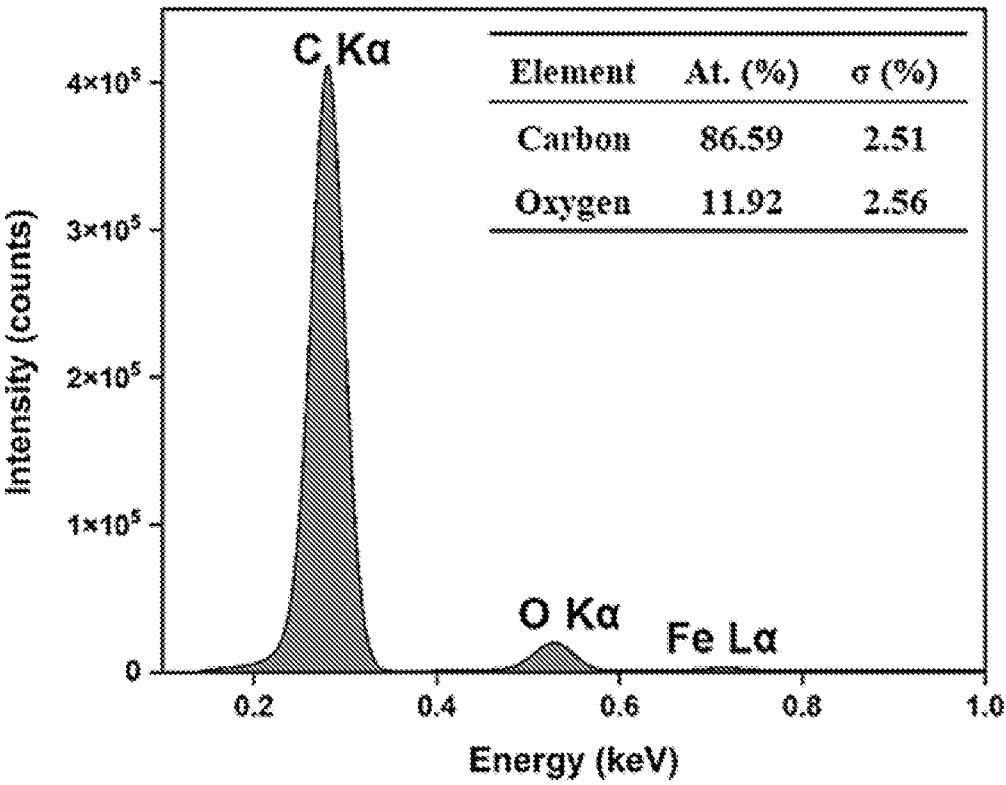


FIGURE 10D

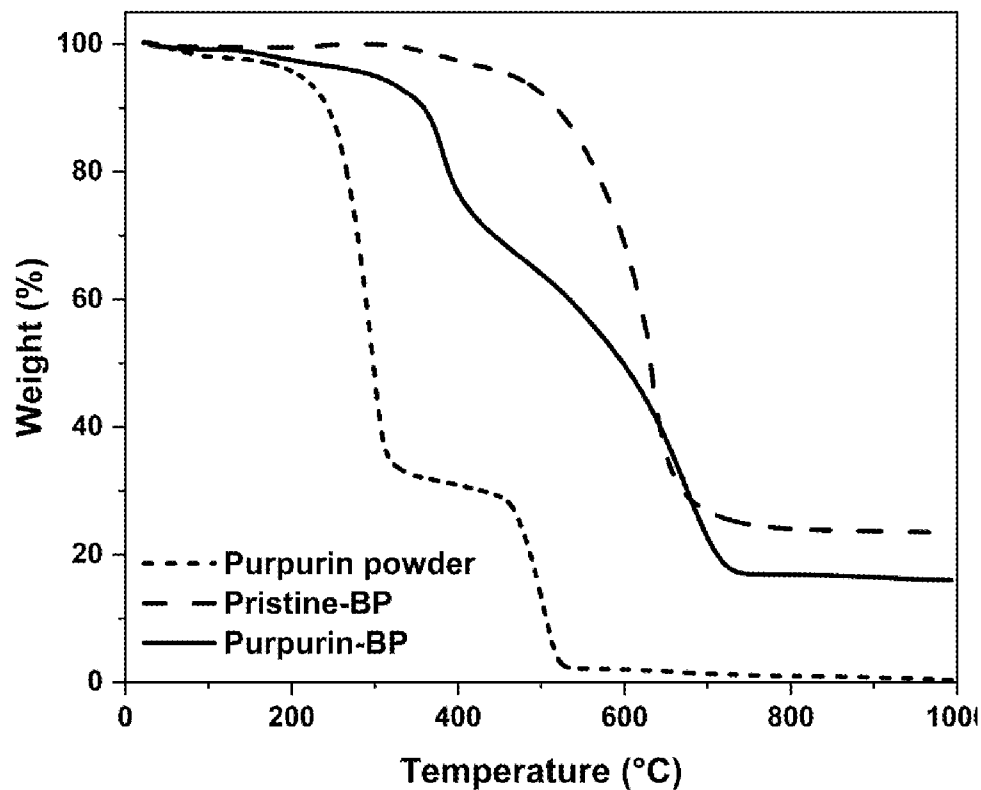


FIGURE 11A

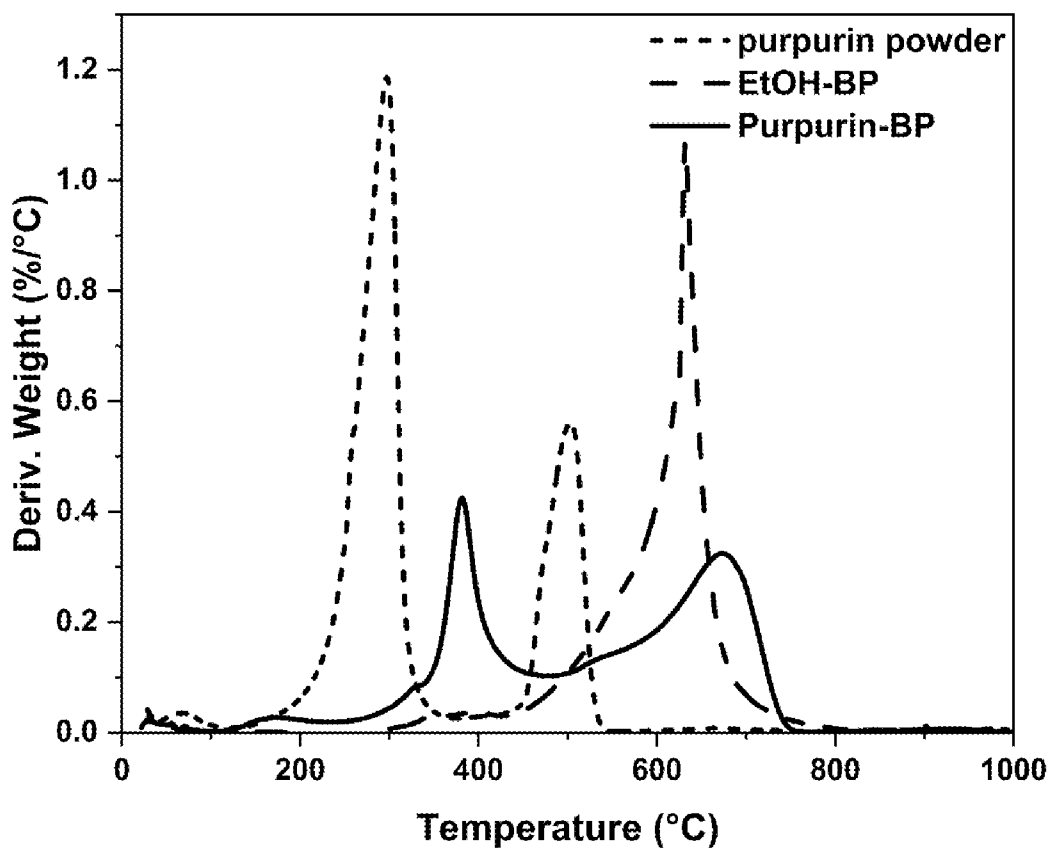


FIGURE 11B

