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(57) Abstract: The invention generally relates to novel composites of conductive polymers and inorganic nanostructures, such as inorganic nanotubes and fullerene-like materials, and their uses in the preparation of electronic or opto-electric devices.



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- 1 -

MATERIALS AND COMPOSITES OF CONDUCTIVE POLYMERS AND INORGANIC NANOSTRUCTURES

TECHNOLOGICAL FIELD

5 This invention generally relates to novel composites of conductive polymers and inorganic nanostructures, such as inorganic nanotubes and fullerene-like materials.

BACKGROUND OF THE INVENTION

Transition metal dichalcogenides and halides such as MX_n (e.g., $\text{M}=\text{W}$, Mo ; $\text{X}=\text{S}$, Cl etc) possess a layered structure, i.e. strong covalent bonds occur between atoms
10 within the layer and weak van der Waals forces stack the planar sheets together. The driving force for the formation of hollow closed nanostructures stems from the high energy of the dangling bonds at the periphery of the nanoparticles, a property which is common to highly anisotropic layered materials, such as WS_2 , MoS_2 , NiBr_2 and others. These materials have been shown to create a variety of close caged nanostructures such
15 as inorganic nanotubes (INTs) and inorganic fullerenes (IFs).

The number of experimental studies on the electronic, optical and magnetic properties of such INTs and IFs is still very small. In particular, the issue of contacting carbon nanotubes (CNT) still involves a large amount of ongoing research with a focus
20 on matching the contact material work-function with that of the measured material, as well as matching the Fermi surfaces in order to reduce electron scattering at the interface.

Intrinsically conducting polymers combine many advantages of plastics, e.g. flexibility and processing from solution, with the additional advantage of conductivity either in the metallic or semiconducting regimes. This class of materials is of great
25 interest for the development of thin film plastic opto-electronic devices including light-emitting devices and photovoltaic cells.

Among the conducting polymers, polyaniline (PANI) is one of the most studied intrinsically conducting polymers, owing to its ease of synthesis, remarkable environmental stability and high conductivity in the doped form. While it is long known
30 that proton-doping can make PANI conducting, the possibility of using non-protonic dopants such as electron-deficient Lewis acids was demonstrated only very recently [1].

- 2 -

These composites are expected to be different from the conventional protonated PANI owing to a qualitatively different chemical interaction between the dopant and the polymer.

PANI exists in a variety of forms that differ in chemical and physical properties.

5 It is already established that the addition of acid (HCl, HClO₄) to the basic form of PANI, Emeraldine base (EB), leads to protonation of the imine moieties rather than the amine moieties, thus forming the conductive Emeraldine salt (ES) (as shown in **Fig. 1**- a transition from structure 2 to structure 3).

10 The resulting material appears to have a significant electron delocalization in the polymer backbone. Previous studies have also showed conductivity of PANI in the presence of CNT [2-5].

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- 3 -

SUMMARY OF THE INVENTION

Electronic and opto-electric devices based on plastic materials are of increasing interest in this industry, as they permit to exploit the advantages of plastics such as flexibility, easy processing and cost. Conducting polymers play a great role in this field
5 as they possess the metallic-like or semiconducting-like properties.

The invention disclosed herein concerns conductive materials, and compositions of matter, having improved electronic properties (conductivity). The materials of the invention comprise conductive polymers and inorganic nanoparticles as doping components (dopants), such as inorganic fullerenes and nanotubes. The inorganic
10 nanoparticles have the advantage of a desirable physical structure, which permits percolation of charge carriers, as well as the desired electronic structure, which permits charge transfer within the conductive material.

Thus, in one aspect the invention provides a conductive material comprising at least one polymer doped with at least one inorganic nanostructure. By some
15 embodiments, the inorganic nanostructure has a closed-cage structure. The conductive polymer and the nanostructures may be associated through coordinative or ionic association (bond or interaction).

In another aspect, the invention provides a composite comprising a conductive material of the invention.

20 In a further aspect, the invention provides a composite comprising at least one conductive polymer and at least one inorganic closed-cage nanostructure. In a composite of the invention, the conductive polymer and the nanostructures exhibit induction of charge carriers therebetween.

In yet a further aspect, the invention provides a conductive polymer associated
25 with at least one inorganic nanostructure.

Without wishing to be bound by theory, the association between the at least one conductive polymer and the at least one (i.e. one or more) inorganic closed-cage nanostructure in a material or composite according to the invention, results from an acid-base interaction, causing association, via chemical bond (e.g., ionic or coordinative
30 bond) between the two moieties. This association results in a charge carrier transfer between the polymer and the inorganic closed-cage nanostructures.

The term "*doping*", or any lingual variation thereof, will be used in the context of the invention to denote the introduction of inorganic nanostructures, as defined, into

- 4 -

the conductive material for the purpose of altering the polymer's electronic/electric properties.

In some embodiments, the induced charge carrier transfer is an electron transfer process from the polymer (which acts as a donor or a Lewis base) to the inorganic nanostructure (which acts as an acceptor or a Lewis acid). In some embodiments, the induced charge carrier transfer is an electron transfer process from the inorganic nanostructure (which acts as a donor or a Lewis base) to the polymer (which acts as an acceptor or a Lewis acid).

The "*conductive polymer*" employed in the materials and composites according to the invention, is any conductive polymer known in the art. Typically, the conductive polymer employed is selected to comprise at least one moiety permitting charge transfer between the components of the composition. In some embodiments, the conductive polymers are selected amongst polymers comprising an atom such as O, N, and S or a moiety comprising such an atom. In some embodiments, the conductive polymer is selected from polypyrrole, polythiophene and polyaniline.

In some other embodiments, the conductive polymer is polyaniline (PANI).

The interaction between the polymer and the inorganic nanostructure, as described above, may results in changes (typically improvement) in the polymer electronic properties (e.g., conductivity). Thus, in another aspect the invention provides a conductive material comprising a conductive polymer doped with inorganic nanostructures, typically closed-cage nanostructures, wherein the conductivity of the material is enhanced as compared to the un-doped conductive polymer.

In yet another aspect, the invention provides a composite comprising a conductive polymer doped with inorganic nanostructures, typically closed-cage nanostructures, wherein the conductivity of the material is enhanced as compared to the un-doped conductive polymer.

Without wishing to be bound by theory, the improved conductivity of the doped polymer (composite) may be attributed to the characteristics of the inorganic nanoparticles. The "*inorganic nanoparticles*" (for brevity used interchangeably hereinfort with the term "*nanoparticles*") are hollow, in some cases closed-cage nanoparticles of transition metal chalcogenides, metal dichalcogenides or metal halides, which may be single or multi-layered, having structures such as nanospheres, nanotubes, nested polyhedra, onion-like (multiwalled and singlewalled) and the like.

- 5 -

As a person skilled in the art would appreciate, the term "*nanoparticle*" should not be regarded as limiting the average size of the particles to the nanoscale. While in some embodiments the nanoparticles employed in accordance with the invention are fully in the nanoscale regime, in some other embodiments, particularly those relating to
 5 nanotubes, at least one of the particles' dimensions is in the nanoscale (e.g., width) while other dimensions (e.g., length) may be at the microscale.

In some embodiments, the nanoparticles are inorganic nanotubes (INT) or inorganic fullerene-like nanoparticles (IF).

In some embodiments, the nanoparticles are of the general formula ML_n ,
 10 wherein M is a transition metal, L is a chalcogen and n is the number of chalcogen atoms L per each atom of the transition metal M . A transition metal includes all the metals in the periodic table from titanium to copper, from zirconium to silver and from hafnium to gold. In some embodiments, the transition metals are selected from Sn, In, Ga, Bi, Mo, W, V, Zr, Hf, Pt, Pd, Re, Nb, Ta, Ti, Cr and Ru. The chalcogen is selected
 15 from S, Se and Te.

In some embodiments, the metal chalcogenides and dichalcogenides are selected from TiS_2 , $TiSe_2$, $TiTe_2$, WS_2 , WSe_2 , WTe_2 , MoS_2 , $MoSe_2$, $MoTe_2$, SnS_2 , $SnSe_2$, $SnTe_2$, RuS_2 , $RuSe_2$, $RuTe_2$, GaS , $GaSe$, $GaTe$, InS , $InSe$, HfS_2 , ZrS_2 , VS_2 , ReS_2 and NbS_2 . In some other embodiments, the metal chalcogenides and dichalcogenides are selected
 20 from WS_2 and MoS_2 .

In additional embodiments, the inorganic nanoparticles are selected from WS_2 , MoS_2 , $NiBr_2$, $NiCl_2$, VS_2 , TiS_2 and InS .

In some embodiments, the inorganic nanoparticles are of the general formula $A_{1-x}B_x$ -chalcogenide, wherein A is either a metal or a transition metal or an alloy of such a
 25 metal/transition metal, B is a metal or a transition metal, and x being ≤ 0.3 and different from zero, provided that: $A \neq B$.

The metal or transition metal or an alloy of metals or transition metals are selected from the following atoms: Mo, W, Re, Ti, Zr, Hf, Nb, Ta, Pt, Ru, Rh, In, Ga, InS, InSe, GaS, GaSe, WMo, and TiW.

30 B is a metal or transition metal selected from the following: Si, Nb, Ta, W, Mo, Sc, Y, La, Hf, Ir, Mn, Ru, Re, Os, V, Au, Rh, Pd, Cr, Co, Fe, and Ni.

Within the nanostructure $A_{1-x}B_x$ -chalcogenide, B and/or B -chalcogenide are typically incorporated within the A_{1-x} -chalcogenide. The chalcogenide is selected from

- 6 -

S, Se and Te. For example, IF nanostructure to be used in the preparation of materials and composites of the invention may be IF-Mo_{1-x}Nb_xS₂, IF-Mo(W)_{1-x}Re_xS₂, the alloys of WMoS₂, WMoSe₂, TiWS₂ and TiWSe₂, where Nb or Re are doped therein.

The term “*incorporated*” means that the B and/or B-chalcogenide are doped or
5 alloyed uniformly within the A_{1-x}-chalcogenide lattice. The B and/or B-chalcogenide substitute the A atom within the lattice. Such substitution may be continuous or alternate substitutions. Continuous substitution are spreads of A and B within each layer alternating randomly (e.g., (A)_n-(B)_n, n>1). Depending on the concentration of incorporated B, it may replace a single A atom within A_{1-x}-chalcogenide matrix forming
10 a structure of (...A)_n-B-(A)_n-B(...). Alternate substitution means that A and B are alternately incorporated into the A_{1-x}-chalcogenide lattice (...A-B-A-B...). It should be noted that other modes of substitution of the B in the A-chalcogenide lattice are possible according to the invention. Since the A-chalcogenide has a layered structure, the substitution may be done randomly in the lattice or every 2, 3, 4, 5, 6, 7, 8, 9 or 10
15 layers.

The conductive materials and composites of the invention may comprise any weight % of nanoparticles. In some embodiments, the conductive materials or composites of the invention comprise between 0.5 and 5 wt% nanoparticles. In some
20 embodiments, the amount of nanoparticles in the composite is between 0.5 and 3 wt%. In further embodiments, the amount of nanoparticles is between 0.5 and 1.5 wt%. In additional embodiments, the amount of nanoparticles is 0.5 and 1wt%.

In some embodiments, the conductive material or composite of the invention comprises PANI and inorganic nanotubes.

In some embodiments, the conductive material or composite comprises PANI
25 and WS₂ inorganic nanotubes (INT-WS₂).

In some embodiments, the conductive material or composite of the invention comprises at least one conductive polymer and INT-WS₂.

In another aspect of the invention, there is provided use of a conductive material or composite according to the invention for the manufacture of a device. The device
30 may be any electronic or optoelectronic device.

Thus, the invention also provides a device comprising a layer or an element of a conductive material or composite thereof.

- 7 -

In some embodiments, the device is an electronic device comprising a material or a composite of the invention. In other embodiments, the device is an opto-electric device comprising a material or a composite of the invention.

In some embodiments, the device may comprise an element or a layer made of
5 or comprising a conductive material or a composite of the invention. The device may be a flexible or a rigid device.

In some embodiments, the device incorporating a conductive material or composite according to the invention is a sensor device.

The structure of the conductive polymers of the invention renders them with
10 increased sensitivity to chemical or electrochemical redox states. As the fluctuations from an oxidation to a reduction state may be reversible, the conductive materials of the invention permit control over electrical and optical properties. Thus, the materials of the invention may additionally be used in a variety of applications such as in electrostatic materials, in electromagnetic shielding, conductive materials, in molecular electronics,
15 in printing circuit boards, electronic displays, as sensors for a variety of chemical or biochemical applications, in energy storage such as rechargeable batteries and solid electrolytes, in the construction of electronic elements such as transistors and diodes and switches, and so forth.

BRIEF DESCRIPTION OF THE DRAWINGS

20 In order to better understand the subject matter that is disclosed herein and to exemplify how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Fig. 1 shows molecular structures of PANI in its various forms: **(a)** PANI-leucoemeraldine, white/clear to colorless, fully reduced, insulating; **(b)** PANI-Emeraldine base, blue, partially oxidized, insulating; **(c)** PANI-Emeraldine salt, green, partially oxidized, conducting; and **(d)** PANI-pernigraniline (PNB), fully oxidized, violet, insulating.

Fig. 2 shows the molecular structure of PANI in its emeraldine base **(EB)** form
30 and in its doped Emeraldine salt **(ES)** form.

Fig. 3 is a SEM image of PANI powder on carbon tape as purchased from Sigma Aldrich, showing worm-like structures.

- 8 -

Fig. 4 is a UV-Vis spectrum of PANI in DMF: (■) corresponds to Emeraldine base; (—) corresponds to Emeraldine salt pH1.

Fig. 5 is a picture of 3 solutions: (a) PANI solution in DMF; (b) PANI solution after addition to IF-WS₂; (c) clear DMF solution after centrifugation, the IF-WS₂ particles precipitated with the absorbed PANI.

Fig. 6A presents a SEM image of reference sample of IF-WS₂ powder; **Fig. 6B** shows IF-WS₂ treated with acidic pH1 solution and with PANI; and **Fig. 6C** shows IF-WS₂ treated with basic solution of pH9 and with PANI.

Figs. 7A-B present close up images of fullerenes coated with PANI.

Figs. 8A-B are TEM images of PANI/IF-WS₂ composite.

Figs. 9A-D are SEM images of PANI/Re:IF-MoS₂ composites exhibiting rejection between the two components.

Fig. 10 shows an absorbance curve: (—) synthesized PANI, and (■) purchased PANI.

Figs. 11A-B are SEM images of synthesized PANI.

Fig. 12A is a SEM image of PANI/INT 0.8 wt% using the in-lens detector; **Fig. 12B** is a SEM image of PANI/INT 3 wt% of embedded nanotube in PANI matrix, using the backscattering detector.

Figs. 13A-B are TEM images of PANI/WS₂ cast from a suspension of the powder in ethanol.

Fig. 14 shows Raman spectra: (a) PANI; (b) INT-WS₂; and (c) PANI/INT-WS₂ sample.

Fig. 15 is a UV-Vis spectrum of EB (---) and ES (—), the arrow points the intensity for ~633 nm.

Fig. 16 shows the conductivity vs. IF wt%.

Fig. 17 shows the conductivity vs. Re:IF-MoS₂ wt%.

Fig. 18 presents oxidized N contents as a function of W contents (at%).

Fig. 19 is an energy diagram of Fermi levels of INT-WS₂, PANI and the produced composite material containing both materials.

Figs. 20A-20B show PANI/INT-WS₂ composites conductivity vs. INT weight percent.

Fig. 21 is the averaged conductivity of each wt% and its deviation.

Fig. 22 presents chemical structure of PANI doped with Lewis acid.

Fig. 23A shows a post treatment suspension; and **Fig. 23B** shows suspension prior to treatment.

DETAILED DESCRIPTION OF EMBODIMENTS

5 **Synthesis**

IF-PANI hybrid experiment

In the first step the possibility of adsorbing PANI onto the pristine IF-WS₂ was explored. IF-WS₂ nanoparticles were synthesized according to a published procedure [6]. Polyaniline $M_w \sim 20,000$ (g/mole) was purchased at Sigma-Aldrich Co. N,N-dimethylformamide (DMF) was selected as the solvent of choice permitting high solubility of the polymer.

IF-WS₂ (20mg) powder was added to PANI solution in DMF (1.3mg/30ml) and suspended using ultrasonic bath for 1 hour. The sample was centrifuged for 1.30 min at rpm=27 to receive a sediment of the synthesized product. The solvent was removed and the product was washed with water and ethanol by shaking and centrifugation repeatedly. The solid residue was dried in a vacuum oven over night at room temperature.

PANI/WS₂ “in situ” composite synthesis

The synthesis of PANI was based on a common procedure [8]. Aniline hydrochloride was used as a monomer due to its solubility in aqueous solutions. In addition, the handling of solid anilinium salt is preferred compared to on liquid aniline from the toxic hazards point of view and the high tendency of the liquid aniline to oxidize. Peroxydisulfate is the most commonly used oxidant, and its ammonium salt was preferred to the potassium counter cation because of its better solubility in water. The concentration of aniline hydrochloride was set to be 0.025 M.