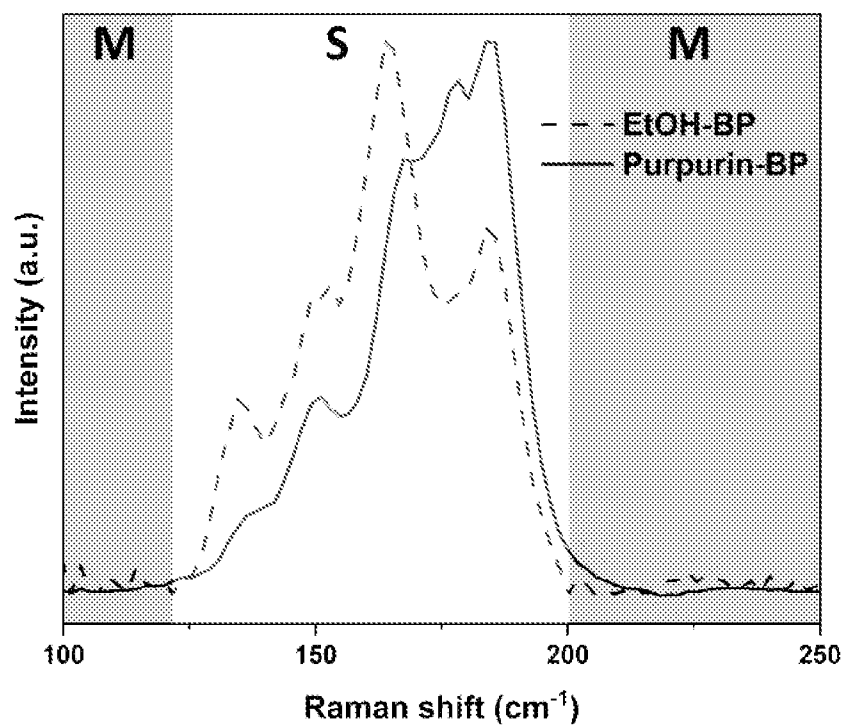
$\lambda = 532 \text{ nm}$ 

FIGURE 12A

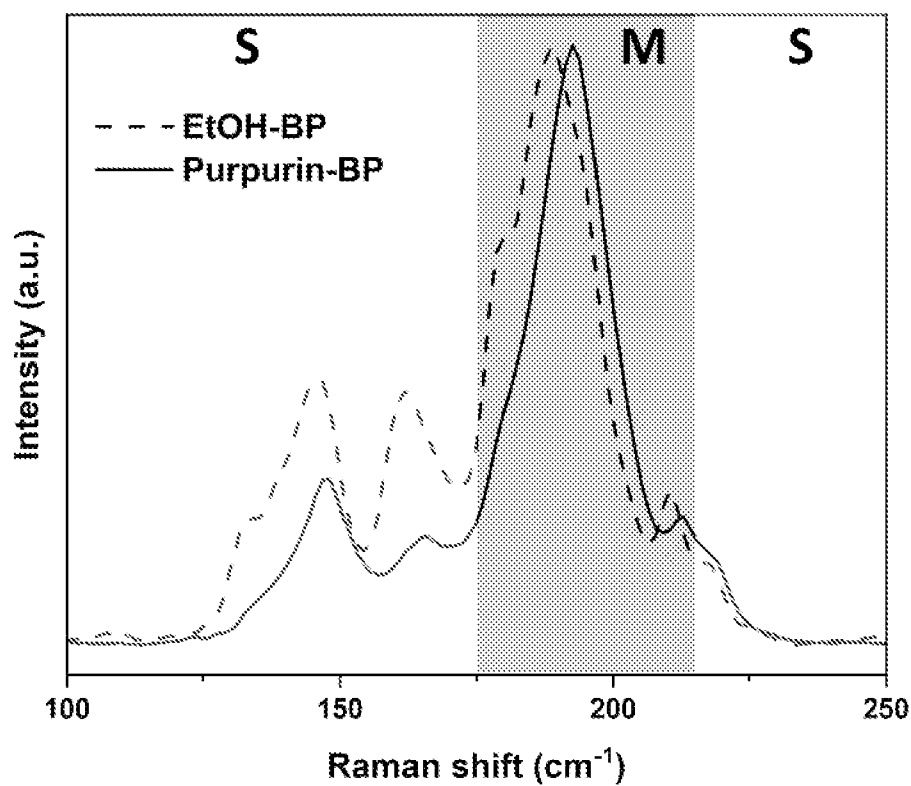
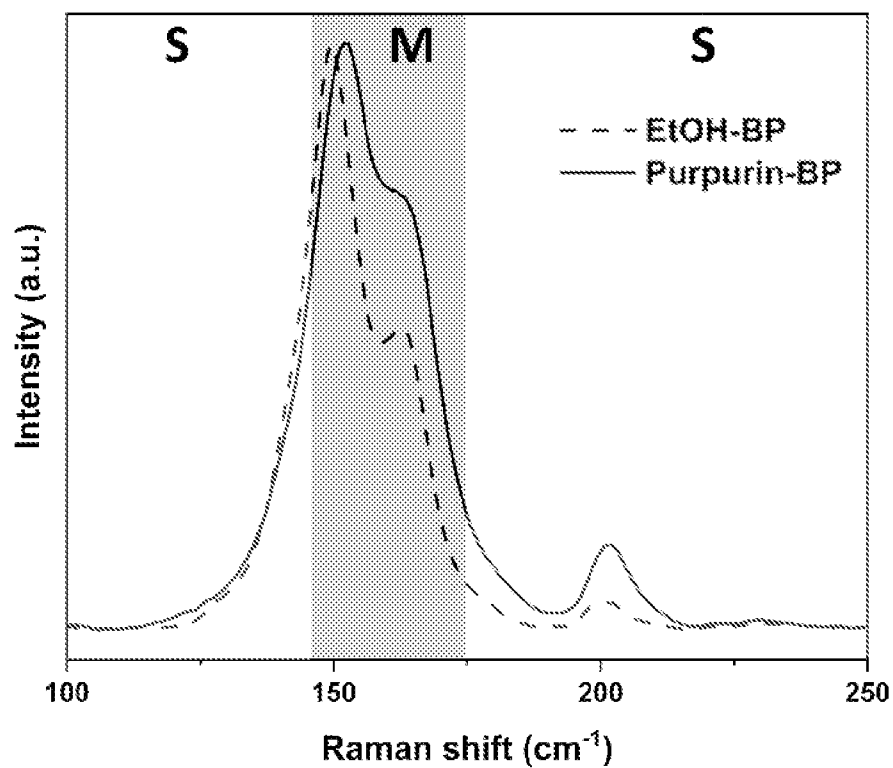
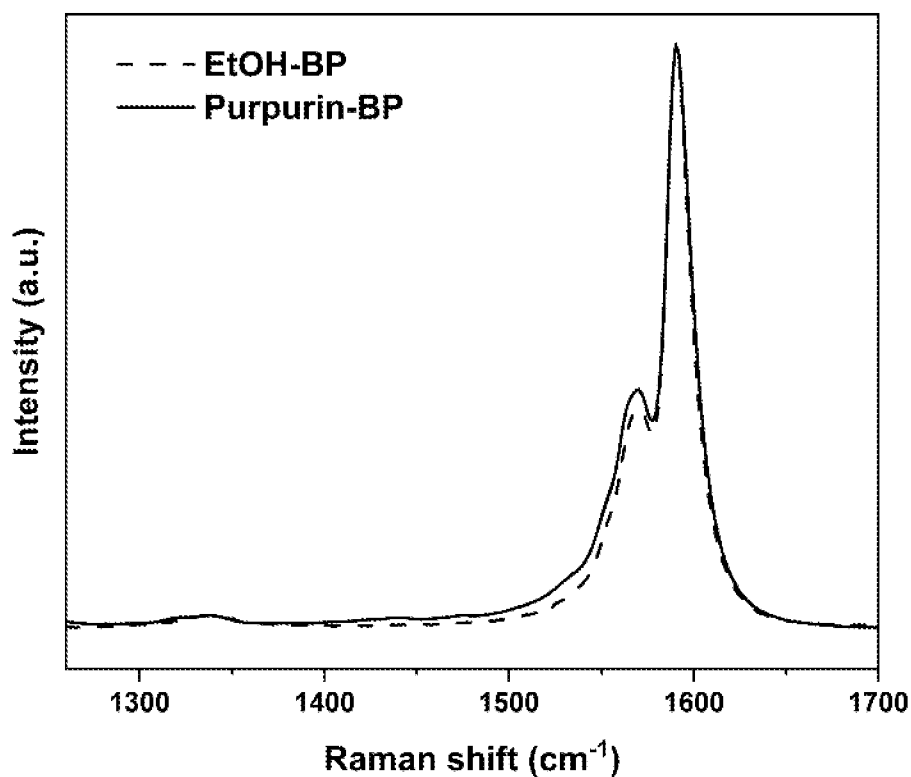
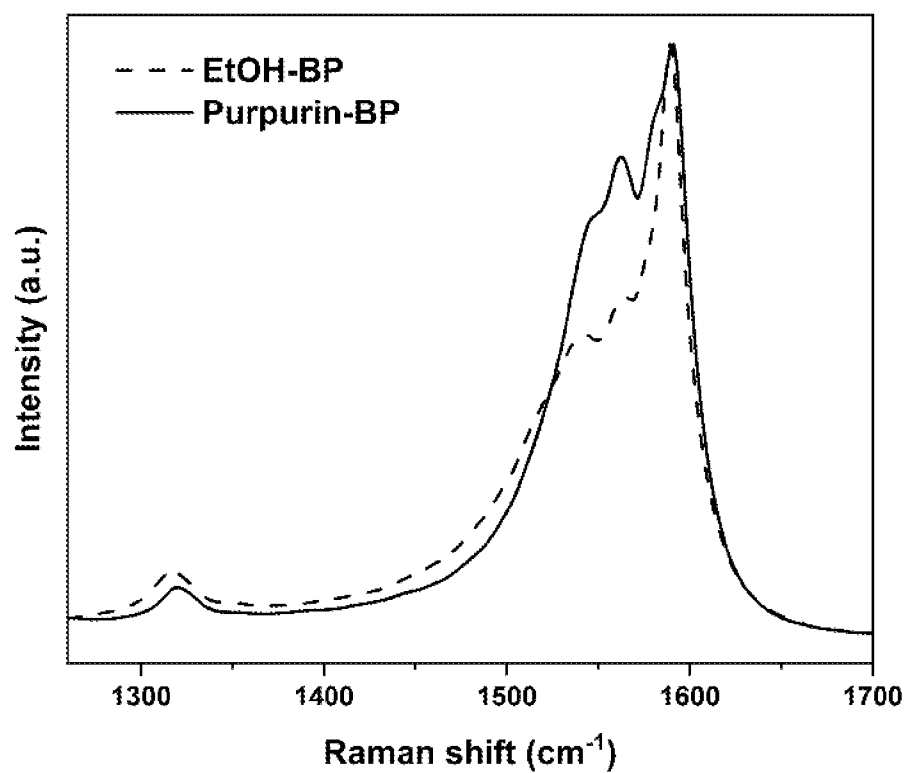
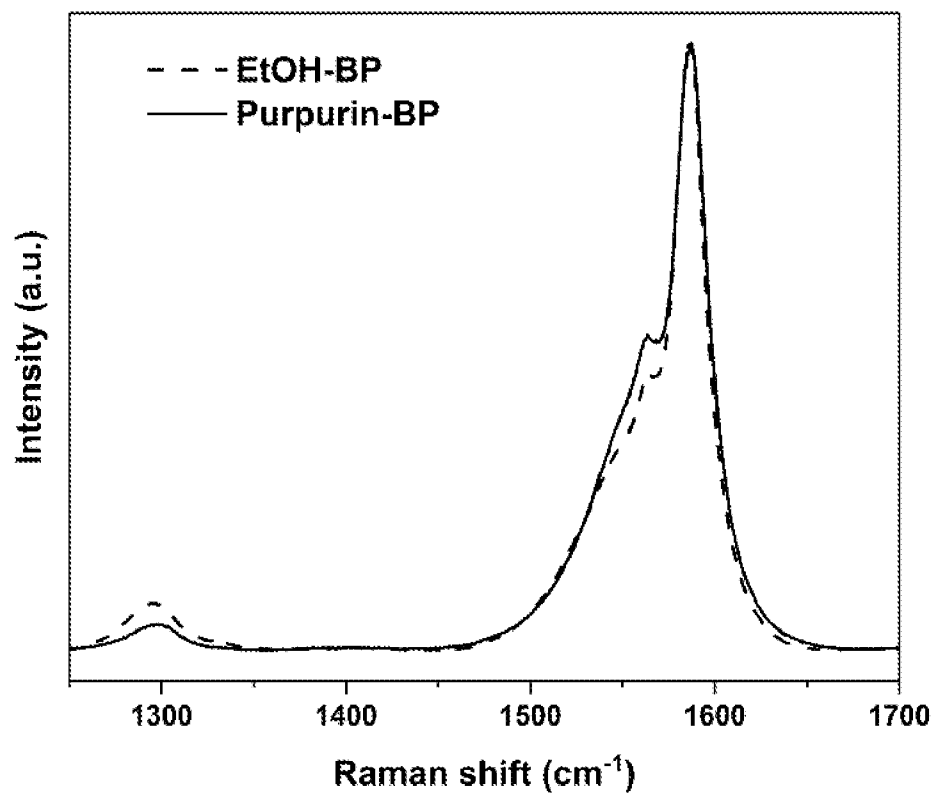
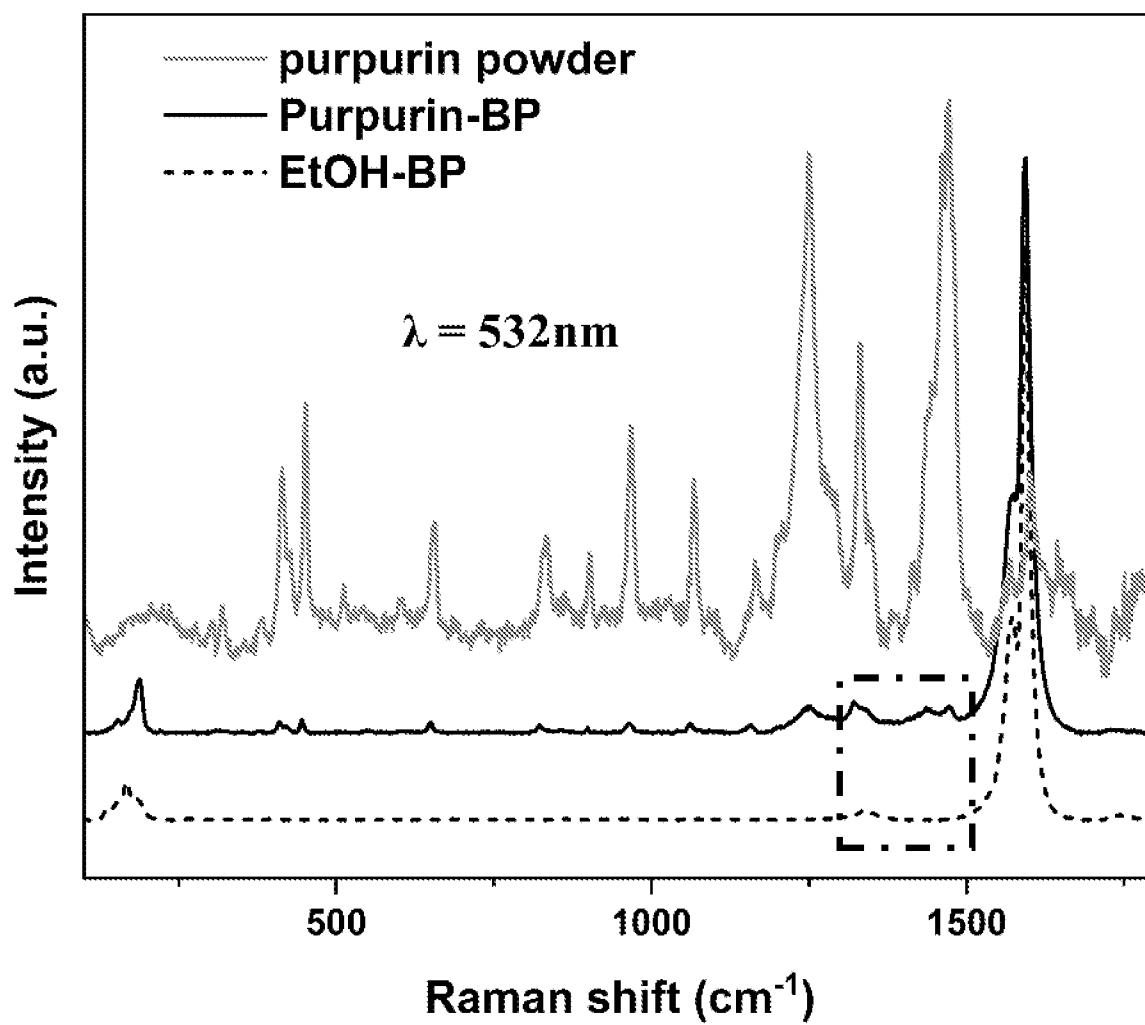
 $\lambda = 633 \text{ nm}$ 