To minimize the presence of residual aniline and to obtain the best yield of PANI, the stoichiometric peroxydisulfate/aniline ratio of 1.25 was used, so the concentration of ammonium peroxydisulfate was set to 0.031 M.

Aniline hydrochloride (Sigma; 0.259 g, 2 mmol) was dissolved in distilled water in a volumetric flask to 10 mL of solution. Ammonium peroxydisulfate (Sigma; 0.571g, 2.5 mmol) was dissolved in 10 mL of water. Both solutions were kept for 1 h at room temperature (~18-24 °C).

- 10 -

Inorganic nanoparticles of WS₂ (IF-WS₂) were suspended in 20 mL of water for 15 min. Anilinium hydrochloride was added to this suspension in order to keep the particles suspended homogeneously with the aniline molecules and was further dispersed in an ultrasonic bath for 1 h. The ultrasonic bath was cooled with ice during this process in order to avoid an increase in the temperature of the water inside the bath and keep it at room temperature. A solution of the oxidant, ammonium persulphate was added to this reaction mixture drop wise with continuous stirring for 30 min at 0-5°C. A color change from yellow to pale green to deep green was observed.

The mixture was left to polymerize for 2 h with continuing stirring at room temperature. The PANI/INT-WS₂ precipitated out and was collected on a vacuum filter, washed with water (3x20 mL) followed by (3x20 mL) ethanol wash to remove the excess of the water. The PANI/INT-WS₂ powder was dried in air and then in vacuum oven at 100°C for 24 h until a constant weight was obtain.

In order to calculate the wt% amount of nanoparticles for each of the samples, PANI was synthesized several times. The average yields of PANI experiments, using the same concentrations of the monomer and oxidizing agent without nanoparticles was found to be 176.3 ± 1.3 (mg) (68% chemical yield, average of 6 samples). The different amounts of INT and IF were calculated according to this weight.

Inorganic Fullerenes

IF-WS₂ samples were prepared according to a published procedure. **Table 1** presents the composite samples prepared.

IF (wt%)	1%	2%	4%	5%	6%	10%	15 %	20%	22 %	25 %	27%	30 %	35 %	50 %
IF (mg)	2	3.5	7	8.8	10.5	17.5	26	35.2	38.7	44	47.5	53	62	88

Table 1: IF-WS₂ content for PANI/IF-WS₂ composites samples; the amount of anilinium chloride (259 mg) and ammonium peroxy sulfate (571 mg) was constant

The total volume of each experiment was 40 mL yielding concentration of 0.025M and 0.031M for anilinium chloride and ammonium peroxy sulfate respectively.

IF-MoS₂

Doping of the IF nanoparticles of MoS₂ with minute amounts (<0.1 wt%) of Re atoms has been demonstrated. The Re (rhenium) atoms reside in substitutional (Mo) sites leading to an excess of negative charge carriers which are trapped at the nanoparticle's surface. It was considered that this surface charge may affect the obtained composite material in terms of electrical properties.

PANI/Re:IF-MoS₂ was synthesized according to the described procedure above.

Table 2 presents the composite sample prepared.

IF (wt%)	5%	10%	20%
IF-Re:MoS ₂ (mg)	8.8	17.6	35.2

Table 2: IF contents for PANI/IF-Re:MoS₂ composite samples; the amount of anilinium chloride and ammonium peroxydisulfate was constant and the total volume of 40 mL

Inorganic Nanotubes

A composite material of PANI containing INT-WS₂ was prepared by the same procedure as described above (except for the chemical treatment). Pure multiwall INT-WS₂ was obtained from NanoMaterials Ltd. (Israel), synthesized according to a published procedure [9-10]. The nanotubes were typically 30-100 nm (nanometers) in diameter and 1-20 μm (micrometers) long, comprising of approximately 30 WS₂ layers and frequently containing a WO_{3-x} sub oxide core.

PANI/INT-WS₂ composites were prepared in weight percent ratio in which the concentration of INT-WS₂ was varied (0.5, 0.85, 1.5, 2.5, 3, 5, 20, 40 and 100 wt %) where the concentration of anilinium chloride and ammonium peroxydisulfate were kept constant. Table 3 below presents the wt% amount of INT taken for preparation of each sample.

INT (wt%)	0.5%	0.85%	1.5%	2.5%	3%	5%	20%	40%
INT (mg)	0.8-0.9	1.4-1.5	2.7	4.5-4.7	5.2-5.3	8.8	35	70-71

Table 3: WS₂-INT contents for PANI/INT-WS₂ composites samples; the amount of monomer (259 mg) and oxidizing agent (571 mg) remained constant for all experiments, all dissolved at a final volume of 40 mL

Results and Discussion

IF Characterization

5 Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties. It is already established that the addition of acid (HCl, HClO₄) to the basic form of PANI, emeraldine base (EB) leads to protonation of the imine moiety rather than the amine one to form the conductive emeraldine salt (ES) (**Fig. 2**). PANI was commercially available, in its reduced state-emeraldine base.

10 The resulting material appears to have a significant electron delocalization in the polymer backbone. It results in the formation of an environmentally stable nitrogen base salt.

Initial characterization of the as-purchased PANI by UV-Vis absorption spectroscopy was done by dissolving the material in DMF in various concentrations. 15 The UV-Vis spectrum of PANI, in the base form is dominated by two absorption peaks at ca. 320 nm (Band I) and ca. 610 nm (Band II), respectively. Band I is often assigned to p-p* transition in the benzenoid structure. The absorption in the visible range, i.e. Band II, is ascribed to exciton formation in the quinonoid rings (**Fig. 2**). These results are concurrent with previous optical studies made on PANI. PANI can be produced as 20 granular or fibrous shape as shown in **Fig. 3**.

At acidic pH 1, the band at 620 nm disappears and a new absorption band at 430 nm is found together with the band at 850 nm (also existed at the EB). These bands correspond to a certain, possibly partial, protonation stage of the imine structural units in the PANI chain. In the literature, it is often interpreted as 25 excitations to the polaron band (**Fig. 4**).

A bluish color solution (EB) was obtained when dissolving PANI in DMF which converted to green color (ES) when a few drops of HCl 0.1M were added (pH 1) (see **Fig. 2**).

PANI solution in DMF (1.3mg/30ml) was added directly to IF-WS₂ powder and 30 the bluish color of the solution turned green. This is due to the acidic pH of IF-WS₂ in solution (pH 1-2). The mixture suspended by ultrasonic bath for 1 hour at room temperature followed by centrifugation (rpm-5, 5min). The resulting colorless solution (**Fig. 5**) suggests complete adsorption of PANI to the WS₂ nanoparticles.

- 13 -

In order to further study the adsorption process of PANI onto the IF-WS₂ and examine the possibility of chemical linkage (or interaction) between them, the adsorption process was performed at two different pH solutions: acidic and basic.

In both pH samples, colorless solutions were observed after centrifuging, indicating that the adsorption step is independent of the initial pH of the WS₂ nanoparticles.

SEM images of the matrix of PANI/IF were taken for both basic and acidic pretreatment of the IF nanoparticles. There were no significant structural differences shown in the nanocomposites; the initial pH of the nanoparticles does not affect the morphology of the obtained composite. In both cases the polymer (PANI) is within the WS₂ particles, as contrast to the bare WS₂ that were not treated with PANI (Figs. 6A-C).

Using SEM and TEM at a higher magnification of PANI treated with WS₂ NP clearly show that the WS₂ nanoparticles are submersed in the PANI film (Figs. 7-8).

Table 4 below presents the atomic concentration (%) of PANI-IF as derived from XPS elemental analysis. The same results were obtained for the acidic and basic pretreatment.

	O	C	N	S	W _s	W _{ox}	S/W _s	C/N	W _{ox} /W _s
PANI/IF	18.9	9.9	1.7	43.6	19.5	5.4	2.2	5.7	0.2

Table 4: Elemental analysis of PANI-IF sample (at%)

20

In the above **Table 4**, W_s stands for the tungsten signal associated with the WS₂ phase. The W_{ox} signal is associated with the WO_{3-x} core of the particles (uncompleted oxygen to sulfur conversion). The C and N signals show the ratio of 1:6 as expected from the PANI's structure (**Fig. 2**) and the existences of Ws and S at the ratio of approximately 1:2. The atomic concentration of the oxygen can be accounted for from the WO_{3-x} core of the particles and from water molecules that are chemisorbed to the defect sites on the surface or inner location of the fullerenes or polymer. The S: Ws ratio suggests a higher amount of S which will be further checked.

25

Re: IF-MoS₂

Electron microscopy characterization of PANI/Re:IF-MoS₂ composite material shows coated particles resembling to the images obtained from PANI/IF-WS₂. A closer

30

- 14 -

view of these coatings reveals existence of gaps between the IF and the PANI coatings as can be seen by **Fig. 9**.

INT-WS₂/PANI nanocomposite

5 Considering the possibility that the structure of the particle can affect the layout of the composite material and later on the conductivity, introducing inorganic nanotubes to the polymer was suggested. The INT-WS₂ with their high aspect ratio (*ca.* 10³) may increase the conductivity of the composite material by arranging with certain directionality, thus facilitating the electron transport across the sample.

10 Prior to characterizing the composite material, UV-Vis measurement of the polymerized PANI without nanoparticles was done and compared with the purchased one to verify the success of the polymerization. UV-Vis spectra clearly indicate the synthesis of PANI. Two fundamental absorption bands appear in the spectra centered at; 320 nm and 610 nm. SEM images of the produced PANI reveal granular morphology of
15 the polymer. (**Fig. 11**).

 The SEM studies performed with all the composite samples of PANI/INT-WS₂ reveal that the WS₂ tubes are embedded in the PANI matrix (**Fig. 12A**). In the lower weight samples, the nanotubes are mostly separated or in small bundles. As the amount of nanoparticles increases, the clusters become more frequently seen in the sample and
20 the nanotubes are less separated (**Fig. 12B**).

 TEM images (**Figs. 13A and B**) of PANI/WS₂ nanocomposite suggest that the WS₂ nanotubes are coated with PANI and thus create an interface layer between the tubes and the polymer.

 Raman spectroscopy was used to verify the contents of INT-WS₂ and PANI in
25 the composite material and compared with the pristine INT and PANI. **Fig. 14** shows the Raman spectra of PANI/WS₂ composite material. The bands at 354-587 cm⁻¹ region are associated with the E_{2g} and the A_{1g} lines, respectively, of the WS₂ nanotubes as was shown before [11]. The bands from 1167 cm⁻¹ to 1600 cm⁻¹ are assigned to the PANI structure according to **Table 5**.

30

- 15 -

Raman band (cm^{-1})	Possible assignment
354	WS ₂ nanotubes
420	
523	
587	
1167	C-H stretch 1027-1170 (1/cm)
1348	C-N stretch 1324-1375 (1/cm)
1477	C=N stretch 1450-1500 (1/cm)
1560	Quinonoid ring C=C stretch
1600	Benzoid ring C=C

Table 5: Main Raman bands and their possible assignments

These observations offered strong evidence for the presence of PANI and INT-WS₂ in the composite material and revealing that PANI was successfully synthesized.

By observing the intensities of PANI in the composite and the pristine PANI, one can notice a large difference in the intensity of the signals and their clarity. The pristine PANI (a) reaches intensities of approximately 2000 compared to the PANI/INT-WS₂ (c) which its intensities reach almost 8000. This large difference may be explained by the UV-Vis absorption of the two forms of PANI, EB and ES as seen by **Fig. 15**.

The wavelength of the Laser beam at the Raman measurement instrument was 633 nm. As seen by **Fig. 15**, the absorption of EB at this wavelength is very high compared to the absorption of the ES. This fact causes most of the coming light to be absorbed by the sample, get lower penetration depth into the sample and as a result, to receive smaller scattering intensities. The ES absorption at 633 nm is much lower (for the same concentration), thus the intensity of the scattered light is expected to be larger, as seen by **Fig. 14**.

XPS analysis of the surface of PANI/INT was conducted to investigate the elemental composition of the composites. **Table 6** presents the results of three different samples. Each sample was tested in various areas and the quoted result represents an average of the three separate measurements.

	O	C	N	S _{ox}	S _{INT}	W _s	W _{ox}	Cl	C/N	S/W
PANI	13.03	72.88	10.92	2.57	-	-	-	0.59	6.7	-
PANI + 3% INT	9.18	76.61	11.75	2.02	0.06	0.03	0.03	0.35	6.5	2
PANI + 40% INT	13.25	68.28	10.07	2.67	3.68	1.75	0.12	-	6.8	2.1

Table 6: Elemental analysis

The results of elemental analysis clearly indicate the presence of oxygen in PANI (520 eV) (which is far more than the oxygen originating from the core of the nanotubes, as verified by analysis of the W line). This may be due to bound water molecules or, more likely, to partial oxidation of the PANI chains. The presence of sulfur in the PANI sample is partly due to the residual sulfate counter ions produced by the reduction of peroxydisulfate during polymerization.

There is also evidence for some chlorine residues in PANI from using anilinium chloride monomer even after several washings of the samples, indicating a partial benzene-ring substitution with chlorine.

Another noticeable fact is that the INT wt% in the 3% and 40% samples is not compatible with the actual amount of INT nanoparticles which were added to each of the experiments. This deviation can be explained by the existence of INT in bundles; thus creating areas depleted of particles contrary to large bundles of them. The size of the scanning beam in the XPS is around 500 μ and it averages the information it collects at this scanning radius. This implies that the above sample are highly non homogenous.

Properties

IF-WS₂

PANI/IF conductivity was measured for the 15 samples. **Fig. 16** presents the conductivity behavior of the composites. There exists a clear increase in conductivity of the composites compared with the pristine PANI. The highest conductivity achieved was for 1 wt% IF (10.46 ± 0.32 S/cm), two orders of magnitude higher than the conductivity of pristine PANI (0.16 ± 0.05 S/cm), as can be seen in **Table 7**.

IF-SW ₂ (wt%)	Conductivity (S/cm)	SD (S/cm)
0	0.16	0.056
1	10.5	0.324
2	9.56	0.479
4	7.58	3.24
5	0.712	0.858
6	2.93	1.33
10	0.061	0.011
15	2.51	0.413
20	0.096	0.014
22	0.943	0.982
25	0.481	0.110
27	0.122	0.031
30	0.025	0.002
35	1.05	0.147
50	0.0003	0.00004

Table 7: Conductivity values for PANI/IF-WS₂ composite

- 5 Important note to consider is the value of the deviation for each of the measured samples. Although 3-4 experiments were performed for each composition and 3 pellets were tested for each experiment, repeatability could not be easily achieved.

IF-MoS₂

- Conductivity values of the PANI/Re: IF-MoS₂ composite material were plotted
10 vs. the wt% of IF nanoparticles in each sample. **Fig. 17** presents the results.

The appeared conductivity of the samples clearly indicates that the existence of Re: IF-MoS₂ NP decreases the conductivity of PANI tremendously. The greatest decrease obtained for the 20 wt% sample, lowering the conductivity by approximately 5 orders of magnitude as can be seen by **Table 8**.

15

IF-MoS ₂ (wt%)	Conductivity (S/cm)	SD (S/cm)
0	0.132	0.013
5	0.004	0.003
10	0.0001	0.00001
20	0.00009	0.00004

Table 8: Conductivity values for PANI/Re: IF-MoS₂ composite

These results, combined with electron spectroscopy characterization demonstrate that the negative charge accumulated on the surface of the particle has a large affect on the composite material obtain, both in terms of morphology and conductivity. Creating a hybrid material between PANI and Re:IF-MoS₂ nanoparticles is not favorable due to, presumably, electrostatic repulsion between the two components. PANI exists in its undoped, nonconductive form (EB) in the composite material. Addition of Re: IF-MoS₂ nanoparticles to EB results in additional interference to the transport of electrons, presumably, due to creation of grain boundaries and barriers.

INT

XPS analyses of the surfaces of PANI/INT-WS₂ were conducted to investigate variations at nitrogen binding sites. A sample of 40 wt% PANI/INT-WS₂ was examined by XPS. Three different grains of the sample were studied. **Table 9** presents the elemental contents of the examined grains and compared with the undoped PANI sample.

(wt%)	C	N	W	S	S/W	C/N
PANI/INT-WS ₂ (1)	86.39	13.14	0.14	0.34	2.4	6.6
PANI/INT-WS ₂ (2)	80.82	15.41	1.27	2.51	1.9	5.2
PANI/INT-WS ₂ (3)	83.26	16.20	0.54	1.08	2	5.1
PANI	83	14	-	-	-	6.1

Table 9: Elemental composition of 3 samples of PANI/INT-WS₂ 40% wt and of PANI

The Carbon/Nitrogen ratio is approximately as predicted from the PANI structure (**Fig. 1**), 6 Carbon atoms for each Nitrogen atom. Shifts from the value of 6 may be due to contaminations of Carbon or Nitrogen absorbed on the sample from the air prior to measurements. The S/W is also compatible with the WS₂ phase.

It is important to notice the large differences in atomic percentage of W and S between the three spots of the same 40% wt sample. These large differences arise from the fact that a sample of composite material containing a great amount of nanoparticles is bound to create large aggregates of the nanoparticles which in turn creates areas depleted of nanoparticles, areas abundant with INT and a measured average of particles in the polymer.

Observing the PANI/INT-WS₂ 40 wt% sample which contains the greatest amount of nanotubes, revealed that the nitrogen signal was split into two. To understand this interesting observation, the band of N_{1s} was deconvoluted and the different sub-bands were fitted with peaks at 398.8, 399.6, 400.7, and 401.8 eV, which corresponded to quinonoid imine (=N-), benzenoid amine (-NH-), protonated amine (-N⁺), and protonated imine (=N⁺), respectively.

Kumar et al. [12] attributed the last two peaks to the presence of polarons (radical cations) and bipolarons (dications), respectively. The ratio of these two N components at 400.7 and 401.8 eV (positively charged nitrogen atoms) could be considered as a direct manifestation of the doping level of PANI (see also Fig. 2). The area ratios of the four nitrogen constituents in PANI were calculated; the results were listed in Table 10.

	N (at%)				[(=N ⁺)+(-N ⁺)]/N
	=N ⁺ 401.8 eV	-N ⁺ 400.7 eV	-NH- 399.6 eV	=N- 398.8 eV	
PANI/INT-WS ₂ (1)	4.7	22.6	19.1	53.7	27.3
PANI/INT-WS ₂ (2)	3.6	52.7	7.4	36.7	56.3
PANI/INT-WS ₂ (3)	2.96	27.4	10.6	43.8	30.36
PANI	8.0	18.7	15.0	58.4	26.7

Table 10: Four Nitrogen constituents of PANI for PANI/INT-WS₂ and PANI (=N⁺ protonated imine; -N⁺ protonated amine; -NH- benzenoid amine; =N- quinonoid imine)

The pure PANI was synthesized in the presence of HCl (by using anilinium chloride as a monomer), hence the nitrogen atoms are partially protonated in the polymer, representing a certain degree of doping. To estimate the doping level of PANI originating from the presence of the INT-WS₂ we compared it to the undoped PANI. To calculate the doping level which occurred only by the presence of INT, we subtracted the ratios of the protonated amine (-N⁺) and protonated imine (=N⁺) components which were received from the pure PANI (as a result of protonation by HCl) from the results received by the composite material. The doping level for PANI/INT-WS₂ (27%-56%) was higher than that for the undoped PANI (26%).

Fig. 18 presents the correlation between the INT-WS₂ content and the degree of doping of the PANI. CREM can provide us with the work function of a sample. Work functions for both INT and PANI were measured separately. The obtained work

- 20 -

functions are displayed in **Fig. 19**. The energy of the valence band was obtained from XPS for both components. The band gap was obtained from UV-Vis spectra together with previous studies.

The obtained work functions for both INT-WS₂ and PANI reveal a significant difference, larger than 0.5 eV. Therefore, it was suggested that an electron transfer process from PANI to INT-WS₂ should occur naturally. The obtained work function for PANI/INT-WS₂ was 4.72 eV which stands in the middle between the work functions of PANI and INT/WS₂. The work function values support the probability of electron transfer process from PANI to INT-WS₂.

The splitting of the nitrogen signal of PANI verifies the oxidation process of one of the nitrogen atoms in PANI structure. This oxidation is known as the process of doping which took place with priority on one site (the imine nitrogen). No evidence of acceptance of electrons on the tungsten or sulfur atoms of INT was observed. It is assumed this may be due to the fact that the reference measurements of INT were done mostly on aggregates of INT and surroundings of them. In the measurement of INT in the composite of PANI/INT-WS₂, the chemical surrounding of the INT was different, smaller aggregates and PANI setting.

The electrical conductivity of PANI and PANI/WS₂ nanocomposites are presented in **Fig. 20**. The addition of INT-WS₂ nanoparticles into polyaniline shows a very peculiar behavior. First the addition of the nanotubes leads to increasing electrical conductivity of the nanocomposites, which peaks at ~0.85 wt% nanoparticles. At higher nanotube concentration the conductivity decreases as the amount of INT-WS₂ becomes larger. **Fig. 20** presents the conductivity data. Three samples were synthesized for each concentration. Three different pellets were prepared from each synthesized sample and their conductivity was measured. Thus each point in the graph represents an average from three tested pellets. **Fig. 22** presents the average of each set of points and their standard deviation.

The inset on **Fig. 20** presents the conductivity for the samples with wt% greater than 5% up to 100% of INT. **Table 11** summarizes the conductivity data using the average conductivities of each sample as also presented in **Fig. 20**.

INT-WS ₂ (wt%)	Conductivity (S/cm)	SD (S/cm)
0	0.153	0.044
0.5	4.566	0.033
0.85	12.73	0.961
1.5	4.217	0.254
2.5	3.701	0.306
3	1.994	0.774
5	0.706	0.292
20	0.049	0.011
40	0.168	0.012
100	0.0095	0.011

Table 11: Conductivity and standart deviation of synthesized composite samples

The effect of the INT-WS₂ nanotubes on the PANI is clearly seen from the conductivity behavior of the composite. The average electrical conductivity of PANI thus prepared (average of 10 separate experiments and 30 samples, synthesized and measured at the same conditions described at the experimental section) was 0.15 ± 0.04 S/cm. The largest increase in conductivity of the composite is achieved for the ~0.85 wt% INT-WS₂ concentration which gave 12.73 ± 0.96 S/cm, two orders of magnitude higher than the pristine PANI hydrochloride. As the amount of nanoparticles in the composite increases, the conductivity is decreases even below the conductivity of undoped PANI.

To explain the obtained results, an “acid-base” reaction between PANI and INT was proposed. PANI can be considered as Lewis base due to a lone electron pair on the nitrogen atoms of PANI (**Fig. 2**). Recently, it was evidenced that the PANI can be doped with Lewis acids, like BF₃, FeCl₃ or SnCl₄ and form acid- base complexes. The general structure of PANI doped with Lewis acid (LA) is presented in **Fig. 21**. Similarly to the case of protonation, one molecule of dopant is coordinated to nitrogen atom of PANI, but contrary to the protonation, both types of nitrogen atoms of PANI (amine as well as imine ones) may be coordinated by LA.

Lewis acid-doped PANI systems are expected to be different from the conventional protonated PANI owing to a qualitatively different chemical interaction between the dopant and the polymer; for instance, the absence of any counter ion in these systems may have different influence on the properties of the polymer.

- 22 -

In this work, we suggested that, INT-WS₂ can also form a complex with PANI. This may explain the increase in conductivity for the ~0.85% INT. WS₂ nanotubes, due to their structure and high aspect ratio; have strong van der Waal forces which results in their tendency to form bundles. At polymer samples with 0.5%-3% INT content, the
5 tendency to form bundles is smaller due to the larger average distance between the nanotubes and their strong acid-base interaction with the polymer. As the INT concentration increases, the chance of creating large bundles also increases. This in turn lowers the active surface area of the tubes and in addition, creates grain boundaries which scatter the conduction electrons and results in lowering of the composite
10 conductivity.

It has been shown that INT-WS₂ nanoparticles were successfully embedded in a conductive, organic polymer matrix. In the scope of the experimental work it was shown that these particles may serve as an inorganic dopant material for PANI and thus
15 increase its conductivity. The conductivity of PANI/INT-WS₂ was investigated and compared to PANI without furthered doping. It was further shown that doping PANI with 0.8 wt% INT-WS₂ increases the conductivity of the polymer by two orders of magnitude compared with the non-treated polymer (i.e., undoped polymer).

It was also found that, the type of additive has a considerable effect on
20 morphology of resultant products. When using a prepared polymer (commercially purchased), the resulting composite material was not homogeneous and it appears as there is no connection between the two species.

XPS and conductivity measurements results from the *in situ* polymerized composite material reveal an electron transfer process from the nitrogen atoms of the
25 polymer to the INT. The anilinium chloride monomer molecules can interact with the nanotubes via electron transfer from the nitrogen atoms to the nanoparticle; creating an electron donor acceptor complex, followed by the subsequent formation of PANI. The fact that only a small amount of INT may increase the conductivity of the polymer by two orders of magnitude suggests that the IF/INT nanoparticles can serve as promising
30 candidates for other composites of conductive polymers such as polypyrrole and polythiophenes.

- 23 -

The improvements made in the conductivity properties of the present PANI/INT-WS₂ enhance the application potential of the conducting polymer without hampering the chemical and physical properties of both moieties.

CLAIMS:

1. A conductive material comprising at least one conductive polymer doped with at least one inorganic closed-cage nanostructure.
2. The conductive material of claim 1, wherein the conductive polymer are associated with the nanostructures through coordinative or ionic association.
3. The conductive material of claim 1 or 2, wherein the conductive polymer and the at least one inorganic closed-cage nanostructure are associated by acid-base interaction.
4. The conductive material of any one of the preceding claims, wherein the conductive polymer has at least one moiety permitting charge transfer between the conductive polymer and the inorganic closed-cage nanostructures.
5. The conductive material of claim 4, wherein the conductive polymer comprises an atom selected from O, N, and S, or comprises a moiety comprising such an atom.
6. The conductive material of claim 5, wherein the conductive polymer is selected from polypyrrole, polythiophene and polyaniline.
7. The conductive material of claim 6, wherein the conductive polymer is polyaniline (PANI).
8. The conductive material of any one of the preceding claims, wherein the inorganic closed-cage nanoparticles are hollow nanoparticles selected from metal chalcogenides, metal dichalcogenides, and metal halides.
9. The conductive material of any one of the preceding claims, wherein the inorganic closed-cage nanoparticles are single or multi-layered nanoparticles.
10. The conductive material of claim 9, wherein the inorganic closed-cage nanoparticles are selected from nanospheres, nanotubes, nested polyhedra, and onion-like.
11. The conductive material of claim 10, wherein the inorganic closed-cage nanoparticles are inorganic nanotubes (INT) or inorganic fullerene-like nanoparticles (IF).
12. The conductive material of any one of the preceding claims, wherein the inorganic closed-cage nanoparticles are of the general formula ML_n , wherein M is a transition metal, L is a chalcogen, and n is the number of chalcogen atoms L per each atom of the transition metal M.

- 25 -

13. The conductive material of any one of the preceding claims, wherein the inorganic closed-cage nanoparticles are of the general formula $A_{1-x}B_x$ -chalcognide, wherein A is either a metal or a transition metal or an alloy of such a metal/transition metal, B is a metal or a transition metal, and x being ≤ 0.3 and different from zero, provided that $A \neq B$.
14. The conductive material of any one of the preceding claims, wherein the material comprises between 0.5 and 5 wt% nanoparticles.
15. The conductive material of claim 14, wherein the material comprises between 0.5 and 3 wt% nanoparticles.
16. The conductive material of claim 15, wherein the amount of nanoparticles in the material is between 0.5 and 1.5% wt.
17. The conductive material of claim 16, the amount of nanoparticles in the material is between 0.5 and 1% wt.
18. The conductive material of any one of the preceding claims, comprising PANI and inorganic nanotubes.
19. The conductive material of claim 18, comprising PANI and WS_2 nanotubes (INT- WS_2).
20. The conductive material of any one of claims 1 to 17, comprising at least one conductive polymer and INT- WS_2 .
21. The conductive material of any one of the preceding claims, wherein the conductivity of the conductive material is enhanced as compared to un-doped conductive polymer.
22. A conductive material comprising a conductive polymer doped with inorganic closed-cage nanostructures, wherein the conductivity of the conductive material is enhanced as compared to non-doped conductive polymer.
23. A composite comprising at least one conductive material according to any one of claims 1-22.
24. A composite comprising at least one conductive polymer and at least one inorganic closed-cage nanostructure.
25. A composite comprising at least one conductive polymer and at least one inorganic closed-cage nanostructure, exhibiting induction of charge carriers therebetween.

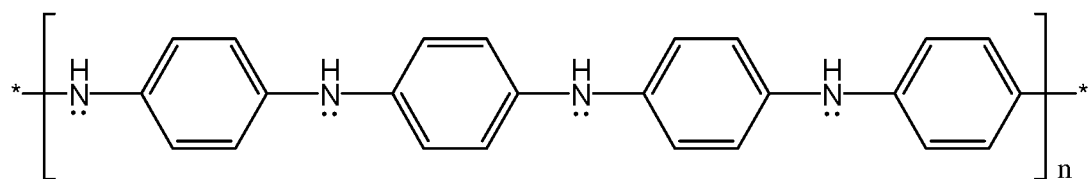
- 26 -

26. The composite of claim 24 or 25, wherein the conductive polymer and the nanostructures are associated with the nanostructures through coordinative or ionic association.
27. The composite of claim 24 or 25, wherein the conductive polymer and the at least one inorganic closed-cage nanostructure are associated by acid-base interaction.
28. The composite of any one of claims 24 to 27, wherein the conductive polymer comprises an atom selected from O, N, and S, or comprises a moiety comprising such an atom.
29. The composite of claim 28, wherein the conductive polymer is selected from polypyrrole, polythiophene and polyaniline (PANI).
30. The composite of any one of claims 24 to 29, wherein the inorganic closed-cage nanoparticles are hollow nanoparticles selected from transition metal chalcogenides, transition metal dichalcogenides, and transition metal halides.
31. The composite of claim 30, wherein the inorganic closed-cage nanoparticles are inorganic nanotubes (INT) or inorganic fullerene-like nanoparticles (IF).
32. The composite of claim 30 or 31, wherein the inorganic closed-cage nanoparticles are of the general formula ML_n , wherein M is a transition metal, L is a chalcogen, and n is the number of chalcogen atoms L per each atom of the transition metal M.
33. The composite of claim 30 or 31, wherein the inorganic closed-cage nanoparticles are of the general formula $A_{1-x}B_x$ -chalcogenide, wherein A is either a metal or a transition metal or an alloy of such a metal/transition metal, B is a metal or a transition metal, and x being ≤ 0.3 and different from zero, provided that $A \neq B$.
34. The composite of any one of claims 24-33, comprising PANI and WS_2 nanotubes (INT- WS_2).
35. The composite of any one or claims 24 to 34, comprising between 0.5 and 5 wt% nanoparticles.
36. An electronic device comprising the material of any one of claims 1 to 22 or the composite of any one of claims 23 to 35.
37. An opto-electric device comprising the material of any one of claims 1 to 22 or the composite of any one of claims 23 to 35.
38. A device comprising a layer or an element of a conductive material of any one of claims 1 to 22 or a composite of any one of claims 23 to 35.

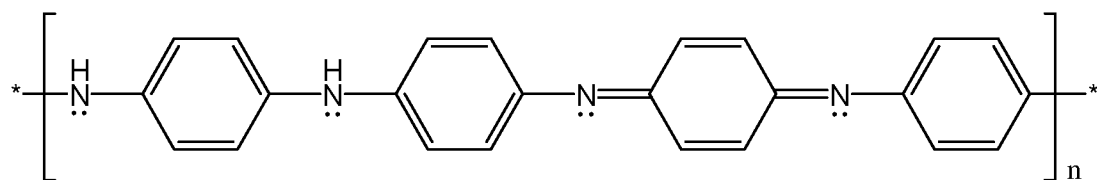
- 27 -

- 39. The device of any one of claims 36 to 38, being a flexible device.
- 40. Use of a conductive material of any one of claims 1 to 22 or a composite of any one of claims 23 to 35 in the manufacture of a device.
- 41. The use of claim 40, wherein the device is selected from an electronic device and an opto-electric device.