FIGURE 12B

$\lambda = 785 \text{ nm}$ **FIGURE 12C****FIGURE 12D**

**FIGURE 12E****FIGURE 12F**

**FIGURE 12G**

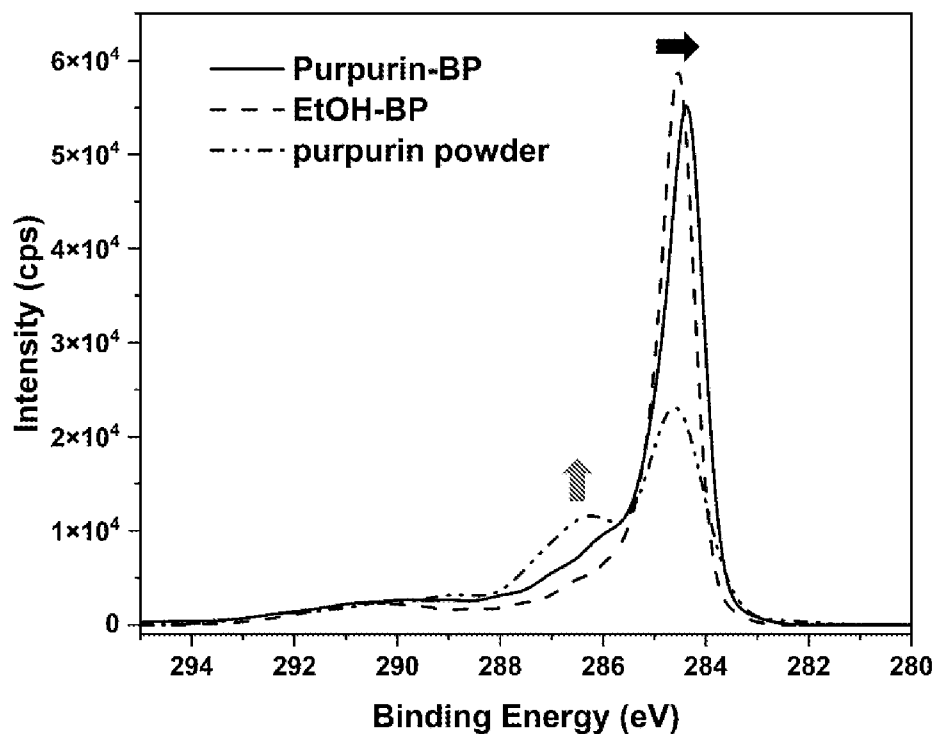


FIGURE 13A

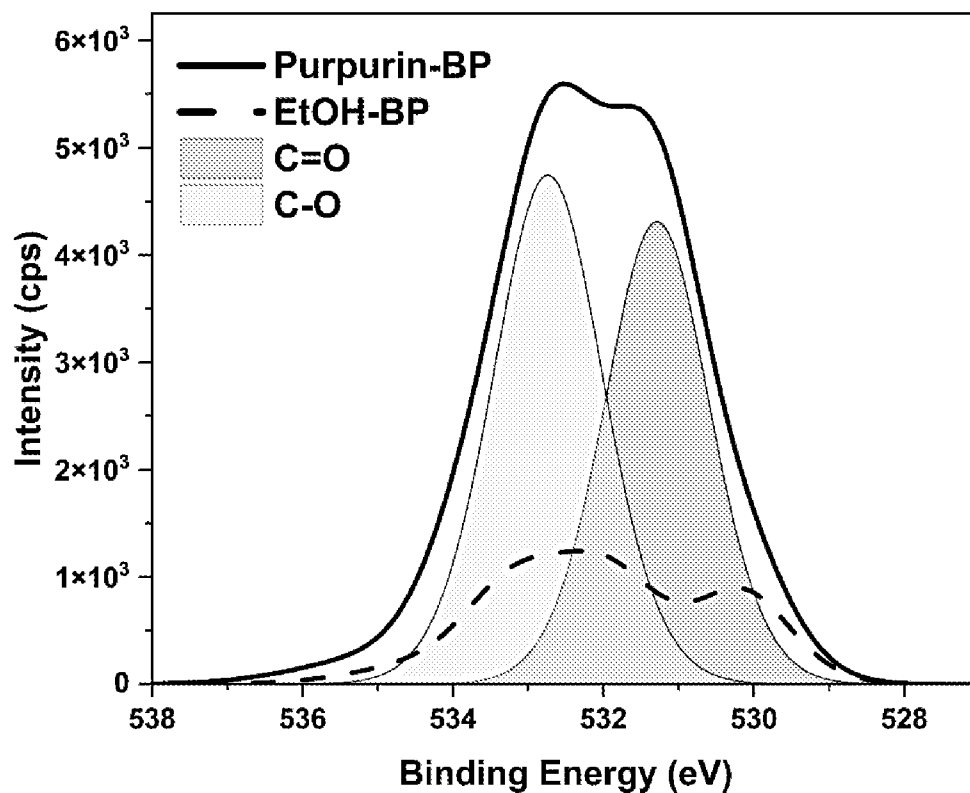


FIGURE 13B

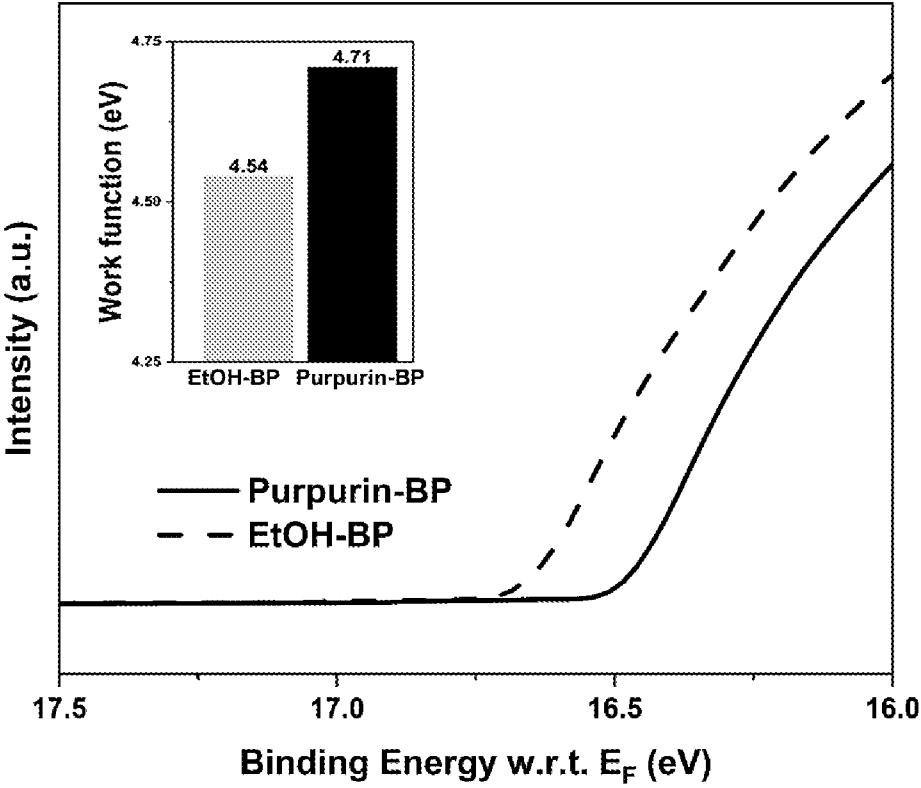
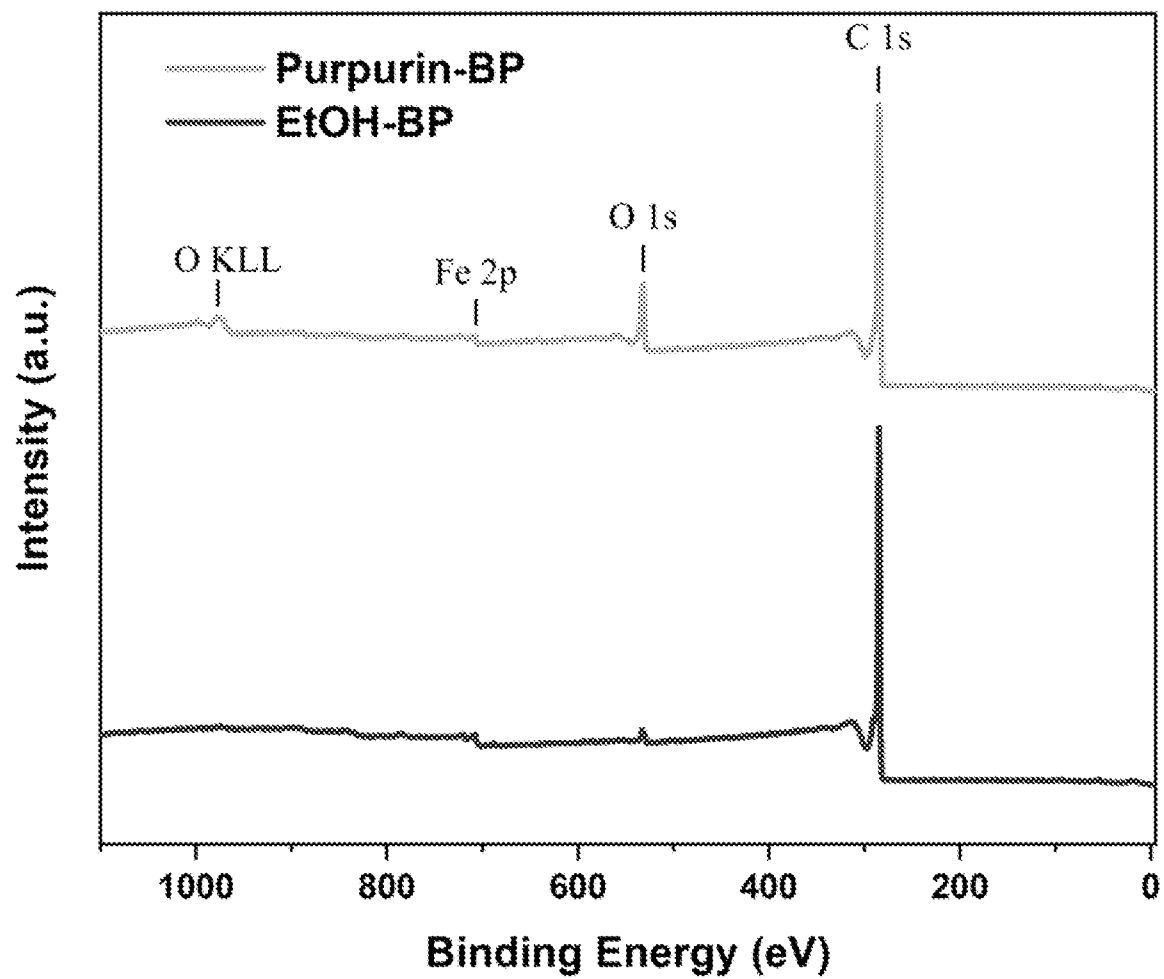