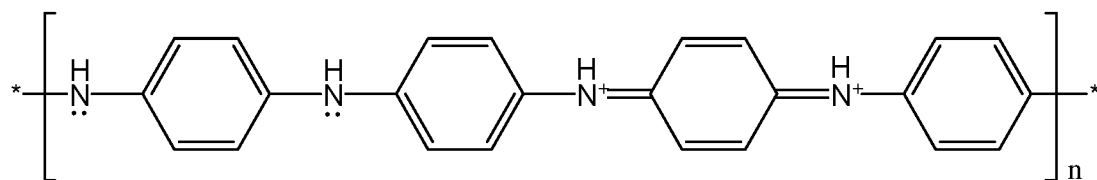
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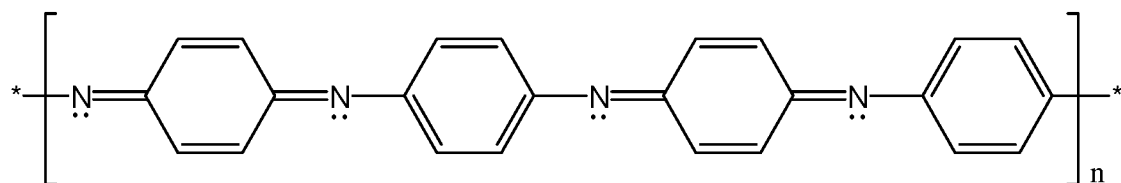
(a)



(b)



(c)



(d)

Fig. 1

2/26

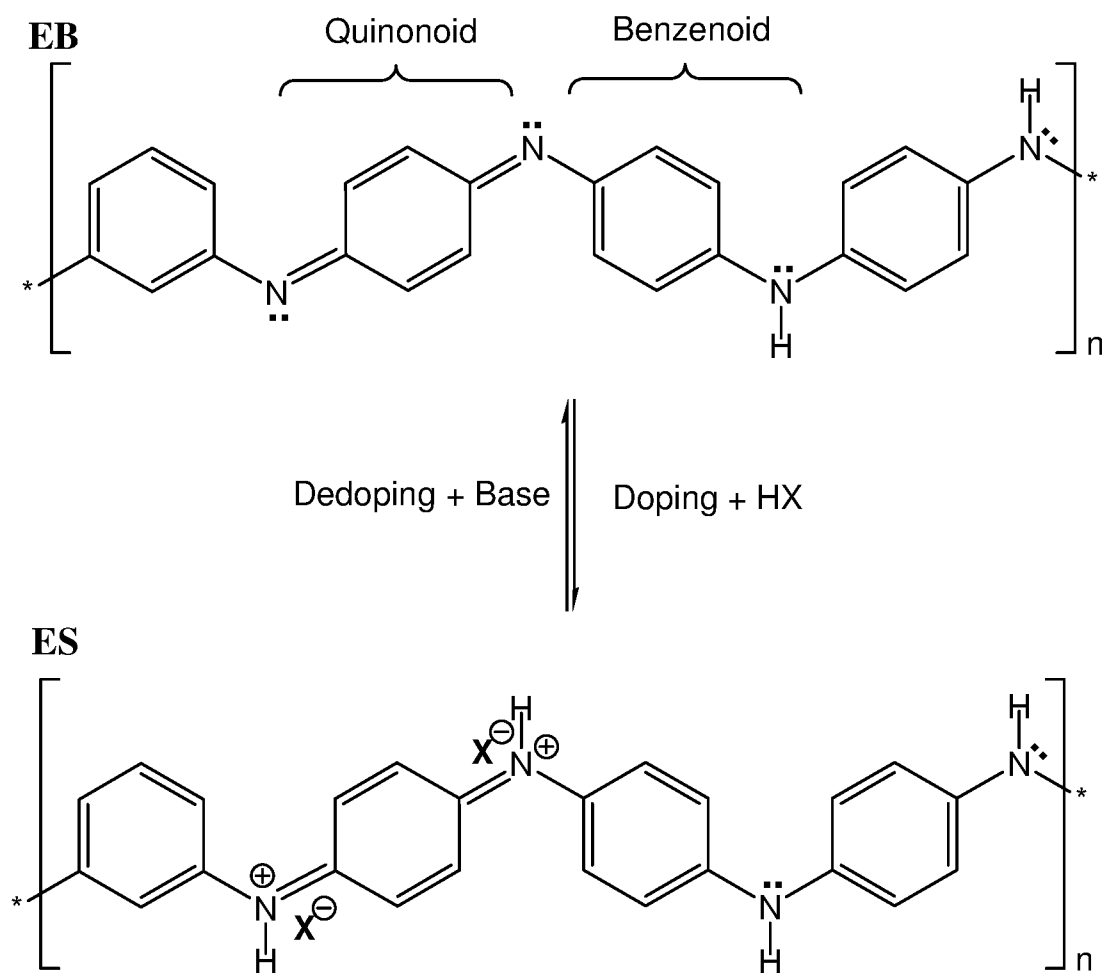


Fig. 2

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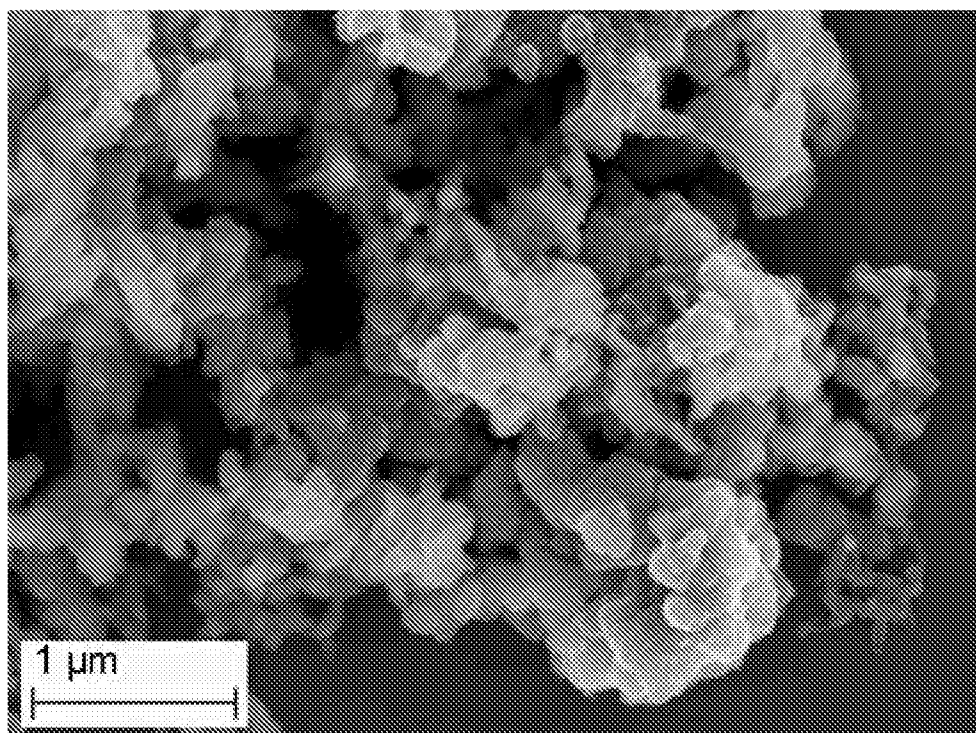


Fig. 3

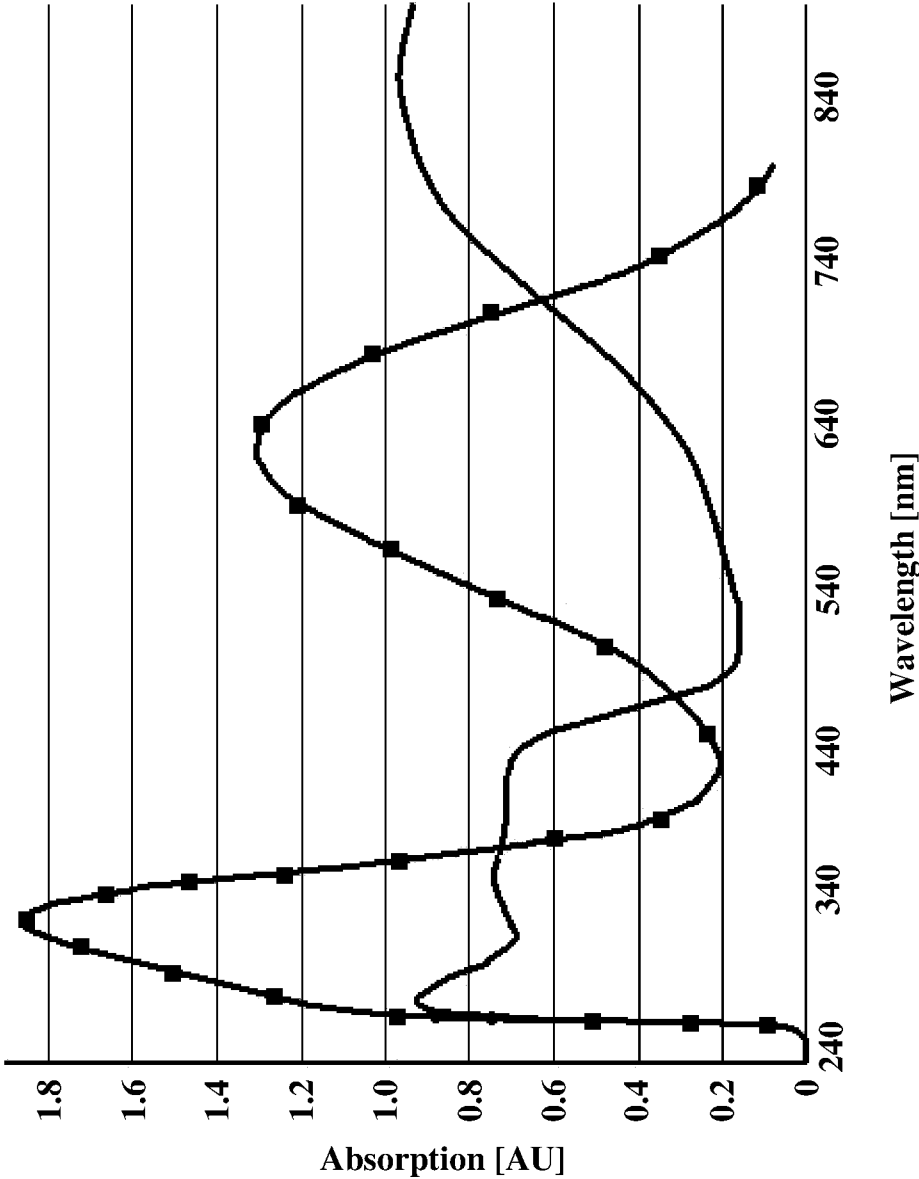


Fig. 4

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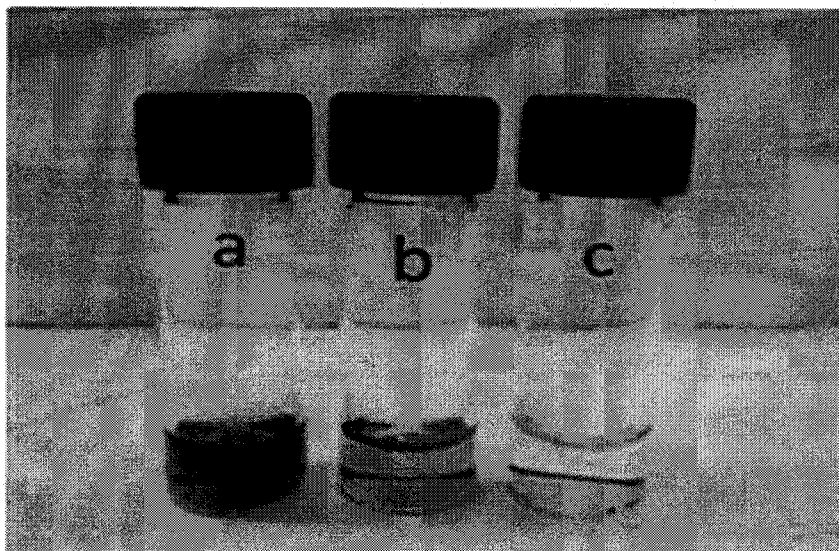


Fig. 5

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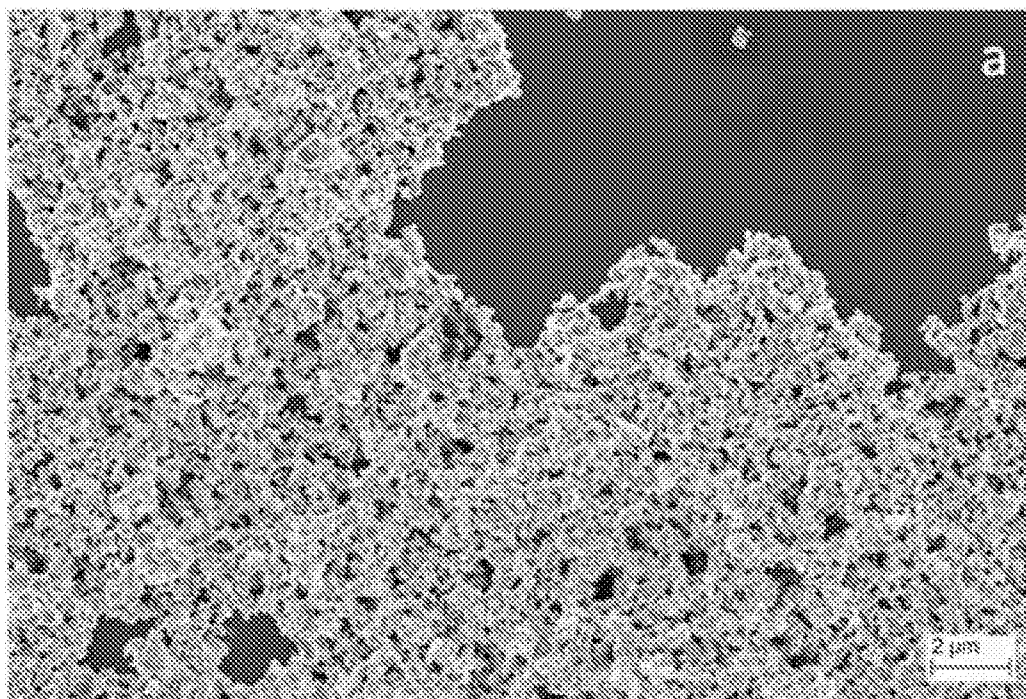