FIGURE 13C

**FIGURE 14**

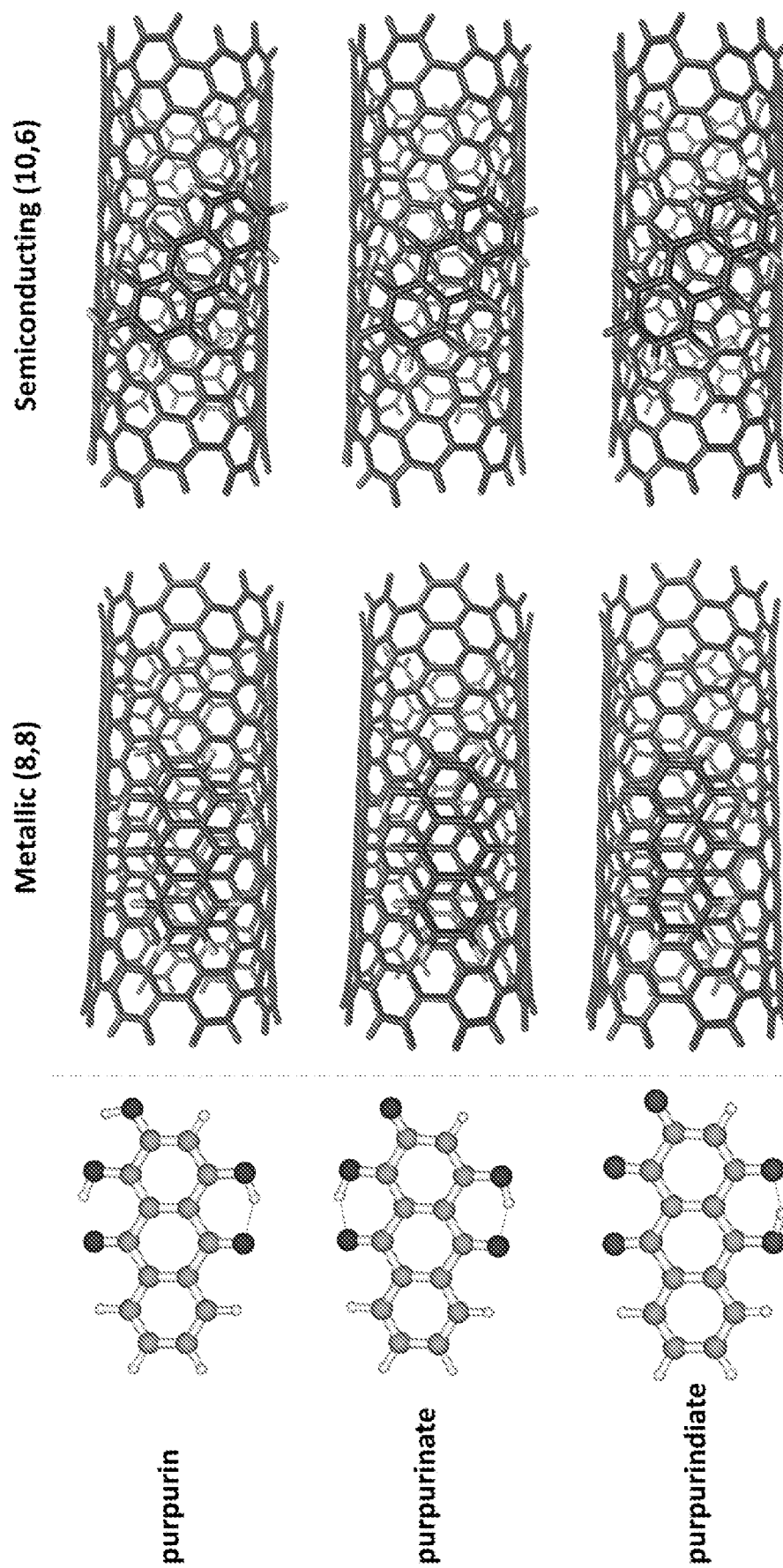


Figure 15

	Centrifugation	DMSO wash
EtOH-BP	✗	—*
Purpurin-BP	✓	✓
P-BP1	✗	✗
P-BP2	✗	✓
P-BP3	✓	✗