Fig. 6A

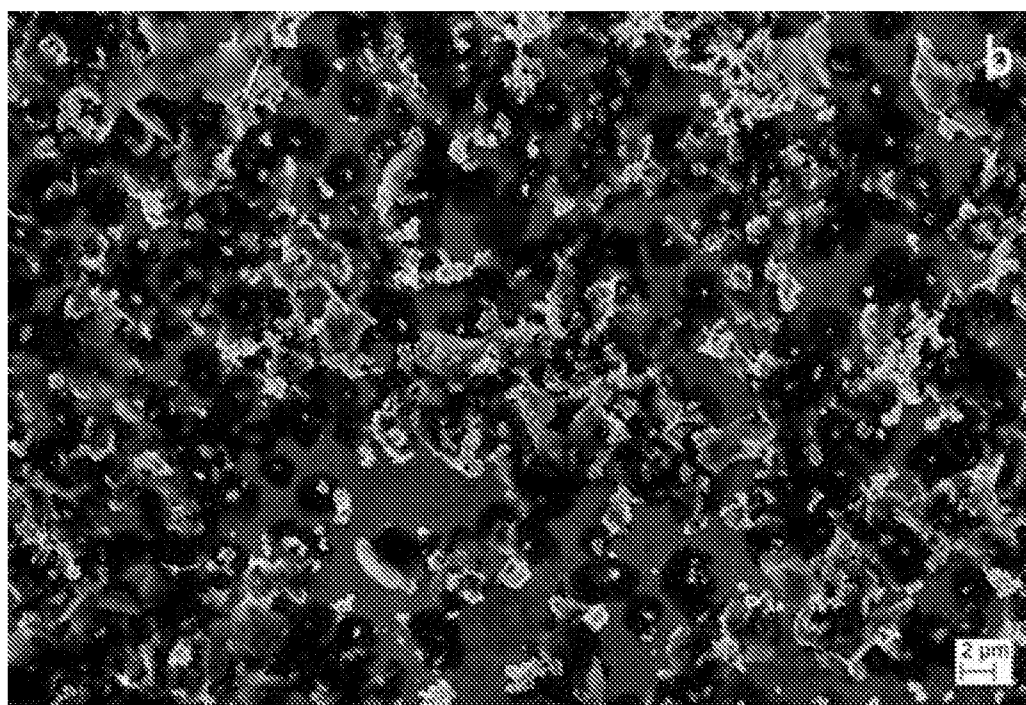


Fig. 6B

7/26

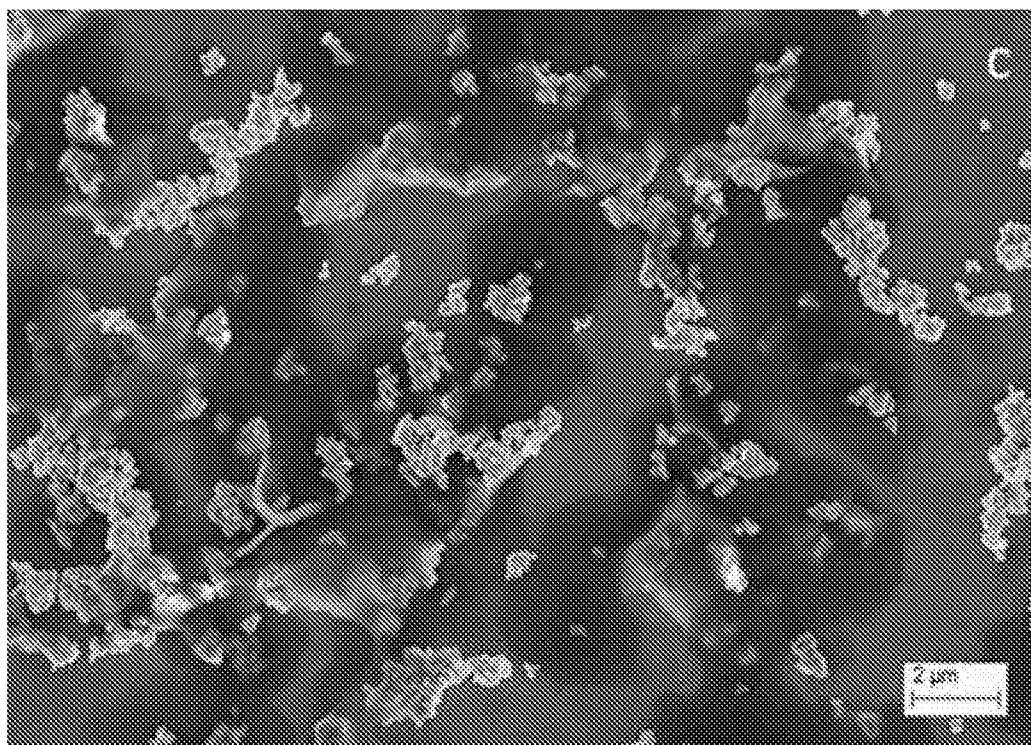


Fig. 6C

8/26

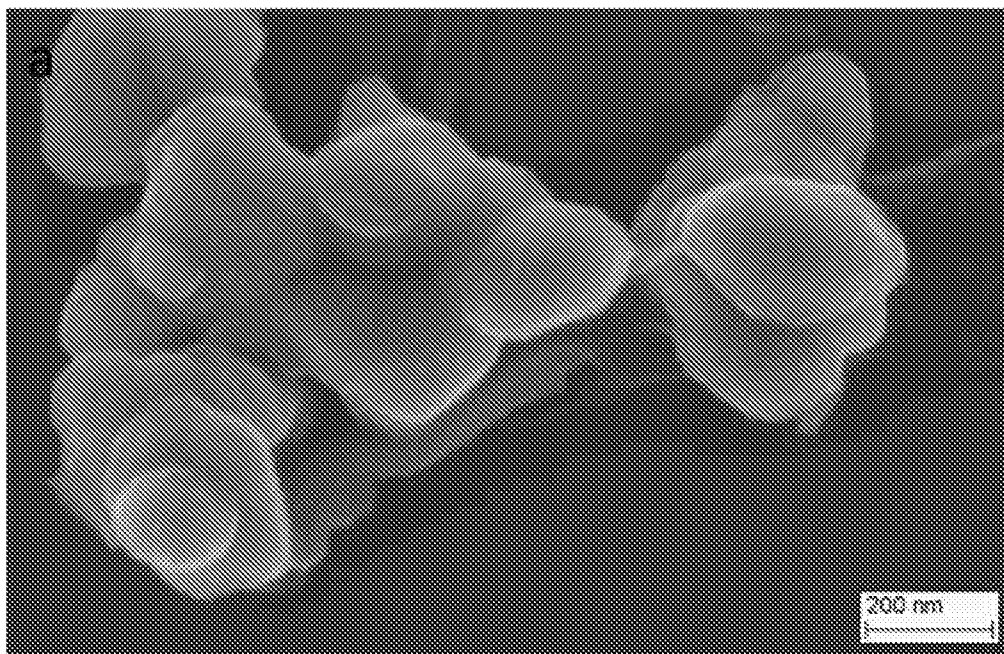


Fig. 7A

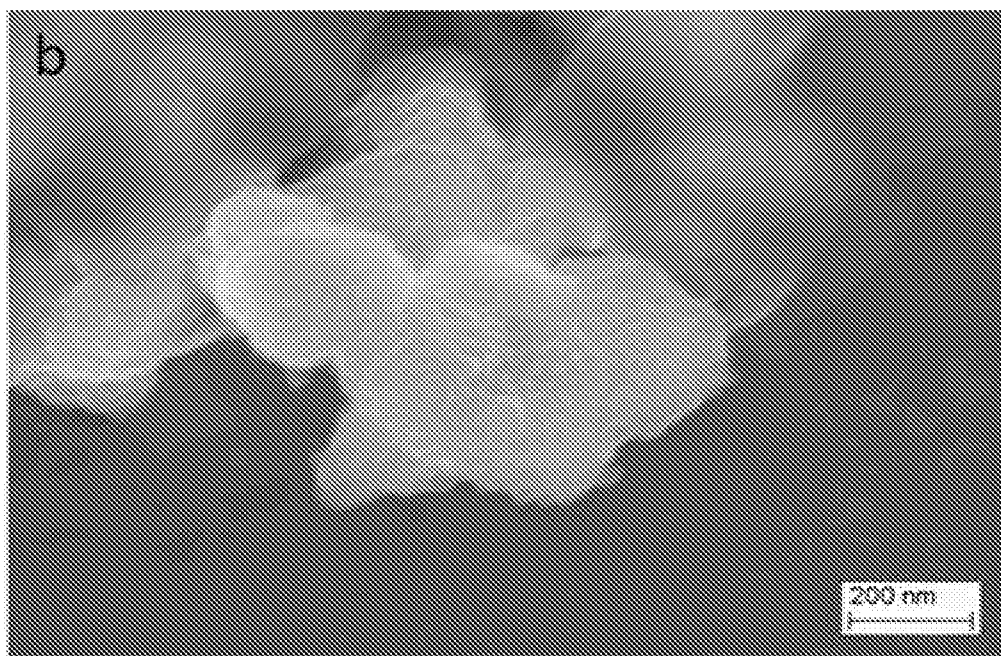


Fig. 7B

9/26

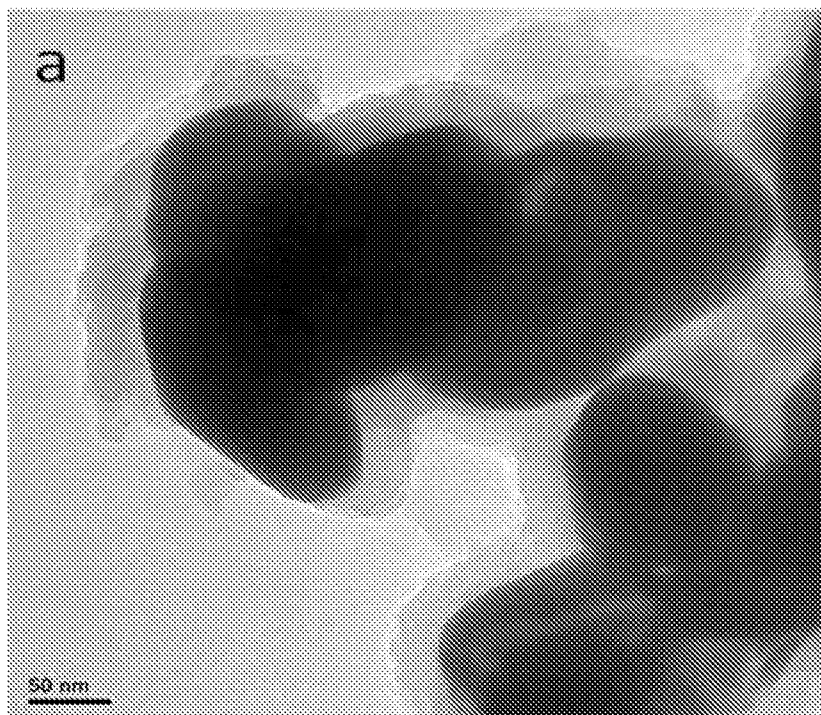


Fig. 8A

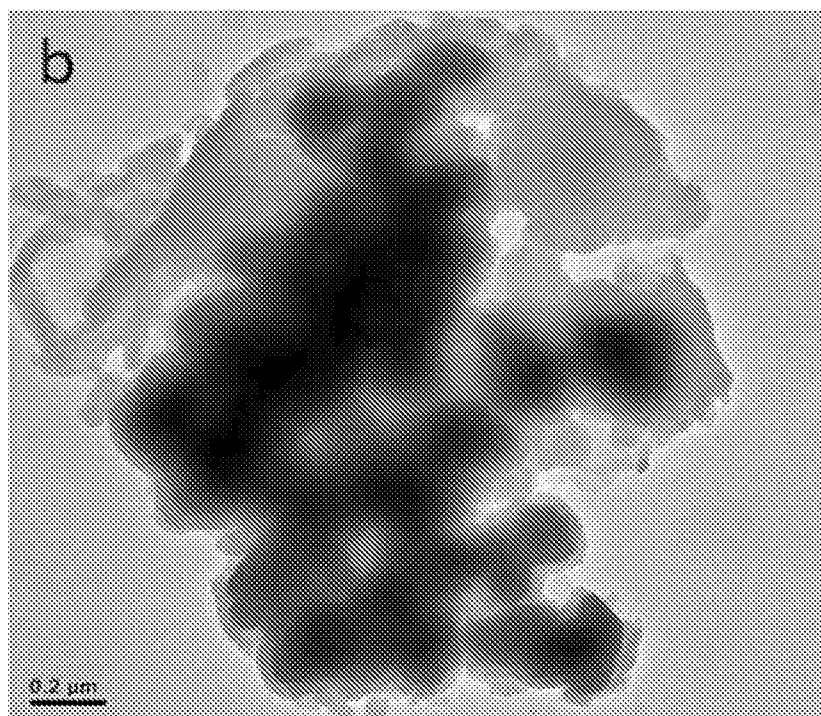


Fig. 8B

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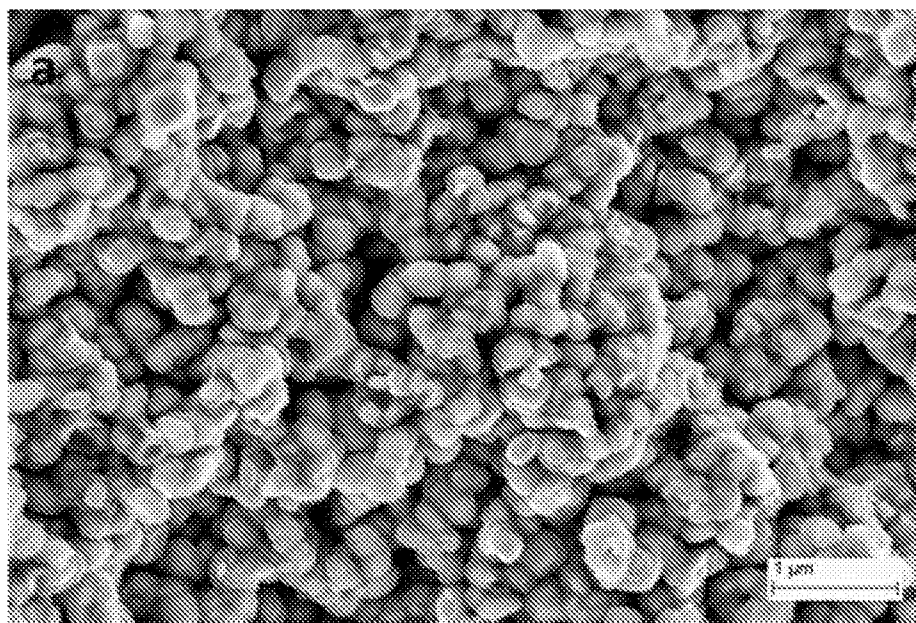


Fig. 9A

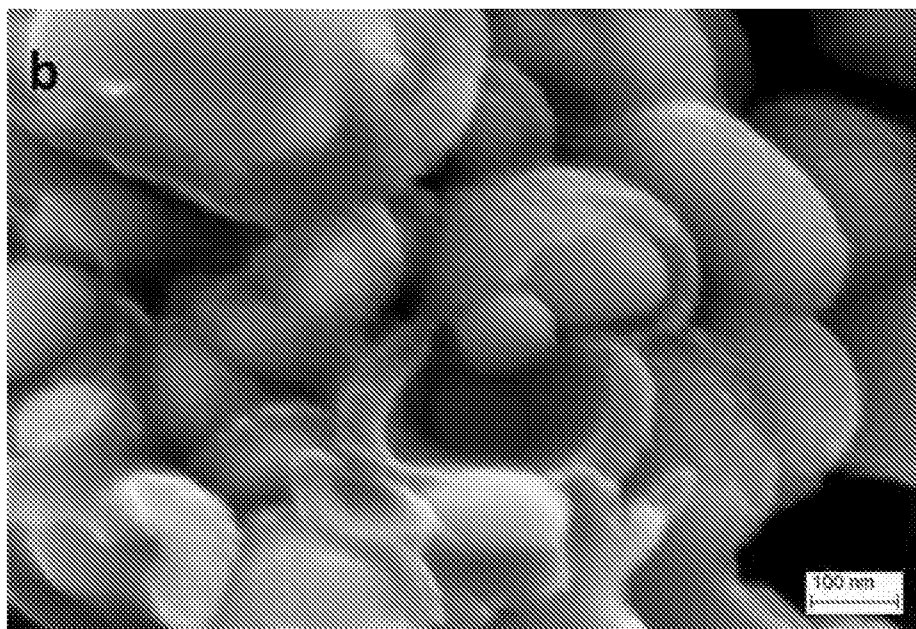


Fig. 9B

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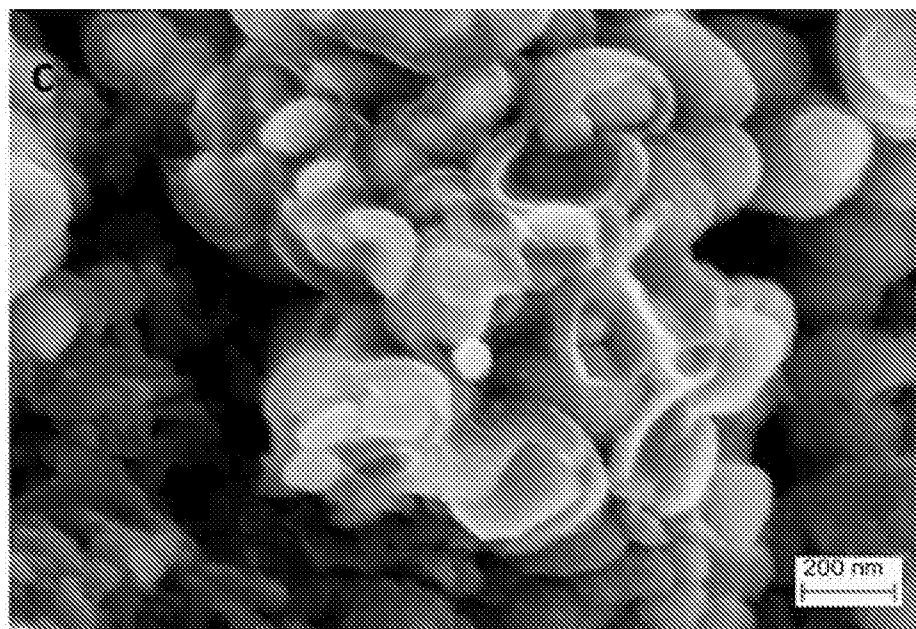


Fig. 9C

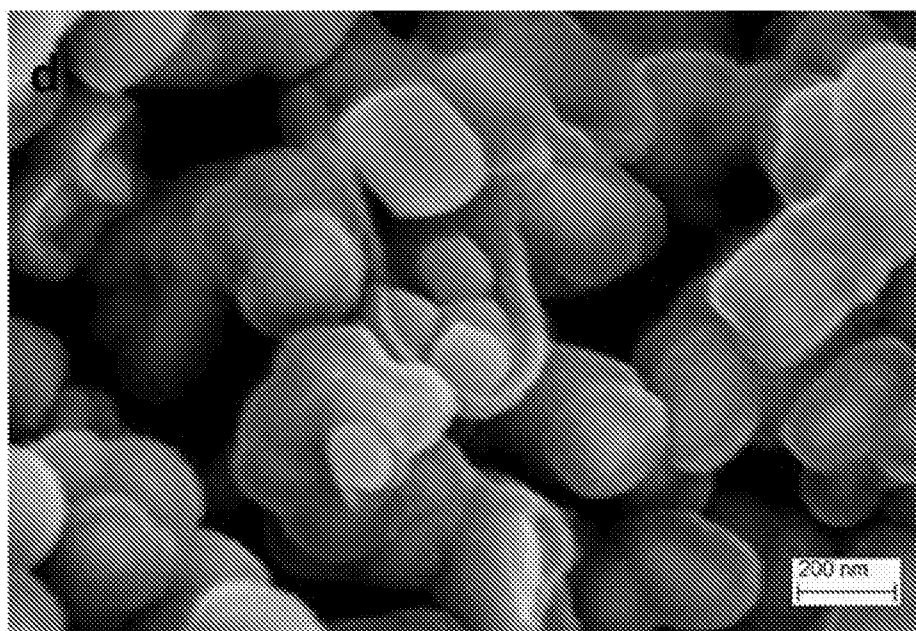


Fig. 9D

12/26

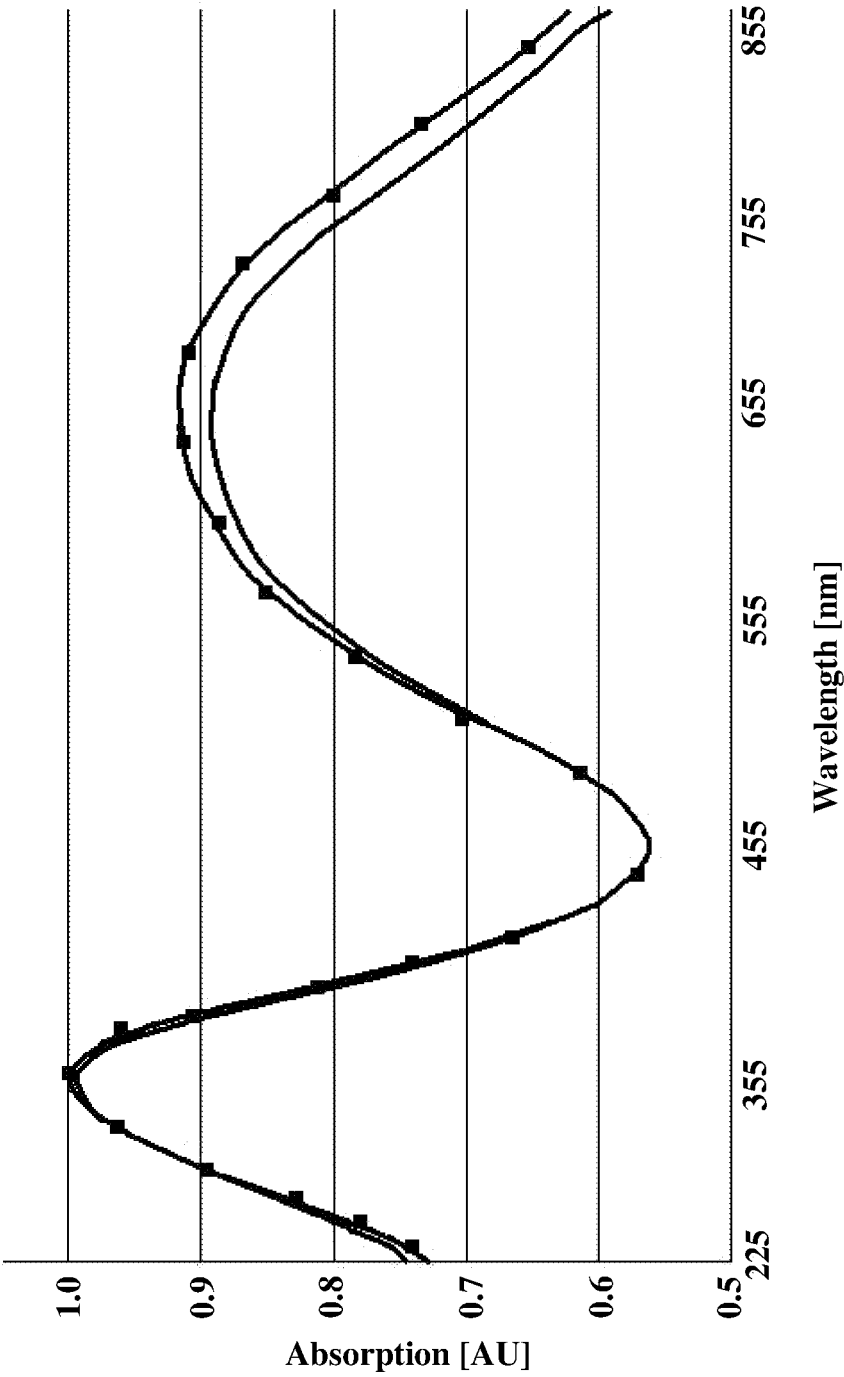


Fig. 10

13/26

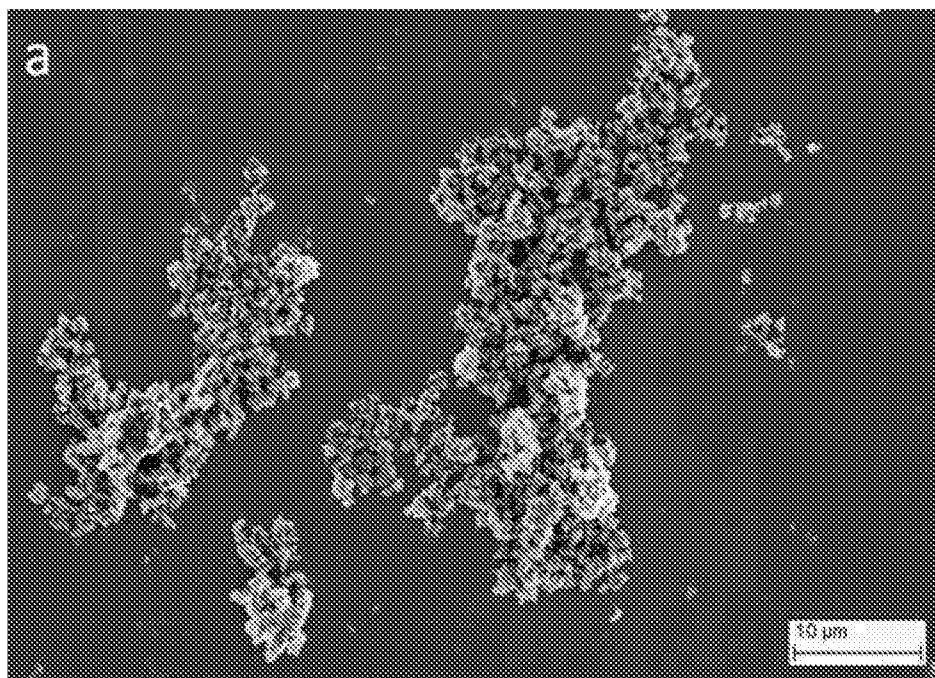


Fig. 11A

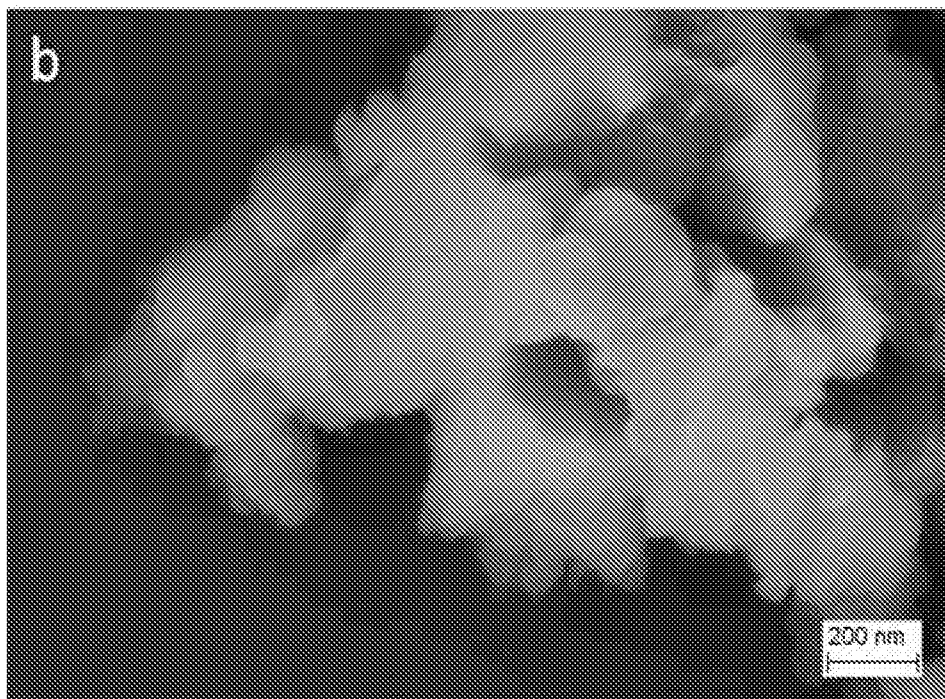


Fig. 11B

14/26

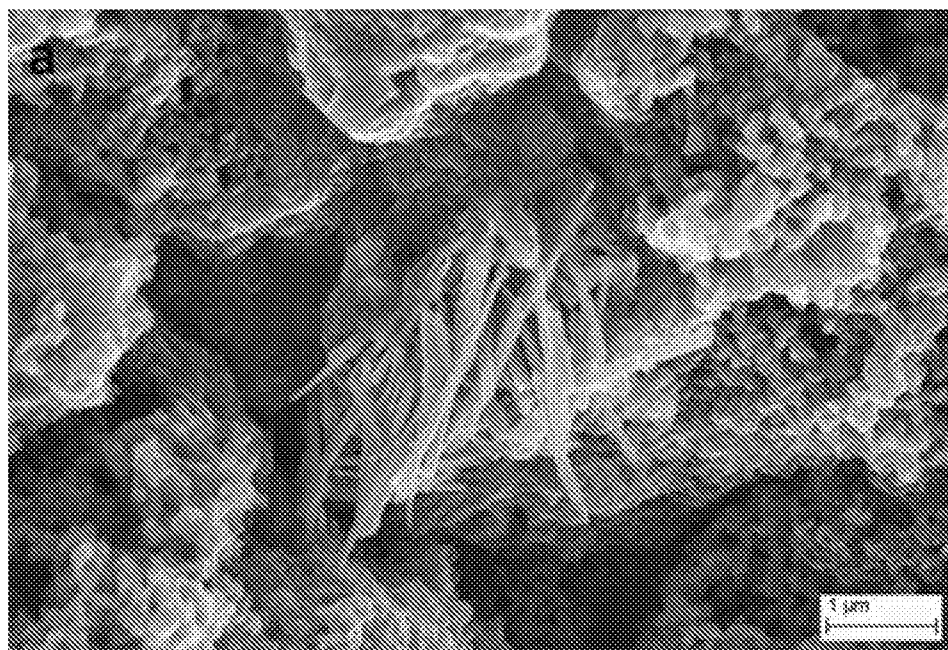


Fig. 12A

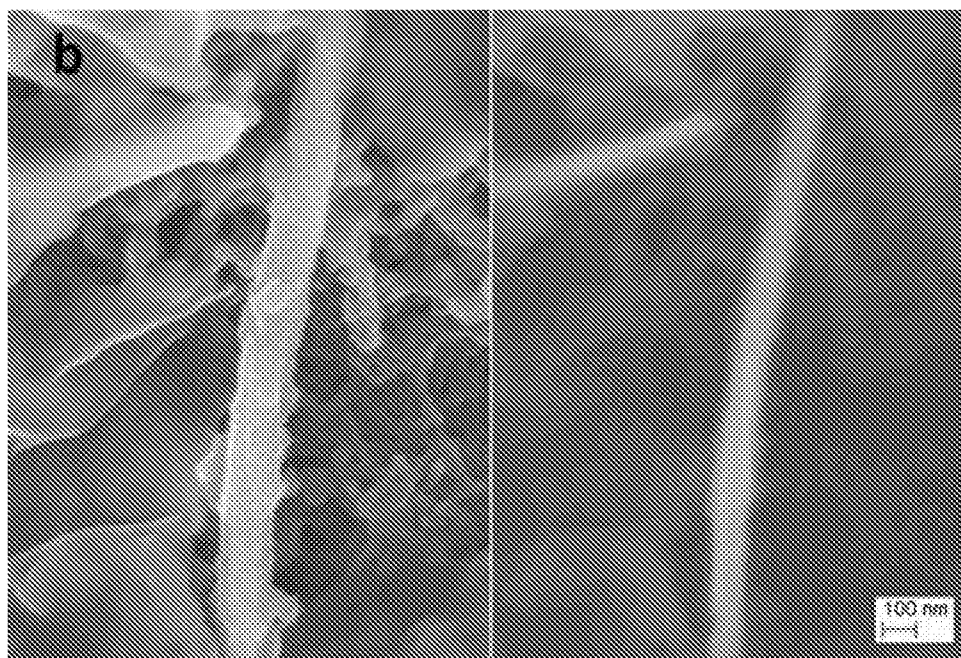


Fig. 12B

15/26

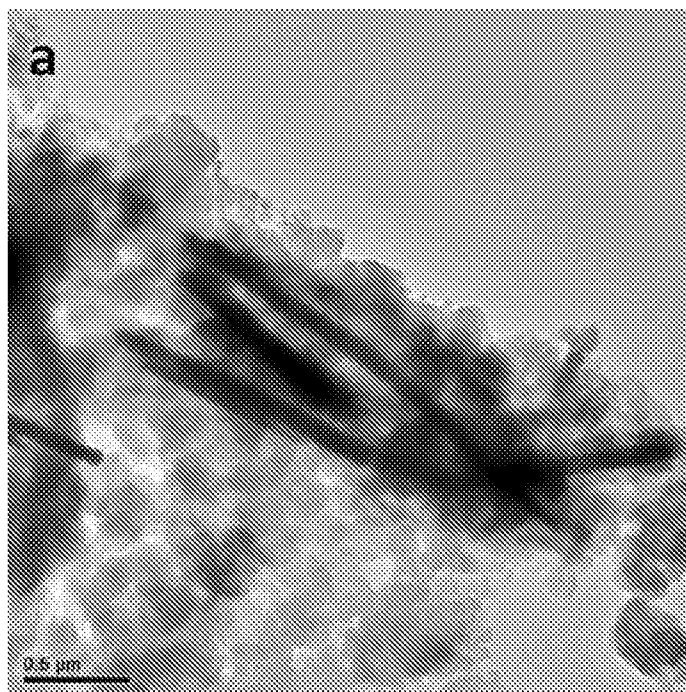


Fig. 13A

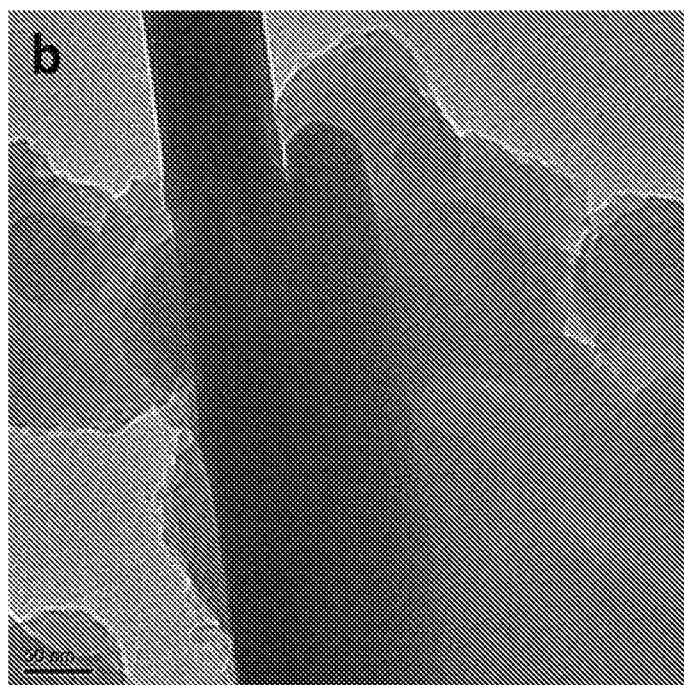


Fig. 13B

16/26

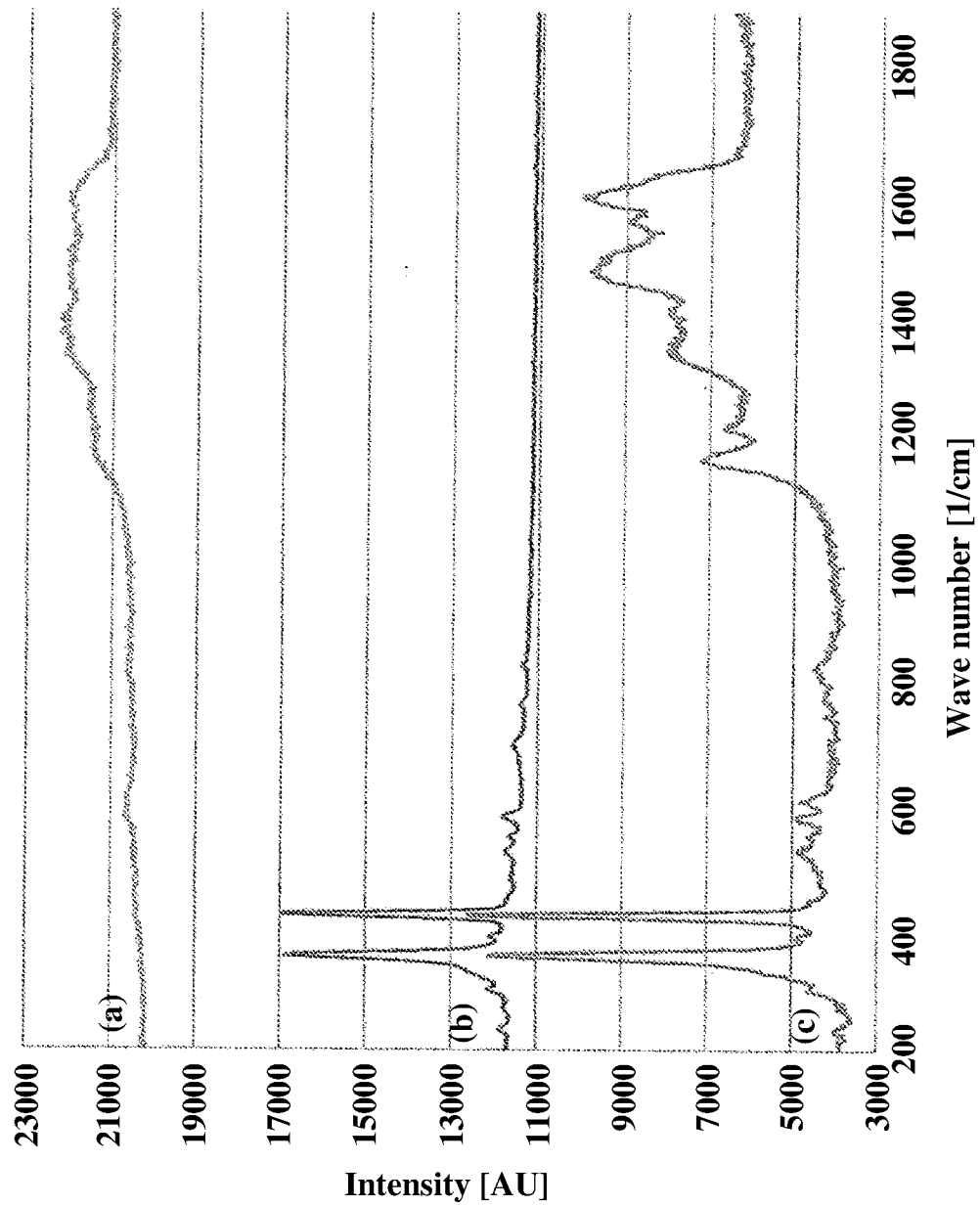


Fig. 14

17/26

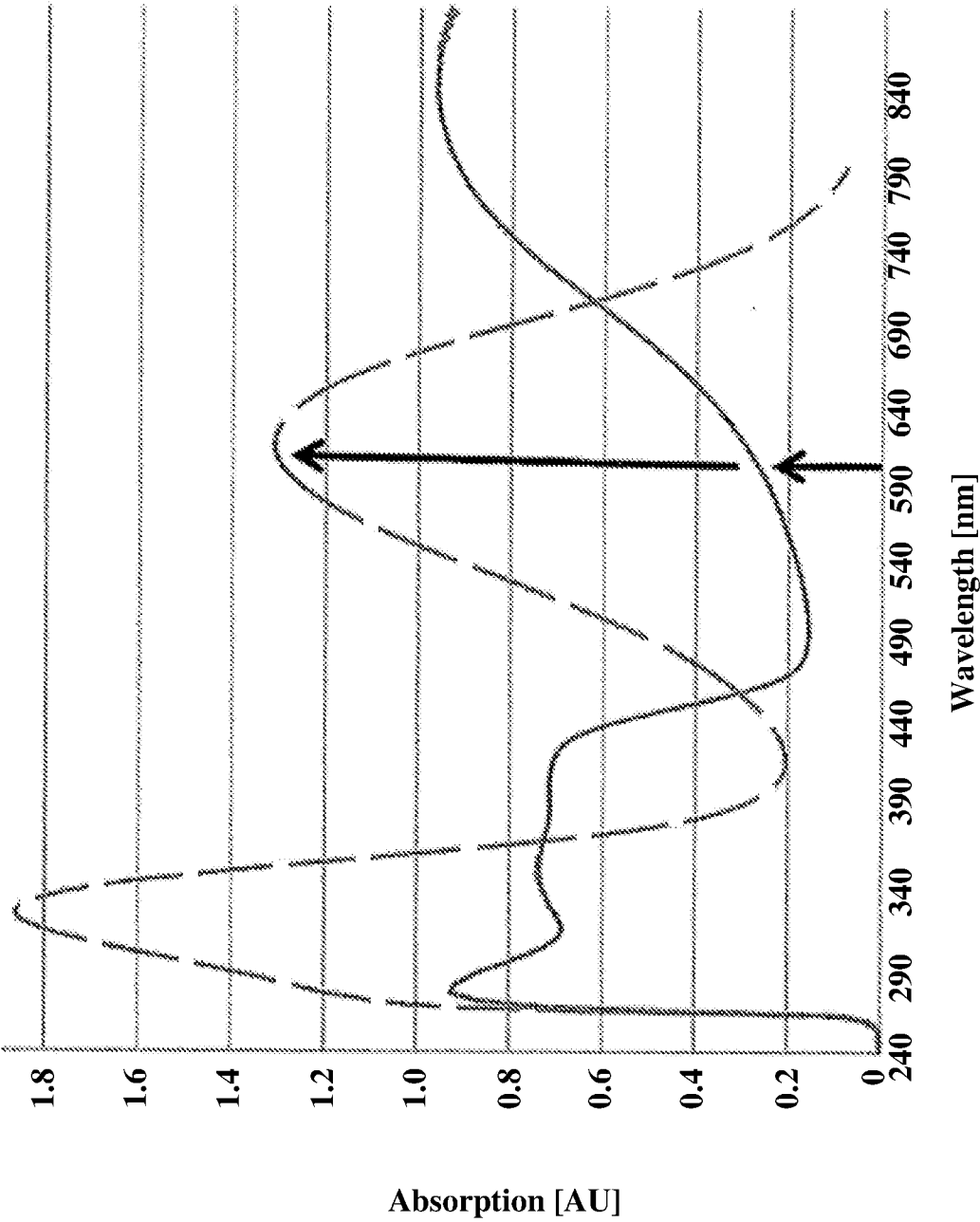


Fig. 15

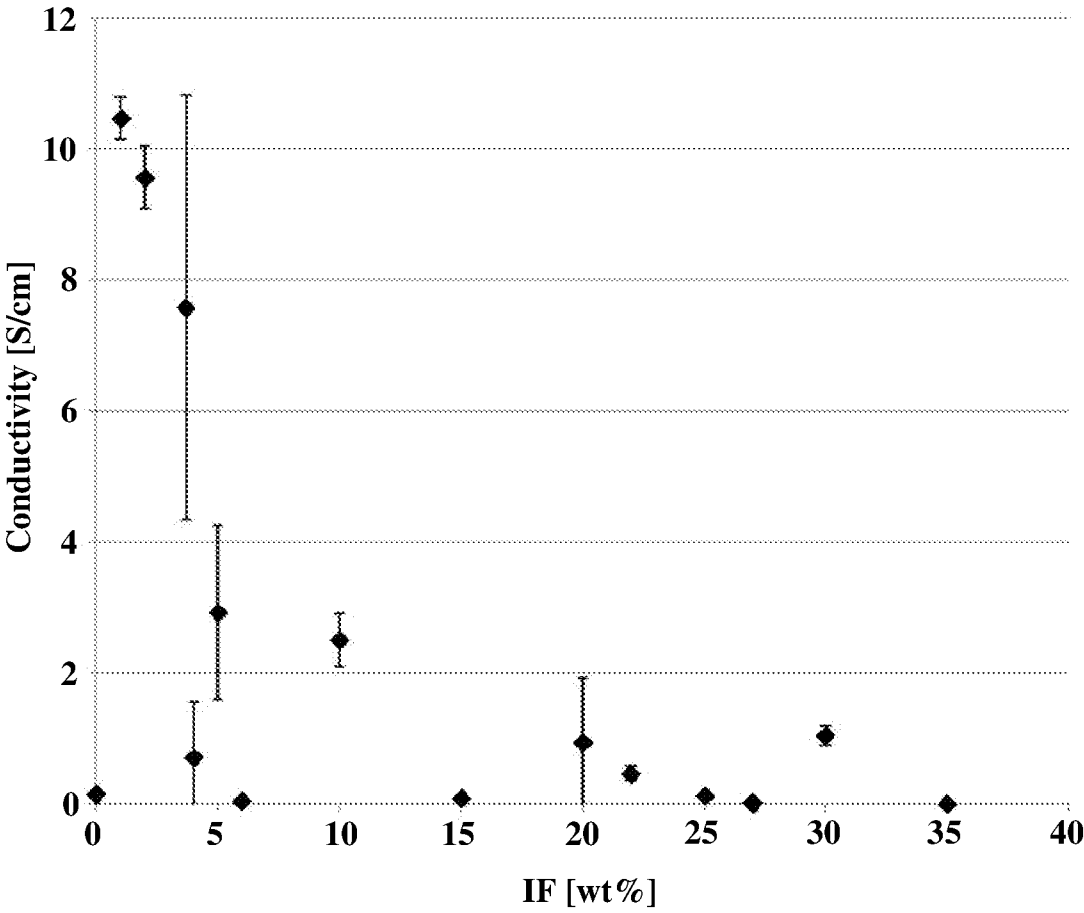


Fig. 16

19/26

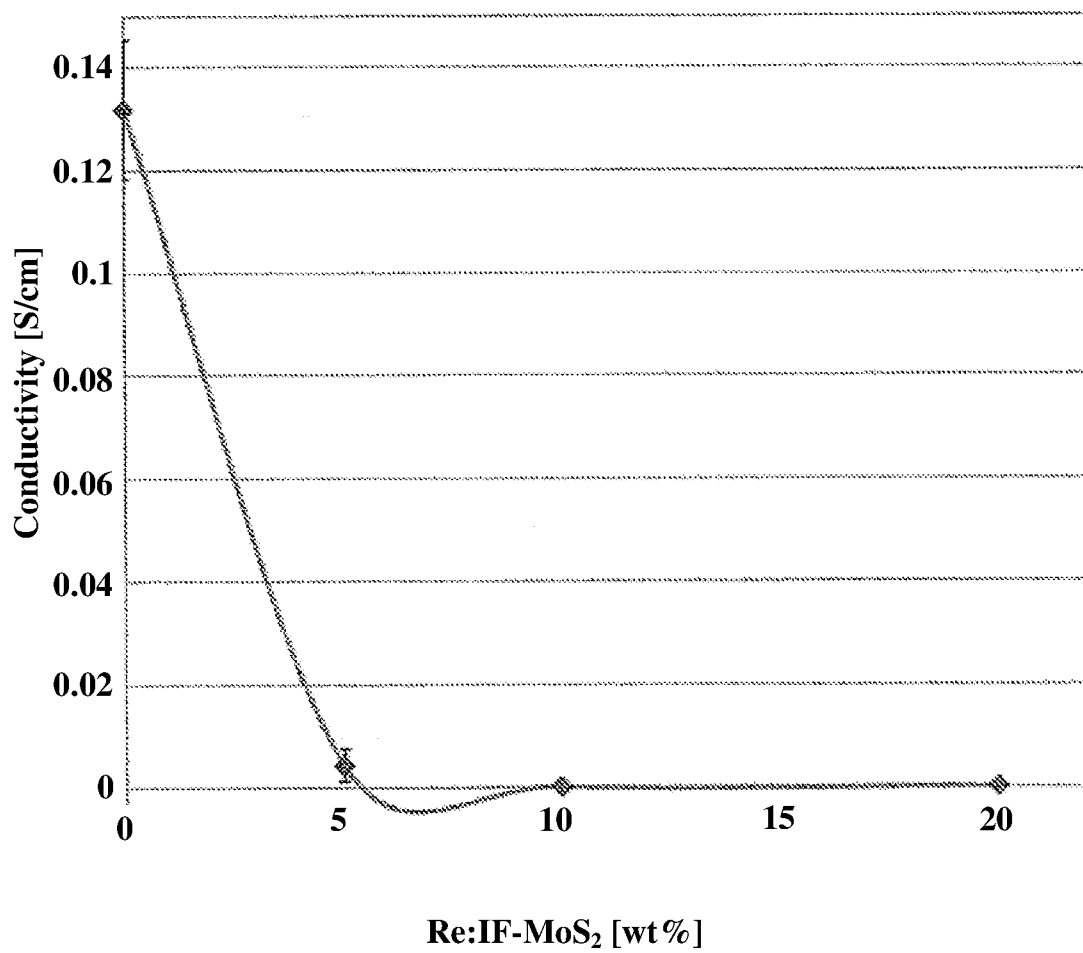


Fig. 17

20/26

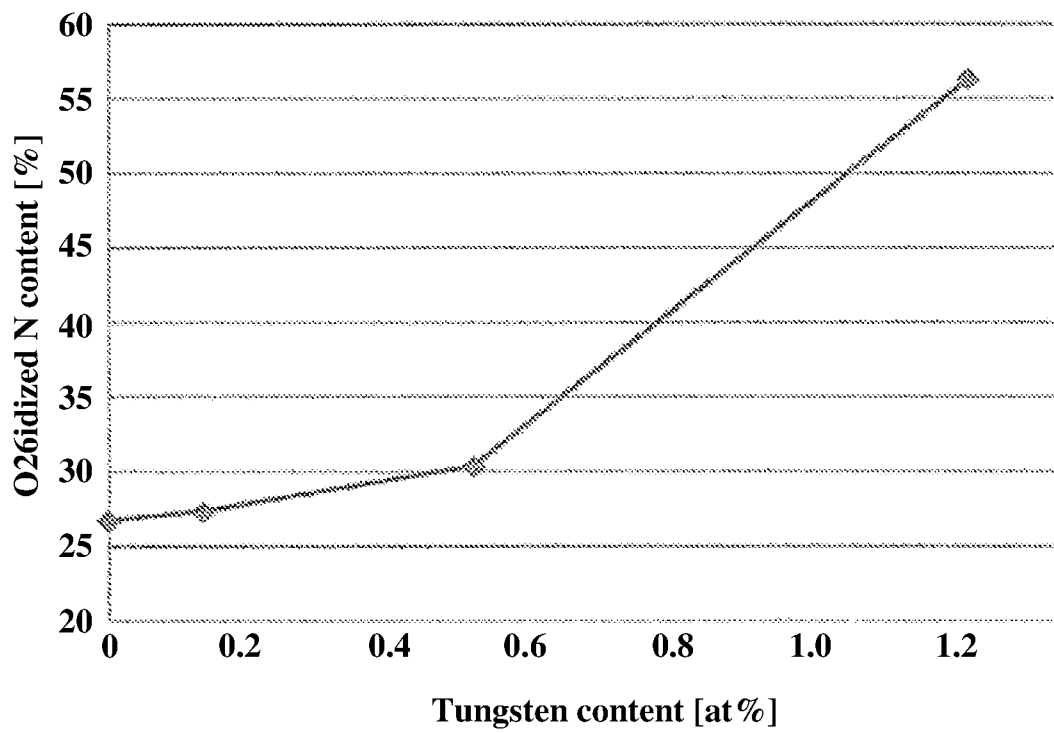


Fig. 18

21/26

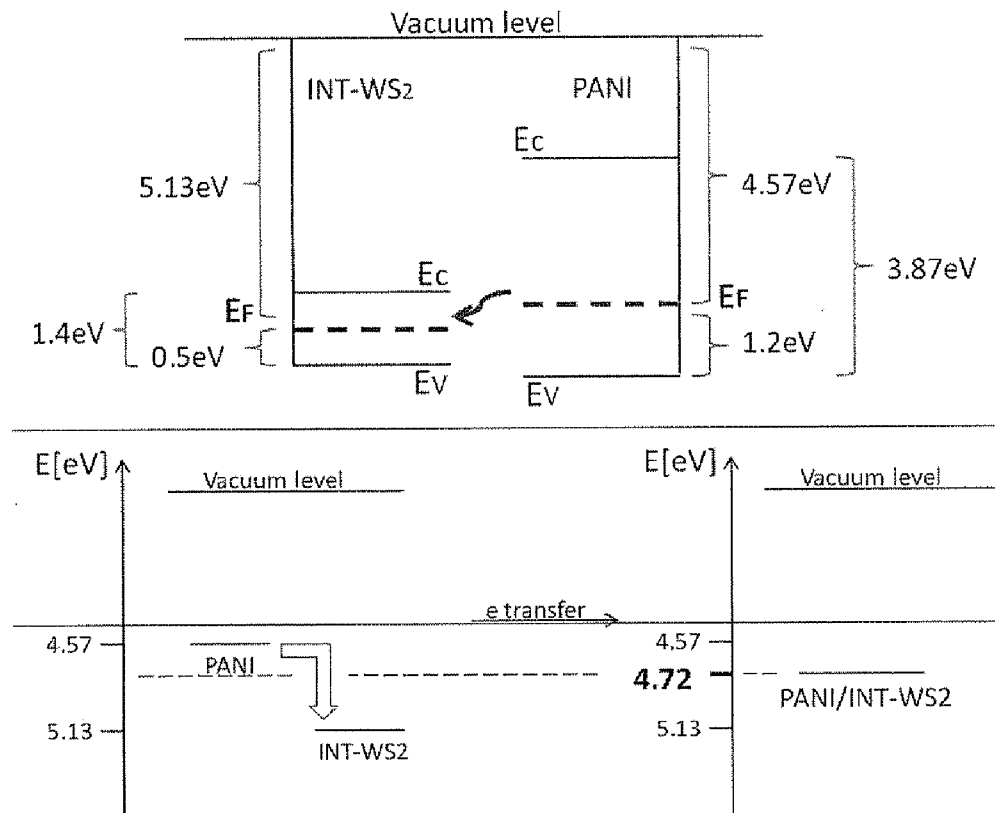


Fig. 19

22/26

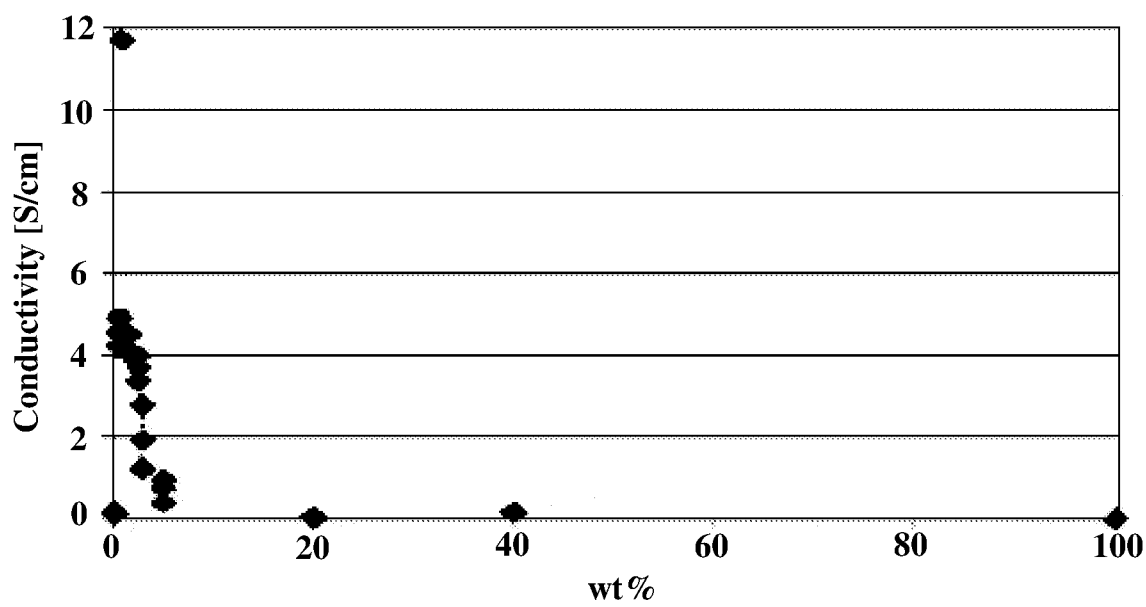


Fig. 20A

23/26

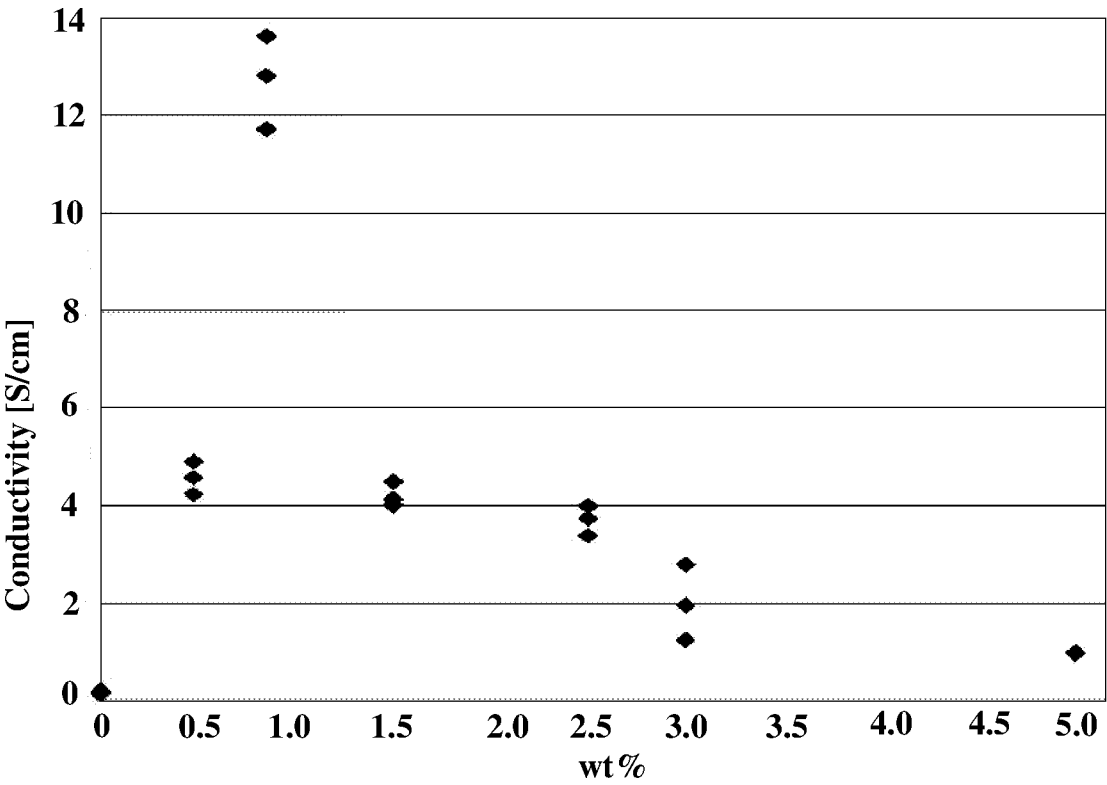


Fig. 20B

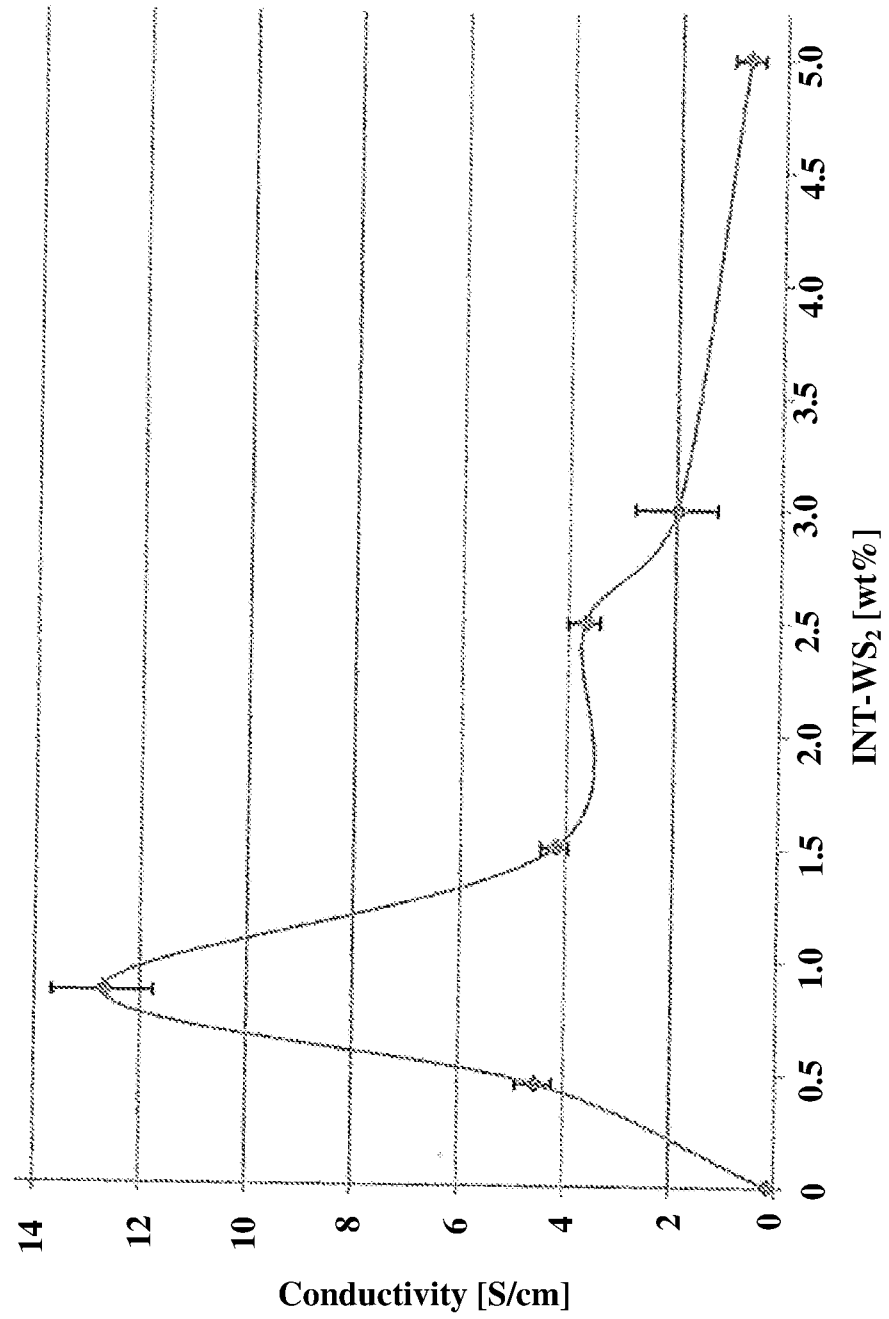