*not relevant as purpurin was not used

FIGURE 16A

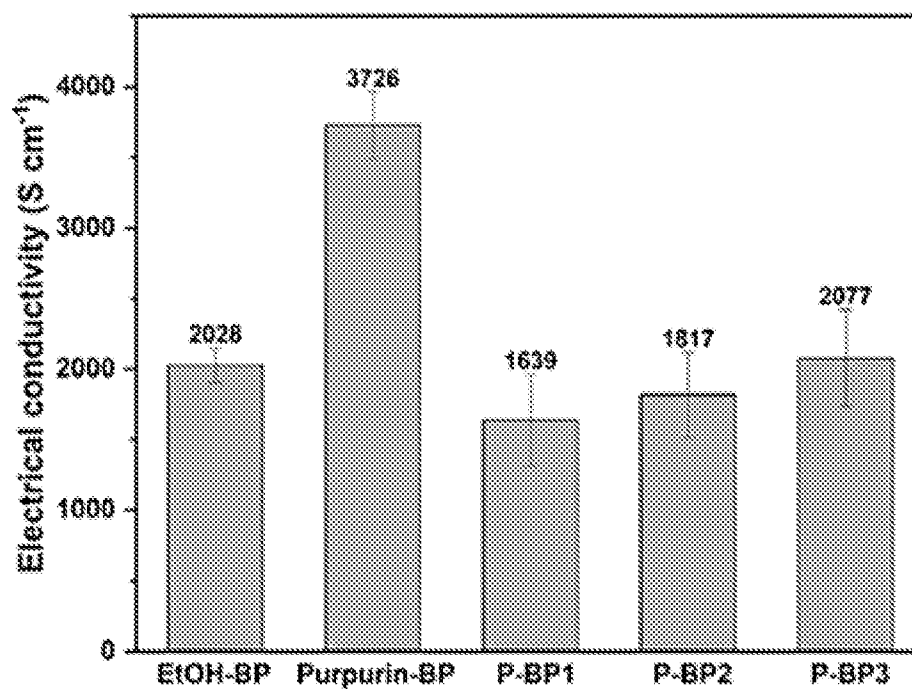


FIGURE 16B

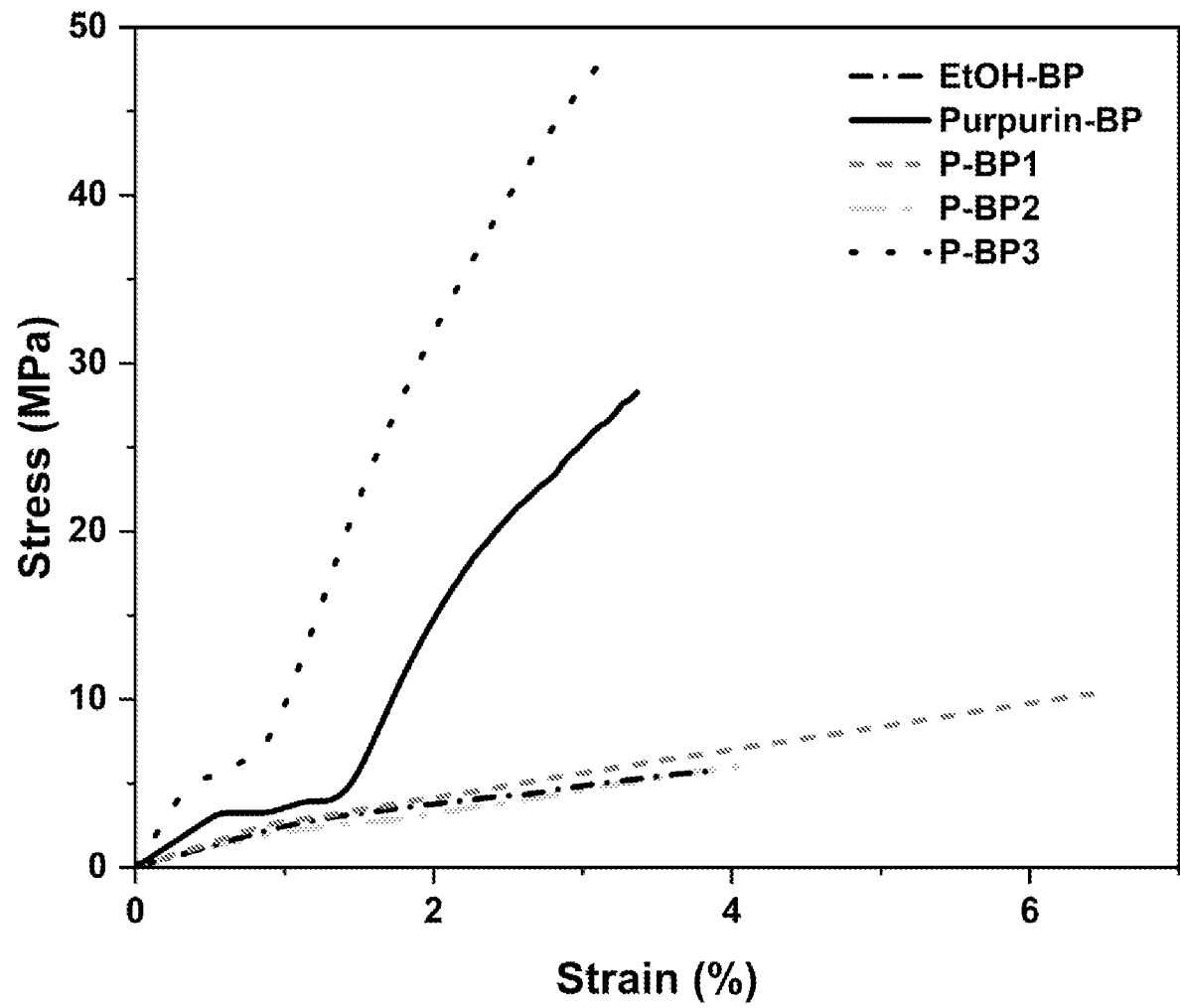


FIGURE 16C

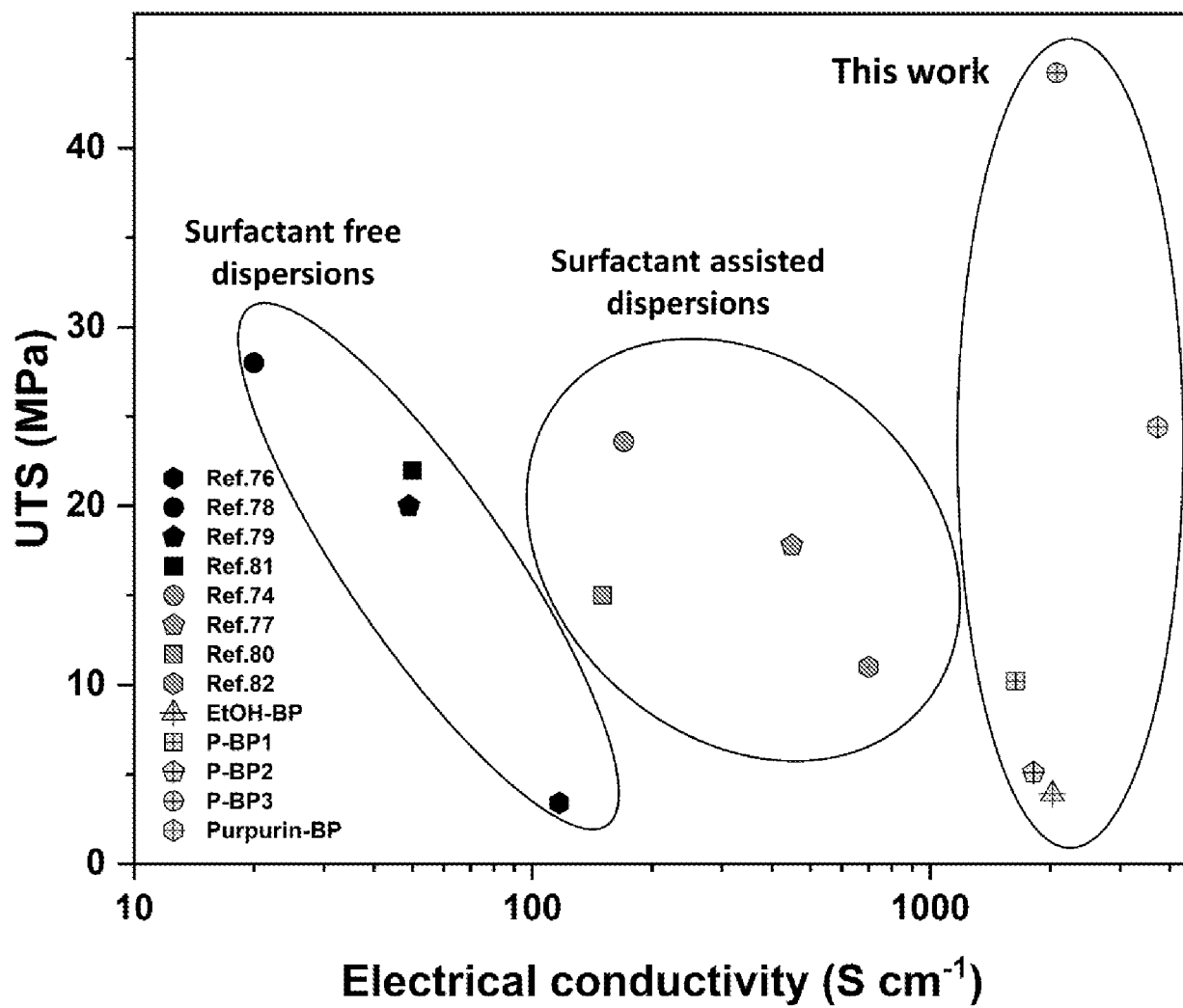


FIGURE 17

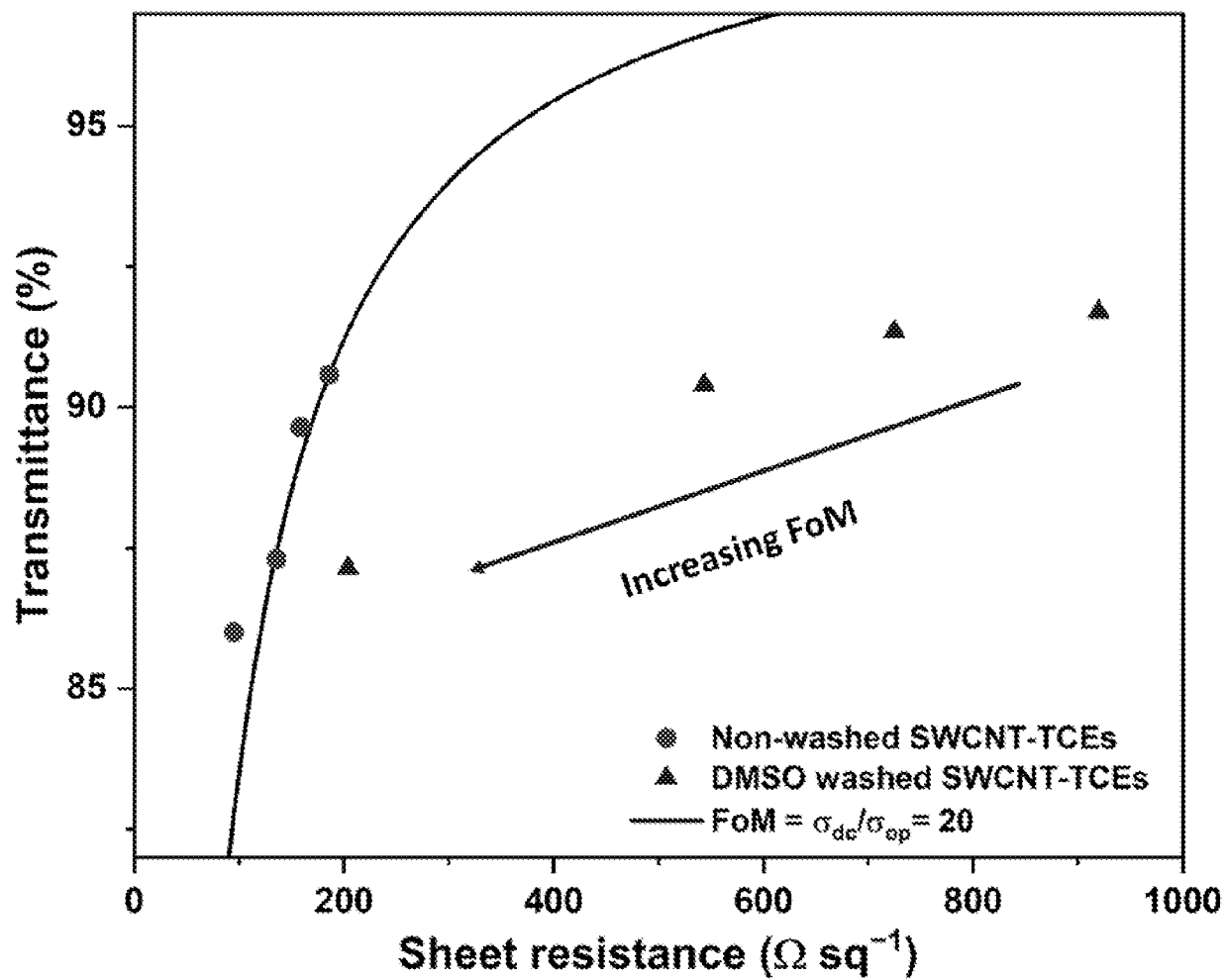


FIGURE 18

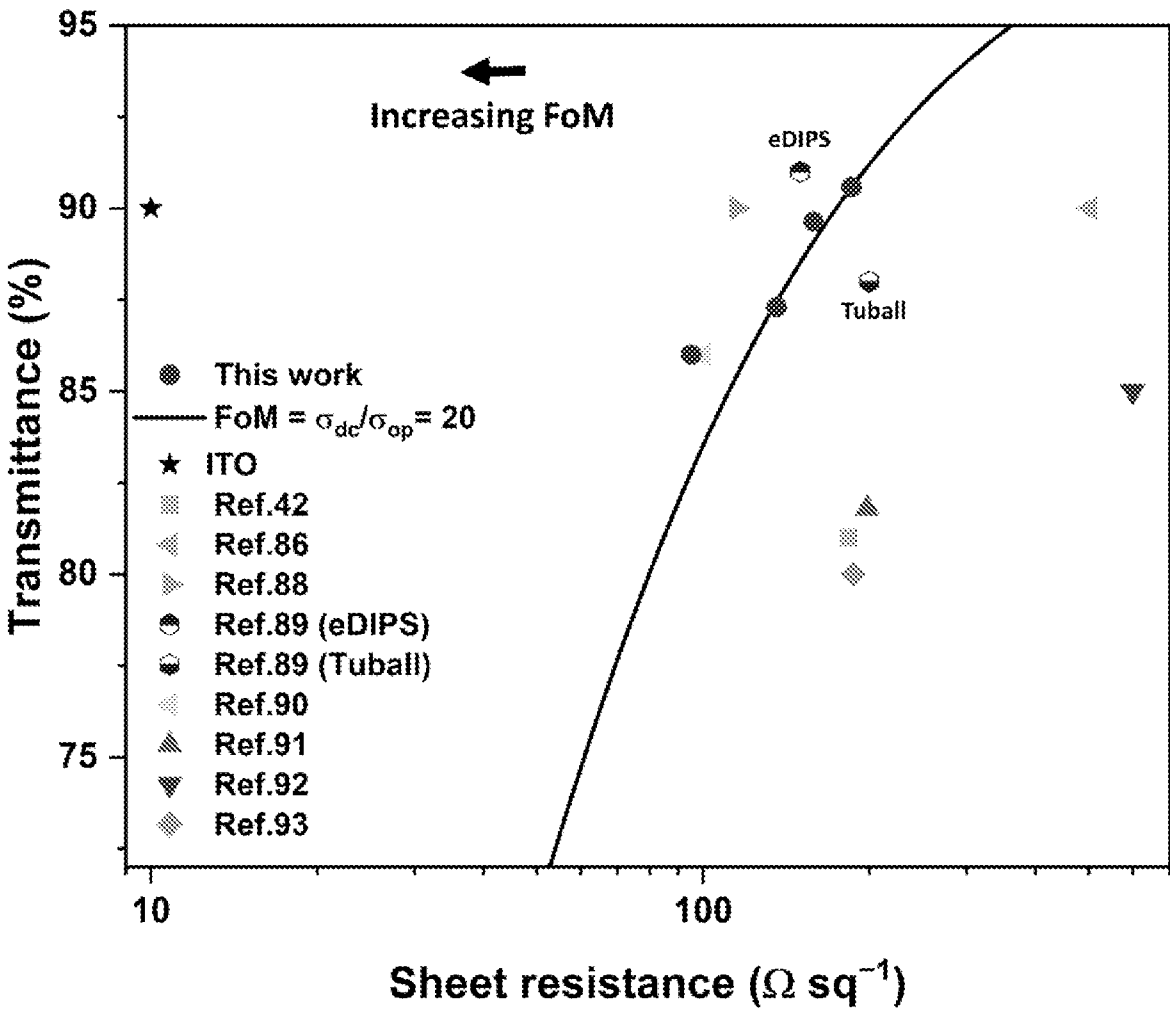


FIGURE 19

INTERNATIONAL SEARCH REPORT

International application No

PCT/IL2023/050800

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01B1/24 C01B32/158

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01B C01B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/189335 A1 (CENTRE NAT RECH SCIENT [FR]) 17 December 2015 (2015-12-17) claims 1, 50, 53, 65, 66, 72 the whole document ----- -/--	1, 2, 4, 5, 7-15, 17-35



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

9 October 2023

Date of mailing of the international search report

16/10/2023

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer

Ziegler, Jan

INTERNATIONAL SEARCH REPORT

International application No

PCT/IL2023/050800

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ATA MUSTAFA S ET AL: "New developments in non-covalent surface modification, dispersion and electrophoretic deposition of carbon nanotubes", CARBON, ELSEVIER