Fig. 21

25/26

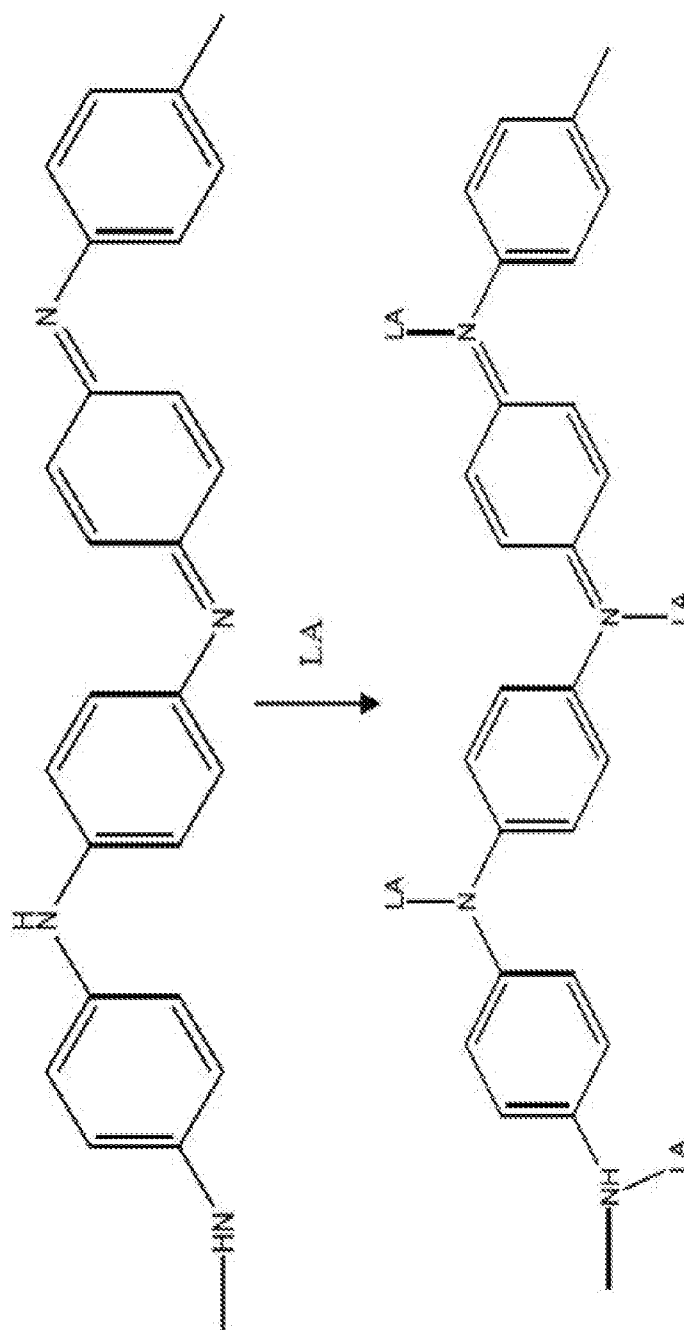


Fig. 22

26/26

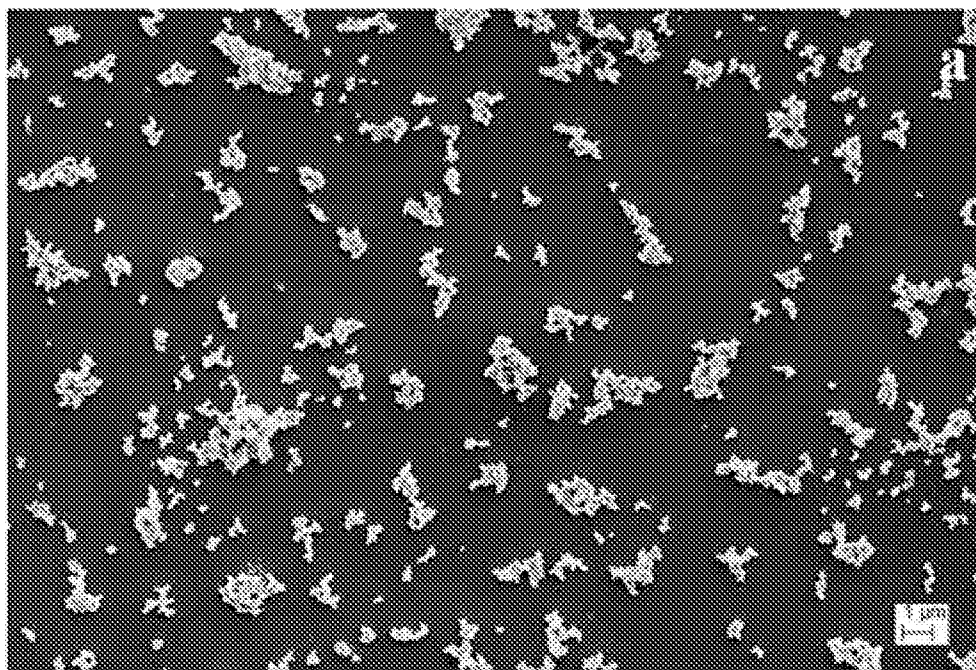


Fig. 23A

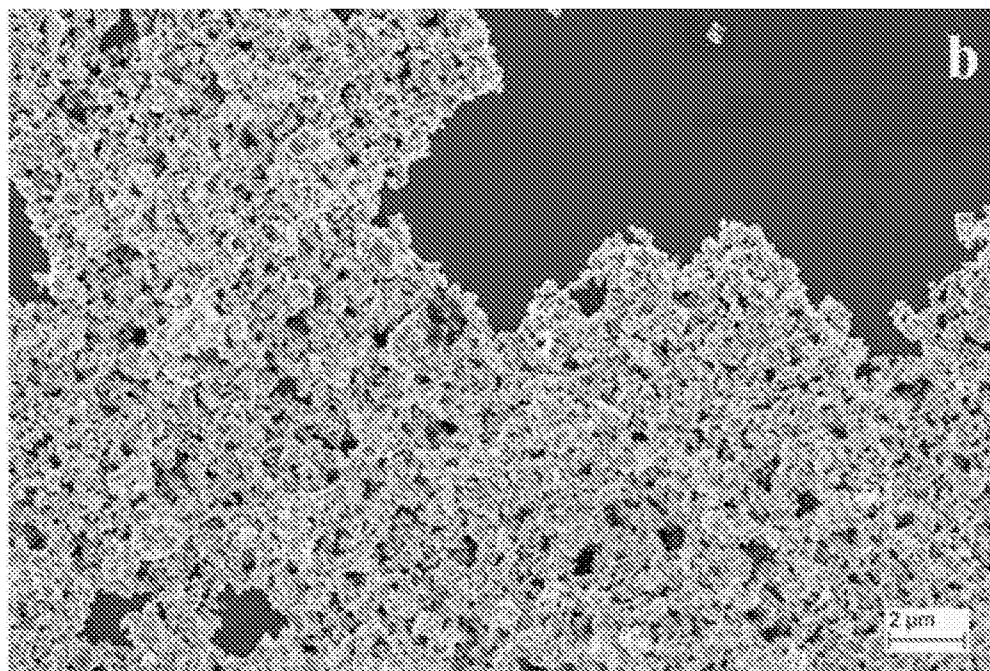


Fig. 23B

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2013/050933

A. CLASSIFICATION OF SUBJECT MATTER INV. C08K3/30 C08L65/00 C08L79/02 H01B1/12 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) C08G C08K C08L C09D H01B H01L		
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, CHEM ABS Data, 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 03/073538 A1 (INST JOSEF STEFAN [SI]; KEMIJSKI INST [SI]; DOMINKO ROBERT [SI]; GABER) 4 September 2003 (2003-09-04) abstract page 6, line 3 - page 10, line 15 -----	23-33, 35-41
X	KUMAR S ET AL: "Dispersion of WS2 nanotubes and nanoparticles into conducting polymer matrices for application as LED materials", THE EUROPEAN PHYSICAL JOURNAL B ; CONDENSED MATTER PHYSICS, EDP SCIENCES, LE, vol. 85, no. 5, 22 May 2012 (2012-05-22), pages 1-7, XP035058544, ISSN: 1434-6036, DOI: 10.1140/EPJB/E2012-20453-4 the whole document ----- -/-	1-6, 8-17, 20-28, 30-33, 35-41
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 23 January 2014	Date of mailing of the international search report 03/02/2014	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Meiners, Christian	

INTERNATIONAL SEARCH REPORT

International application No

PCT/IL2013/050933

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DOMINKO ET AL: "Carbon nanocoatings on active materials for Li-ion batteries", JOURNAL OF THE EUROPEAN CERAMIC SOCIETY, ELSEVIER SCIENCE PUBLISHERS, BARKING, ESSEX, GB, vol. 27, no. 2-3, 19 November 2006 (2006-11-19), pages 909-913, XP005729683, ISSN: 0955-2219, DOI: 10.1016/J.JEURCERAMSOC.2006.04.133 abstract	23-33, 35,36, 38-40
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International application No

PCT/IL2013/050933

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