OXFORD, GB, vol. 130, 30 January 2018 (2018-01-30), pages 584-598, XP085346294, ISSN: 0008-6223, DOI: 10.1016/J.CARBON.2018.01.066 dispersion comprising Alizarin red, CNT and water; table 2 the whole document -----	1-5, 7-15, 17-35
X	ARCILA-VELEZ M R: "Design and synthesis of polymer, carbon and composite electrodes for high-energy and high-power supercapacitors", THESIS, CLEMSON UNIVERSITY, US, 1 December 2015 (2015-12-01), pages 1-201, XP009500251, ISBN: 978-1-339-37847-3 Retrieved from the Internet: URL:https://tigerprints.clemson.edu/all_dissertations/1572 [retrieved on 2023-10-06] page 133 - page 144 the whole document -----	1-35
X	US 2010/244655 A1 (KIM JI SUNG [KR] ET AL) 30 September 2010 (2010-09-30) paragraph [0054]; claims 1,2,12 the whole document -----	1-5,7-35
X	EP 2 833 542 A1 (NAT INST OF ADVANCED IND SCIEN [JP]) 4 February 2015 (2015-02-04) paragraphs [0032], [0034]; claims 1,2 the whole document -----	1,2,4,5, 7-15, 17-35
X	EP 1 699 736 A2 (CENTRE NAT RECH SCIENT [FR]) 13 September 2006 (2006-09-13) claims 1, 4, 13, 15 the whole document -----	1-5, 7-15, 17-35
X	JP 2003 301141 A (SUMITOMO METAL MINING CO) 21 October 2003 (2003-10-21) claims 1,2,3,4 the whole document -----	1,4,5, 7-35
1	X US 2007/151601 A1 (JUNG WON CHEOL [KR] ET AL) 5 July 2007 (2007-07-05) paragraph [0046]; claims 1,3,5 the whole document -----	1,4,5, 7-35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IL2023/050800

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015189335 A1	17-12-2015	CN 106660800 A	10-05-2017
		EP 3166886 A1	17-05-2017
		JP 6825781 B2	03-02-2021
		JP 2017528395 A	28-09-2017
		TW 201605724 A	16-02-2016
		US 2017121179 A1	04-05-2017
		WO 2015189335 A1	17-12-2015
US 2010244655 A1	30-09-2010	CN 101866707 A	20-10-2010
		JP 5680323 B2	04-03-2015
		JP 2010245044 A	28-10-2010
		KR 20100108985 A	08-10-2010
		US 2010244655 A1	30-09-2010
EP 2833542 A1	04-02-2015	EP 2833542 A1	04-02-2015
		JP 6416358 B2	31-10-2018
		JP 6713693 B2	24-06-2020
		JP 2018016811 A	01-02-2018
		JP 2019048982 A	28-03-2019
		JP WO2013147031 A1	14-12-2015
		US 2015061457 A1	05-03-2015
		US 2019356242 A1	21-11-2019
		WO 2013147031 A1	03-10-2013
EP 1699736 A2	13-09-2006	CA 2551443 A1	11-08-2005
		EP 1699736 A2	13-09-2006
		FR 2864454 A1	01-07-2005
		JP 4737091 B2	27-07-2011
		JP 2007516925 A	28-06-2007
		US 2007189954 A1	16-08-2007
		WO 2005073127 A2	11-08-2005
JP 2003301141 A	21-10-2003	NONE	
US 2007151601 A1	05-07-2007	KR 20070070797 A	04-07-2007
		US 2007151601 A1	05-07-2007